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The Chemistry of Metal Carbonato and Carbon Dioxide Complexes

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A. Carbon Dioxide Dissolution Equilibria	655	A general review ¹ of the chemistry of metal carbonato complexes appeared in the literature in 1969, and in the same year a detailed review devoted entirely to cobalt(III) complexes was also published. ² Since this time the field has undergone tremendous growth, with abundant new data available on the physical properties of these compounds. Changes have occurred in how the mechanisms of metal carbonato formation reactions are perceived and the entire discipline of metal carbon dioxide complexes (organometallic chemistry) has virtually been created. ³ Certainly the environmental impact of the industrial CO ₂ output and the growing shortage of strategic materials, and the problems associated with nuclear waste storage have led to a greater interest by environmental chemists, geochemists, oceanographers, and biologists in the applied aspects of metal carbonate chemistry.	
B. Carbonic Acid Ionization	655	In compiling the material for this presentation we have surveyed the literature in <i>Chemical Abstracts</i> from 1969 to 1981 and have attempted to include the most relevant publications appearing in 1982. In many cases it was found necessary to include data prior to 1969, although we have avoided duplicating material already covered by Krishnamurthy, Harris, and Sastri ¹ where possible. As we cataloged in excess of 1400 references within this 11-year period, some of these studies that did not bear directly on the subject matter had to be deleted. For example, the role of CO ₂ in the atmosphere will not be treated in this text. ⁴⁻¹⁰	
C. Aqueous Carbon Dioxide Ionization	656	To break down briefly the sequence of topics treated here, we first deal with the physical properties, aqueous equilibria, and kinetics of CO ₂ (aq) and its hydrolysis products in order to provide some background for the subsequent sections. The metal carbonato complexes are then introduced by tabulating their preparative procedures, spectral characteristics, and X-ray crystallographic structures. As will be seen, a large number of natural minerals are included in the latter that could have otherwise been included in the later geochemical section. However, in keeping with our policy throughout the review, we have tried to centralize such material in the appropriate specific section to make comparisons easier and to avoid unnecessary duplication of discussion. Solid-state thermal reactions are then discussed in the light of their potential for producing certain carbonato complexes and with the intention of using the decomposition temperatures as rough fingerprints	
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of such carbonato complexes. The equilibrium section serves mainly to list current values of stability constants, ion-pair formation constants and solubility data, and the related thermodynamic data, for metal carbonato complexes. The section on kinetics gives a detailed discussion of the individual modes of reaction with present-day concepts of the mechanisms involved in these processes and how the data for each type of reaction can be correlated. The relatively new field involving metal–carbon dioxide complexes is divided into three sections which describe the preparation and characterization of these species, followed by discussions of CO₂ fixation and insertion reactions, with again much

of the data being presented in tabular form. Finally, the applied sections on geochemistry, oceanography, and biochemistry are not meant to provide researchers active in these areas with a comprehensive review of the literature, but rather to give research chemists an insight into some of the applied aspects and implications of carbonato metal chemistry in these areas.

There are still minor topics within this framework that are difficult to qualify precisely. It is hoped that a significant degree of cross referencing will help elevate this problem. Furthermore, during the literature survey we discovered numerous papers that dealt with chemical systems in which CO₂ is produced as a product. Although such systems were not reported to involve the direct participation of metal carbonato or metal–CO₂ complexes, this possibility cannot be ruled out completely. Carbon dioxide is usually one of the main products during the thermal or photochemical oxidation of carboxylic acids in the presence of metal ions. Many papers describe the oxidation of oxalic acid and oxalate bound to metal centers.^{11–15} The radical, CO₂[·], usually participates in such processes, and much chemistry has been developed around this species,¹⁶ especially in cases where it is produced via the radiolysis of formic acid^{17–23} and oxalate complexes.²⁴ Similarly, the uranyl-sensitized photolysis of carboxylic acids also produces CO₂ via the CO₂[·] radical.^{25–28} Alternative systems involve the application of photocatalytic, photosynthetic, or radiolytic techniques.^{29–33} Reduction of CO₂ and subsequent reactions must also be considered during thermal and photochemical activation^{34–36} and radiolysis.³⁷

Finally, it is also the intention of this review to bring the large body of data on metal carbonato and metal carbon dioxide systems to the attention of other research workers who are concerned with other or closely related aspects of this general topic.

The Chemistry of Carbonates

II. Physical Properties of Carbonates

In this section we present a compact summary of the physical properties of CO₂, HCO₃[−], and CO₃^{2−}. This includes the various spectroscopic characterization data and electrochemical analytical methods; structural information; solubility in aqueous salt and mixed solvent solutions; thermodynamic data; miscellaneous physical properties; and thermal decomposition properties.

A. Spectroscopic Characterization

IR and Raman spectroscopy are among the methods adopted most commonly for the characterization of the different carbon dioxide/carbonate species. The CO₂ molecule ($D_{\infty h}$) in the gas phase has three normal vibrational modes,³⁸ the symmetric stretching mode ν_1 , the bending mode ν_2 , and the antisymmetric stretching mode ν_3 . ν_1 is Raman active while ν_2 and ν_3 are infrared active and typical values are summarized in Table I. Information on the rotational structure of these bands for CO₂ gas has been published^{39–43} and the pressure dependence up to 12 GPa has also been investigated.^{38,44,45} It was found that the stretching modes stiffen and the bending mode softens with pressure.³⁸ Until recently, spectroscopy could not show the existence of H₂CO₃ molecules in aqueous solutions of CO₂.^{46,47}

TABLE I. IR and Raman Spectra Data on CO₂

phase	spectra	frequencies, cm ⁻¹			comments	ref
		ν_1	ν_2	ν_3		
gas	IR	1337	667	2349 2326 2326	studied up to 3.2 MPa	70 45 42 38 47
		1333	667	2349		46
		1388	1285 ^a			38
		1388, 1409	1265, 1285 ^a			47
		1390, 1411	1266, 1386 ^a			46
	R	1388	1286 ^a		500 kPa	46
		1381	1274 ^a		12-18 °C, 4-176 MPa	b 44
		1386-1388				47
		1384	1280 ^a		in D ₂ O, 4.5 MPa	47
		1383	1274 ^a		in H ₂ O, 4.5 MPa	47
aq soln	R	1386, 1405	1279 ^a		in D ₂ O	46
		1384	1276 ^a		in H ₂ O	46
		1352, 1347	660, 655	2354	0.6-12 GPa	38
			639		¹³ C ¹⁶ O ₂	38

^a 2 ν_2 . ^b Fenner, W. R.; Hyatt, H. A.; Kellam, J. M.; Porto, S. P. S. *J. Opt. Soc. Am.* 1973, 63, 173.

However, in a high temperature, high-pressure study, Kruse and Franck⁴⁸ recently reported a band at 1017 cm⁻¹ in the Raman spectrum of a CO₂ solution and ascribed this to the C-OH stretching vibration of H₂CO₃.

In aqueous solution, carbonic acid deprotonates to produce HCO₃⁻ and CO₃²⁻ (see section III). In addition to the spectral information included as a comparison in section V, a number of studies have reported the IR and Raman bands of these species.⁴⁸⁻⁵⁴ Note that in aqueous solution (H₂O and D₂O) the IR and Raman bands of the alkali metal carbonates (Li-Cs)⁴⁹ correspond closely to those observed in the solid state, D_{3h} point group, except that the ν_3 band is consistently split by ca. 55 cm⁻¹ for which carbonate-water interaction is believed responsible. For example, in 2 M solutions bands are found at: 1060 (ν_1); 880 (ν_2); 1425 and 1370 cm⁻¹ (ν_3) in the IR; 1066 (ν_1), 1435 and 1380 (ν_3), 686 cm⁻¹ (ν_4) in the Raman spectrum. The Raman inactive band does appear at very high concentrations of >6 M at 880 cm⁻¹, in keeping with the general observation that all the peak intensities increase linearly with concentration. No splitting of the weak ν_4 band in the Raman spectra was observed, indicating that ion pairing is probably not substantial, despite the high concentrations of up to 8 M employed in this study.⁴⁹ The lack of any significant dependence of the spectra on the nature of the cation tends to support this view.

For the alkali metal bicarbonate salts in solution (H₂O and D₂O), again no positive evidence for ion-pair formation was observed^{46,49} and the positions of the bands appeared independent of the nature of the metal ion. In accordance with the C_s symmetry for the HCO₃⁻ ion, the following assignments were made: 1630 R, 1620 IR (ν_2) asymmetric C-O stretch; 1360 R, 1355 IR (ν_3) symmetric C-O stretch; 1302 R, 1300 IR (ν_4) COH bend; 1017 R, 1000 IR (ν_5) C-OH stretch; 841 R, 840 IR (ν_6) CO₃ out-of-plane deformation; 672 R (ν_7) CO₂ bend; 632 cm⁻¹ R (ν_7) (OH)CO bend.⁴⁶

The UV absorption characteristics of CO₂(aq), HC-O₃⁻, and CO₃²⁻ form the basis of a spectrophotometric titration method.^{55,56} A detailed review of the electronic spectra of CO₂ has also been published.⁵⁷ Additional spectroscopic characterization methods include: ¹³C NMR,^{54,58} ¹⁷O NMR,⁵⁹ mass spectrometry,^{60,61} EPR,⁶² photoelectron emission spectroscopy,⁶³ and X-ray

techniques.⁶⁴ A number of electrodes have been developed for the selective identification of carbonate species in solution.^{65,68}

Structural studies⁶⁹ indicate that CO₂ is a symmetrical linear molecule with no dipole moment and a C-O distance of 1.159 Å. In the case of the carbonate ion, the distance is 1.32 Å and the bond angle 120°.⁷⁰ (See section VB.) In addition, a recent report⁶⁴ reviews the stereochemical aspects of 34 well-known carbonate groups.

B. Solubility Characteristics

The solubility of CO₂ in aqueous solutions depends strongly on the temperature and applied CO₂ pressure. Various research groups have studied solubility phenomena, and a summary of the most recent work is presented in Table II. In a quite recent review paper⁷¹ it was demonstrated that the mole fraction (x) of dissolved CO₂ at 1 atm partial pressure of CO₂ can be expressed as

$$R \ln x = A + BT^{-1} + C \ln (T/K) + DT \quad (1)$$

over the temperature range 273-353 K with $A = -1327.8$ J K⁻¹ mol⁻¹, $B = 72611.6$ J mol⁻¹, $C = 179.99$ J K⁻¹ mol⁻¹, and $D = -0.009159$ J K⁻² mol⁻¹ for water as solvent. The corresponding values for D₂O as solvent over the temperature range 298-353 °C are -1256.2, 71255.6, and 167.75 for A , B , and C , respectively. Malinin⁷² developed a general equation for the salting out of CO₂ in aqueous solutions of NaCl and CaCl₂ over a wide temperature range (25-300 °C) and chloride concentration range (up to 5-7 M):

$$\log \frac{x_{\text{CO}_2}^{\text{L}}}{x_{\text{CO}_{2,s}}^{\text{L}}} = K_{\text{sh}}^{\text{m}} m + K_x \Delta x_{\text{CO}_2}^{\text{L}} + K_v (P - P_s) \quad (2)$$

where K_{sh}^{m} = salting-out coefficient corrected for the activity of CO₂ in solution; $x_{\text{CO}_2}^{\text{L}}$ = solubility of CO₂ in the pure liquid phase (mole fraction); $x_{\text{CO}_{2,s}}^{\text{L}}$ = $x_{\text{CO}_2}^{\text{L}}$ for the electrolyte solution; $\Delta x_{\text{CO}_2}^{\text{L}} = x_{\text{CO}_{2,s}}^{\text{L}} - x_{\text{CO}_2}^{\text{L}}$; P = overall pressure; P_s = saturated vapor pressure of the electrolyte solution; and K_x , K_v = constants which are functions of temperature. Typical values for K_{sh}^{m} , K_x , and K_v are 0.07, 2.9, and 0.0, respectively, for the solubility of CO₂ in a 3 M NaCl solution at 150 °C.

TABLE II. Solubility Measurements of CO₂ in Aqueous Solution

authors	soln composition	temp range, °C	P _{CO₂} , MPa	range, ref
Matous et al. (1969)	pure H ₂ O	30-80	0.1-4	a
Stewart and Mungal (1970)	pure H ₂ O, synthetic seawater	-5-25	1-4.5	b
Mungal and Stewart (1971)	pure H ₂ O, seawater	-5-25	0.1-4.5	c
Malinin and Savelyeva (1972)	0.4 M NaCl, 0.4-3.4 M CaCl ₂	25-75	~5	d
Krestov and Nedelko (1972)	0.5-6 M various electrolytes	15-25	0.1	e
Malinin and Kurovskaya (1975)	0-6 M NaCl 1-6 M CaCl ₂	25-150 100-150	~5	f
Yasunishi and Yoshida (1979)	16 electrolytes	15-35	~0.1	g
Sada and Yasunishi (1980)	7 binary salt solutions	25	~0.1	h
Sada et al. (1981)	molten alkali halides and nitrates	300-1000	0.1	i
Zawisza and Malesinska (1981)	pure H ₂ O	50-200	0.2-5.0	j
Drummond (1981)	0-6 M NaCl	50-400	3.0-15.0	118

^a Matous, J.; Sobr, J.; Novak, J. P.; *J. Collect. Czech. Chem. Commun.* 1969, 34, 3982. ^b Stewart, P. B.; Mungal, P. K. *J. Chem. Eng. Data* 1970, 15, 67. ^c Mungal, P. B.; Stewart, P. B. *J. Chem. Eng. Data* 1971, 16, 170. ^d Malinin, S. D.; Savelyeva, N. I. *Geokhimiya* 1972, 643. ^e Krestov, G. A.; Nedel'ko, B. E. *Tr. Ivanov. Khim.-Tekhnol. Inst.* 1972, 32. ^f Malinin, S. D.; Kurovskaya, N. A. *Geokhimiya* 1975, 547. ^g Yasunishi, A. *Kenkyu Hokoku-Asahi Garasu Kogyo Gijutsu Shoreikai* 1980, 36, 25; *Chem. Abstr.* 1982, 95, 226522v. ^h Sada, E.; Yasunishi, A.; *Kenkyu Hokoku-Asahi Garasu Kogyo Gijutsu Shoreikai* 1980, 36, 25; *Chem. Abstr.* 1982, 95, 226522v. ⁱ Sada, E.; Katoh, S.; Yoshii, H.; Takemoto, I.; Shiomi, N. *J. Chem. Eng. Data* 1981, 26, 279. ^j Zawisza, A.; Malesinska, B. *J. Chem. Eng. Data* 1981, 26, 388.

TABLE III. Thermodynamic and Related Properties

substance	properties	temp range, °C	pressure range, MPa	ref
CO ₂	ΔH _{sub}	-80 to -233	<0.1	a
	PVT	-50 to 1000	0.1-1000	80
	PVT	-50 to 50	<250	b
	PVT, γ	<500	<3000	c
	PVT	0 to 600	0-15	89
	PVT	0 to 1030	0.1-100	d
	ΔH _f °, S°	25	0.1	81
	γ	450 to 800	0-50	e
	f	180 to 1030	0.1-1000	f
	f, G	50 to 1000	2.5-140	g
	C _p	0 to 6000	0.01-100	h
	C _p , H, G, S	0-1230, 600-5700, 5700-20 000	i	
NaHCO ₃	vapor/liquid distribution const	100-340		521
	C _p	25	0.1	108
	ΔH _f °, S°	25	0.1	81
	γ	25	0.1	91, j
	γ, φ	25	0.1	84
	γ, φ	25	0.1	79
	γ	25	0.1	91
	ΔH _f °, S°	25	0.1	81
	C _p	25	0.1	108
	C _p , a, φ, γ	25	0.1	82
	γ, φ	25	0.1	83
K ₂ CO ₃				

^a Angus, S.; Armstrong, B.; de Reuck, K. M. IUPAC International Thermodynamic Tables of the Fluid State Carbon Dioxide; Pergamon Press: New York, 1976; Vol. 3, p 3, 380. ^b Vasserman, A. A.; Golovskii, E. A.; Tsymarnyi, V. A. *Inzh.-Fiz. Zh.* 1971, 20, 734. ^c Lentz, H.; Franck, E. U. "High Pressure Science and Technology"; Timmerhaus, K. D., Barber, M. S., Eds.; Plenum Press: New York, 1977; Vol. 1 p 539. ^d Altunin, V. V.; Gadetskii, O. G. *Tr. Mosk. Energ. Inst.* 1970, 3. ^e Greenwood, H. J. *Am. J. Sci.* 1973, 273, 561. ^f Shmulovich, K. I.; Schmonov, V. M. *Geochem. Int.* 1975, 202. ^g Majumdar, A. J.; Roy, R. *Geochim. Cosmochim. Acta* 1956, 10, 311. ^h Kessel'man, P. M.; Afanas'ev, M. M.; Bestukhev, A. S.; Blank, Yu. I.; Gorykin, S. F.; Kotlyarevskii, P. A.; Chernyshev, S. K.; Shchekatolina, S. A. *Teplo-Massoperenos, Dokl. Vses. Soveshch.*, 3rd 1968, 7, 142; *Chem. Abstr.* 1971, 74, 16343c. ⁱ Maslov, P. G. *Termodin. Termokhim. Konstanty* 1970, 235; *Chem. Abstr.* 1971, 74, 16302p. ^j Pitzer, K. S.; Pelper, J. C. *J. Phys. Chem.* 1980, 84, 2396.

The solubility of CO₂ has also been measured for aqueous solutions of ethanol,^{73,74} propanol,^{74,75} glycol,⁷⁶ glycerol,⁷⁶ 1,5-pentanediol,⁷⁶ ethylene carbonate,⁷⁷ ethylene oxide,⁷⁷ diethylene glycol,⁷⁶ ethanolamine,⁷⁶ binary mixed solvents including CCl₄, various alcohols, and formamide,⁷⁴ and a series of heavy hydrocarbons.⁷⁸ Finally the solubility of Na₂CO₃ in water at 25 °C was found to be 2.767 mol kg⁻¹,⁷⁹ which is in good agreement with a series of values dating back as far as 1911.⁷⁹

C. Thermodynamic and Related Properties

A variety of thermodynamic and related properties of CO₂, HCO₃⁻, and CO₃²⁻ have been investigated. A

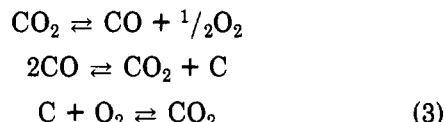
summary of the most recent studies is given in Table III. These properties include heat of sublimation (ΔH_{sub}), heat of formation (ΔH_f°), free energy (G), entropy (S), heat capacity (C_p), activity coefficient (γ), fugacity coefficient (f), and osmotic coefficient (φ). In this respect we would like to draw attention to a number of recent papers in which the mentioned properties are reviewed in detail.⁸⁰⁻⁸⁴ Other properties that have been reported include diffusion coefficient,^{74,85} thermal conductivity,⁸⁶ refractive index,⁸⁷ viscosity,⁸⁸ compressibility,^{89,90} ion-pair formation,⁹¹ thermal expansion coefficients in the solid state,⁹² and critical properties.⁹³⁻⁹⁵ Some of the important physical constants for

CO_2 can be summarized as follows:⁹⁵ molecular mass, 44.009 g mol⁻¹; ΔH_{sub} at 0 K, 26 250 J mol⁻¹; critical temperature, 304.21 K; critical pressure, 7.3825 MPa; critical density, 0.010 59 mol cm⁻³; triple-point temperature, 216.58 K; triple-point pressure, 518.5 kPa.

The molar volume of $\text{CO}_2(\text{g})$ has been determined in a number of ways as a function of temperature and pressure.⁹⁶⁻⁹⁸ The partial molar volume of dissolved CO_2 was reported to vary between 31.3 and 37.6 cm³ mol⁻¹ at 25 °C.⁹⁹⁻¹⁰⁶ The effect of temperature up to 400 °C and pressure up to 700 MPa on $\bar{V}(\text{CO}_2)$ has also been studied.^{106,107} Similar data have been reported for the molar volumes of NaHCO_3 , KHCO_3 , Na_2CO_3 , and K_2CO_3 .^{100,108,109}

D. Thermal Decomposition of CO_2

The thermal decomposition of CO_2 to CO and O has been studied by various groups.¹¹⁰⁻¹¹² Theoretical calculations¹¹² have predicted Arrhenius parameters for the dissociation and recombination of CO_2 up to 6000 K which are in good agreement with those measured experimentally.^{110,111,113} Typical activation energies are 535 and 13 kJ mol⁻¹ for the dissociation and recombination of CO_2 at 1500 K, respectively.¹¹² Lietzke and Mullins¹¹⁴ described the thermal decomposition in terms of the following mechanism:



The equilibrium constants were calculated over a wide range of temperature and pressure, using the relationship

$$\ln K_i = a_i/T + b_i + c_i T + d_i T^2 \quad (4)$$

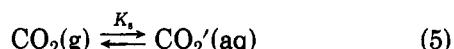
for which the various constants a_i , b_i , c_i , and d_i were reported.¹¹⁴

III. Carbonic Acid, Bicarbonate, and Carbonate Hydrolysis Equilibria

Equilibrium constants referred to here are in molality units unless stated otherwise.

A. Carbon Dioxide Dissolution Equilibria

Any consideration of the "carbonate" equilibria must deal with the Henry's law constants for the equilibration of gaseous CO_2 with $\text{CO}_2(\text{aq})$. We refer to $\text{CO}_2(\text{aq})$ as the total dissolved carbon dioxide which is the sum of $\text{CO}_2(\text{aq})$ and H_2CO_3 , but does not include the ionized forms, HCO_3^- and CO_3^{2-} . Thus, the solubility equilibrium can simply be represented by



The numerous studies of this equilibrium have been thoroughly appraised by Berg and Vanderzee¹¹⁵ who, in some cases, applied corrections to the reported constants, and arrived at a mean value for K_s° of $(0.034\ 16 \pm 0.000\ 15)$ mol kg⁻¹ atm⁻¹ and a $\Delta \bar{H}_s^\circ = -(19.74 \pm 0.17)$ kJ mol⁻¹ at 25 °C and 101.325 kPa (1 atm). Note that Hu et al.¹¹⁶ selected a K_s° value of $0.034\ 16$ mol dm⁻³ atm⁻¹. From their previous calorimetric measurements,¹¹⁷ which should generally be more reliable, these same authors¹¹⁵ calculated a remarkably similar value

for $\Delta \bar{H}_s^\circ$ of $-(19.75 \pm 0.17)$ kJ mol⁻¹. Moreover, Wilhelm et al.⁷¹ earlier reviewed a narrower range of data and reported a value for $\Delta \bar{H}_s^\circ$ of -19.79 kJ mol⁻¹. The maximum temperature considered in any of these treatments was about 80 °C. Drummond¹¹⁸ has since extended the temperature range of these measurements to 400 °C using PVT methods.

The solubility of $\text{CO}_2(\text{g})$ in seawater has been determined in terms of the apparent equilibrium constant, $K_s' = [\text{CO}_2(\text{aq})]/p_{\text{CO}_2}$, calculated¹¹⁹ as a function of temperature and ionic strength using the data of Harned and Davis:¹²⁰

$$\begin{aligned}pK_s' = -2385.73/T + 14.0184 - 0.0152642T + \\ I(0.28596 - 6.167 \times 10^{-4}T) \quad (6)\end{aligned}$$

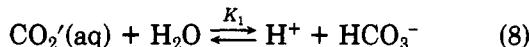
where the ionic strength of seawater can be represented as a function of chlorinity, Cl, by the equation

$$I = 0.00147 + 0.03592 \text{Cl} + 6.8 \times 10^{-5} \text{Cl}^2 \quad (7)$$

For comparison of K_s' values, correction may be needed depending on how the standard state for the original potentiometric measurements is defined.¹¹⁹ Edmond and Gieskes also acknowledged the criticism¹²¹ that seawater would have a different salting-out effect than those of pure NaCl solutions. This restriction notwithstanding, eq 6 represents a good first-order approximation of seawater.

B. Carbonic Acid Ionization

Although expressed as carbonic acid ionization, the majority of studies consider the first ionization constant in the following form:



The distinction will be readdressed in the subsequent section on the kinetics of these processes where a consideration of the actual rate-determining step is critical to the elucidation of the reaction mechanism. Patterson and co-workers^{122,123} determined the true ionization constant for H_2CO_3 by high field conductivity methods in accordance with eq 9. The K_0° value at 25 °C was



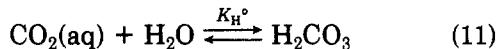
determined to be $(1.72 \pm 0.05) \times 10^{-4}$ mol kg⁻¹ [cf. 1.6×10^{-4} mol kg⁻¹ evaluated at 25 °C and ca. 0.01 ionic strength by the pressure jump, conductometric technique;¹²⁴ and $(2.5 \pm 0.3) \times 10^{-4}$ mol kg⁻¹ at 0 °C in the presence of NaCl, by a flow thermoelectric method¹²⁵]. Of the techniques mentioned, the conductivity method of Wissburn, French, and Patterson¹²² must be considered as the most precise. They measured the temperature dependence of K_0° over the range 5–45 °C and found a small trend in the values with a maximum at ca. 17 °C. This allowed them to calculate $\Delta \bar{H}^\circ$ values which ranged from 2.4 kJ mol⁻¹ at 0 °C to -3.7 kJ mol⁻¹ at 37 °C. However, in the light of results presented later in this section,¹²⁶ if $\log(K_0^\circ/K_w^\circ)$ is plotted against $1/T$, where K_w° is the dissociation constant of water, a straight line results with a slope of $(2.98 \pm 0.04) \times 10^3$ and intercept of 0.25 ± 0.13 (correlation coefficient = 0.99965). This is equivalent to writing eq 9 in the form:



As has been demonstrated by Patterson et al.,¹²⁶ this behavior is typical of acid and base dissociation equi-

libria. Thus, rearranging the equations into their anionic and cationic forms and thereby equalizing the charges on both sides of the equation, reduces $\Delta\bar{C}_p$ to ca. 0. This allows for a more exact linear extrapolation of the temperature dependence data.

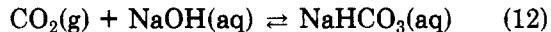
This result may be applied to the equilibrium



which has been likened to a hydration reaction. The equilibrium constant can be determined from the quotient K_1°/K_0° . Thus, at 25 °C, $K_{\text{H}}^{\circ} = (4.48 \times 10^{-7})/(1.74 \times 10^{-4}) = 2.58 \times 10^{-3}$, while at 300 °C, $K_{\text{H}}^{\circ} = (3.18 \times 10^{-9})/(1.38 \times 10^{-3}) = 2.31 \times 10^{-3}$ (the values used for each numerator came from ref 126), so that despite the length of the extrapolation it is clear that K_{H}° varies only slightly with temperature as would be expected for a hydration reaction. This finding justifies the use of eq 8 to describe the overall behavior of $\text{CO}_2(\text{aq}) + \text{H}_2\text{CO}_3$ over a wide range of temperature. Raman spectroscopy^{46,47,54} had confirmed that the only detectable species in such aqueous solutions at ambient conditions is the linear symmetrical CO_2 molecule. However, Kruse and Franck⁴⁸ have now reported a small band at 1017 cm⁻¹ in the Raman spectrum of $\text{CO}_2(\text{aq})$ attributable to the C-OH stretching vibration of H_2CO_3 or HCO_3^- . This band was observed at <40 °C and up to 200 MPa, indicating about 2–3% H_2CO_3 was present at room temperature and 100 MPa. Bar and Sasson⁵⁸ reported an analysis of the ¹³C NMR spectra of $\text{HCO}_3^-/\text{CO}_3^{2-}$ solutions indicating the existence of both H_2CO_3 and dissolved CO_2 at virtually negligible levels at 31 °C. Abbott and co-workers⁵⁴ could not detect either species by this technique.

C. Aqueous Carbon Dioxide Ionization

Considerable attention has been paid to the exact measurements of K_1° at ambient conditions using mainly potentiometric techniques,^{120,127–132} with perhaps the study of Harned and Davis¹²⁰ being the most noticeable. Berg and Vanderzee¹¹⁵ combined three sets of emf data^{120,130,131} to obtain the thermodynamic parameters for the hydrolysis of $\text{CO}_2(\text{g})$ to form $\text{H}^+(\text{aq})$ and $\text{HCO}_3^-(\text{aq})$. This calculation depended on a knowledge of the standard enthalpy for the reaction



i.e., $\Delta\bar{H}^{\circ} = -(66.40 \pm 0.14) \text{ kJ mol}^{-1}$, which was determined by calorimetry, as well as the standard enthalpy for the ionization of water $-(55.81 \pm 0.42) \text{ kJ mol}^{-1}$. Combination of these parameters resulted in a $\text{p}K_1^{\circ}$ value of 6.351 (cf. the model of Peiper and Pitzer,¹³³ $\text{p}K_1^{\circ} = 6.355$, which incorporated very recent emf measurements by Roy et al.¹³² at high concentration levels), a $\Delta\bar{H}_1^{\circ}$ of $9.155 \pm 0.063 \text{ kJ mol}^{-1}$, and $\Delta\bar{S}_1^{\circ}$ of $-(90.9 \pm 0.3) \text{ J K}^{-1} \text{ mol}^{-1}$ at 25 °C. Note that Millero¹³⁴ has since reanalyzed the data base and arrived at a similar value of $\Delta\bar{H}_1^{\circ}$ of 9.33 kJ mol^{-1} . The $\text{p}K_1^{\circ}$ value reported by Berg and Vanderzee is very close to the original values of Harned and Davis¹²⁰ (6.352) and MacInnes and Belcher¹³¹ (6.343) who each used their own measured values of K_s° . Two sets of conductance measurements resulted in $\text{p}K_1^{\circ}$'s of 6.365^{102} and 6.382^{135} . Slightly more recent conductance measurements,¹³⁶ which extended the conditions to 101.325 MPa and 300 °C, diverged substantially from the above parameters

TABLE IV. Partial Molar Volume Changes for the Dissociation of "Carbonic Acid" at 101.325 kPa

method	temp, °C	$-\Delta\bar{V}_1^{\circ}, \text{cm}^3 \text{ mol}^{-1}$	ref
glass electrode	22.0	25.4 (buffered)	129
	22.0	25.5 (buffered)	a
	22.0	26.6 (unbuffered)	a
conductance	25.0	26.5 (27.7) ^b	138
	25.0	27.6	102
density	25.0	29.0	137

^a Distéche, A.; Distéche, S. *J. Electrochem. Soc.*, 1965, 112, 350. ^b Recalculated by Read¹⁰² from Ellis's original data.¹³⁸

at 25 °C and 101.325 kPa, e.g., $\text{p}K_1^{\circ} = 6.37$, $\Delta\bar{H}_1^{\circ} = 6.78 \text{ kJ mol}^{-1}$, and $\Delta\bar{S}_1^{\circ} = -382 \text{ J K}^{-1} \text{ mol}^{-1}$, and even greater discrepancies at 300 °C,¹²⁶ cast doubt on the validity of these results.¹³⁶

The heat capacity data are based on the free-energy measurements, and therefore subjected to possible error as discussed later in this section. The original $\Delta\bar{C}_p$ value of Harned and Davis¹²⁰ is $-374 \text{ J K}^{-1} \text{ mol}^{-1}$ compared to recent interpolated values of $-377 \text{ J K}^{-1} \text{ mol}^{-1}$ ¹³⁴ and $-388 \pm 27 \text{ J K}^{-1} \text{ mol}^{-1}$ ¹²⁶ at 25 °C and 101.325 kPa.

The partial molal volume change associated with eq 8 has been determined by a number of methods, with again the preponderance involving emf measurements. The results summarized in Table IV are generally in good agreement, except for the early density measurements of Owen and Brinkley.¹³⁷ The observation by Ellis¹³⁸ that $\Delta\bar{V}_1$ increases with increasing pressure ($\Delta\bar{V}_1^{\circ} = -20.7 \text{ cm}^3 \text{ mol}^{-1}$ at 303.975 MPa and 25 °C) was substantiated by Read.¹⁰² However, Read¹⁰² investigated the temperature dependence of K_1° over a much larger temperature range of 25.0–250.1 °C and found that $\Delta\bar{V}_1^{\circ}$ decreases markedly with increasing temperature at constant pressure ($\Delta\bar{V}_1^{\circ} = -88 \text{ cm}^3 \text{ mol}^{-1}$ at 250 °C and 303.975 MPa), so that obviously no evidence for a maximum as suggested by Ellis¹³⁸ was observed. Typical of other weak acids and bases, such as acetic acid,¹³⁹ a linear relationship exists between $\Delta\bar{V}_1^{\circ}$ and $\Delta\chi_1^{\circ}$, the standard partial molar compressibility change, at constant pressure up to 250 °C, and the slopes of these isobars become less with increasing pressure.¹⁰² Contributing somewhat to this temperature dependence of $\Delta\bar{V}_1^{\circ}$, the partial molar volume of $\text{CO}_2(\text{aq})$ was calculated to increase from 34.3 (33.2¹⁰¹) to 47.4 $\text{cm}^3 \text{ mol}^{-1}$ over the range 25–200 °C.¹⁰² Note, however, that literature values for $\bar{V}^{\circ}(\text{CO}_2(\text{aq}))$ at 25 °C vary sharply. Millero and Berner¹⁴⁰ proposed that $\bar{V}^{\circ}(\text{H}_2\text{CO}_3) = \bar{V}^{\circ}(\text{CO}_2(\text{aq})) = 31.3 \text{ cm}^3 \text{ mol}^{-1}$.

The discussion of reaction 8 has been limited to this point to results extrapolated to infinite dilution. Patterson et al.¹²⁶ recently reported the results of a potentiometric study of this reaction in NaCl media, up to 5 m, and to temperatures of 300 °C at the saturated vapor pressures of these solutions. These data are of more practical interest. Two sets of equations were presented to model these data as well as the results of some previous research.^{102,117,130,131,138} Both models have in common a Bronsted-Guggenheim expression for ionic activity coefficients to calculate the activity coefficient quotient for eq 8. The difference in the two models is that one is based on the expression

$$\partial^2 \ln K / (\partial T \partial(1/T)) p_{\text{sat}} = a_1 + a_2 T + a_3 / T^2 \quad (13)$$

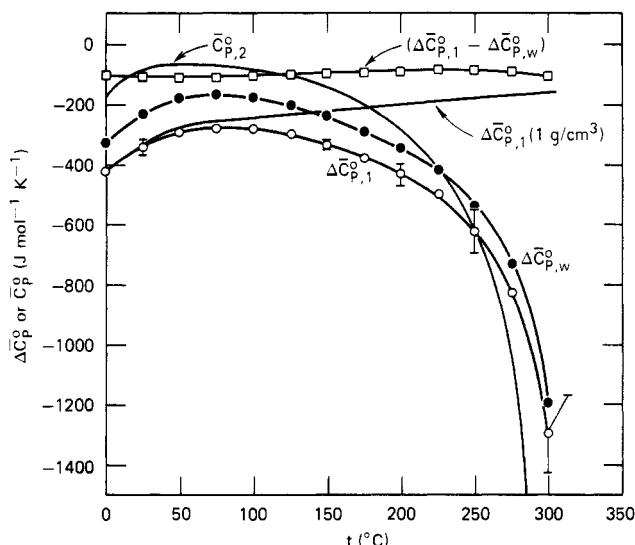
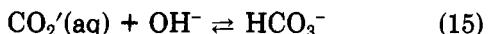


Figure 1. Heat capacity functions at infinite dilution along the saturation vapor pressure curve and at unit density: $\Delta\bar{C}_p,1^\circ$, the change in heat capacity for the first ionization of aqueous carbon dioxide; $\Delta\bar{C}_{p,w}^\circ$, the change in heat capacity for the ionization of water; $\bar{C}_{p,2}^\circ$, the partial molar heat capacity of sodium chloride in water. Reprinted with permission from ref 126. Copyright 1982, Pergamon Press Ltd.

whereas the basic assumption in the other involves the partial molal volumes of ions

$$\bar{V}_1^\circ = b_{1,i} - b_{2,i}\beta + b_{3,i}\bar{V}_w^\circ \quad (14)$$

where β is the compressibility coefficient and \bar{V}_w° is the molar volume of water. As a check of the models, the $\Delta\bar{H}_1^\circ$ value obtained from an analysis of all these data is $9.06 \pm 0.12 \text{ kJ mol}^{-1}$ at 25°C , which compares favorably with the value of Berg and Vanderzee¹¹⁵ shown above. As alluded to earlier in this section, the values of $\Delta\bar{C}_p^\circ$ and $\Delta\bar{V}_1^\circ$ decrease dramatically as the temperature approaches 300°C along the saturation vapor pressure curve. This behavior, which is illustrated in Figures 1 and 2, was said to stem from the temperature dependencies of the first and second derivatives of the dielectric constant of water with respect to T .¹²⁶ In keeping with this explanation, the heat capacity and volume changes were virtually constant over the same temperature range when calculated at unit density. Alternatively, when eq 8 is written in its anionic form



which essentially removes the contributions to $\Delta\bar{C}_p^\circ$ and $\Delta\bar{V}_1^\circ$ from the ionization of water, both parameters are substantially less dependent on temperature and salt concentration. In fact, $\Delta\bar{C}_p \approx -100 \text{ J K}^{-1} \text{ mol}^{-1}$ over the entire range, while $\Delta\bar{V} \approx -7 \text{ cm}^3 \text{ mol}^{-1}$ up to 100°C , then decreases to $-20 \text{ cm}^3 \text{ mol}^{-1}$ at $I = 0$ and 300°C , and to $-60 \text{ cm}^3 \text{ mol}^{-1}$ at 5 M at 300°C . The authors¹²⁶ tabulate the parameters of $\log K_1$, $\Delta\bar{G}_1$, $\Delta\bar{H}_1$, $\Delta\bar{S}_1$, $\Delta\bar{C}_p$, and $\Delta\bar{V}_1$, based on model I, at 25°C intervals over the range 0 – 300°C , at ionic strengths of 0 , 0.1 , 0.5 , 1.0 , 3.0 , and 5.0 . The immediate conclusion of this work is that "carbonic acid" becomes weaker with increasing temperature and decreasing pressure or salt concentration.

A further practical aspect of eq 8 concerns the role played by this reaction in seawater. Potentiometric studies^{121,129,141–144} have dealt with this problem directly. For comparison, $I = 0.75$ (NaCl), which corresponds approximately to the ionic strength of seawater at a chlorinity of 20.0% , Distèche and Distèche¹²⁹ reported

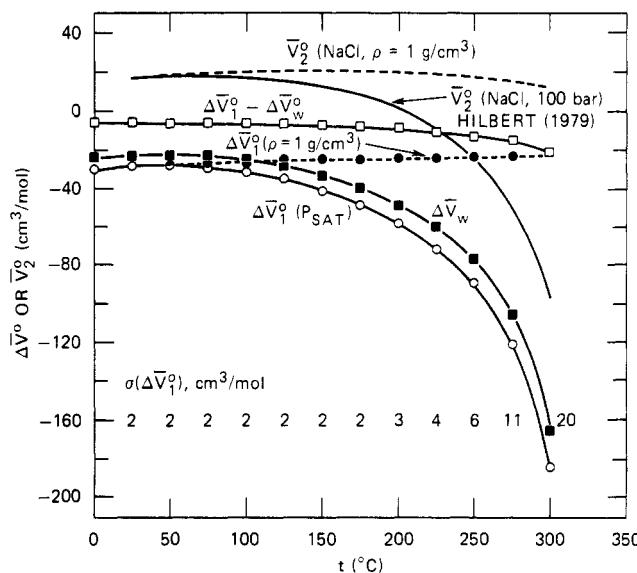


Figure 2. Volume functions along the saturation vapor pressure curve and at unit density; subscripts as in Figure 1. Uncertainties (3σ) are shown by the row of numbers across the figure. Reprinted with permission from ref 126. Copyright 1982, Pergamon Press Ltd.

a pK_1° of 5.995 at 22°C and 101.325 kPa (K_1° , concentrations in units of molarity). In natural seawater, the effects of the divalent ions Mg^{2+} , Ca^{2+} , and SO_4^{2-} must be considered as well as the additional buffering capacity of boric acid. Millero¹³⁴ treats the additional complication of the different standards used to calibrate the pH electrodes, namely the NBS and Tris pH scales, with the latter preferred by Hansson¹⁴³ as it maintains a continuity of medium because the standardizing buffer solution is made up in seawater. Millero¹³⁴ concluded in favor of the NBS system. An apparent dissociation constant, K_1' , is defined as $a_{\text{H}^+}[\text{HCO}_3^-]_{\text{total}}/[\text{CO}_3^{2-}(\text{aq})]_{\text{total}}$, where [] refers to concentrations in molarity units. Some typical values of pK_1' at 25°C , atmospheric pressure, and 20% chlorinity are: 5.93 ,¹⁴³ 6.000 ,¹⁴¹ 6.06 ,¹⁴⁴ 6.08 ,¹²¹ and 6.00 (22°C),¹²⁹ where the first value was measured on the Tris scale which indeed reads lower (e.g., 25°C and $\text{Cl} = 19.4\%$, $\Delta\text{pH} = 0.144$).¹³⁴ At 100 MPa , $\text{Cl} = 20\%$ and 22°C , $pK_1' = 5.663$ ¹²⁹ so that it is clear that increasing chlorinity¹⁴³ and pressure cause "carbonic acid" to become a stronger acid in seawater, thus complying with the behavior in "pure" water. However, over the narrow temperature range investigated (5 – 35°C), which is of relevance to the seawater system, increasing temperature increases the strength of "carbonic acid" in seawater.

On a more quantitative basis, Edmond and Gieskes¹¹⁹ combined earlier results^{121,129,130,144} in the following empirical equation using the temperature dependence established for K_1° .¹³⁰

$$\begin{aligned} pK_1' = & 3404.71/T + 0.032786T - 14.7122 - 0.19178\text{Cl}^{1/3} \\ & (16) \end{aligned}$$

Millero¹³⁴ used a somewhat different equation to fit previous data over the range 0 – 50°C and $0 \leq \text{SI} \leq 40\%$ with the generalized equation

$$\ln K_1' - \ln K_w = (a_0 + a_1/T + a_2 \ln T)\text{SI}^{1/2} + b_0\text{Cl} \quad (17)$$

where a_0 , a_1 , a_2 , and b_0 are constants ($a_2 = 0$ in this case), and $\ln K_w$ is determined from a similar equation, and SI is the salinity of the seawater and is equivalent to 1.80655 (Cl ‰).

A general equation¹⁴⁵ to rigorously describe the pressure dependence of K_1^0 in seawater is

$$\ln (K_i^P/K_i^0) = -(\Delta \bar{V}_i/RT)P + (0.5\Delta \bar{\kappa}_i/RT)P^2 \quad (18)$$

where $\Delta \bar{V}_i$ and $\Delta \bar{\kappa}_i$ are the changes in the volumes and compressibilities for ionization. The values of $\Delta \bar{V}_1'$ and $\Delta \bar{\kappa}_1'$ are obtained from the following:

$$-\Delta \bar{V}_1' = 25.50 + 0.151(\text{SI} - 34.8) - 0.1271t \quad (19)$$

$$-10^3 \Delta \bar{\kappa}_1' = 3.08 + 0.578(\text{SI} - 34.8) - 0.0877t \quad (20)$$

At $t = 25^\circ\text{C}$ and $\text{Cl} = 19.26\%$, $\Delta \bar{V}_1' = -22.3 \text{ cm}^3 \text{ mol}^{-1}$ and $\Delta \bar{\kappa}_1' = 9 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ atm}^{-1}$. Based on the partial molal volumes of the individual species,¹⁴⁰ $\Delta \bar{V}_1 = -21.7 \text{ cm}^3 \text{ mol}^{-1}$, which assumes $\bar{V}[\text{H}^+(\text{aq})] = -3.7 \text{ cm}^3 \text{ mol}^{-1}$, $\bar{V}[\text{CO}_2'(\text{aq})] = 31.3 \text{ cm}^3 \text{ mol}^{-1}$. By ignoring the effects of change in salinity and by considering the solvated species to be incompressible, a simple expression for $\Delta \bar{V}_1$ can be presented, viz.¹¹⁹

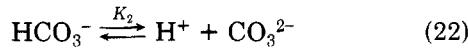
$$\Delta \bar{V}_1' = -(24.2 - 0.085t) \quad (21)$$

which at $t = 25^\circ\text{C}$ results in a $\Delta \bar{V}_1' = -22.1 \text{ cm}^3 \text{ mol}^{-1}$. Note eq 19 gives a value of $-20.1 \text{ cm}^3 \text{ mol}^{-1}$ at the lower chlorinity of 11.1‰, so that eq 21 represents at least a good first-order approximation of $\Delta \bar{V}_1'$. These values appear preferable to $-18.8 \text{ cm}^3 \text{ mol}^{-1}$ derived^{119,140} from the pressure study of Distèche and Distèche¹²⁹ at $\text{Cl} = 20\%$ and 22°C .

It is often assumed that divalent metal ions can form ion pairs with carbonate ions at ambient conditions, an assumption of particular importance in modeling seawater equilibria. However, their existence and more particularly those of alkali metal carbonate and bicarbonate ion pairs under these conditions is disputable. Nevertheless, Nakayama^{127,146} recalculated the original results of Harned and Davis¹²⁰ by allowing for the formation of NaHCO_3^0 ion pairs in the mass and charge balance equations. The $\text{p}K_1$ value was only slightly affected (6.356 at 25°C) and, as expected, the association constant proved to be very small, viz. 1.5 ± 0.2 . Independent potentiometric measurements by Butler and Huston⁹¹ gave similarly small values for the formation of NaHCO_3^0 ion pairs of 0.5 and 0.8. Although, as these authors⁹¹ point out, these data can be equally well or better fitted to the conventional model which does not include ion pairs. This important, general statement is appropriate to all the ion pairs at ambient conditions discussed here, such that until a more precise solution theory is developed to prove otherwise, such apparent effects are better described by conventional activity coefficients of the individual ionic species.

D. Bicarbonate Ion Ionization

The most generally accepted^{115,147} equilibrium constant for this reaction (eq 22) was determined poten-



tiometrically by Harned and Scholes¹⁴⁸ to be 4.69×10^{-11} (4.60×10^{-11} ¹³³ and 4.68×10^{-11} ¹³⁴) at 25°C and atmospheric pressure. This is reasonably close to pre-

vious work of MacInnes and Belcher¹³¹ who reported a value of 5.61×10^{-11} for the potassium rather than the sodium salt, but in the main their values over the temperature range 0 – 50°C are lower than previously reported. However, there is excellent agreement with the conductivity data of Ryzhenko,¹³⁵ $K_2^\circ = 4.70 \times 10^{-11}$. Again a recalculation of Harned's value¹⁴⁸ by Nakayama^{127,146} led to an ion-pair association constant for NaCO_3^- of 3.6 which compares to 8 ± 2 derived by Butler and Huston.⁹¹

It is noteworthy that Plummer and Busenberg¹⁴⁹ have also reevaluated the data for K_s° , K_1° , and K_2° and report these values in the general form

$$\log K^\circ = A + BT + C/T + D \log T + E/T^2 \quad (23)$$

and claim validity for this expression to 250°C at the appropriate vapor pressure for water. They also derived similar expressions for the association constants of the ion pairs CaHCO_3^+ and CaCO_3^0 as a function of pressure, except that $E = 0$ in these equations (see section VII for more details), but again these values are too small to definitely establish their existence.

Berg and Vanderzee^{115,117} recorded a standard enthalpy of ionization of $(14.70 \pm 0.10) \text{ kJ mol}^{-1}$ with a corresponding entropy of $-148.4 \pm 0.4 \text{ J K}^{-1} \text{ mol}^{-1}$ at 25°C and 101.325 kPa . Millero's¹³⁴ treatment of the earlier data¹⁴⁸ yielded 15.1 kJ mol^{-1} for $\Delta \bar{H}_2^\circ$.

Flow calorimetric measurements by Larson and co-workers¹⁴⁷ were used to derive a $\Delta \bar{C}_p^\circ$ value of $-247 \pm 8 \text{ J K}^{-1} \text{ mol}^{-1}$ at 25°C . Earlier estimates were based on the double differentiation of $\log K = f(T)$ with respect to T by Harned and Scholes¹⁴⁸ and others,¹³⁴ resulting in a range of values, -272 ,¹⁴⁸ -280 , and $-213 \text{ J K}^{-1} \text{ mol}^{-1}$.¹³⁴ However, the latter method can give rise to large uncertainties in $\Delta \bar{C}_p$ in those cases where the parameters in the equation of $\log K = f(T)$ are strongly correlated.^{150,151} Therefore, the calorimetric measurements are intrinsically more reliable. Larson et al.¹⁴⁷ recalculated the results of a previous calorimetric study of Perron, Desnoyers, and Millero¹⁰⁸ to obtain a corrected $\Delta \bar{C}_p^\circ$ of $-249 \text{ J K}^{-1} \text{ mol}^{-1}$.

Larson, Zeeb, and Hepler¹⁴⁷ measured a $\Delta \bar{V}_2^\circ$ at 25°C of $-(29.2 \pm 1.2) \text{ cm}^3 \text{ mol}^{-1}$ from density measurements of $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ buffers. Much earlier less negative values of 27.7 and $25.6 \text{ cm}^3 \text{ mol}^{-1}$ were reported from density¹⁵² and potentiometric methods.¹²⁹ The partial molar volumes reported for NaHCO_3 and Na_2CO_3 would result in a $\Delta \bar{V}_2^\circ = -28.4 \text{ cm}^3 \text{ mol}^{-1}$ assuming $\bar{V}^\circ[\text{H}^+(\text{aq})] = 0$ and $\bar{V}^\circ[\text{Na}^+(\text{aq})] = -1.2 \text{ cm}^3 \text{ mol}^{-1}$. In summary, Larson et al.¹⁴⁷ combined their results with selected values in the literature¹⁰⁸ to give preferred values of $\Delta \bar{C}_p^\circ = -250 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta \bar{V}_2^\circ = -28.7 \text{ cm}^3 \text{ mol}^{-1}$ at 25°C and 101.325 kPa . Their experimental values for the individual ions are: $\phi_c^\circ = -55 \{\text{HCO}_3^-(\text{aq})\}$ and $-302 \text{ J K}^{-1} \text{ mol}^{-1} \{\text{CO}_3^{2-}(\text{aq})\}$; and $\phi_v^\circ = 24.8$ and $-4.4 \text{ cm}^3 \text{ mol}^{-1}$, respectively, based on the assumption $\phi^\circ \{\text{H}^+(\text{aq})\} = 0$.

Potentiometric measurements of the dissociation of DCO_3^- in D_2O over the range 5 – 50°C led to the constants shown in Table V.¹⁵³ The preferred parameters for eq 22 are also listed for comparison. It is interesting that in comparison with other acids such as acetic, acetic- d_3 , and H_2PO_4^- the differences in $\Delta \bar{S}^\circ (\text{D}_2\text{O}) - \Delta \bar{S}^\circ (\text{H}_2\text{O})$ and $\Delta \bar{C}_p^\circ (\text{D}_2\text{O}) - \Delta \bar{C}_p^\circ (\text{H}_2\text{O})$ are all small and the values are equal within the experimental un-

TABLE V. Comparison of the Standard Thermodynamic Constants for the Dissociation of HCO_3^- in water and DCO_3^- in Deuterium Oxide¹⁵³ at 25 °C and 101.325 kPa

constant	HCO_3^-	DCO_3^-
$\text{p}K_2^\circ$	10.329	11.076 (11.00, ^a 10.85 ^b)
$\Delta\bar{H}_2^\circ$ (kJ mol ⁻¹)	14.70	17.62 ± 0.03
$\Delta\bar{S}_2^\circ$ (J K ⁻¹ mol ⁻¹)	-148.4	-153.0 ± 0.1
$\Delta\bar{C}_p^\circ$ (J K ⁻¹ mol ⁻¹)	-250	-257 ± 4
$\Delta\bar{V}_2^\circ$ (cm ³ mol ⁻¹)	-28.7	

^a Glasoe, P. K.; Schaleger, L. L.; Long, F. A. *J. Am. Chem. Soc.* 1964, 86, 1. ^b Curry, J.; Hugus, Z. *Z. Z. J. Am. Chem. Soc.* 1944, 66, 653.

certainties. The equivalent term for $\Delta\bar{H}^\circ$ is considerably greater than HCO_3^- .

Empirical equations were again proposed by Edmond and Gieskes,¹¹⁹ and Millero¹³⁴ to quantify these relationships. The former equation is as follows:

$$\text{p}K_2' = 2902.39/T + 0.02379T - 6.4710 - 0.4693\text{Cl}^{1/3} \quad (24)$$

while Millero's equation again takes the form of eq 17 with $a_2 = 0$. Mehrbach and co-workers¹⁴¹ have proposed a much more elaborate equation involving the independent variables T and Sl , leading to a $\text{p}K_2'$ value of 9.115 at 25 °C and $\text{Sl} = 35\%$.

The partial molar volume changes are also calculated in the same two ways described for carbonic acid, viz.^{119,134}

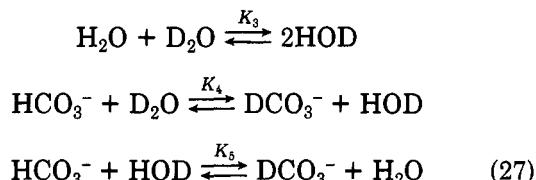
$$\Delta\bar{V}_2' = -(16.4 - 0.04t) \quad (25)$$

$$-\Delta\bar{V}_2' = 15.82 - 0.321(\text{Sl} - 334.8) + 0.0219t \quad (26)$$

Thus, at 25 °C and $\text{Sl} = 35\%$, $\Delta\bar{V}_2' = -15.4 \text{ cm}^3 \text{ mol}^{-1}$ ¹¹⁹ and $-16.4 \text{ cm}^3 \text{ mol}^{-1}$.¹³⁴ From partial molal volume data of the individual ions, $\Delta\bar{V}_2' = -15.9 \text{ cm}^3 \text{ mol}^{-1}$,¹⁴⁰ assuming $\bar{V}_2[\text{CO}_3^{2-}(\text{aq})] = 19.2 \text{ cm}^3 \text{ mol}^{-1}$.¹³⁴ These values are in marked disagreement with the $\Delta\bar{V}_2'$ value of $-10.8 \text{ cm}^3 \text{ mol}^{-1}$ at 22 °C and $\text{Sl} = 35\%$. Note also that eq 25 and 26 predict opposite temperature effects, but the absolute changes are small in both cases, i.e., $\leq 0.8 \text{ cm}^3 \text{ mol}^{-1}$ for 15–35 °C. The dominant effect is the salinity; thus, at lower values, i.e., $\text{Sl} = 20\%$, $\Delta\bar{V}_2'$ according to eq 26 becomes $-21.1 \text{ cm}^3 \text{ mol}^{-1}$ at 25 °C leading to larger discrepancies between eq 25 and 26.

E. Isotopic Exchange Equilibria

These equilibria have been represented by Oliver and Davis⁴⁹ as follows:



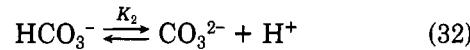
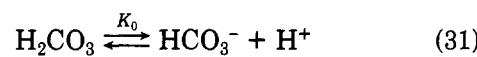
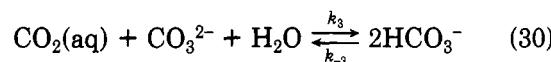
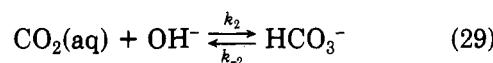
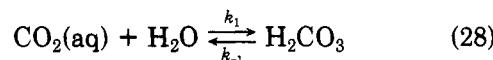
They used Raman spectroscopy to monitor the 1017-cm⁻¹ band associated with HCO_3^- and then obtained a quantitative measure of the DCO_3^- concentration after subtracting the HCO_3^- contribution from the band centered at 1030 cm⁻¹, which is attributable to DCO_3^- . From the known value for K_3 of 3.8 at 25 °C, values for K_4 and K_5 were estimated at 1.9 ± 0.2 and 0.50 ± 0.05 , respectively, for 1 M NaHCO_3 solutions.

Similar values were obtained for 2.9 M KHCO_3 solutions.

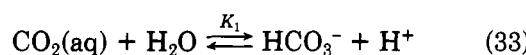
IV. Kinetics of Carbon Dioxide Hydrolysis and Carbonic Acid Dehydration

The rates of the reactions within this system have been studied extensively by many researchers using a wide variety of techniques.^{69,154,155} The history of these endeavors up until 1960 has been particularly well documented by Kern,¹⁵⁴ who gave a critical evaluation of the experimental methods. The inordinate depth of these kinetic data is primarily due to their importance in biological and environmental sciences, and partially to the fact that they are convenient for examining new rapid-response techniques and improvisations. Note that the biological aspects of these reactions, involving mainly enzyme catalysis, are discussed in section XIII.

The following set of equations adequately describes the entire "uncatalyzed" system:



Below a pH of ca. 7.4, coincidentally the pH of blood, eq 28 and 31 dominate. Indeed, carbonic acid never represents more than 1% of the total dissolved CO_2 because $k_{-1} >> k_1$. In addition, calculations based on Coulombic interactions for diffusion-controlled processes yield¹⁵⁶ a value for the rate of protonation of HCO_3^- of ca. $6.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, in good agreement with the value reported by Eigen¹⁵⁷ of $4.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ which he obtained from an electrical-jump relaxation technique. This emphasizes the speed of reaction 31, and by inference eq 32, and permits the estimation of the rate constant for the protolytic dissociation of carbonic acid ($1.5 \times 10^7 \text{ s}^{-1}$) when coupled with the value of K_0 . Thus H_2CO_3 acts as an intermediate in the net reaction



with K_1 being referred to as the "apparent" acid dissociation constant.

Kern¹⁵⁴ has cataloged the problems in the interpretation of the pioneer work in this field and declared that it was not until the meticulous study of Faurholt¹⁵⁸ in 1924 that a meaningful value for k_{-1} was reported. A summary of the subsequent rate data is given in Table VI.

Of the principal methods utilized, spectrophotometric measurements invariably involved the use of indicators to transpose the change in pH associated with reaction 33 into a spectral signal. Conductivity provides a direct response to the decrease in charge accompanying reaction 33. It is significant that the applicability of oxygen-exchange studies relies on the slow rate of oxygen exchange between either HCO_3^- or CO_3^{2-} with

TABLE VI. Summary of Kinetic Data for the Dehydration of Carbonic Acid at 25 °C

year	k_{-1} , s ⁻¹	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , J K ⁻¹ mol ⁻¹	method	ref
1924	29.3 ^{a,b}			quenching	158
1927	17.4 ^b			H ₂ -electrode and conductometric	c
1933	21.7			manometric and spectrophotometric	d
1941	27.1 ^b	68.1	11	flow thermometric	125
1953	24.4 ^b	68.2	10	flow spectrophotometric	e
1957	24.4 ^a	68.2	10	stopped-flow glass electrode	f
1958	23.0 ^b	62.9	-8	flow spectrophotometric	g
1961	15.1			temperature-jump spectrophotometric	h
1969	22.2			stopped-flow calorimetric	i
1970	27.9 ^b	60.8	-13	stopped-flow spectrophotometric	j
1972	16.7			stopped-flow spectrophotometric	k
1973	22.1	52.7	-42	concentration-jump spectrophotometric	155
1973	29.4	51.4	-46	pressure-jump conductometric	155
1973	21.0	55.2	-35	stopped-flow spectrophotometric	155
1978	12.4 ^l			rapid mixing-pH statt	161
1979	25.1	73.4	28	stopped-flow spectrophotometric	m
1980	28.0			pressure-jump conductometric	156
1981	25.7 ⁿ			stopped-flow calorimetric	o
1982	18.7			stopped-flow spectrophotometric	163

^a Corrected by the factor 2.3 as described.¹⁵⁴ ^b Interpolated from the temperature dependence of k_{-1} . ^c Saal, R. N. J. *Recl. Trav. Chim. Pay-Bas* 1928, 47, 264. ^d Brinkman, R.; Margaria, R.; Roughton, F. J. W. *Philos. Trans. Soc. London* 1933, A232, 65. ^e Dalziel, K. *Biochem. J.* 1953, 55, 79. ^f Sirs, J. A. *Trans. Faraday Soc.* 1958, 54, 207. ^g Scheurer, P. G.; Brownell, R. M.; Lu Valle, J. E. *J. Phys. Chem.* 1958, 62, 809. ^h Eigen, M.; Kustin, K.; Maass, G. *Z. Phys. Chem. (Wiesbaden)* 1961, 30, 130. ⁱ Balko, B.; Berger, R. L.; Friau, W. *Anal. Chem.* 1969, 41, 1506. ^j Soerensen P. E.; Jensen, A. *Acta. Chem. Scand.* 1970, 24, 1483. ^k Lal, L. C.; Maren, T. H. *Biochim. Biophys. Acta* 1972, 261, 70. ^l Calculated by assuming $K_1 = 2.49 \times 10^{-4}$ at 25 °C,¹²² corrected to an ionic strength of 0.1. ^m Morelli, B. *Anal. Chim. Acta* 1979, 106, 73. ⁿ 24 °C. ^o Balko, B.; Bowen, P.; Berger, R. L. *J. Biochem. Biophys. Methods* 1981, 4, 1.

TABLE VII. Summary of Kinetic Data for the "Acid" Hydrolysis of CO₂ at 25 °C and I = 0

year	$10^2 k_1$, s ⁻¹	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , J K ⁻¹ mol ⁻¹	method	ref
1940	2.75	67.9	-46	¹³ C and ¹⁸ O exchange	a
1951/1956	2.57	61.1 ^b	-71 ^b	manometric	165, 166
1967	2.70 ^c	71.1 ^c	-36 ^c	¹⁸ O exchange	159
1969	3.13 ^d	67.8	-46	¹⁸ O exchange	167
1969	5.00 ^b			manometric	173
1977	2.6 ^e			quenching, titration	162
1982	3.7			pH statt	558

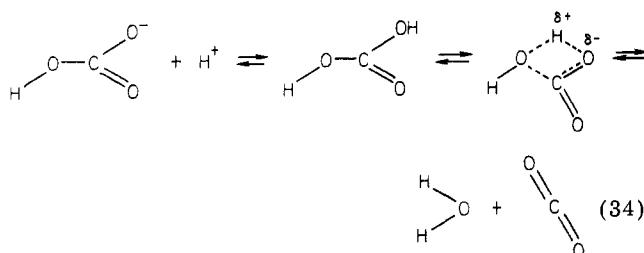
^a Mills, G. A.; Urey, H. C. *J. Am. Chem. Soc.* 1940, 62, 1019. ^b Recalculation¹⁶⁶ of original results¹⁶⁵ led to ΔH^\ddagger being temperature dependent with the resulting empirical equation: $\log k_1 = 329.85 - 110.541 \ln T - 17265.4/T$; cf. $\log k_1 = 195.3 - 63.590 \ln T - 11715.8/T$.¹⁷³ ^c $I = 1.5$ M. ^d Interpolated to 25 °C. ^e $I = 1.0$ M.

water, such that the rate of hydrolysis through CO₂ is rate-determining. Manometric methods take advantage of the rapid transfer of CO₂(gas) ⇌ CO₂(aq) from well-stirred solutions to provide a discernible pressure change during the reaction. Considering the diversity of techniques and their degrees of sophistication, the agreement between the k_{-1} values in Table VI is quite remarkable. This comparison can be more freely made with the knowledge that k_{-1} is relatively insensitive to variations in ionic strength, as demonstrated by Atkinson et al.¹⁵⁵ for ionic strengths from 5×10^{-3} to 3 M NaCl or NaBr, for which ΔG^\ddagger remained constant at ca. 66 kJ mol⁻¹. A fit of the combined data in Table VI gave the activation parameters, $\Delta H^\ddagger = 60.7 \pm 1.8$ kJ mol⁻¹ and $\Delta S^\ddagger = -15 \pm 6$ J K⁻¹ mol⁻¹, while k_{-1} at 25 °C was interpolated at 23.7 s⁻¹.

In the majority of cases, the hydration rate constant, k_1 , was determined from the relationship $k_1 = k_{-1}K_H$, where K_H is the hydrolysis equilibrium constant (28). A typical K_H value at 25 °C and zero ionic strength is 2.6×10^{-3} ,¹²² leading to an average value of k_1 of 6.2×10^{-2} s⁻¹ under these conditions. However, there are three examples where hydration was studied directly, and these data are shown in Table VII. In contrast to dehydration, hydration rate constants are greatly affected by variations in ionic strength,^{155, 159} despite the

fact that the reactants are neutral species. The combined data^{155, 159} show an approximate linear decrease in k_1 with increasing ionic strength over the range 0.005 to 3.0 M, with the relationship being: $k_1 = -(8 \pm 3) \times 10^{-3}I + (3.9 \pm 0.5) \times 10^{-2}$ s⁻¹. As will be shown for k_2 , the ionic strength effect remains somewhat controversial as Dennard and Williams¹⁶⁰ observed no change in k_1 at 0 °C within an overall uncertainty of ± 4.7% up to $I = 1$ M (KCl) at different pH values. The rate of CO₂ hydration has been compared to the hydration rates of some carbonyl compounds and shown to be not only slower, but also not strongly acid catalyzed. These effects were attributed to the unique linear structure of the CO₂ molecule.

On a mechanistic level, the dehydration (dehydrolysis, decarboxylation, or decomposition) rate of HCO₃⁻ in H₂O and D₂O at 25 °C was compared with the corresponding reaction of the alkyl carbonates, CH₃OCO₂⁻, C₂H₅OCO₂⁻, and sec-C₄H₉OCO₂⁻, based on pH-statt data.¹⁶¹ For the acid-catalyzed reaction analogous to reaction 33, $k_{-1}(H_3O^+)/k_{-1}(D_3O^+)$ averaged 0.6^{161, 162} which, when coupled with the observed acid-catalysis effect, implied a mechanism intermediate between a preequilibrium proton transfer and the other extreme of a rate-determining proton-transfer step. Therefore, the mechanistic form of eq 33 becomes



where H would be replaced by an alkyl group in the case of the alkyl carbonates.

A study¹⁶³ of the effect of pressure on k_{-1} yielded an activation volume of $+6.4 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$ (25°C and $I = 0.5 \text{ M}$). This is considered as direct evidence for a dissociative mechanism with the volume increase mainly reflecting the elongation of the C–O bond as shown in eq 34. When an interpolated value for ΔV (eq 28) of $-17.2 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$ (25°C and $I = 0.5 \text{ M}$) was used, a ΔV^* for the hydrolysis reaction was calculated as $-10.8 \pm 1.9 \text{ cm}^3 \text{ mol}^{-1}$, which is also compatible with the overriding effect of C–O bond formation in the transition state. Secondary contributions to ΔV^* from proton transfer, where bonds are partially formed and broken, will tend to cancel out, while electrostriction increases due to partial charge separation are small and negative in both directions.

The value of k_{-1} was also measured as a function of the alcohol content of the solution.¹⁶⁴ In both mixtures of water/methanol and water/*tert*-butyl alcohol, maxima in ΔH^* with increasing alcohol content were observed. On the other hand, ΔS^* increased monotonically in the former [$x(\text{CH}_3\text{OH})$, 0–0.8], but showed a maximum in the latter at $x(\text{BuOH}) = 0.06$. Based on similarities to organic solvolysis reactions, these results were construed as evidence for a decrease in polarity and hydrogen bonding as the initial state, H_2CO_3 , rearranges to the transition state. This interpretation is also compatible with the formulation in eq 34.

In the general pH range 7–10, eq 28–32 contribute to the dynamics of aqueous CO_2 chemistry, while beyond a pH of 10, eq 29, 30, and 32 are alone responsible. The kinetic parameters associated with eq 29 are presented in Table VIII. Combining all these data leads to the activation parameters: $\Delta H^* = 54.4 \pm 2.4 \text{ kJ mol}^{-1}$ and $\Delta S^* = 12 \pm 8 \text{ J K}^{-1} \text{ mol}^{-1}$. It appears generally accepted that the most reliable set of data is that reported by Pinsent et al.^{165,166} They¹⁶⁶ also present the most extensive results on the ionic strength dependence of k_2 , although there is considerable discrepancy as to the magnitude, and even the sign, of the dependence.¹⁵⁹ The combined results¹⁶⁶ for NaCl, KCl, and Na_2CO_3 as the inert salts can be fitted to a quadratic equation of the form

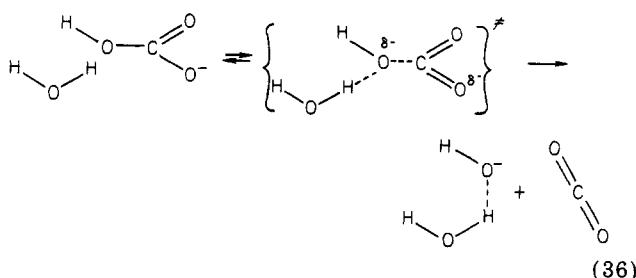
$$\log k_2 = 3.773 + (0.213 \pm 0.013)I - (0.0214 \pm 0.0028)I^2 \quad (35)$$

Specific catalysis by certain salts can modify this relationship. This aspect is discussed in more detail in this section.

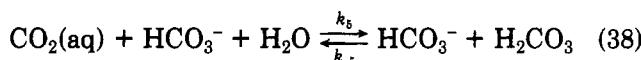
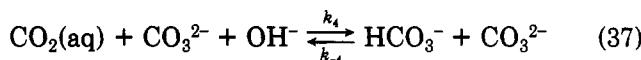
Welch et al.¹⁶⁷ reported a value for k_{-2} of $2.25 \times 10^{-4} \text{ s}^{-1}$ at 25°C , corrected for the contribution of k_{-1} in the pH range 8.5 to 9.3, based on the exchange rate of oxygen-15 between CO_2 and water. Good agreement was obtained with the k_{-2} value of $2.91 \times 10^{-4} \text{ s}^{-1}$ derived from the mean k_2 value from Table VIII ($7740 \text{ M}^{-1} \text{ s}^{-1}$

at 25°C), and the equilibrium constant for eq 29 of $2.66 \times 10^7 \text{ M}^{-1}$. Activation parameters were determined from the values of k_{-2} at three temperatures: $\Delta H^* = 93 \pm 9 \text{ kJ mol}^{-1}$ and $\Delta S^* = 0 \pm 29 \text{ J K}^{-1} \text{ mol}^{-1}$.

A study¹⁶¹ of the deuterium isotope effect on the respective rate constants k_2 and k_{-2} has established a $k(\text{H}_2\text{O})/k(\text{D}_2\text{O})$ ratio of 0.6 and 1.8, where the latter was derived by analogy to the “water-catalyzed” decarboxylation of alkyl carbonates. Atkinson et al.¹⁶⁵ report a range of values from 1.4 to 2.0 over the temperature range $3.5\text{--}38.5^\circ\text{C}$ which they ascribe to $k_{-1}(\text{H}_2\text{O})/k_{-1}(\text{D}_2\text{O})$; whereas, as discussed earlier, a value of 0.6 was assigned to the ratio $k_{-1}(\text{H}_3\text{O}^+)/k_{-1}(\text{D}_3\text{O}^+)$.¹⁶¹ However, both groups agree that ca. 1.8 is in keeping with the predicted secondary-isotope effect for the removal of an –OH vs. an –OD group from a molecule (theoretical 2.02).¹⁵⁵ In other words, these results are compatible with reaction 29 and the proposed mechanism:¹⁶¹



Logically, the presence of excess carbonate in solution would lead to the increasing importance of eq 30 in the overall scheme. However, some authors^{160,168} have concluded that the contribution from such a path, also referred to as carbonate catalysis, is negligible; a position that is substantiated by Pinsent et al.¹⁶⁶ in their ionic strength dependence study described earlier. Nevertheless, Poulton and Baldwin¹⁵⁹ argue that the uncertainties of the manometric method^{160,168} are large enough to mask such small catalytic effects which could be quantitatively assessed from their oxygen-18 exchange data. They went on to assign a value to k_3 (eq 30) of ca. $1.2 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C [this value represents the average of three values at ionic strengths of 0.5, 1.5, and 2.5 M (NaCl)]. Moreover, two more reactions involving other permutations of carbonate species were proposed¹⁵⁹



for which the average values (25°C , $I = 0.5\text{--}2.5 \text{ M}$) of k_4 and k_5 are $1.4 \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$ and $4.7 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, respectively. Therefore, unless a “carbonate” buffer is used, these three reactions would provide negligible contributions to the established rate expressions for reactions 28 and 29. This subject will be treated again later in this section.

More recent investigations by Silverman et al.^{169,170} have brought these processes more into perspective by fixing the rate of intermolecular exchange between $\text{CO}_2(\text{aq})$ and CO_3^{2-} in slightly alkaline solution using both ^{18}O -labeled and ^{13}C -enriched carbonate. The exchange rate constant at 25°C is $114 \pm 11 \text{ M}^{-1} \text{ s}^{-1}$ which, although slower than the rate of exchange via eq 29 at higher pH values, is considerably faster than the re-

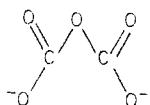
TABLE VIII. Summary of Rate Data for the Base Hydrolysis of CO₂ at 25 °C

year	<i>I</i> , M	<i>k</i> ₂ , M ⁻¹ s ⁻¹	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , J K ⁻¹ mol ⁻¹	method	ref
1924	.22/.11	4563 ^{a,b}			quenching, titration	158
1928	0.01	3700 (13.7 °C)			conductometric	c
1933	<0.21	2820 ^a			gas evolution spectrophotometric	d
1951	0	6771 ^a			manometric	165
1956	0	8430 ^e	52.8	7	thermal method	
	0	8500 ^f	52.7	7	manometric	166
1958	<0.01	7610 ^e	61.2	35	photoelectric	
		7515 ^e	49.4	-5	conductometric	g
1963	0	8100 (25.1 °C)			gas absorption: ¹⁴ C tracer	178
1966	0	1100 (0 °C) ^h			manometric	160
1967	1.5	8000	48.1	-9	mass spectroscopy, ¹⁸ O tracer	159
1973	0	8049	43.3	-25	manometric	i
1982	0	7043			pH statt	558

^a Interpolated from two data points. ^b Data corrected by a factor of 2.303 and using more recent values for K_2^{148} and K_w at 0 °C and 18 °C (Marshall, W. L.; Franck, E. U. "Water and Steam"; Pergamon Press: New York, 1980, p 506).

^c Saal, R. N. J. *Recl. Trav. Chim. Pays-Bas* 1928, 47, 264. ^d Brinkman, R.; Margaria, R.; Roughton, F. J. W. *Philos. Trans. R. Soc. 1933, A232*, 65. ^e Interpolated to 25.0 °C. ^f Appendix to ref 166 by E. Meda. ^g Sirs, J. A. *Trans. Faraday Soc.* 1958, 54, 201. ^h Equilibrium constant values for K_1 and K_2 at 25 °C were used. ⁱ Pohorecki, R.; Moniuk, W. *Pr. Inst. Inz. Chem. Politech. Warszaw* 1972, 1, 69; *Chem. Abstr.* 1973, 79, 35528m.

maining hydrolysis reactions. Albeit bicarbonate ion does not enter into the intermolecular exchange process, it still undergoes oxygen exchange with water.¹⁶⁹ A labile dimeric intermediate with the structure



was considered as one possible intermediate in the exchange for which an activation energy of 63 kJ mol⁻¹ was recorded.¹⁷⁰

Catalysis of the hydration reactions of CO₂(aq) is of obvious interest to industry. Nonenzymatic catalysis has been studied by a considerable number of workers (ref 69,160,162,165,168,171–174) using mainly manometric techniques. A general relationship for the observed rate constant for CO₂ hydrolysis can be expressed in terms of the contributions of the concentrations of base B and its conjugate acid, HB.^{160,162}

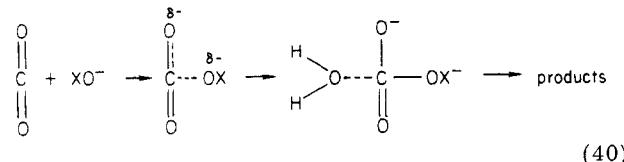
$$k_{\text{obs}} = k_1 + k_2[\text{OH}^-] + k_{\text{HB}}[\text{HB}] + k_B[\text{B}] \quad (39)$$

For example, for HB = H₂PO₄⁻, $k_{\text{HPO}_4^{2-}} = 0.3 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{H}_2\text{PO}_4^-} \approx 0$ at *I* = 1.0 and 25 °C,¹⁶² whereby HPO₄²⁻ is considered a weak catalyst.¹⁶⁰

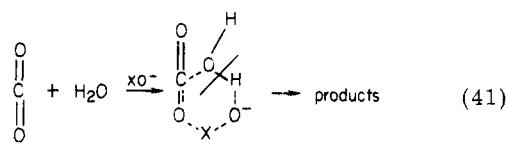
Despite the wide range of bases investigated by Sharma and Danckwerts,¹⁷⁴ their finding that the Bronsted relationship holds for certain bases which have in common a high degree of localized negative charge on an oxygen atom has been criticized¹⁶⁰ because the pH range chosen was too low relative to the $\text{p}K_a$ values of the conjugate acids. However, the general classification of bases according to their catalytic effect and structure was substantiated.¹⁶⁰ In addition, strong acid anions, as well as carbonate, cyanide, and hydrogen sulfide, are not effective catalysts, a fact which validates the ionic strength effects discussed previously and eq 35 in particular. Dennard and Williams¹⁶⁰ laid down the following criteria for bases to be good catalysts:

(1) For oxyanions with the nonmetal in its highest oxidation state there can be no resonant form for the basic oxygen atom, i.e., [OTe(OH)₅]⁻, [OGe(OH)₃]⁻, and [OSi(OH)₃]⁻ are good catalysts, while HPO₄²⁻ and HAsO₄²⁻ are only weak catalysts despite the similar basicity of all five.

(2) The oxyanions of nonmetals in lower oxidation states with at least one lone pair of electrons are the best catalysts, e.g., SO₃²⁻, AsO₂⁻, ClO⁻, and BrO⁻. The authors¹⁶⁰ point out that these rules can be related to specific properties of the bases. For the majority of cases, the nucleophilicity and ability of the anion to act as a leaving group are paramount and consistent with the favored mechanism:¹⁶⁰



Furthermore, certain oxyanions with lower oxidation state centers, class 2, can act as electrophilic agents (e.g., SO₃²⁻ or ClO⁻), compliant with the following mechanism:



McLachlan's work¹⁷² on the catalysis of reaction 28 by As(OH)₂O⁻ and ClO⁻ in carbonate buffers bears directly on the general topic of catalysis, as well as "carbonate" catalysis in the form of eq 37.¹⁵⁹ Using gas absorption techniques he was able to demonstrate that catalysis under these conditions obeys a third-order rate law which is first order with respect to the base B⁻, [As(OH)₂O⁻], or [ClO⁻], and [CO₃²⁻]. A linear least-squares fit of McLachlan's results for $k[B^-]$ vs. [CO₃²⁻] yielded the rate constants: $k_{\text{As(OH)}_2\text{O}^-} = 393 \pm 13 \text{ M}^{-2} \text{ s}^{-1}$ (25 °C and *I* = 1.4–5.1) and $k_{\text{ClO}^-} = 7300 \pm 400 \text{ M}^{-2} \text{ s}^{-1}$ (25 °C and *I* = 0.45–5.03 M). These constants are obviously insensitive to ionic strength and bicarbonate concentration, albeit the latter increases sharply in the presence of chloride ion which most likely reflects a change in the oxidation state of ClO⁻. Note also that $k_{\text{As(OH)}_2\text{O}^-}$ values could be calculated from two earlier measurements of Danckwerts et al. and gave a fair fit to the third-order model, whereas the value of 6670 M⁻¹ s⁻¹ reported¹⁷¹ for ClO⁻ catalysis in mixtures of 1 M

$\text{KHCO}_3/1 \text{ M K}_2\text{CO}_3$ at 25 °C is in excellent agreement with the calculated k_{ClO_4} -value. These authors¹⁷¹ also report a second-order rate constant for BrO^- under the same conditions of $6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

Of direct application to the earlier discussion on carbonate catalysis is McLachlan's¹⁷² plot of k_{obs} vs. $[\text{CO}_3^{2-}]^2/[\text{HCO}_3^-]$ which includes the results of five other investigators¹⁷⁵⁻¹⁷⁷ who used potassium or sodium carbonate buffers, but no other catalysts. A good straight line results and translates into a slope of $0.99 \pm 0.03 \text{ M}^{-2} \text{ s}^{-1}$ (25 °C and $I = 1.0-6.4 \text{ M}$), which, in turn, gives a third-order rate constant for reaction 37 of $(4.7 \pm 0.1) \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$ (K_2 and K_w values at $I = 0$, 25 °C were used). This value is 2 orders of magnitudes greater than reported by Poulton and Baldwin,¹⁵⁹ but must be considered more accurate as it was determined directly. It is difficult to speculate on what role carbonate plays in the detailed mechanisms 40 and 41, although it appears logical that it involves interaction of either carbonate or B^- with the type of intermediate (viz., $\text{C}_2\text{O}_5^{2-}$) proposed for intermolecular oxygen exchange, which is first-order in both $[\text{CO}_2]$ and $[\text{CO}_3^{2-}]$, and is also independent of $[\text{HCO}_3^-]$.

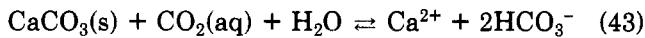
Catalysis by coordinated metal ions is well documented and is discussed in section VIII.

A brief mention of the rate of CO_2 absorption into solution should be made as it is technologically important and central to many of the hydrolysis studies discussed here. In alkaline solutions the rate of absorption of gaseous CO_2 is given by the following equation in units of $\text{mol cm}^{-2} \text{ s}^{-1}$,

$$\text{rate} = [\text{CO}_2(\text{aq})](k_L^2 + Dk_2[\text{OH}^-])^{1/2} \quad (42)$$

where k_L represents the individual mass-transfer coefficient for CO_2 in solution and D is the diffusivity of CO_2 in solution with typical values ranging from 1×10^{-5} to $2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 25 °C. Depletion of $[\text{OH}^-]$ from the surface layer can present a problem at high rates of absorption or low agitation rates as the reaction proceeds. Notwithstanding this retardation effect, in eq 29 k_2 is generally considered to be rate-determining. Numerous investigations have been reported on this subject.¹⁷⁵⁻¹⁸⁵ However, note that in view of the exchange studies of Silverman et al.^{169,170} and the above-mentioned rapid equilibration of $\text{CO}_2(\text{gas}) \rightleftharpoons \text{CO}_2(\text{aq})$, the recently reported¹⁸⁵ relaxation time of ca. 13.4 min (15–18 °C) for ^{13}C exchange for this process appears much too slow, even at pH values of 8.5. This discrepancy can probably be traced to the aforementioned diffusion problems in the solution. However, Szaran and Zuk¹⁸⁵ did determine the equilibrium fractionation factor $\delta^{13}\text{C}$ for $\text{CO}_2(\text{gas})$ vs. mainly HCO_3^- over the temperature range 0–52 °C. The fractionation factor proved to be a linear function of temperature, t (°C), e.g., $\delta^{13}\text{C} = 10.2 \pm 0.1 - (0.090 \pm 0.006)t$ (%); an equation which is consistent with previous work.¹⁸⁶

As a final comment, the rate of dissolution of calcium carbonate in relatively neutral solutions (pH 6.5–8) is apparently diffusion controlled;^{187,188} i.e., the overall hydrolysis reaction (eq 43) in this case is faster than the



rate of diffusion of $\text{CO}_2(\text{aq})$, or more explicitly the

proposed reactant H_2CO_3 , to the surface of the crystal.

The Chemistry of Metal Carbonato Complexes

V. Preparation and Characterization

A. Preparation and Spectroscopic Data

The preparative techniques have been described in some detail in previous reviews.^{1,2} Conventional solution methods basically rely on carbon dioxide uptake by the hydroxo form of the parent transition-metal compound¹⁸⁹ (the mechanism of which is explained in section VIII), or involve using the carbonato complex as the starting materials, as in the case of $\text{Co}(\text{CO}_3)_3^{3-}$,¹⁹⁰ and substituting other ligands into such species. High pressures of CO_2 and high temperatures are generally required for solid-state conversions to form carbonates (see section VI).

We have attempted to summarize the spectroscopic properties of metal carbonato complexes in Tables IX–XIII with particular emphasis on the most recent results. The preparative methods are referenced in these Tables and, in a number of cases, represent only one of a number of published techniques.

The spectroscopic data can serve most readily to fingerprint the species. The visible and UV spectra are particularly useful for this purpose, but will not be discussed further in this review except to point out that a practical test for the existence and, to certain extent, the purity of a soluble carbonato complex is to acidify an aqueous solution containing the suspected complex and then compare the spectrum of the generated aquo species with the known spectrum of the aquo complex obtained directly.

The infrared and Raman spectra have more general application and will therefore be discussed in more detail.

(1) **Infrared and Raman Spectroscopy.** Infrared and Raman spectroscopy are the traditional means of ascertaining the bonding modes of coordinated carbonates. As the free ion, carbonate has a D_{3h} symmetry and four bands may be assigned to the following vibrational modes: ν_1 , the C–O symmetrical stretch at $\sim 1065 \text{ cm}^{-1}$; ν_2 , the CO_3 out-of-plane deformation at $\sim 880 \text{ cm}^{-1}$; ν_3 , the C–O asymmetrical stretch at $\sim 1400 \text{ cm}^{-1}$; and ν_4 , the CO_3 in-plane deformation (or rocking) mode at $\sim 685 \text{ cm}^{-1}$. The ν_2 mode should be inactive in the Raman. On this basis, the spectral data in Table XIV for the alkali metal carbonates confirm that the ν_2 mode is absent from the Raman spectrum; however, the ν_1 mode is generally of medium to weak intensity in the IR which may indicate a lowering of the D_{3h} symmetry. It can also be seen that the range of frequencies cited in Table XIV embrace the values quoted above, viz. the mean values are 1064 (20), 861 (22), 1417 (33), and 696 (19) cm^{-1} , respectively. Temperature affects the energy of these transitions slightly, whereas the degree of hydration generally has a much stronger effect.

As was observed in the spectra of alkali metal carbonates in aqueous solution,⁴⁹ the D_{3h} symmetry is also lowered in the molten state.¹⁹¹ This is thought to be due largely to the anisotropic nature of the melt.

The IR and Raman spectra of a series of compounds with calcite and aragonite structures led Donoghue et

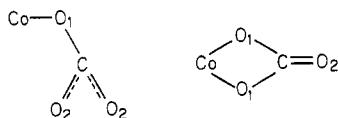
TABLE IX. Spectroscopic Properties of Monodentate Carbonato Complexes

compd	prepn ref	vis/UV, nm ($M^{-1} \text{cm}^{-1}$)	ref	IR, cm^{-1}	ref	comments
<i>cis</i> - $K_2[\text{Co}(\text{H}_2\text{O})_4\text{CO}_3]_{\text{NO}_3\cdot 1.5\text{H}_2\text{O}}$	^a ^b	505 (94), 237 (13 800)	333	1482, 1365, 1052, 856, 738, 690 1453, 1373	195 340	
<i>cis</i> [$\text{Co}(\text{en})_2(\text{NH}_3)\text{CO}_3\text{JBr}\cdot 0.5\text{H}_2\text{O}$	189					
<i>trans</i> - $[\text{Co}(\text{en})_2(\text{NH}_3)\text{CO}_3\text{JClO}_4$	189					
<i>trans</i> - $[\text{Co}(\text{NH}_3)_4(\text{CN})\text{CO}_3]$	^c	458 (109)	353			
<i>trans</i> - $[\text{Co}(\text{en})_2(\text{Cl})\text{CO}_3\text{JH}_2\text{O}$	353	~578 (~74), ~450 (~25)	353			
<i>trans</i> - $[\text{Co}(\text{en})_2(\text{Cl})(\text{CO}_3\text{H})]^+$	^d	510 (21.2)	^d			
<i>cis</i> - $[\text{Co}(\text{en})_2(\text{OH})\text{CO}_3]$	353	~512 (~114), ~361 (~110)	353			
<i>trans</i> - $[\text{Co}(\text{en})_2(\text{OH})\text{CO}_3]$	^e	532 (~81)	353			
<i>trans</i> - $[\text{Co}(\text{en})_2(\text{HCO}_3)]^+$	^f	510 (65.1)	^d			
<i>cis</i> - $\alpha\beta\text{S}[\text{Co}(\text{tetren})\text{CO}_3\text{JClO}_4\cdot 3\text{H}_2\text{O}$	189	500 (198)	327	1458, 1340	327	
<i>cis</i> - $[\text{Co}(\text{tren})(\text{OH})(\text{HCO}_3)]^+$	^e	530 (120), 430 (20)	352			
<i>cis</i> - $[\text{Co}(\text{tren})(\text{OH})(\text{HCO}_3)]^+$	^f	515 (155), ~350 (130 sh)	352			
<i>cis</i> - $[\text{Co}(\text{tren})(\text{OH})(\text{CO}_3\text{H})]^+$	^e	520 (144), 367 (117 sh)	328			
<i>cis</i> - $[\text{Co}(\text{cyclam})(\text{OH})(\text{CO}_3\text{H})]^+$	314	~525 (~222), ~365 (~194 sh)	314			
<i>trans</i> - $[\text{Co}(\text{cyclam})(\text{OH})(\text{CO}_3\text{H})]^+$	^e	~555 (~45), ~438 (~33)	314			
<i>trans</i> - $[\text{Co}(\text{cyclam})(\text{OH})(\text{CO}_3\text{H})]^+$	^f	~562 (~50), ~453 (~29)	314			
$[\text{Cu}(\text{NH}_3)_2(\text{CO}_3\text{H})_2]$	480					
$[\text{Cu}(\text{PPh}_3)_2(\text{CO}_3\text{H})_2]$						
<i>cis</i> - $[\text{M}(\text{dmpe})_2(\text{CO}_3\text{H})_2]$	^g					
$[\text{RhH}_2(\text{P}(\text{i-Pr})_3)_2(\text{CO}_3\text{H})]$	403					
$[\text{RhH}_2(\text{PPh}(t\text{-Bu})_2)_2(\text{CO}_3\text{H})]$	403					
$[\text{RhH}_2(\text{P}(\text{c-C}_6\text{H}_5)_2)_2(\text{CO}_3\text{H})]$	403					
$[\text{Rh}(\text{CO})(\text{P}(\text{c-C}_6\text{H}_{11})_2)_2(\text{CO}_3\text{H})]$	403					
$[\text{Rh}(\text{CO})(\text{P}(\text{i-Pr})_3)_2(\text{CO}_3\text{H})]$	403					
$[\text{Rh}(\text{NH}_3)_2(\text{CO}_3\text{H})_2(\text{CO}_3\text{H})]$	^h	325 (178)	1455			
<i>cis</i> - $[\text{Rh}(\text{en})_2(\text{H}_2\text{O})\text{CO}_3\text{JClO}_4$	ⁱ	332 (224)	ⁱ			
<i>trans</i> - $[\text{Rh}(\text{en})_2(\text{CO}_3)_2]$	322	347 (146)	322			
<i>trans</i> - $[\text{Rh}(\text{en})_2(\text{H}_2\text{O})\text{CO}_3\text{JClO}_4$	322	345 (101)	322			
<i>trans</i> - $[\text{Rh}(\text{en})_2(\text{OH})\text{CO}_3]$	322	346 (121)	322			
<i>trans</i> - $[\text{Rh}(\text{en})_2(\text{Cl})\text{CO}_3]$	315	376 (118)	315			
<i>trans</i> - $[\text{Rh}(\text{en})_2(\text{Br})\text{CO}_3]$	315	384 (141)	315			
<i>trans</i> - $[\text{Rh}(\text{en})_2(\text{I})\text{CO}_3]$	315	456 (232), 415 (216)	315			
<i>trans</i> - $[\text{Pd}(\text{PPh}_3)_2(\text{Me})\text{CO}_3\text{H}]$	^j					
$[\text{Ir}(\text{NH}_3)_2(\text{CO}_3\text{H})_2\text{ClO}_4]$	^h	262 (125)	1370			

^a Reynolds, W. C. *J. Am. Chem. Soc.* **1898**, *73*, 262. ^b Lamb, A. B.; Mysels, K. J. *J. Am. Chem. Soc.* **1945**, *67*, 468. ^c Krishnamoorthy, C. R.; Palmer, D. A.; van Eldik, R.; Harris, G. M. *Inorg. Chim. Acta* **1979**, *35*, L361. ^d Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1978**, *17*, 1348. ^e As mentioned in the discussion, we prefer the form, $\text{ML}_4(\text{H}_2\text{O})\text{CO}_3$. ^f Tsuda, T.; Chujo, Y.; Sagusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 431. ^g Connor, J. A.; Riley, P. I. *J. Chem. Soc., Dalton Trans.* **1979**, *1231*. ^h Palmer, D. A.; Harris, G. M. *Inorg. Chem.* **1974**, *13*, 965. ⁱ Palmer, D. A.; van Eldik, R.; Lock, C. J. L. *Inorg. Chim. Acta* **1977**, *24*, L15.

al.¹⁹² to favor a C_3 symmetry for these carbonates. They list the positions of the bands for the ν_1 , ν_2 , and ν_4 modes of these compounds in the calcite form where $M = Mg$, Ca , Mn , Zn , Cd : $\nu_1 = 1074$ (10) IR, 1091 (4) R; $\nu_2 = 872$ (9), 845 (7) IR; $\nu_3 = 730$ (13) IR, 720 (8) cm^{-1} R; and in the aragonite form where $M = Ca$, Sr , Ba , Pb : $\nu_1 = 1065$ (14) IR, 1065 (9) R; $\nu_2 = 851$ (7), 839 (10) IR; $\nu_4 = 697$ (14), 686 (7) IR, 690 (11) cm^{-1} R. Note that the ν_4 band is split in some cases. Donoghue et al.¹⁹² suggest that the second peak at the ν_2 frequency could be due to a combination with a lattice mode. Coincidentally, the lower energy band corresponds exactly to that reported by Sterzel¹⁹³ for the ν_2 ^{13}C absorption such that for calcite $\Delta\nu_2$ (^{12}C – ^{13}C) = 27 cm^{-1} and 11 cm^{-1} for aragonite.

Coordination lowers the symmetry of the carbonate further from D_{3h} to C_{2v} , or possibly C_s , for monodentate coordination and thereby results in the splitting of each of the degenerate ν_3 and ν_4 modes into two. Gatehouse, Livingstone, and Nyholm¹⁹⁴ categorize six fundamental frequencies associated with C_{2v} symmetry: ν_4 , asym stretch, 1577–1493 cm^{-1} ; ν_1 , CO_2 sym stretch, 1338–1260 cm^{-1} ; ν_2 , CO stretch, 1082–1055 and 1050–1021 cm^{-1} ; ν_6 , nonplanar rock, 889–824 cm^{-1} ; ν_3 , CO_2 bend, and ν_5 , planar rock, 809–738 cm^{-1} , all of which are both IR and Raman active. Fujita, Martell, and Nakamoto¹⁹⁵ used the normal coordination treatment to calculate the theoretical band assignments and force constants for cobalt(III) carbonato complexes. Although they obtained a satisfactory agreement for the C_{2v} symmetry in both the monodentate and bidentate cases, the C_s model gave better agreement for the ν_4 frequency in the former case. The notation derived by Fujita et al.¹⁹⁵ is different from that described above,¹⁹⁴ and is shown in Table XV along with the calculated frequencies and the experimental values for the examples of mono- and bidentate coordination. The authors adopted the following reference structures (see Tables XVIII and XIV for bond lengths and angles):



The magnitude of the split between the ν_1 and ν_5 modes is a function of the carbonato ligand polarization and the M–O bond strength, and is greater for bidentate bonding than for monodentate bonding, given that the two first mentioned independent variables are constant.¹⁹⁶ The examples cited in Table XV attest to the validity of this postulate. Other more subtle distinctions exist between the spectra resulting from these two forms of coordination.¹⁹⁶ These criteria are generally met for all the compounds listed in Tables IX and X. Similar bidentate characteristics are expected to be observed for the bridged carbonato complexes in Table XI. From the limited data available it can be seen that the splitting of the degenerate ν_3 is ambiguous in many cases with $|\Delta(\nu_1 - \nu_5)|$ values lying between the extremes quoted in Table XV. Note the example of the $\{[\text{Co}(\text{diars})_2\text{HCO}_3]_2(\mu-\text{CO}_3\text{H})\}^{3+}$ cation is complicated by the presence of monodentate carbonate.¹⁹⁷

The majority of the lanthanide and actinide complexes shown in Tables XII and XIII exhibit complex spectra associated with mixed mono- and bidentate ligands. Although Caro et al.¹⁹⁸ favor monodentate

bonding in the series of complexes, $\text{Ln}_2(\text{CO}_3)_x(\text{OH})_{2(3-x)}\cdot n\text{H}_2\text{O}$, $\text{Ln} = \text{Pr}$, Nd , Sm , Tb , Dy , and Nd-Tb , on the basis of their IR spectra which closely resemble that of $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{Br}$, with modifications due to the existence of two crystallographic sites for the two rare earth atoms. This lanthanide formula also raises the point that in some of the complexes found in Tables XII and XIII, the participation of one or more "waters of crystallization" in the first coordination sphere of the metal ion cannot always be ruled out. On the other hand, the IR spectra of the sodium pentacarbonato-thorate(IV) hydrates suggest strongly that only bidentate coordination is present.¹⁹⁹ The same is true for $\text{Na}_4[\text{UO}_2(\text{CO}_3)_3]$ for which the ν_3 splitting is strong (1560–1342, 1630–1358 cm^{-1}).²⁰⁰

A matrix isolation IR spectroscopic study²⁰¹ of the vaporization of the alkali metal carbonates $\text{Cs}_2(\text{CO}_3)$, $\text{Rb}_2(\text{CO}_3)$, and $\text{K}_2(\text{CO}_3)$ showed evidence for molecular carbonates with the C_{2v} symmetry discussed above for bidentate complexes.

(2) **Other Methods.** ^1H and ^{13}C NMR spectroscopy provide a more exact description of the configuration of ligands around the metal center and have been used for this purpose for carbonato metal complexes (see Tables IX–XI). Similarly ESR, magnetic, and conductometric properties have been recorded and ORD and CD measurements made where appropriate. These properties are referred to in Tables IX–XI and XIII.

However, as these properties are generally associated with the molecule as a whole, we feel they are outside the immediate scope of this review so that we have limited ourselves to merely indicating in the tables where such data are available.

B. Structure

The unit cell parameters determined from X-ray crystallography for a wide range of carbonato complexes, including a number of naturally occurring minerals, are listed in Table XVI. The corresponding bond lengths and angles for these complexes are given in Tables XVII–XXIV, with the main emphasis on the carbonato ligand itself. Obviously space does not permit a complete breakdown of these structures in terms of bond lengths and angles, but it is hoped that where just mean values for these measurements are given this will convey the degree of distortion, if any, as reflected by the standard deviation. In other words, even though average values are listed, this is not meant to imply equality.

For ease of comparison, the structures of the bicarbonate and carbonate salts of the alkali and alkaline earth metals are given separately in Table XVII. They warrant a brief clarification because the sodium and potassium (rubidium) salts exhibit different structures.

Sass and Scheuerman²⁰² determined the CO_3 group in NaHCO_3 to have a C_{2v} symmetry (planar within 0.01 Å) with two oxygens hydrogen bonded; viz., O_3 covalently and O_2 electrostatically. Thus, in this classical picture, the C– O_3 bond has approximately 14% double bond character (cf. the expected bond length for a single C–O bond of 1.43 Å), while the remaining two C–O bonds have ca. 50% double bond character, based on an estimate for a double bond length of 1.255 Å.

The structure of potassium bicarbonate is different in that it consists of H-bonded dimers reminiscent of

TABLE X. Spectroscopic Properties of Bidentate Carbonato Complexes

compd	prepn ref	vis/UV, nm (M ⁻¹ cm ⁻¹)	ref	IR, cm ⁻¹	ref	comments
K ₂ [Co(CO ₃) ₂]·4H ₂ O	<i>a</i>			1338 m, 1082 m, 1049 m, 884 m, 799 s, 766 m	194	
[Co(HDPA)(H ₂ O) ₂ CO ₃]·0.5H ₂ O	<i>b</i>			1065 sh, 1277, 842	<i>b</i>	1320, 1110, 535, 488, 395, 347 nm, diffuse reflectance spectrum
Nd ₃ [Co(CO ₃) ₃]·3H ₂ O	190 640 (154), 440 (166), 260 (10 ⁵) 640 (162), 440 (173) 645 (155), 439 (166)	364 367 <i>c</i>		1600, 1495, 1335 1527 s, 1330 s, 1080 w, 1037, 851 m, 809 m	358 194	optically resolved
K ₃ [Co(CO ₃) ₃]·3H ₂ O	364			1585 s, 1265 s	<i>d</i>	$\tilde{\nu}_{\text{max}} = 17.8$ (-2.32)
[⁵⁸ Li(-) ⁵⁸ K][Co(NH ₃) ₂ (CO ₃) ₂] cis-K[Co(NH ₃) ₂ (CO ₃) ₂] (blue)		<i>d</i>		362	1623, 1597, 1265, 1026, 839,	195
K[Co(NH ₃) ₂ (CO ₃) ₂]·H ₂ O (violet)				359	763, 744, 673	362
cis-K[Co(py) ₂ (CO ₃) ₂]·0.5H ₂ O	362	574 (138), 390 (251)		359	1370, 970, 740, 690	
cis-K[Co(py) ₂ (CO ₃) ₂]·2H ₂ O	364	540 (63), 374 (110), 234 (13 800)		359		
trans-K[Co(py) ₂ (CO ₃) ₂]·3H ₂ O	364	561 (165), 388 (232)		366		
K[Co(bpy)(CO ₃) ₂]·2H ₂ O	366	568 (178), 392 (251)		366		
K[Co(phen)(CO ₃) ₂]·1H ₂ O	366	549 (100), 417 sh, 372 (107)		366		
K ₂ [Co(picolo)(CO ₃) ₂]·0.5H ₂ O	366	549 (89.1), 426 (36.3), 375 (72.4)		366		
[Co(en) ₃] ⁺ ·cis-[Co(CN) ₃]·2H ₂ O	366	549 (151), 391 (240 sh)		366		
cis-Na[Co(en)(CO ₃) ₂]·H ₂ O	366	568 (151), 394 (251 sh)		366		
cis-K[Co(en)(CO ₃) ₂]·H ₂ O	366	588 (145), 415 (191)		366		
cis-[Co(en)(CO ₃) ₂]·H ₂ O	366	546 (91), 444 (107), 363 (158)		366		
cis-[Co(en)(CO ₃) ₂]·H ₂ O	366	568 (154), 395 (173)		366		
cis-[Co(en)(CO ₃) ₂]·H ₂ O	366	31, 570 (148), 390 (214), 239 (28 800)		366		
cis-[Co(en)(CO ₃) ₂]·H ₂ O	366	359, 570 (148), 390 (214), 239 (28 800)		366		
cis-[Co(en)(CO ₃) ₂]·H ₂ O	366	220, 567 (159), 394 (164)		220		
cis-[Co(en)(CO ₃) ₂]·H ₂ O	366	334, 567 (104), 394 (164)		334	1598, 1035, 765	334
cis-[Co(en)(CO ₃) ₂]·H ₂ O	366	367 (520)		367	1593, 1265, 1030, 834, 760, 673	195
cis-[Co(en)(CO ₃) ₂]·H ₂ O	366	<i>m</i>		<i>m</i>	$\tilde{\nu}_{\text{max}} = 18.1$ (-0.59), 20.3 (+0.92), 27.8 (-0.28)	
cis-[Co(en)(CO ₃) ₂]·H ₂ O	366	<i>m</i>		<i>m</i>	$\tilde{\nu}_{\text{max}} = 20.0$ (+1.87), 27.4 (-0.36)	
cis-[Co(en)(CO ₃) ₂]·H ₂ O	366	<i>n</i>		<i>n</i>		
mer-[Co(py) ₃ (Cl)CO ₃]·H ₂ O	366	536 (~89), 388 (~111)		<i>f</i>	ϵ values multiplied by 2.5	
mer-[Co(py) ₃ (Cl)CO ₃]·H ₂ O	366	536 (87), 388 (107)		<i>f</i>	ϵ values multiplied by 2.5	
[Co(py) ₃ (H ₂ O)CO ₃]Cl·H ₂ O	366	577 (125), 409 (150)		<i>o</i>	ϵ values multiplied by 2.5	
cis-[Co(py) ₄ CO ₃]ClO ₄ ·H ₂ O	366	582 (113), 401 (142)		<i>p</i>		
cis-[Co(py) ₄ CO ₃]ClO ₄ ·H ₂ O	366	540 (119), 380 (138)		<i>p</i>		
cis-[Co(NH ₃) ₂ (bpy)CO ₃]Cl·2H ₂ O	366	530 (170), 378 (189)		342	1650 s, 1625 br, 1250 s 1680 br, 1640 s, 1240 sh	<i>p</i>
cis-[Co(NH ₃) ₂ (bpy)CO ₃]Cl·3H ₂ O	366	530 (172), 379 (187)		366		$\tilde{\nu}_{\text{max}} = 19.0$ (+2.03), 25.3 (+0.25), 29.2 (-0.66)
[Co(terpy)(OH)CO ₃]·4H ₂ O	366	513 (117)		<i>m</i>	¹³ C NMR spectrum ³²¹	
[Co(HDPA) ₂ CO ₃]ClO ₄	366	<i>s</i>		<i>m</i>		
cis,cis-Na[Co(NH ₃) ₂ (CN) ₂ CO ₃]·2H ₂ O	366	<i>b</i>		<i>b</i>	510, 400 (sh), 342 nm, diffuse reflectance spectrum	
mer(N)-[Co(bpy) ₂ CO ₃]Cl·3H ₂ O	366	<i>t</i>		<i>t</i>	$\tilde{\nu}_{\text{max}} = 20.9$ (+0.98), 24.1 (-1.11), 29.7 (+0.245)	
[Co(NH ₃) ₃ (CN) ₂ CO ₃]·H ₂ O	366	<i>c</i>		<i>c</i>		
mer(N)-[Co(NH ₃) ₃ (CN) ₂ CO ₃]·2H ₂ O	366	<i>u</i>		<i>u</i>		

$\text{fac}(N)\text{-}[\text{Co}(\text{NH}_3)_3(\text{CN})\text{CO}_3]$	<i>u</i>	495 (107), 345 (158), 377 (sh)	<i>u</i>	$[\alpha]^{25}\text{D} -1331^\circ(\text{H}_2\text{O})^w$
$\text{K}[\text{Co}(\text{NH}_3)_3\text{NO}_2]_3\text{CO}_3\text{-H}_2\text{O}$	360	472 (219), 347 (7410), 259 (25700)	360	1643, 1285, 1267, 833, 757, 673
$\text{cis-}[\text{Co}(\text{en})_2\text{CO}_3]\text{ClO}_4$	<i>v</i>	511 (133), 359 (122)	336	1577 s, 1290 sh, 1278 s, 1055 m,
$\text{cis-}[\text{Co}(\text{en})_2\text{CO}_3]\text{Cl}$	<i>v</i>		1034 m, 824 s, 756 m	194
$\text{cis-} (+)_{ss}\text{-}[\text{Co}(\text{en})\text{CO}_3]^+$		515 (145), 361 (132)	<i>m</i>	
$\text{cis-} (+)_{ss}\text{-}[\text{Co}(\text{NH}_3)_2(\text{en})\text{CO}_3]\text{Cl}\cdot\text{H}_2\text{O}$	<i>m</i>	515 (120), 358 (120)	<i>m</i>	
$\text{cis-}[\text{Co}(\text{NH}_3)_2(\text{en})\text{CO}_3]\text{ClO}_4\cdot 2\text{H}_2\text{O}$	355	504 (125), 347 (148)	355	
$\text{trans-}[\text{Co}(\text{NH}_3)_2(\text{en})\text{CO}_3]\text{Cl}\cdot\text{H}_2\text{O}$	355	500 (125)	326	
$\mu\text{-} \text{fac}(N)\text{-}[\text{Co}(\text{NH}_3)_2(\text{en})\text{(CN)}\text{CO}_3]\text{Cl}\cdot\text{H}_2\text{O}$	<i>u</i>	485 (117), 345 (145), 377 (sh)	<i>u</i>	
$\text{mer}(N)\text{-}[\text{Co}(\text{NH}_3)_2(\text{en})\text{(CN)}\text{CO}_3]\text{Cl}\cdot\text{H}_2\text{O}$	<i>u</i>	485 (115), 347 (120)	<i>u</i>	
$\text{trans-}[\text{Co}(\text{NH}_3)_2(\text{tn})\text{CO}_3]\text{Cl}\cdot\text{H}_2\text{O}$	355	520 (95)	326	
$\text{cis-}[\text{Co}(\text{phen})_2\text{CO}_3]\text{Cl}\cdot 3\text{H}_2\text{O}$	38	509 (109)	38	
$\text{K}(+)\text{-}_{ss}\text{-}[\text{Co}(\text{NH}_3)_2(\text{ox})\text{CO}_3]\text{H}_2\text{O}$	<i>x</i>	565 (123), 389 (151)	<i>m</i>	
$\text{K}(-)_{ss}\text{-}[\text{Co}(\text{en})_3]\text{[(Co(NH}_3)_2(\text{ox})\text{CO}_3]\text{H}_2\text{O}$	<i>y</i>	535 (79), 435 (117), 356 (178)	<i>y</i>	
$\text{cis-K}_3[\text{Co}(\text{ox})(\text{NO})_2\text{CO}_3]$	<i>c</i>	565 (123), 388 (151)	<i>c</i>	
$\text{K}[\text{Co}(\text{en})(\text{NO}_2)_2\text{CO}_3]$	<i>m</i>	560 (148), 382 (200)	<i>c</i>	
$\text{K}(-)_{ss}\text{-}[\text{Co}(\text{en})(\text{ox})\text{CO}_3]\text{H}_2\text{O}$	<i>x</i>	552 (145), 391 (178)	<i>m</i>	
$\text{cis-K}_3[\text{Co}(\text{ox})(\text{NO})_2\text{CO}_3]$	<i>c</i>	535 (182)	<i>c</i>	
$\text{cis-}[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{cis-} (+)_{ss}\text{-}[\text{Co}(\text{py})_2\text{:}$	<i>m</i>	556 (138), 391 (191)	<i>m</i>	
$(\text{ox})\text{CO}_3\text{-}2\text{H}_2\text{O}$	<i>g</i>	549 (66.1), ~420, 374 (63.1)	<i>g</i>	
$\text{trans-K}[\text{Co}(\text{py})(\text{ox})\text{CO}_3]\text{-}2.5\text{H}_2\text{O}$	<i>m</i>	562 (120), 388 (195)	<i>m</i>	
$\text{Na}(+)_{ss}\text{-}[\text{Co}(\text{tn})(\text{ox})\text{CO}_3]\text{H}_2\text{O}$	<i>x</i>	562 (100), 389 (138)	<i>x</i>	
$[\text{Co}(\text{en})_2\text{ox}] (+)_{ss}\text{-}[\text{Co}(\text{NH}_3)_2(\text{mal})\text{CO}_3]\text{-}$				
$2\text{H}_2\text{O}$				
$\text{trans-(N)}\text{-}[\text{Co}(\text{picol})\text{CO}_3]^-$	<i>i</i>	549, 397	<i>i</i>	
$\text{C}_1\text{-} \text{cis}(N)\text{-K}[\text{Co}(\text{picol})\text{CO}_3]\text{-}2\text{H}_2\text{O}$	<i>i</i>	549 (155), 395 (186)	<i>i</i>	
$\text{C}_2\text{-} \text{cis}(N)\text{-K}[\text{Co}(\text{picol})\text{CO}_3]\text{-}1.5\text{H}_2\text{O}$	<i>i</i>	543 (115), 397 (200)	<i>i</i>	
$\text{mer, cis}(\text{NH}_3)_2\text{-}[\text{Co}(\text{NH}_3)_2(\text{picol})\text{CO}_3]$	<i>i</i>	546 (105), 373 (182)	<i>i</i>	
$\text{mer, trans}(\text{NH}_3)_2\text{-}[\text{Co}(\text{NH}_3)_2(\text{picol})\text{CO}_3]\text{-}$	<i>i</i>	521 (110), 400 (sh)	<i>i</i>	
$\text{fac-}[\text{Co}(\text{NH}_3)_2(\text{picol})\text{CO}_3]\text{-H}_2\text{O}$	<i>i</i>	529 (117), 372 (170)	<i>i</i>	
$\text{cis-K}_2[\text{Co}(\text{acac})(\text{NO}_2)_2\text{CO}_3]\text{-H}_2\text{O}$	<i>c</i>	534 (151)	<i>c</i>	
$\text{K}_2[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_3\text{CO}_3]\text{-H}_2\text{O}$	<i>c</i>	471 (135)	<i>c</i>	
$\text{mer, cis}(\text{NH}_3)_2\text{-}[\text{Co}(\text{NH}_3)_2(\text{gly})\text{CO}_3]$	<i>aa</i>	530 (85.1), 401 (39.8), 367 (70.8)	<i>aa</i>	
$\text{mer, trans}(\text{NH}_3)_2\text{-}[\text{Co}(\text{NH}_3)_2(\text{gly})\text{CO}_3]$	<i>aa</i>	533 (107), 377 (178)	<i>aa</i>	
$\text{fac-}[\text{Co}(\text{NH}_3)_2(\text{gly})\text{CO}_3]$	<i>aa</i>	533 (110), 374 (135)	<i>bb</i>	
$\text{cis, cis-}[\text{Co}(\text{NH}_3)_2(\text{CN})\text{CO}_3]$	<i>c</i>	499 (91), 431 (105), 336 (sh)	<i>c</i>	
$\text{cis-K}[\text{Co}(\text{gly})_2\text{CO}_3]\text{-H}_2\text{O}$	<i>cc</i>	556 (147), 391 (163)	<i>cc</i>	
$\text{cis-Ag}_3[\text{Co}(\text{L-asp})_2\text{CO}_3]\text{-}4\text{H}_2\text{O}$	<i>c</i>			
$\beta\text{-} \text{mer}(N)\text{-}[\text{Co}(\text{adao})\text{CO}_3]\text{-H}_2\text{O}$	<i>dd</i>	526 (162), 379 (177)	<i>dd</i>	
$\beta\text{-} \text{fac}(N)\text{-}[\text{Co}(\text{adao})\text{CO}_3]\text{-}2\text{H}_2\text{O}$	<i>dd</i>	526 (206), 369 (160)	<i>dd</i>	
$\text{mer}(N)\text{-}[\text{Co}(\text{i-dtma})\text{CO}_3]$	<i>ee</i>	516 (132), 364 (95.5)	<i>ee</i>	
$\text{fac}(N)\text{-}[\text{Co}(\text{i-dtma})\text{CO}_3]$	<i>ee</i>	517 (162), 368 (129)	<i>ee</i>	
$\text{mer, cis}(\text{NH}_3)_2\text{-}[\text{Co}(\text{NH}_3)_2(\text{val})\text{CO}_3]$	<i>bb</i>	555 (93.3), 373 (120)	<i>bb</i>	
$0.5\text{H}_2\text{O}$	<i>bb</i>	532 (79.4), 416 (sh), 366 (63.1)	<i>bb</i>	

$\nu_{\text{max}} = 18.7 (+3.70), 25.6 (+0.27),$
 $27.5 (-0.10), 29.1 (+0.1)$
 $\nu_{\text{max}} = 18.8 (+1.53), 25.5 (+1.30),$
 $27.4 (-0.05), 30.1 (+0.11)$

$^{13}\text{C NMR spectrum}^{38}$

$\nu_{\text{max}} = 17.3 (+1.74), 23.6 (+0.22),$

25.8 (0.11), 28.3 (+0.09)

$\nu_{\text{max}} = 19.3 (-1.74), 22.9 (2.17),$

28.4 (-0.57)

$\nu_{\text{max}} = 17.2 (+3.43), 23.9 (+0.33),$

25.9 (-0.07), 28.3 (+0.21)

$\nu_{\text{max}} = 18.4 (+0.87), 25.9 (-0.10)$

$\nu_{\text{max}} = 18.3 (+1.27), 23.8 (+0.09),$

25.8 (-0.06)

$\nu_{\text{max}} = 16.5 (-1.21), 18.4 (+0.81),$

23.9 (-0.28), 27.2 (-0.26)

TABLE X (*Continued*)

compd	prepn ref	vis/UV nm (M ⁻¹ cm ⁻¹)	ref	IR, cm ⁻¹	ref	¹ H NMR spectrum $\tilde{\nu}_{\text{max}} = 17.9$ (+ 3.55)	comments
iac-[Co(NH ₃) ₃ (val)CO ₃]· 3.5H ₂ O	bb cc	532 (110), 371 (135) 552 (172), 392 (163)	bb cc	1595	cc	¹ H NMR spectrum $\tilde{\nu}_{\text{max}} = 17.9$ (+ 3.55)	
mer,cis(NH ₃)-[Co(NH ₃) ₂ (α -ala)CO ₃]H ₂ O	bb	550 (93.3), 378 (129)	bb			¹ H NMR spectrum	
mer,trans(NH ₃)-[Co(NH ₃) ₂ (α -ala)CO ₃]· fac-[Co(NH ₃) ₂ (α -ala)CO ₃] iac-[Co(NH ₃) ₂ (β -ala)CO ₃]	bb bb bb bb	531 (100), 414 (sh), 366 (110) 533 (141), 369 (158) 537 (148), 375 (151) 555 (97.7), 375 (126)	bb bb bb			¹ H NMR spectrum	
mer,cis(NH ₃)-[Co(NH ₃) ₂ (β -ala)CO ₃]· mer,trans(NH ₃)-[Co(NH ₃) ₂ (β -ala)CO ₃] 0.5H ₂ O	bb cc	547 (129), 372 (141)	bb	1600, 1270, 1030, 760	bb	¹ H NMR spectrum	
is-K[Co(β -ala) ₂ CO ₃]·3H ₂ O	cc					¹ H NMR spectrum	
Co(DH) ₂ (py) ₂ [Co(DH) ₂ CO ₃] Co(DH) ₂ (β -picoline) ₂ [Co(DH) ₂ CO ₃] [Co(DH) ₂ (PhNH ₂) ₂]cis-[Co(DH) ₂ CO ₃] [Co(DH) ₂ (p-CIC ₆ H ₄ NH ₂) ₂]cis-[Co(DH) ₂ CO ₃] [Co(DH) ₂ (p-BrC ₆ H ₄ NH ₂) ₂]cis-[Co(DH) ₂ CO ₃] trans(N)-K[Co(mda)(NH ₃)CO ₃]·2.5H ₂ O	u ff gg	543 (115), 379 (98), 418 (sh) ~571 (~146), ~378 (~128) 570 (109), 520 (90 sh), 385 (150)	ff ff gg	1670 sh, 1605 s, 1010, 765	ff	¹³ C NMR spectrum; $\tilde{\nu}_{\text{max}} = 17.2$ (- 3.04), 24.0 (- 0.31), 26.0 (+ 0.10)	
cis-K ₂ [Co(nta)CO ₃]H ₂ O	u					¹ H NMR and CD spectra	
Δ-cis- α -Na[Co(pren)CO ₃]·3H ₂ O	u					¹ H NMR and CD spectra	
γ -cis-K[Co(edda)CO ₃]·4H ₂ O	hh	565 (114), 382 (128)	hh	359			
β -cis-K[Co(edda)CO ₃]·H ₂ O	hh	545 (96), 385 (138)	hh	359			
β -fac(N)-[Co(dien)(CN)CO ₃] mer(N)-[Co(dien)(CN)CO ₃] is-[Co(tren)CO ₃]ClO ₄ ·H ₂ O	u u ii	481 (162), 345 (182), 377 (sh) 490 (151), 350 (158) 504 (130), 354 (110)	u u ii	359 359 325			
+) _{3,9} cis- β -[Co(3,8-dimethien)CO ₃]ClO ₄ cis-[Co(dmt) ₂]ClO ₄ ·H ₂ O	320 320 320 320 jj	505 (132), 354 (111) 503 (134), ~354 (~112) 504 (132) 503 (124) 503 (180)	328 328 326 326 jj	328 326 326 326 jj		CD spectrum $k \cdot k$ CD spectrum $k \cdot k$	
γ -cis-[Co(trien)CO ₃]ClO ₄ ·H ₂ O β-cis-[Co(trien)CO ₃]ClO ₄ ·H ₂ O +) _{3,9} cis- β -[Co(3,8-dimethien)CO ₃]ClO ₄ cis-[Co(dmt) ₂]ClO ₄ ·H ₂ O	214 214 214 214 mm	530 (280), 368 (210)	mm	1653 s, 1605 br, 831 m, 752 m, 676 m	mm	¹ H NMR spectrum $\Lambda = 81 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$ (H ₂ O)	
Co([13]aneN ₄)CO ₃ ClO ₄	nn	501 (178), 356 (133)	nn	1660 vs, 1630 m, 810 m, 755 m	nn	¹ H NMR spectrum ^{ss}	
is-[Co(Me ₄) ₁₄]dieneN ₄)CO ₃ ClO ₄ · 1.5H ₂ O	oo	504 (133), 360 (167), 244 (18 000), 233 (16 000 sh)	338	1660 vs, 1630 m, 820 m, 750 ms	tt	¹ H NMR spectrum	
is-[Co(cyclam)CO ₃]ClI	pp	~51.7 (~204), ~360 (~183)	314		tt	¹ H NMR spectrum	
is-[Co(trans)[14]dieneN ₄]CO ₃ ClO ₄	qq	500 (121), 350 (135), 243 (16 000), 192 (~10 000)	rr	1660 vs, 1630 m, 820 m, 750 ms	rr	¹ H NMR spectrum	
is-[Co(Me ₄) ₁₄]diene)CO ₃]ClO ₄ ·2H ₂ O	tt	506 (126), 364 (176)	314		tt	¹ H NMR spectrum	
is-[Co(Me ₄) ₁₄]diene)CO ₃]ClO ₄	351	500 (121), 350 (135), 243 (16 000), 192 (10 000)	rr	1630, 830, 755, 675 1665	tt	¹ H NMR spectrum	
is-[Co([15]aneN ₄)CO ₃]ClO ₄ ·1.5H ₂ O	nn	528 (138), 366 (182)	nn	1662 s, 1621 br, 828 m, 750 m, 676 m	nn	¹ H NMR spectrum	

$\text{cis-}[\text{Co}(\text{1,16-aneN}_4)\text{CO}_3]\text{ClO}_4$	<i>nn</i>	540 (146), 375 (197)	<i>nn</i>	1656 s, 1613 br, 828 m, 752 m, 672 m	<i>nn</i>	$\Lambda = 95 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1} (\text{H}_2\text{O})$
$\Delta \cdot \beta \cdot [\text{Co}(5R,7R\text{-Me}_2\text{-}2,3,2\text{-tet})\text{CO}_3]\text{Cl}\cdot$ $1.5 \text{ H}_2\text{O}$	<i>uu</i>	515 (158), 360 (132)	<i>uu</i>			$\tilde{\nu}_{\text{max}} = 18.35 \text{ } (+2.47), 20.49$ (-1.51), 25.51 (+2.47), 28.57 (+0.41); ${}^1\text{H NMR}$ spectrum
$\Delta \cdot \beta \cdot [\text{Co}(1,5R,7R,11\text{-Me}_4\text{-}2,3,2\text{-tet})\text{CO}_3]\text{Cl}\cdot$ $\text{ClO}_4 \cdot \text{H}_2\text{O}$	<i>uu</i>	530 (174), 372 (148)	<i>uu</i>			$\tilde{\nu}_{\text{max}} = 18.05 \text{ } (+2.19), 20.37$ (-0.46), 25.13 (+0.55), 28.01 (+0.42); ${}^1\text{H NMR}$ spectrum
$\text{cis-}[\text{Co}(3,2,3\text{-tet})\text{CO}_3]\text{ClO}_4$	<i>vv</i>	520 (127), 360 (125)	<i>vv</i>			$\Lambda = 90 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1} (\text{H}_2\text{O})$
$\alpha\text{-}cis\text{-}[\text{Co}(\text{tetb})\text{CO}_3]\text{ClO}_4$	<i>ww</i>	554 (200), ~387 (~185)	<i>ww</i>			
$\beta\text{-}cis\text{-}[\text{Co}(\text{tetb})\text{CO}_3]\text{ClO}_4$	<i>ww</i>	551 (184), ~381 (~180)	<i>ww</i>			
$\text{cis-}[\text{Co}(\text{tetd})\text{CO}_3]\text{ClO}_4$	<i>ww</i>	~553 (~188), ~385 (~171)	<i>xx</i>			
$(+)\Delta \cdot cis\text{-}\beta\text{-}R,R:S,S[\text{Co}(3,2,3\text{-tet})\text{CO}_3]\text{-}$ $\text{ClO}_4 \cdot \text{MeOH}$	<i>yy</i>		<i>yy</i>			$[\alpha]_{\text{D}} 21^\circ \text{ (0.01 M H}_2\text{O)}$
$\text{cis-}\beta\text{-}R,R:S,S[\text{Co}(R,S,S,R,S,R,S\text{-ch-}$ $3,2,3\text{-tet})\text{CO}_3]\text{ClO}_4$	<i>yy</i>		<i>yy</i>			$\Delta M = 85 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1} (\text{H}_2\text{O})$
$\text{cis-}\beta\text{-}R,R:S,S[\text{Co}(R,S,R,S\text{-ch-}3,2\text{-}$ $\text{tet})\text{CO}_3]\text{ClI}$	<i>yy</i>		<i>yy</i>			$\Delta M = 73 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1} (\text{H}_2\text{O})$
$(+)\Delta \cdot cis\text{-}\beta\text{-}R,R:[\text{Co}(R,S,R,S\text{-ch-}3,2\text{-}$ $\text{tet})\text{CO}_3]\text{BPh}_4$	<i>yy</i>		<i>yy</i>			$[\alpha]_{\text{D}} + 92^\circ \text{ (0.002 M H}_2\text{O)}$
$\text{cis-}\beta\text{-}R,R:S,S[\text{Co}(R,S,R,S\text{-ch-}3,2,3\text{-}$ $\text{tet})\text{CO}_3]\text{ClO}_4$	<i>yy</i>		<i>yy</i>			$[\alpha]_{\text{D}} + 63^\circ \text{ (0.001 M MeOH)}$
$(-\Delta \cdot cis\text{-}\beta\text{-}S,S[\text{Co}(R,S,R,S\text{-ch-}3,2,3\text{-}$ $\text{tet})\text{CO}_3]\text{ClO}_4 \cdot \text{H}_2\text{O}$	<i>yy</i>		<i>yy</i>			not active
$\text{cis-}[\text{Co}(\text{diars})_2\text{CO}_3]\text{PF}_6$	<i>yy</i>		<i>yy</i>			
<i>197</i>				1675 s, 1190 m, 982 w, 890 sh, 732 m, 665 m, 449 m	<i>197</i>	mp 142°; ${}^1\text{NMR}$ spectrum
$\text{cis-}[\text{Co}(\text{diars}),\text{CO}_3]\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2$	<i>zz</i>					
$\text{cis-}\beta\text{-}[\text{Co}(R,R,S,S\text{-tetars})\text{CO}_3]\text{ClO}_4$	<i>aaa</i>					
$\text{cis-}\alpha\text{-}[\text{Co}(R,R,S,S\text{-tetars})\text{CO}_3]\text{ClO}_4$	<i>aaa</i>					
$\Delta \cdot cis\text{-}\beta\text{-}[\text{Co}(R,R\text{-tetars})\text{CO}_3]\text{ClO}_4$	<i>aaa</i>					
$\wedge \cdot cis\text{-}\alpha\text{-}[\text{Co}(R,R\text{-tetars})\text{CO}_3]\text{ClO}_4$	<i>aaa</i>					
$\text{cis-}\beta\text{-}[\text{Co}(R,S\text{-qars})\text{CO}_3]\text{ClO}_4$	<i>bbb</i>					
$\text{cis-}\beta\text{-}[\text{Co}(R,S\text{-qars})\text{CO}_3]\text{ClO}_4 \cdot 0.25\text{NaClO}_4$	<i>bbb</i>					
$\text{cis-}\beta\text{-}[\text{Co}(\text{dtnd})\text{CO}_3]\text{ClO}_4$	<i>ccc</i>	524 (387), 368 (485 sh)	<i>ccc</i>	1655 s, 1630 vs, 1610 vs, 823	<i>ccc</i>	
$\text{K}_3[\text{VO(O}_2)_2\text{CO}_3]$	<i>ddd</i>	524 (387), 368 (485 sh)	<i>ddd</i>	1575 vs, 1358 s, 1337 s, 1048 m, 690 w	<i>ddd</i>	232
$\text{cis-K[Cr(ox)}_2\text{CO}_3\text{]} \cdot 3\text{H}_2\text{O}$	<i>ddd</i>	577 (69), 415 (108), 265 (1040 sh)	<i>ddd</i>	1505 s, 1380 s, 1080 s, 858 s, 835 s, 707 m	<i>ddd</i>	350
$\text{K}_6[\{\text{Fe(OH)}_2\text{CO}_3\}_2\text{CO}_3] \cdot \text{H}_2\text{O}$	<i>ddd</i>	577 (69), 415 (108), 265 (1040 sh)	<i>ddd</i>	1025 s, 1340 s, 1058 s, 840 s 1517 s, 1340 s, 1058 s, 840 s	<i>ddd</i>	
$\text{Na}_2[\text{Fe}_2\text{O}_3(\text{OH})_2(\text{CO}_3)_2]$	<i>ddd</i>		<i>ddd</i>	1340 s, 1085 s, 837 s, 700 w	<i>ddd</i>	
$\text{K}_3[\text{Co}(\text{NH}_3)_6]\text{[Fe}_3(\text{OH})_4(\text{CO}_3)_6]$	<i>ddd</i>		<i>ddd</i>	1335 s, 1070 w, 853 m	<i>ddd</i>	
$\text{K}_3[\text{Co}(\text{NH}_3)_6]\text{[Fe}_3(\text{OH})_4(\text{CO}_3)_6]$	<i>ddd</i>		<i>ddd</i>	1600 s, 1340 sh, 1068 w, 696 m	<i>ddd</i>	
$\text{NH}_4[\text{Co}(\text{NH}_3)_6]\text{[Fe}_2(\text{OH})_4(\text{CO}_3)_3]$	<i>ddd</i>		<i>ddd</i>	1350 s, 1090 s, 855 s	<i>ddd</i>	
CuCO_3	<i>eee</i>		<i>eee</i>	1460 s, 1420 s, 1090 w, 860 m, 760 w, 743 w	<i>eee</i>	
$\text{Na}_2[\text{Cu}(\text{CO}_3)_2] \cdot 3\text{H}_2\text{O}$	<i>fff</i>		<i>fff</i>	1525 s, 1385 s, 1355 s, 1330 s, 1070 m, 1055 m, 855 s, 750 s, 700 m, 645 w	<i>fff</i>	Raman: 1523, 1395, 1330, 1071, 766, 750, 697 (cm^{-1})
$\text{[Cu(NH}_3)_2\text{CO}_3]$	<i>ggg</i>	635	<i>ggg</i>	282 [$\nu (\text{Cu-O})$] 1518 vs, 1022 w, 860 vs, 747 s, 708 s	<i>ggg</i>	
$[\text{C}(\text{NH}_2)_3]_2[\text{Cu}(\text{CO}_3)_2]$	<i>hhh</i>		<i>hhh</i>	1540, 1470, 1380, 1100, 860, 770, 725	<i>iii</i>	
$\text{NH}_4[\text{Ga}(\text{OH})_2\text{CO}_3]$	<i>jjj</i>			1040, 1012, 860, 755	<i>kkk</i>	CO_3 bands only

TABLE X (*Continued*)

acetic acid in the vapor phase. More recent X-ray and neutron diffraction data^{203,204} led to a refinement of this structure with the hydrogen atoms, or deuterium atoms, occupying two possible sites with an approximate probability ratio of 4:1. This gives rise to a degree of disorder in the dimer, $(\text{HCO}_3)_2^{2-}$.²⁰⁴ The authors²⁰⁴ did point out, however, that the degree of disorder may be specimen dependent. Note that RbHCO_3 also has this dimeric structure.²⁰⁵

Sodium carbonate monohydrate consists of sheets of CO_3^{2-} groups with H bonding between the layers of the O_1 and O_3 oxygen atoms.²⁰⁶ These oxygens are also bound to sodium atoms, whereas the O_2 oxygen is bound only to four sodiums in an approximate planar configuration. Anhydrous K_2CO_3 is symmetrical and planar with a D_{3h} symmetry.

Consideration of the various magnesium, calcium, strontium, and barium carbonates in Table XVII shows the carbonate to be, or very close to, planar and trigonal, with C–O bond lengths that vary only slightly. In fact, for the majority of carbonates and bicarbonates considered up to this point in the discussion, the average C–O bond length is (1.285 ± 0.021) Å and the average O–C–O angle is $(120.0 \pm 2.1)^\circ$, which compares almost exactly with the mean values computed by Zemann⁶⁴ for 34 carbonates of (1.284 ± 0.018) Å and $(120.0 \pm 2.1)^\circ$. From these two values, an average O–O distance within the carbonate of (2.22 ± 0.17) Å can be derived.

A more detailed examination of these data in Table XVII reveals that in dolomite, for example, the carbonate group has a slight pyramidal shape with the carbon atom 0.018 Å out from the plane of the oxygen atoms,²⁰⁷ whereas fairchildite exhibits a somewhat larger deviation of 0.038 (9) Å.²⁰⁸ Another finer aspect of these structures is that the arrangement of six oxygen atoms around the Mg^{2+} ion has a more exact octahedral symmetry than for the larger Ca^{2+} ion. Moreover, in our example of dolomite, the Mg–O bond lengths are shorter than they are in magnesite, while the Ca–O bond lengths are longer than in calcite. In the other example of fairchildite, $\text{K}_2\text{Ca}(\text{CO}_3)_2$,²⁰⁹ is in fact a double salt of potassium and calcium carbonate which therefore contains two distinct carbonate groups as shown in Table XVII.

Pauling²¹⁰ used measurements of the diamagnetic anisotropy of the minerals calcite, aragonite, strontianite, and witherite to estimate the degree of covalency within the metal–oxygen bonds, amounting to 20.6, 20.6, 15.4, and 14.2%, respectively. This allowed him to further calculate the resultant charge on the metal atoms.

All three monodentate carbonato complexes shown in Table XVIII are involved in extensive hydrogen bonding. For the Pd(II) complex, intermolecular H bonding between O_2 and O_3 of a pair of such complexes leads to a structure similar to that of KHCO_3 . Intramolecular H bonding for the two cobalt complexes is observed between the carbonate oxygens, O_2 , and the protons on the axial ligands. Of particular interest is the trans effect of the carbonate ligand in the $[\text{Co}(\text{NH}_3)_5\text{CO}_3]^+$ moiety, where the trans $\text{Co}-\text{NH}_3$ bond is weakened to 1.98 (3) Å compared to 1.96 (2) Å for the four cis ligands.²¹¹ Some distortion of octahedral symmetry occurs in this case with the $\text{O}_1\text{CoN}_{\text{cis}}$ angle being 89.9 (1.2)°.

From the data listed in Table XIX it can be seen that the bidentate carbonate creates the largest distortion in the symmetry of the metal ion by imposing such a narrow O_1MO_2 angle. It is therefore somewhat surprising that the O_1MO_2 angle and, for that matter, the MO_1C angle remain so constant for metal complexes with coordination numbers 4 through 6, i.e., mean values for these two angles are 68.0 (18)° and 90.3 (8)°, respectively. The origin of this consistency can be easily traced to the O_1CO_2 angle that is not reduced below 108° for any of the complexes listed in Table XIX. In fact, for the larger central metal ions with their longer $\text{M}-\text{O}_1$ distances (such as $\text{W}^{\text{IV}}-\text{O}_{1,2}$) the O_1MO_2 angle becomes quite narrow at ca. 53° while maintaining an O_1CO_2 angle of ca. 114° . The narrowest O_1CO_2 angle in this group is reported for $[\text{Co}(\text{phen})_2\text{CO}_3]\text{Cl}\cdot 3\text{H}_2\text{O}$ where the strain due to the planar phenanthroline ligands is quite acute leading to two distinct phen ligands and large differences in the $\text{C}-\text{O}_1$, $\text{C}-\text{O}_2$ bond lengths.²¹² Note that these two bonds are generally almost equal except where the remaining ligands are asymmetrical, such as in the example of $\text{K}[\text{Co}(\text{L-val})_2\text{CO}_3]\cdot 2\text{H}_2\text{O}$.²¹³ In this particular case, the *cis*(*N*)-*cis*(*O*) configuration could in fact be inferred from this inequality. Complexes in this group with coordination numbers 5 and 6 all have longer $\text{C}-\text{O}_1$, $\text{C}-\text{O}_2$ bonds (1.315 (15), 1.312 (18) Å) relative to their $\text{C}-\text{O}_3$ bonds (1.234 (20) Å) as a direct result of $\text{M}-\text{O}_{1,2}$ bonding, with the exception of the aforementioned valinato complex. In other words, this reflects the enhanced double bond character of the $\text{C}-\text{O}_3$ bond. For most of the remaining complexes of higher coordination number, hydrogen bonding tends to cloud this picture.

Distortion of the symmetry of the complex at the metal center is manifested in the angle of twist of the MCO_3 plane. For the cobalt(III) complexes this can be measured relative to the plane of the ML_1L_2 plane, where L_1 and L_2 are the ligands trans to O_1 and O_2 . The angle of twist may be as great as 4.3° as in the case of *cis*- β -[$\text{Co}(3,8\text{-Me}_2\text{trien})\text{CO}_3$] ClO_4 .²¹⁴ However, no elongation of the $\text{M}-\text{L}_{1,2}$ bonds due to the trans effect of the oxygen atoms, O_1 and O_2 , was observed. In general, the coordinated bidentate amine ligands, phen, bpy, tn, etc., are asymmetrical. In the particular example of *cis*-[$\text{Co}(\text{tn})_2\text{CO}_3$] ClO_4 , the two six-membered CoN_2C_3 rings adopt their configurations, with one flatter than the other.²¹⁵

Little comment can be made concerning the bonding in the remaining bridged carbonato complexes summarized in Tables XXI–XXIV, except one is immediately struck by the incredible diversity of the carbonate ligand as it displays such a range of bonding modes. The complexes in Table XXI establish that the bonding angle, MO_1C , of the bridge in this particular group is close to 120° , especially where M–M bonding is involved, e.g., in the Cr(II) and two Rh(III) complexes. Where metal–metal bonding does not occur, this MO_1C angle is extended to ca. 127° . In addition, the carbonate group has close to trigonal symmetry and the $\text{C}-\text{O}_{1,2}$, $\text{C}-\text{O}_3$ bonds are similar to those recorded for mononuclear bidentate complexes (viz., 1.301 (15), 1.260 (17) Å).

A comparison of the structure of $[\{\text{Rh}(\text{H}_2\text{O})_2(\mu\text{-CH}_3\text{CO}_2)\}_2]^{2+}$ ²¹⁶ with that of $\text{Cs}_4[\{\text{Rh}(\text{H}_2\text{O})_2(\mu\text{-CO}_3)\}_2]\cdot 6\text{H}_2\text{O}$ shown in Table XXI establishes the close similarity of

Table XI. Spectroscopic Properties of Bridged Carbonato Complexes

compd	prep ref	vis/UV, nm ($M^{-1} \text{ cm}^{-1}$)	ref	IR, cm^{-1}	ref	comments
$[\{\text{Ti}(\text{cp})_2\}_2(\mu\text{-CO}_3)]_2$	402	1475 ms, 1425 vs	402			
$[\{\text{Cr}([9]\text{-aneN}_3)\}_2(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$	345	510 (101), 373 (84), 335 (41 sh)	345			I ₂ ·3H ₂ O salt also prepared
$[\text{Cr}_2(\text{CO}_3)_3]_2 \cdot [\text{Co}(\text{NH}_3)_3]_2(\mu\text{-OH})_2(\mu\text{-CO}_3)_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$	590, 407, 353	347 ~520 (~122), ~294 (~3200 sh)	a	1600, 1480, 1270, 825	347	
$[\{\text{Co}(\text{NH}_3)_5\}_2(\mu\text{-CO}_3)_2](\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	b	505 (151), 350 (170)	c	1480, 1340, 1030, 830, 760, 670	c	
	d	505 (138), 350 (sh), 255	d			
	e	510 (151)	e			
$\wedge\wedge\text{-cis}(N)\text{-trans}(O)\text{-}[(S\text{-pra})_2\text{Co}(\mu\text{-CO}_3)(\mu\text{-OH})\text{-Co}(S\text{-pra})(S\text{-praH})] \cdot 2\text{H}_2\text{O}$	f					vis, IR, and CD spectra
$\wedge\wedge\text{-cis}(N)\text{-cis}(O)\text{-}[(S\text{-pra})_2\text{Co}(\mu\text{-CO}_3)(\mu\text{-OH})\text{-Co}(S\text{-pra})(S\text{-praH})]$	f					vis, IR, and CD spectra
$\wedge\wedge\text{-cis}(N)\text{-trans}(O)\text{-}[(S\text{-pra})(S\text{-praH})\text{Co}]_2$	f					vis, IR, and CD spectra
$[(\mu\text{-CO}_3)_2 \cdot 2\text{NaHCO}_3 \cdot 2\text{H}_2\text{O}] \cdot [\text{Co(dials)}_2(\text{CO}_3\text{H})_2(\mu\text{-CO}_3\text{H})](\text{BF}_4)_3$	197					
$[(\text{Co(dials)}_2(\text{CO}_3\text{H})_2(\mu\text{-CO}_3\text{H})](\text{ClO}_4)_3$	197					
$[(\text{Ni(dla})_2(\mu\text{-CO}_3)_2](\text{ClO}_4)_2 \cdot 2\text{DMF}$	g					
$[(\text{Cu}(\text{PPh}_3)_2)_2(\mu\text{-CO}_3)]$	h					
$[(\text{Cu(dia)}_2(\mu\text{-CO}_3)_2](\text{ClO}_4)_2 \cdot \text{DMF}$	i	1053 (50), 645 (300), 373 (5100)	i			
$[(\text{Cu(dia)}_2(\mu\text{-CO}_3)_2)(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$	g					
$[(\text{Cu(teed})\text{Cl}]_2(\mu\text{-CO}_3)]$	j	760 (285), 300 (6700)	j	1530, 840	j	
$[(\text{Cu(tmed})\text{Cl}]_2(\mu\text{-CO}_3)]$	j	750 (570), 375 (2500 sh), 287 (9770)	j	1520, 1380, 810, 745, 515	j	
$[(\text{Cu(teed})\text{Br}]_2(\mu\text{-CO}_3)]$	j	713 (320), 492 (360 sh), 320 (5400), 270 (4560)	j	1535, 830, 510	j	
$[(\text{Cu(tmtd})\text{Br}]_2(\mu\text{-CO}_3)]$	j	744 (590), 380 (5880), 330 (4400), 275 (5060)	j	1560, 1380, 890, 735, 505	j	
$[(\text{Cu(tmtd})\text{(NO}_3)_2]_2(\mu\text{-CO}_3)]$	j	720 (33), 290 (5630), 265 (5125)	j	1580, 1390, 895, 740, 505	j	
$[(\text{Cu(tmtd})\text{Cl}]_2(\mu\text{-CO}_3)]$	k	775 (450), 375 (4475), 300 (5080), 255 (5140)	k	1560 s, 1380 s, 895 m, 730 m	k	diamagnetic mp = 124-126 °C
$[(\text{Cu(tpam})\text{Cl}]_2(\mu\text{-CO}_3)]$	j	719 (156), 294 (33 600), 265 (28 000)	j	1600, 1490	j	magnetic, ESR, emf properties
$[(\text{Cu(tpam})\text{(OAc})]_2(\mu\text{-CO}_3)]$	j	750 (570), 375 (2500 sh), 287 (9770)	j			magnetic, ESR properties
$[(\text{Cu(tpam})\text{Br}]_2(\mu\text{-CO}_3)]$	j	684 (95), 293 (29 200), 266 (23 750)	j	1600, 1490	j	magnetic, ESR properties

$\left[\text{Cu}(\text{pip})(\text{H}_2\text{O})\right]_3(\mu\text{-CO}_3)_2(\text{NO}_3)_4$	1460, 840, 752	I	$(\text{ClO}_4)_4$ salt also isolated
$\left[\text{Cu}(\text{mdpt})\right]_3(\mu\text{-CO}_3)_2(\text{ClO}_4)_4$	1474 s, 1425 vs, 838, 774, 672	g	$\mu_{\text{eff}} = 1.91 \text{ BM}$
$\left[\text{Cu}(\text{dpt})\right]_3(\mu\text{-CO}_3)_2(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$	1475, 1425, 837, 782, 672	m	$\mu_{\text{eff}} = 1.87 \text{ BM (20 }^\circ\text{C)}$
$\left[\text{Cu}(\text{dppt})\right]_4(\mu\text{-CO}_3)_2\text{C}_6\text{H}_5\text{O}$	1540, 1365, 818, 740	m	$\mu_{\text{eff}} = 1.67 \text{ BM (20 }^\circ\text{C)}$
$[\text{Rh}_2(\text{PPh}_3)_5(\mu\text{-CO}_3)_2]\cdot\text{C}_6\text{H}_6$	500	500	Raman: 1660 m, 1300 s (cm^{-1}); $^{31}\text{P}, ^1\text{H}$ NMR spectra
$[\text{Rh}(\text{P}(i\text{-Pr})_3)_2(\text{CO})]_2(\mu\text{-CO}_3)_2$	403	403	^{31}P , ^1H NMR spectra mp = 145 °C
$\text{Cs}_4\text{Na}_2\left[\text{RhCl}(\mu\text{-CO}_3)_2\right]_2\cdot 8\text{H}_2\text{O}$	n	500	^{1}H , ^{31}P NMR data
$\text{Cs}_4\left[\text{Rh}(\text{H}_2\text{O})\right]_2(\mu\text{-CO}_3)_2\cdot 6\text{H}_2\text{O}$	n	o	o
$[\text{Rh}([9\text{-anen}_3])_2(\mu\text{-OH})(\mu\text{-CO}_3)_2]$	p	1540 s, 1460 s, 1380 s, 1095 w, 859 s,	p
$[\text{Mo}_2(\text{PMe}_2\text{Ph})_6(\text{CO})_2(\mu\text{-CO}_3)_2]$	346	826 s, 743 w, 714 m, 675 w	q
$[(\text{PPh}_3)_2(\text{Me})\text{Pd}(\mu\text{-CO}_3)\text{Pd}(\text{PPh}_3)(\text{Me})]$	346	1520 s, 1425 s, 1395 sh, 1395 w, 869 m, 840 m, 775 m, 725 sh, 705 m, 680 w	q
$[\text{Ce}_3\text{Cl}(\text{CO}_3)_4]$	445	1475 s, 1360 m, 820 w	q
$[\text{Ce}_4\text{Cl}(\text{OH})_3(\text{CO}_3)_4]$	403	1690, 1580, 1300, 1260, 1020	q
$[\text{Ce}_4\text{Cl}(\text{CO}_3)_4]$	q	1520 s, 1425 s, 1395 sh, 1395 w, 869 m, 840 m, 775 m, 725 sh, 705 m, 680 w	q

^a Tandon, S. P.; Sule, K. K.; Surana, S. S. *L. Phys. Status Solidi* 1973, 20, K65. ^b Kranig, J. *Ann. Chim. Paris* 1929, 41, 87. ^c Kremer, E.; Mac-Coll, C. R. *P. Inorg. Chem.* 1971, 10, 2182. ^d Abedini, M. *Ibid.* 1976, 15, 2945. ^e Mac-Coll, C. R. *P. Rev. Roum. Chim.* 1979, 24, 575. ^f Nishio, K. *Bull. Chem. Soc. Jpn.* 1977, 50, 2618. ^g Martin, J. W. L.; Curtis, N. L. *Aust. J. Chem.* 1980, 33, 1241. ^h Yamamoto, A. *Bull. Chem. Soc. Jpn.* 1980, 53, 680. ⁱ Davis, A. R.; Einstein, F. W. B.; Curtis, N. F.; Martin, J. W. L. *J. Am. Chem. Soc.* 1978, 100, 6258. ^j Churchill, M. R.; Hutchinson, J. P.; Rupich, M. W. *Inorg. Chem.* 1980, 19, 201. ^k Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. F.; Watkins, K. O. *Ibid.* 1979, 18, 2296. ^l Kolks, G.; Lippard, S. J.; Waszczak, J. V. *J. Am. Chem. Soc.* 1980, 102, 4832. ^m Curtis, N. F.; Hay, R. W.; Curtis, Y. M. *J. Chem. Soc. A* 1968, 182. ⁿ Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* 1980, 19, 320. ^o Ozawa, F.; Ito, T.; Yamamoto, A. *Chem. Lett.* 1979, 735. ^p Singh, N. B.; Singh, R. P.; Singh, J.; Singh, H. C. *J. Solid State Chem.* 1980, 33, 391. ^q Peterson, E. J.; Onstott, E. I. *J. Inorg. Nucl. Chem.* 1979, 41, 517.

the bonding parameters, e.g., Rh-O₂CCH₃ = 2.039 (8) Å, C-O = 1.269 (4) Å, Rh-Rh = 2.39 (8) Å, and the O₁-C-O₂ angle = 1.248 (3)°, and the Rh-O₁-C angle = 119.5 (3) Å. A similarly close relationship is expected for the corresponding formato rhodium(II) complex²¹⁷ and has been established between the Cr(II) complexes, (NH₄)₄[{Cr(H₂O)₂(μ-CO₃)₄}]·H₂O (see Table XXI) and [{Cr(py)₂(μ-CHO₂)₄}]²¹⁸ e.g., Cr-O₂CH = 2.019 (6) Å, C-O = 1.254 (9) Å, O₁-C-O₂ = 126.0 (7)°, and Cr-O₁-C = 120.3 (3)°. The structures of the complexes involved in “bidentate” and “monodentate” carbonate bridging (Table XXII) reflect the angles and bond lengths observed for the individual species, Tables XVIII and XIX, respectively. Although it is not immediately obvious, the same pattern exists for the multinuclear compounds in Tables XXIII and XIV, with the exception of [(dpf)₄Cu₄(μ-CO₃)(μ-Cl)₂]Cl₄·7.5H₂O where bonding of two Cu(II) atoms to O₁ apparently causes the C-O bond to be exceptionally long.²¹⁹ This effect is not observed for malachite, Cu₂(OH)₂CO₃, which has a continuous structure with no discrete units.

Finally, the metal-oxygen bond lengths for the carbonate ligands vary from 1.909 (13) Å for the bidentate cobalt(III) complex to 2.81 (11) Å for BaCO₃. No definite trend could be detected between the relative lengths of monodentate vs. bidentate M-O bonds, but this may well be due to the large experimental uncertainties in the former for which only a limited number of examples are available. The effect of increased charge on the metal decreasing the M-O bond length is quite apparent in every case.

VI. Solid-State Thermal Decomposition

Solid carbonato complexes, with few exceptions, decompose on heating. Consequently, the melting points of these solids are generally not available as an intrinsic property. However, thermal decomposition does provide a “fingerprint” of the solid which may not be precise, but is nevertheless appropriate to this section. Furthermore, numerous examples are to be found where new carbonato complexes have been isolated, and/or characterized, or at least their composition inferred from the decomposition products of similar complexes.

Table XXV lists the abbreviated results of thermolytic studies, the more complicated of which are discussed in the body of this text. In those cases where various heating rates were used, the results of the slowest were chosen. Obviously the heating rate strongly influences the recorded temperature range over which species appear to be stable. The compounds listed under “products” in Table XXV do not necessarily represent all of the residue formed in that particular temperature range. We have not attempted to establish whether the thermal transitions are endo- or exothermic in this brief synopsis. Moreover, the dehydration reactions are not treated, unless they are coupled with a change in coordination of the central metal.

Many reactions that may appear simple from a cursory look at the data in Table XXV involve more complicated mechanisms, as exemplified by the thermal decomposition of MgCO₃·3H₂O.²²⁰ Magnesium carbonate trihydrate can be better represented as containing a bicarbonato and a hydroxo ligand coupled together to form a dimer. Thermolysis results in polymerization

TABLE XII. Infrared Spectral Data of Lanthanide Carbonato Complexes

compd	hyd-rate	prepn ref	IR, cm ⁻¹	ref
Na[La(CO ₃) ₂]	0	250	1500, 1480, 1440, 1088, 1080, 882, 873, 868, 854, 747, 727, 690, 684, (275) ^a	250
	2		1470 vs, 1370 vs, 1080 vw, 850 m, 750 m, 680 vw, (280 m)	b
	6		1470 vs, 1410 vs, 1350 vs, 1090 vw, 1065 vw, 875 sh, 860 s, 750 m, 720 vw, 700 sh, 680 vw, (315 s, 250 vw)	b
K[La(CO ₃) ₂]	2		1470 vs, 1410 vs, 1360 vs, 1085 vw, 1060 w, 870 sh, 850 s, 760 sh, 735 m, 700 m, 670 m, (280 s)	b
	3		1470 vs, 1410 vs, 1360 vs, 1090 vw, 1060 sh, 870 sh, 850 s, 760 w, 735 m, 700 m, 670 w, (280 m)	b
	x		1440, 1370, 1060, 870, 720, 675	c
[C(NH ₂) ₃] ₅ [La(ox) ₂ (CO ₃) ₂] [La ₂ (CO ₃) ₃]	8	d-f	1460 s, 1360 s, 1330 m, 1075 m, 860 w, 850 s, 743 m, 675 m	198
	8		1470 vs, 1370 vs, 1085 vw, 1075 vw, 875 w, 850 s, 750 vs, 680 vw, (290 m, 225 sh)	b
Na[Sc(CO ₃) ₂]	1		1500 vs, 1490 vs, 1410 vs, 1100 m, 1060 sh, 840 s, 770 w, 700 w, (370 s, 280 s)	b
K[Sc(CO ₃) ₂]	2		1500 vs, 1400 vs, 1085 m, 1050 sh, 865 s, 855 vs, 780 s, 685 w, (380 s, 310 m, 250 w)	b
Na ₅ [Sc(CO ₃) ₄]	0		1550 vs, 1365 vs, 1060 m, 880 s, 860 s, 740 s, 700 w, (370 m)	b
	2		1550 vs, 1415 s, 1350 vs, 1060 m, 870 m, 745 m, 700 w, (360 s, 260 m)	b
	2		1550, 1420, 1360, 1062, 870, 740, 680 (360, 250)	253
	11		1565 vs, 1410 s, 1355 s, 1060 s, 870 s, 750 s, 710 m, (370 s, 260 m)	b
Na[Ce(CO ₃) ₂]	0	250	1500, 1480, 1440, 1089, 1080, 882, 873, 867, 853, 749, 728, 689, 683, 661 (275)	250
[Ce(OH)CO ₃] (A form)	0		1485 s, 1410 s, 1071 m, 850 m, 800 m, 710 sh, 692 m	g
[Ce(OH)CO ₃] (B form)	0		1490 s, 1440 s, 1405 s, 1095 w, 1080 w, 872 m, 848 m, 795 w, 780 w, 739 w, 729 w, 705 m, 690 w	g
[Ce(Cl)CO ₃]	3		1480 s, 1450 s, 1405 s, 1089 w, 860 sh, 851 m, 829 w, 770 w, 748 m, 715 sh, 692 m	g
[Ce ₂ (CO ₃) ₃]	8	f	1470 s, 1370 s, 1340 sh, 1075 w, 845 m, 745 m, 673 w	g
Na[Pr(CO ₃) ₂]	0	250	1500, 1485, 1440, 1092, 1081, 883, 874, 867, 854, 753, 730, 691, 683, 661 (275)	250
	6		1550 sh, 1460 vs, 1405 vs, 1355 vs, 1090 vw, 1060 w, 875 sh, 860 s, 755 m, 720 vw, 685 vw, 670 vw, 660 vw, (320 m, 260 vw)	b
[Pr ₂ (CO ₃) ₃]	5		1550, 1500, 1085, 860, 750, 690	h
	8		1460 s, 1360 s, 845 s, 745 m	198
	10		1655, 1380, 1335, 810, 725, 503	h
Na[Nd(CO ₃) ₂]	0	250	1510, 1495, 1450, 1098, 1087, 888, 878, 872, 858, 760, 735, 693, 687, 665, (280)	250
	6		1550 sh, 1460 vs, 1405 vs, 1355 vs, 1090 vw, 1060 w, 880 s, 875 sh, 760 vw, 750 sh, 730 vw, 710 vw, 690 vw, 670 vw, (320 m, 255 vw)	b
	0		1495, 1425, 1078, 856, 810, 723, 712	310
[Nd ₂ (CO ₃) ₃]	2	e	1480 s, 1410 s, 1070 m, 863 m, 834 s, 782 w, 761 m, 730 w, 685 m	198
	5		1520, 1090, 860, 750, 695	h
	8	d	1470 s, 1370 s, 1340 s, 1080 m, 847 s, 748, 675	198
Na[Sm(CO ₃) ₂]	10		1650, 1370, 1340, 812, 750, 497	h
	0	250	1525, 1465, 1099, 1087, 887, 876, 870, 857, 761, 734, 690, 685, 663, (300)	250
	6		1550 sh, 1460 vs, 1400 vs, 1350 vs, 1090 vs, 1060 w, 875 sh, 860 s, 760 vw, 750 sh, 730 vw, 710 vw, 685 vw, 670 vw, (300 sh, 270 m, 240 vw)	b
K ₅ [Sm(ox) ₂ (CO ₃) ₂] [C(NH ₂) ₃] ₅ [Sm(ox) ₂ (CO ₃) ₂]	5		1480, 1380, 1060, 865, 710, 670	c
	2		1485, 1365, 1050, 868, 730, 685	c
	6		1490 vs, 1390 vs, 1060 m, 880 s, 720 s, 690 s, (260 m)	b
Na ₃ [Sm(CO ₃) ₃]	0		1500 vs, 1380 vs, 1070 m, 850 s, 740 m, 700 w, (280 sh)	b
Na(Eu(CO ₃) ₂)	0	250	1515, 1465, 1101, 1089, 887, 877, 872, 857, 763, 735, 690, 685, 663, (300)	250
	6		1500 vs, 1380 vs, 1090 vw, 1065 w, 875 sh, 860 s, 780 sh, 750 vw, 730 vw, 710 vw, 690 vw, 680 vw, (300 sh, 265 m)	b
	6		1457, 1440, 1067.5, 852, 700.5, 695	j
EuCO ₃	0		1490 vs, 1380 vs, 1060 m, 880 s, 720 s, 690 s, (265 m)	b
	6		1520, 1470, 1101, 1090, 885, 876, 867, 857, 765, 738, 692, 686, 663, (300)	250
Na ₃ [Eu(CO ₃) ₃]	6		1500 vs, 1360 vs, 1070 w, 890 sh, 860 s, 760 vw, 750 vw, 730 vw, 710 vw, 690 vw, 670 vw, (300 sh, 270 m)	b
	0	250	1665, 1380, 1340, 815, 760, 497	h
Na[Gd(CO ₃) ₂]	6		1500 vs, 1360 vs, 1070 w, 890 sh, 860 s, 760 vw, 750 vw, 730 vw, 710 vw, 690 vw, 670 vw, (280 sh, 260 m)	b
	6		1520, 1500, 1360, 1116, 1069, 763, 725	253
Na ₃ [Gd(CO ₃) ₃]	6		1500 vs, 1385 vs, 1060 m, 880 s, 720 s, 690 s, (265 m)	b
	5	d	1550, 1530, 1095, 862, 750, 690	h
Na[Tb(CO ₃) ₂]	10	f	1665, 1380, 1340, 815, 760, 497	h
	0	250	1560, 1520, 1430, 1415, 1395, 1107, 1092, 857, 768, 758, 692, 688, (330, 300)	250
	6		1500 vs, 1370 vs, 1060 w, 880 sh, 855 s, 760 vs, 750 vw, 730 vw, 710 vw, 690 vw, 670 vw, (280 sh, 260 w)	b

TABLE XII (Continued)

compd	hyd-	prepn	IR, cm ⁻¹	ref
	drate	ref		
Na ₃ [Tb(CO ₃) ₃]	6		1495 vs, 1385 vs, 1060 m, 880 s, 720 s, 690 s, (270 m)	b
Na[Dy(CO ₃) ₂]	0	250	1560, 1540, 1435, 1415, 1390, 1112, 1097, 862, 773, 766, 687, 682, (330, 300)	250
	6		1500 vs, 1370 vs, 1060 w, 890 sh, 855 s, 760 vw, 690 vw, 670 vw, (290 w, 260 w)	b
Na ₃ [Dy(CO ₃) ₃]	6		1495 vs, 1390 vs, 1065 m, 880 s, 720 s, 690 s, (270 m)	b
Na[Ho(CO ₃) ₂]	0	250	1565, 1540, 1435, 1410, 1380, 1115, 1095, 860, 773, 765, 685, 680, (330, 300)	250
Na ₃ [Ho(CO ₃) ₃]	6		1510 vs, 1380 vw, 1060 m, 880 s, 720 s, 690 s, (270 m)	b
Na[Y(CO ₃) ₂]	0	250	1545, 1445, 1420, 1400, 1115, 1100, 862, 765, 757, 688, 682, (370, 330, 300)	250
	6		1500 vs, 1370 vs, 1100 vw, 1055 w, 900 vw, 765 vw, 740 vw, 670 vw, (290 w)	b
Na ₃ [Y(CO ₃) ₃] [Y ₂ (CO ₃) ₃]	6		1510 vs, 1400 vs, 1070 m, 880 s, 710 sh, 690 s, (265 m)	b
	2	d, f	1540 w, 1500 s, 1450 sh, 1420 sh, 1087 w, 1062 w, 862 m, 846 s, 835 s, 760 s, 683 s	198
Na[Er(CO ₃) ₂]	0	250	1570, 1550, 1435, 1415, 1385, 1110, 1090, 859, 773, 765, 682, 677, (335, 300)	250
	6		1530, 1370, 1110, 1060, 855, 760, 740, 680, (290, 260)	253
	6		1530 vs, 1370 vs, 1110 w, 1060 w, 930 sh, 855 s, 760 vs, 740 vw, 680 vw	b
Na ₃ [Er(CO ₃) ₃]	6		1500 vs, 1390 vs, 1070 m, 880 s, 720 s, 690 s, (260 m)	b
	6		1500 vs, 1390 vs, 1070, 1064, 880, 860, (260)	253
Na ₅ [Er(CO ₃) ₃]	9		1490 vs, 1390 vs, 1070 m, 900 sh, 870 s, 760 w, 720 m, 690 m, (260)	b
Na[Tm(CO ₃) ₂]	0	250	1550, 1435, 1415, 1380, 1110, 1090, 856, 771, 763, 680, 675, (330, 300)	250
	6		1530 vs, 1360 vs, 1105 vw, 1060 w, 930 sh, 850 s, 770 vw, 760 vw, 690 vw, (290 w, 260 w)	b
Na ₃ [Tm(CO ₃) ₃] Na ₅ [Tm(CO ₃) ₄]	6		1490 vs, 1380 vs, 1070 m, 880 s, 710 sh, 690 s, (260 w)	b
	2		1550 vs, 1380 vs, 1340 vs, 1050 s, 870 s, 740 s, 700 m, 680 w, (300 m, 250 m)	b
[Tm ₂ (CO ₃) ₃]	0		1535 vs, 1385 vs, 1085 w, 850 m, 770 w, 690 w, (300 sh)	b
	3		1520 vs, 1420 vs, 1090 vw, 1070 vw, 845 s, 835 s, 765 w, 690 w, (290 m, 220 sh)	b
Na[Yb(CO ₃) ₂]	0	250	1550, 1440, 1420, 1385, 1112, 1095, 860, 776, 768, 682, 678, (335, 300)	250
	0		1530 vs, 1380 vs, 1070 m, 850 s, 755 m, 700 w, (300 sh)	b
	6		1530 vs, 1360 vs, 1100 vw, 1050 w, 850 s, 770 sh, 760 vw, 690 w, (300 w, 260 sh)	b
Na ₃ [Yb(CO ₃) ₃] [Yb ₂ (CO ₃) ₃]	6		1500 vs, 1400 vs, 1070 m, 880 s, 710 sh, 690 s, (265 m)	b
	0		1550 vs, 1360 vs, 1085 w, 830 s, 770 m, 700 vw, (300 sh)	b
	6		1550 vs, 1430 sh, 1360 vs, 1100 vs, 1080 w, 1060 vw, 860 w, 850 s, 840 s, 770 w, 700 w, (350 sh, 300 m, 260 sh)	b
Na[Lu(CO ₃) ₂]	0		1550, 1445, 1410, 1385, 1117, 1095, 860, 780, 771, 686, 680, (335, 300)	250
Na ₃ [Lu(CO ₃) ₃]	6		1490 vs, 1390 vs, 1060 m, 880 s, 715 s, 690 s, (275 m)	b

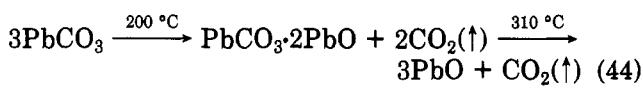
^a Frequencies in parentheses assigned to $\nu(\text{Ln}-\text{O})$ stretch. ^b Taravel, B.; Fromage, F.; Delorme, P.; Lorenzelli, V. *J. Chim. Phys. Physicochim. Biol.* 1971, 68, 715. ^c Thomas, Y.; Taravel, B.; Dumonceau, J.; Fromage, F.; Lorenzelli, V. *J. Mol. Struct.* 1978, 43, 159. ^d Wakita, H.; Nagashima, K. *Bull. Chem. Soc. Jpn.* 1972, 45, 2476. ^e Salutsky, M. L.; Quill, L. L. *J. Am. Chem. Soc.* 1950, 72, 3306. ^f Nagashima, K.; Wakita, H.; Mochizuki, A. *Bull. Chem. Soc. Jpn.* 1973, 46, 152. ^g Peterson, E. J.; Onstott, E. I. *J. Inorg. Nucl. Chem.* 1979, 41, 517. ^h Karyakin, A. V.; Davitashvili, E. G.; Kublashvili, Z. *Zh. Sh. Bull. Acad. Sci. Georgian SSR* 1969, 55, 297; *Chem. Abstr.* 1969, 71, 117990. ⁱ $\nu_2(^{13}\text{C}) = 837$ and $\nu_2(^{14}\text{C}) = 818.8 \text{ cm}^{-1}$. ^j Sterzel, W.; Schnée, W.-D. *Z. Naturforsch.* 1971, 26, 615.

through the carbonate ligands, followed by partial dehydration and eventually the formation of additional Mg-O-Mg bridges which are characterized by a band at 780 cm⁻¹ in the IR spectrum. Decomposition of the polymer occurs in the range 315–380 °C.²²¹

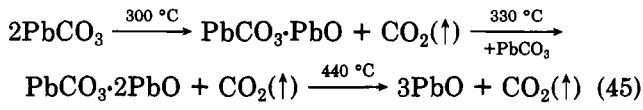
Alkaline earth metal carbonates can also undergo phase rearrangements at elevated temperatures. One such example involved heating SrCO₃ and BaCO₃ to form the solid solution, γ -(Sr,Ba)CO₃ at 500 °C, with another phase change at 800 °C corresponding to the formation of β -(Sr,Ba)CO₃, given a reasonably slow heating rate.²²²

The importance of the presence of CO₂ in the prevailing atmosphere of certain thermolysis processes is clearly illustrated by the decomposition of cerussite, PbCO₃.²²³ Using TG and DTA, combined with X-ray diffraction and SEM of the products, Yamaguchi et

al.²²³ established that for CO₂ pressures less than 1 atm only one intermediate exists



whereas at ca. 1 atm of CO₂, two intermediates are observed



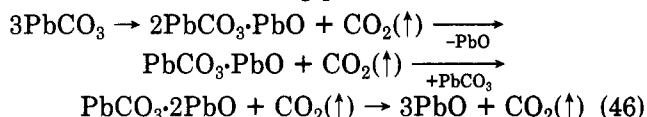
These two reaction paths were also proposed by Ball and Casson,^{224,225} although higher temperatures were generally reported (e.g., reaction 45, 365, 412, and 472 °C, respectively). These authors²²⁴ found white lead, PbCO₃·Pb(OH)₂, behaved similarly with three/four

TABLE XIII. Spectroscopic Properties of Actinide Carbonato Complexes

compd	prepn. ref	vis/UV, nm ($M^{-1} \text{ cm}^{-1}$)	ref	IR, cm^{-1}	ref	comments
[Th(OH) CO_3] $\cdot 2\text{H}_2\text{O}$	^a			1535, 1460, 1380, 1070, 840, 730	199	bi- and unidentate
Na ₆ [Th(CO ₃) ₅] $\cdot 3\text{H}_2\text{O}$	^a			1570, 1375, 1350, 1046, 856, 718	199	bidentate
Na ₆ [Th(CO ₃) ₅] $\cdot 12\text{H}_2\text{O}$	^a			1535, 1378, 1340, 1067, 1054,	199	bidentate
[C(NH ₂) ₃] ₆ [Th(CO ₃) ₅]	^a			1050 sh, 867, 735, 725		
				1590, 1485, 1350, 1059, 1047,	199	bi- and unidentate
		859, 723				
[UO ₂ (CO ₃) ₃] ₂ [UO ₂ (CO ₃) ₃] ²⁻	266	424 466 (13.7), 451 (19.1), 437 (19.9), 424 (18.9)	268			
Na ₄ [UO ₂ (CO ₃) ₃]	266	463 (19.0), 449 (27.0), 435 (24.4), 423 (21.1) 460, 445, 435, 420	266	1560 br, 1460 br, 1340 br, 1070 s, 850 vs, 830 vs, 735, 710	b	luminescence spectrum; 19 931, 19 590, 19 341, 19 202 cm^{-1} Raman: 1630, 1358, 1077, 737,
K ₄ [UO ₂ (CO ₃) ₃]	e		d	1560, 1342, 1062, 821, 732, 700	c	697 cm^{-1} Raman: 1065 sh, 1055 m, 1046 sh, 879 vw, 863 vw, 806 vs, 785 vw, 725 m, 719 w, 693 w, cm^{-1} ^e
[UO ₂ (CDMBA)(CO ₃) ₃] [(UO ₂) ₃ (CO ₃) ₆ ⁻ (NH ₄) ₂ [UO ₂ (neocupferron) ₂ CO ₃] ₁ ·H ₂ O	f	459 (29.9), 445 (44.8) 470 (417) 470 (274), 370 (2540 sh), 365 (2560 sh), 283 (32.730)	270 g h	1600 m, 1550 m, 1358 sh, 1338 m, 1054 sh, 1049 m, 1045 m, 882 s, 855 w, 847 w, 719 s, 694 m 1610, 1551, 1385, 1352	e	vis spectrum in Me ₂ CO $\lambda = 54.6$ (DMF), 134.3 (CH ₃ CN)
Na ₄ [(NP) ₂ (CO ₃) ₃] [Pu(OH)CO ₃] _x H ₂ O	i j			1565, 1535 1620, 1508, 1435, 1370	g	
					j	

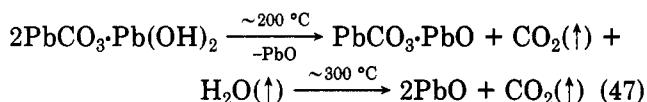
^a Chernyaev, I. I.; Golovnya, V. A.; Molodkin, A. K. *Zh. Neorg. Khim.* 1958, 3, 2671. Chernyaev, I. I.; Molodkin, A. K. *Ibid.* 1961, 6, 587, 809. ^b Novikov, Yu. P.; Gliva, V. B.; Komarevskii, V. M.; Akhmanova, M. V. *Radiokhimika* 1977, 19, 546. ^c Koglin, E.; Schenck, H. J.; Schwochau, K. *Spectrochim. Acta, Part A* 1979, 35A, 641. ^d Gao, H.-C.; Zhang, M.-L.; Pen, Q.-X.; Pen, L.-E.; Wang, W.-Q. *Heh Hua Hsueh Yu Fang She Hua Hsueh* 1981, 3, 88; *Chem. Abstr.* 1981, 95, 194031r. ^e Anderson, A.; Chieh, C.; Irish, D. E.; Tong, J. P. K. *Can. J. Chem.* 1980, 58, 1651. ^f Vera Palomino, J.; Galiano Sedano, J. A.; Parellada Bellido, R.; Bellido Gonzalez, A. *Junta Energ. Nucl., Junta Energ. Nucl. Chem.* 1979, 18A, 62. ^g Kundu, P. C.; Roy, P. S.; Banerjee, R. K. *J. Inorg. Nucl. Chem.* 1980, 42, 851. ^h Dzyubenko, V. I.; Karaeva, S. A.; Peretrukhin, V. F.; Krot, N. N. *Dokl. Akad. Nauk. SSSR* 1979, 248, 1362. ⁱ Hagan, P. G.; Navratil, J. D.; Cichorz, R. S. *J. Inorg. Nucl. Chem.* 1981, 43, 1054.

decomposition steps in a CO_2 atmosphere but only three in nitrogen (see Table XXV). For CO_2 pressures exceeding 4 atm (405.3 kPa), three intermediates were detected and the temperatures of these transformations increased with increasing pressure.²²³

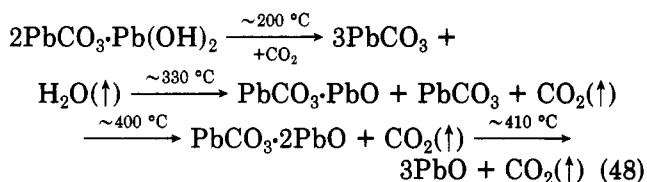


An equally detailed study²²⁶ of the thermal decomposition of hydrocerussite, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, at four pressures revealed a similar reaction sequence at $p(\text{CO}_2)$ of 0.304–2.533 MPa with PbCO_3 as the common intermediate. The complete reactions are as follows:

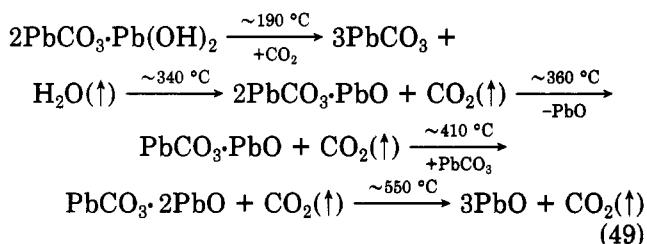
in air



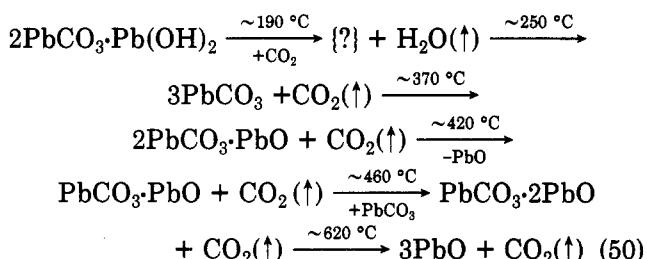
$$p(\text{CO}_2) = 304 \text{ kPa}$$



$$p(\text{CO}_2) = 912 \text{ kPa}$$



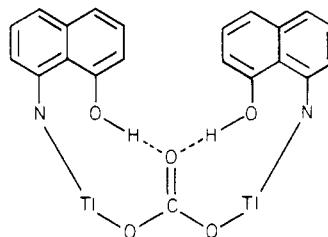
$$p(\text{CO}_2) = 2.533 \text{ MPa}$$



Kato and Mizutani²²⁶ concluded that lead carbonates, together with some of the rare earth carbonates, exhibit the common behavior of losing all of the H_2O and some CO_2 initially, with the loss of CO_2 being dependent on the partial pressure of CO_2 . Other basic carbonates may lose all the H_2O and CO_2 at one temperature, e.g., those of Co, Ni, and Cu. As discussed earlier, magnesium carbonates behave in a more complicated manner with the loss of CO_2 drastically affected by $p(\text{CO}_2)$.

A rather unique solid-state reaction was reported by Singh et al.^{226a} who reacted thallous carbonate with 8-hydroxyquinoline at temperatures of 40–55 °C to produce a yellow product which analyzed as $[(\text{Ti}(\text{C}_{10}\text{H}_6\text{NOH}))_2\text{CO}_3]$. X-ray and IR data (3200 br, H-bonded OH; ~1270, $\nu(\text{C}-\text{OH})$; 1690, $\nu(\text{C}=\text{O})$; 1580, 1300, ν_3 ; 1020 cm^{-1} , ν_1) of the solid material and conductivity measurements in nitrobenzene indicate the following

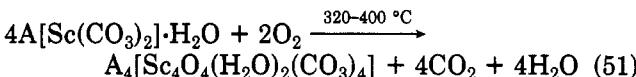
structure with a bidentate, H-bonded carbonate bridge.



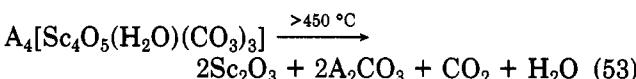
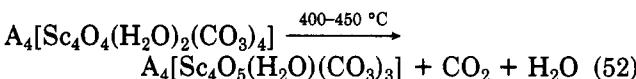
However, the thermal stabilities of transition-metal carbonates, particularly those of the lanthanides and actinides, are of greater interest within the mandate of this review. The discussion of these processes will be subdivided into individual subsections according to the nature of the central metal.

A. Transition-Metal Complexes

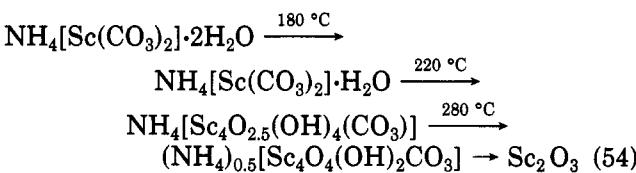
The decomposition of $\text{A}[\text{Sc}(\text{CO}_3)_2] \cdot n\text{H}_2\text{O}$ ($\text{A} = \text{K}$, NH_4 , Rb , or Cs ; $n = 1$ and 2) was studied in dry air and the reaction products characterized by IR, X-ray diffraction, and GC.²²⁷ For the alkali metals the complex maintains its anionic form when heated and yields yet another carbonate, the tetrameric form.



This reaction is manifested in the IR by a shift in the strong band at 1540 cm^{-1} to 1665 cm^{-1} (carbonate) and the appearance of a band at 635 cm^{-1} that can be related to Sc–O–Sc bonding in the tetramer. Subsequent heating produces another carbonate species which then decomposes.



The behavior of the ammonium salt is anomalous in that it decomposes as follows:



The stoichiometry of these reactions is difficult to rationalize. The coordinated carbonate in this tetramer exhibits two strong bands in the IR at 1410 and 1535 cm^{-1} .

It was further suggested²²⁷ that $\text{Na}_5[\text{Sc}(\text{CO}_3)_4] \cdot 11\text{H}_2\text{O}$ decomposes at 250 °C through a similarly coordinated carbonate tetrameric intermediate $[\text{Sc}_4\text{O}(\text{CO}_3)_5(\text{H}_2\text{O})]$ or $[\text{Sc}_4(\text{OH})_2(\text{CO}_3)_5]$. Moreover, the authors²²⁷ observed that heating $\text{Sc}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ to 300 °C in the presence of CO_2 yielded another tetramer, namely $[\text{Sc}_4\text{O}_3(\text{OH})_4\text{CO}_3]$ which decomposed to Sc_2O_3 at 420 °C.

Carbonato complexes are commonly formed during the thermolysis of carboxylato metal complexes. Within this group, oxalato complexes provide the main thermal source of carbonate complexes. One such mechanism involves complexes of the general formula, $\text{A}[\text{MO}(\text{C}_2\text{O}_4)_2] \cdot x\text{H}_2\text{O}$, where $\text{M} = \text{V(IV)}$, $\text{A} = \text{Ba}$ ($x = 4$) or Sr

TABLE XIV. Infrared and Raman Spectra of Alkali Metal Bicarbonates and Carbonates at Room Temperature^j

salts	spec- tra ⁱ	ν_6	$\nu_5^+ (\delta \text{OH})$	ν_1	ν_2	ν_4	ν_3	ref
Bicarbonate								
NaHCO ₃	IR	1655 s, 1617 s	1452 s, 1398 s, 1300 vs	1045 m, 1032 s	836 vs	694 vs	656 s	a
	R	1623 vw	1459 w, 1437 w	1047 vs	834 vw	699 w, 687 m	660 w	a
NaDCO ₃	IR	1620 sh, 1598 vs	1326 vs	1040 sh, 990 m	835 s	686 vs	626 s	a
	R	1597 w	1319 br	1036 vs, 995 vw	835 vw	678 s	627 vw	a
Carbonate								
Li ₂ CO ₃	IR	1495 vs, 1437 vs	1088 m	866 s, 846 w ^b		741 w, 712 w		c
	R	1420	1088	859 m, 847 w ^b		740 m, ^d 713 w		e
Na ₂ CO ₃	IR	1459	1091	n.o. ^f		748, 711		e
	R	1451 vs	1079 vw	881 s, 855 w, ^b 851 w ^b		701 w, 694 w, 691 m		c
K ₂ CO ₃	IR	1481, 1422	1083, 1079	n.o. ^f		702, 698		e
	R	1418, 1408, 1400	1063, 1043	880, 854 ^b		690, 685, 683		g
Rb ₂ CO ₃	IR	1445 sh, 1380 br	1053 vw	879, 852 ^b		688, 684, 681		g
	R	1405, 1395, 1384	1053, 1033 ^h	n.o. ^f		690, 688, 682, 680		g
Cs ₂ CO ₃	IR	1367 m	1041 m	878 s, 851 ^b		679 s, 674 s		i
	R	1391 w, 1381 w	1042 vw, 1020 vw ^h	n.o. ^f		680 m, 674 m		i

^a Bertoluzza, A.; Monti, P.; Morelli, M. A.; Battaglia, M. A. *J. Mol. Struct.* 1981, 73, 19. ^b Generally assigned to ¹³CO₃²⁻ frequency. ^c Buijs, K.; Schutte, C. J. H. *Spectrochim. Acta* 1961, 17, 927. ^d Not assigned. ^e Brooker, M. H.; Bates, J. B. *J. Chem. Phys.* 1971, 54, 4788. ^f Not observed. ^g Brooker, M. H.; Bates, J. B. *Spectrochim. Acta Part A* 1974, 30A, 2211. ^h Assigned to C¹⁶O₂¹⁸O²⁻ ν_1 frequency. ⁱ Hase, Y. *An. Acad. Brasil. Cienc.* 1980, 52, 521. ^j In cm⁻¹.

TABLE XV. Calculated and Experimental Carbonate Infrared Frequencies^a

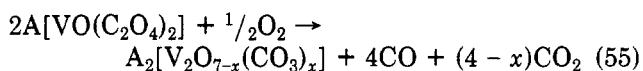
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8
Monodentate Carbonate								
C _s (calcd)	1373	1039	765	369	1483	711	82	
C _{2v} (calcd)	1376	1069	772	303	1483	676	92	
(assignment)	$\nu(\text{C}-\text{O}_2)$	$\nu(\text{C}-\text{O}_1)$	$\delta(\text{O}_2\text{CO}_2)$	$\nu(\text{C}-\text{O}_1)$	$\nu(\text{C}-\text{O}_2)$	P _r (O ₂ CO ₂)	$\delta(\text{CoO}_1\text{CO}_2)$	π
(Co(NH ₃) ₅ CO ₃)Br	1373	1070	756	362	1453	678	b	850
Bidentate Carbonate								
C _{2v} (calcd)	1595	1038	771	370	1282	669	429	
(assignment)	$\nu(\text{C}-\text{O}_2)$	$\nu(\text{C}-\text{O}_1)$	ring deformation	$\nu(\text{Co}-\text{O}_1)$	$\nu(\text{C}-\text{O}_1)$	$\delta(\text{O}_1\text{CO}_2)$	$\nu(\text{C}-\text{O}_1)$	π
+ $\nu(\text{Co}-\text{O}_1)$			+ $\nu(\text{Co}-\text{O}_1)$	+ ring deformation	+ $\delta(\text{O}_1\text{CO}_2)$	+ $\nu(\text{Co}-\text{O}_1)$		
(Co(NH ₃) ₄ CO ₃)Cl	1593	1038	760	395	1265	673	430	834

^a Reference 195, frequency in cm⁻¹. ^b Outside CsBr range.

($x = 4$); M = Zr(IV), A = Ca ($x = 7$) or Sr ($x = 4$). They all undergo dehydration during the initial heating stage (up to ca. 200 °C), but then their chemistries are different in that only in the case of Sr₂[Zr(C₂O₄)₂] was a mixed carbonato-oxalato complex detected, although not isolated, i.e., Sr₂[Zr₂O₂(C₂O₄)₃CO₃].²²⁸ The oxalato and carbonato ligands were characterized by IR bands at 1650 and 1320 cm⁻¹, respectively, but no band was found at ca. 2350 cm⁻¹ which would have indicated the presence of CO₂ trapped in the residue. The mixed complex yielded Sr₂[Zr₂O₅CO₃] on further heating (375–500 °C). Reddy and Mehrotra²²⁹ had previously not observed the mixed complex and reported the direct transformation of the dehydrated oxalato host over a similar temperature range of 325–475 °C to the Sr₂·[Zr₂O₅CO₃]·(CO₂) species in which the CO₂ is trapped within the lattice as evidenced by an IR band at 2310 cm⁻¹. The anhydrous calcium analogue, on the other hand, initially forms Ca[Zr₂O₄(CO₃)₂] at 225–375 °C containing both uni- and bidentate carbonate, then rearranges at 375–500 °C to the common form, Ca₂·[Zr₂O₅CO₃], in which the carbonate is ionic.²²⁸

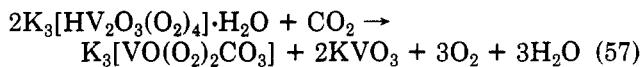
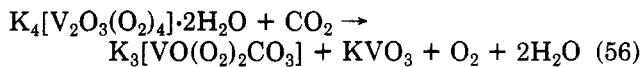
In oxidizing media, the barium and strontium salts of the anhydrous bis(oxalato)vanadium complex decompose at 280 and 300 °C, respectively, to produce the

monodentate vanadium(V) carbonato complex according to the following equation:²³⁰



Conversely, under nonoxidizing conditions at 400 °C, the mononuclear bidentate vanadium(IV) complex is formed, viz. A[V₂O₂CO₃], which in turn converts at 500 °C to A[V₂O₅CO₃], which is the analogue of the zirconium species.²³⁰

Stable vanadium oxycarbonato complexes can also be synthesized by the interaction of vanadium oxide with gaseous CO₂.²³¹



The rates of these reactions were monitored by IR spectroscopy and below 100 °C proved to be dependent on such factors as air humidity, CO₂ partial pressure, sample surface area, etc., whereas the stoichiometry of the products is independent of such factors. The mechanism for CO₂ uptake parallels the reaction in

aqueous solution with CO_2 combining with the terminal OH group formed by O_2 release, H_2O addition, and subsequent proton transfer. Note that $\text{K}_3[\text{VO}(\text{O}_2)_2\text{CO}_3]$ can be more conveniently prepared from aqueous solutions.²³²

A group of oxalato complexes of mainly the first transition series (viz., $\text{K}_3[\text{M}(\text{C}_2\text{O}_4)_3]\cdot x\text{H}_2\text{O}$ for $\text{M} = \text{Al}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Rh}; \text{K}_2[\text{M}(\text{C}_2\text{O}_4)_2]\cdot x\text{H}_2\text{O}$ for $\text{M} = \text{Cu}, \text{Zn}, \text{Pd}, \text{Pt}$) was investigated up to 600 °C by EGA (evolved gas analysis)²³³ and the liberated gases were CO and CO_2 . No evidence for the formation of intermediate carbonato complexes was presented. On the other hand, oxalato complexes of the form $[\text{MC}_2\text{O}_4]\cdot 2\text{H}_2\text{O}$, where $\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$, and Cd, did yield the corresponding carbonato complexes when heated in a CO_2 atmosphere,²³⁴ although the Cu^{II} transformation required the presence of an oxidizing agent. These reactions are outlined in Table XXVI and as intimated, $\text{VC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ and $\text{CrC}_2\text{O}_4\cdot 0.4\text{H}_2\text{O}$ decomposed directly to their oxides with no evidence for carbonate formation. Most of these carbonates can be prepared by an alternative thermolytic route, namely by heating solutions of the metal hydroxide or oxide under CO_2 pressure.²³⁵ These results are summarized in Table XXVII together with the appropriate IR information, which suggests a common calcite structure for Mn-Zn.

As an interesting side issue Moreau²³⁶ established a linear relationship between the carbonate absorption bands in the IR of the complexes, MnCO_3 , FeCO_3 , CoCO_3 , and NiCO_3 , and the radius of their cations.²³⁶ A linear relationship also exists between the cationic radius and the coefficients of thermal expansion in the planes containing the carbonate anions up to temperatures where decomposition begins.

Other carboxylate complexes, such as the iron and cobalt caprylate soaps also decompose on heating in air to form $[\text{Fe}_2(\text{CO}_3)_3]$ at 200–300 °C and CoCO_3 at 390–480 °C, although these observations appear to be based solely on the thermogravimetric record.²³⁷

Another aspect of the solid-state conversion of carbonato complexes is that they can provide a source for other complexes via substitution. For example, heating $[\text{Co}(\text{en})_2\text{CO}_3]\text{NO}_3$ or $[\text{Co}(\text{en})_2\text{CO}_3]\text{Cl}$ to 165 °C for 1–4 h in the presence of NH_4Cl produces *cis*- and *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ as the main products.²³⁸ In the absence of NH_4Cl no reaction occurred at this temperature over 24 h. Another example is the solid-state reaction between thallous carbonate, Tl_2CO_3 , and tungstic oxide at 550 °C to give thallous tungstate, Tl_2WO_4 .²³⁹

B. Lanthanide Complexes

At least over the past decade, the thermal chemistry of these complexes has attracted the most interest.

To begin with, consider the stepwise decomposition of the carbonato complexes themselves. The thermolysis of $[\text{La}_2(\text{CO}_3)_3]\cdot 8\text{H}_2\text{O}$ gives rise to $\text{La}_2\text{O}_2\text{CO}_3$.²⁴⁰ These authors²⁴⁰ were careful to point out that the transition temperatures are strongly influenced by the gas-phase composition (i.e., CO_2 content, presence of oxidizing gases, vacuo, etc.) depending on the stoichiometry and reversibility of the transition. The kinetics of this process can also be affected. In addition, Prodan et al.²⁴¹ showed that for this particular reaction the specific surface changes, which occur during the two

steps of this reaction (i.e., the formation and decomposition of $\text{La}_2\text{O}_2\text{CO}_3$), are modified considerably in the presence of CO_2 .

In their review of the thermal decomposition of lanthanide carbonates, $\text{Ln}_2(\text{CO}_3)_3\cdot x\text{H}_2\text{O}$, including yttrium carbonate, Sharov and Bezdenezhnykh²⁴² demonstrated that the thermal stability of this series of complexes increases with increasing atomic number, e.g., $[\text{La}_2(\text{CO}_3)_3]$ begins to decompose at 495 °C, while $\text{Er}_2(\text{CO}_3)_3$ first decomposes at 770 °C. Consistent with the example of $[\text{La}_2(\text{CO}_3)_3]\cdot 8\text{H}_2\text{O}$ cited above,²⁴⁰ all the lanthanides degenerate following dehydration into $\text{Ln}_2\text{O}_2\text{CO}_3$ in its tetragonal form.²⁴² Given a slow heating rate of 0.6 °C h⁻¹, there is then a phase change to $\text{Ln}_2\text{O}_2\text{CO}_3$ (hexagonal) for $\text{Ln} = \text{La-Pr}$. For Na and Sm-Gd, this phase change does not reach completion before thermal decomposition to Ln_2O_3 begins. The hexagonal form is not encountered for lanthanides smaller than Gd³⁺, but now the initial phase may be either the tetragonal or monoclinic form. Within this group of heavy lanthanides, the thermal stability of either form of $\text{Ln}_2\text{O}_2\text{CO}_3$ decreases markedly from Tb to Lu and is a reflection of a weakening of the $\text{Ln}-\text{CO}_3$ bond with increasing atomic number. Sharov and Bezdenezhnykh²⁴² also cite numerous publications²⁴³ supporting the existence of $\text{Ln}_2\text{O}(\text{CO}_3)_2$ for the light lanthanides as an intermediate prior to the formation of $\text{Ln}_2\text{O}_2\text{CO}_3$. The fact that this intermediate only becomes apparent for light lanthanides is consistent with the concept of $\text{Ln}-\text{CO}_3$ bond strength decreasing as a function of atomic number. Indeed, it was suggested that decomposition of carbonates of heavy lanthanides and yttrium is accompanied by the formation of $\text{Ln}_2\text{O}_3\cdot 2\text{CO}_2$ as well as $\text{Ln}_2\text{O}_2\text{CO}_3$.

Peterson et al.²⁴⁴ examined the thermal decomposition of both $[\text{Ce}_2(\text{CO}_3)_3]\cdot 8\text{H}_2\text{O}$ and $[\text{Ce}(\text{OH})\text{CO}_3]\cdot x\text{H}_2\text{O}$ in vacuo within sealed tubes and were able to establish that the anhydrous form of the latter is an intermediate in the dehydration of the former at 573 °C. $[\text{Ce}(\text{OH})\text{CO}_3]$ decomposes at 773 °C to the familiar $\text{Ce}_2\text{O}_2\text{CO}_3$ form which in turn converts to CeO_2 at 873 °C.

It is worthwhile mentioning at this point that hydroxo carbonates $[\text{Ln}(\text{OH})\text{CO}_3]$, where $\text{Ln} = \text{La, Gd, Er, and Y}$, can be produced by heating solutions of the appropriate tris(carbonato) complex in the presence of ca. 6 M ammonium or potassium salts of chloride or carbonate at 250–500 °C, 100–200 MPa, and over time periods of 27–58 days.²⁴⁵ In addition to $[\text{Ln}(\text{OH})\text{CO}_3]$, the familiar species $\text{Y}_2\text{O}_2\text{CO}_3$, $\text{Gd}_2\text{O}_2\text{CO}_3$, and $\text{Er}_2\text{O}_2\text{CO}_3$ were formed under various combinations of these conditions. Although $\text{La}_2\text{O}_2\text{CO}_3$ was not observed at all, the complex $[\text{La}_3\text{Cl}(\text{CO}_3)_4]$ was detected along with the hydroxo carbonate in the presence of NH_4Cl . SEM photomicrographs established that well-developed crystals were obtained by this method and tentative phase diagrams were also constructed for the systems $\text{Ln}_2\text{O}_3\text{-H}_2\text{O-CO}_2$ at temperatures ranging from 100 to 900 °C.

Thermal decomposition of $[\text{Ln}_2(\text{C}_2\text{O}_4)_3]\cdot x\text{H}_2\text{O}$ occurs with the usual initial dehydration step at low temperatures followed by the formation of $[\text{Ln}_2(\text{CO}_3)_3]$, followed again by the chemistry outlined immediately above.²⁴² The appearance of mixed carbonato-oxalato complexes has been confirmed for the lighter lanthanides. For the heavier lanthanides, when heated in va-

TABLE XVI. Summary of Crystal Data Describing the Unit Cell of Metal Carbonate Compounds

		cryst syst, <i>unso</i>		obsd ^a		<i>a_o, Å</i>		<i>b_o, Å</i>		<i>c_o, Å</i>		β, deg		<i>Z</i>	<i>vol, Å³</i>	<i>d, b g cm⁻³</i>	measd	calcd	ref
compd	space grp	monoc, <i>P</i> 2 ₁ / <i>c</i>	319 (0.108)	3.51 (1)	9.71 (1)	8.05 (1)	111.85	4	255	2.22	2.19	202							
KHCO ₃		monoc, <i>P</i> 2 ₁ / <i>c</i>	15.111 (11)	5.67	3.71	103.75							4	306.62	2.169			^c	²⁰³
		monoc, <i>P</i> 2 ₁ / <i>c</i>	15.1725 (11)	5.6283 (5)	3.7110 (4)	104.631							4	307.27	2.186			²⁰⁴	²⁰³
KDCO ₃		monoc, <i>P</i> 2 ₁ / <i>a</i>	15.1948 (9)	5.6307 (3)	3.7107 (3)	104.567							4	307.27	2.186			²⁰⁴	²⁰⁵
RbHCO ₃		monoc, <i>C</i> 2- <i>C</i> 2 ³	15.05	5.83	4.02	107							4	233.8	2.094			^d	²⁰⁵
Li ₂ CO ₃		monoc, <i>C</i> 2/ <i>c</i>	291 (0.043)	8.3593 (36)	4.9725 (11)	6.1975 (21)	114.83 (3)						4	233.8	2.096				
γ -Na ₂ CO ₃		monoc, C2/ <i>m</i>	313 (0.128)	8.90	5.24	6.04	101.2						4					^e	
Na ₂ CO ₃ ·H ₂ O		ortho, <i>P</i> 2 ₁ <i>a</i> <i>b</i>	1231 (0.034)	6.474 (2)	10.724 (3)	5.259 (2)							4	365.1	2.255			²⁰⁶	
K ₂ CO ₃		monoc, <i>P</i> 2 ₁ / <i>c</i>	316	5.64 (3)	9.80 (4)	6.88 (3)							4	375.78	2.428			^f	
KNa ₂ [Cl(CO ₃) ₂ (SO ₄) ₂] (hanksite) ^b		hex, <i>P</i> 6 ₃ / <i>m</i>	1535 (0.034)	10.490 (1)		21.240 (1)							2					^g	
MgCO ₃ (magnesite) ^k		trig, <i>R</i> ̄(2/ <i>c</i>)	253 (0.020)	4.6328 (2)	15.0129 (5)								6	279.05 (3)				207	
MgCO ₃ (magnesite) ^l		trig, <i>R</i> ̄ <i>c</i>	234 (0.037)	4.6330 (1)	15.016								6					^h	
MgCO ₃ ·3H ₂ O		monoc, <i>P</i> 2 ₁ / <i>n</i>	595 (0.124)	7.7053 (11)	5.3673 (6)	12.1212 (11)	90.451 (13)						4	497	1.85			ⁱ	
(nesquehonite) ^l		monoc, <i>P</i> 2 ₁ / <i>c</i>	2598 (0.052)	10.105 (5)	8.954 (2)	8.378 (4)	114.44 (5)						2	690	2.25			^j	
Mg ₅ (CO ₃) ₄ (OH) ₂ (H ₂ O) ₄ (hydromagnesite) ^k		trig, <i>R</i> ̄ <i>3</i> trig, <i>R</i> ̄ <i>3</i>	210 (0.045)	4.942 (2)	16.406 (7)								3	347.9 (4)				^m	
Na ₂ Mg(CO ₃) ₂ (eliteite) ^l		trig, <i>R</i> ̄ <i>3</i> trig, <i>R</i> ̄ <i>3</i>	210 (0.045)	4.946 (2)	16.422 (4)								16	2785	2.380			ⁿ	
Na ₃ Mg(CO ₃) ₂ Cl (northupite) ^k		isom, <i>F</i> 4 ₃	401 (0.023)	14.069 (2)									16	2785	2.374			^o	
K ₂ Mg(CO ₃) ₂ ·4H ₂ O (baylissite) ^l		monoc, <i>P</i> 2 ₁ / <i>n</i>	1153 (0.045)	11.404 (4)	6.228 (2)	6.826 (2)	99.66 (2)						2	477.9 (3)	2.04			^p	
KHCO ₃ ·MgCO ₃ ·4H ₂ O		tric, ~ <i>P</i> 1	860 (0.075)	6.713 (3)	7.337 (3)	5.364 (1)	108.92 (3)						1	213.6	1.99			^q	
CaCO ₃ (argonite) ^k		ortho, <i>P</i> mcn ortho, <i>P</i> mcn	271 (0.022)	4.9614 (3)	7.9671 (4)	5.7404 (4)							4					^r	
CaCO ₃ (calcite) ^l		trig, <i>R</i> ̄ <i>3</i> trig, <i>R</i> ̄(2/ <i>c</i>)	340 (0.022)	4.9900 (2)		17.002 (1)							6	367.85 (5)				^s	
CaCO ₃ (calcite) ^k		trig, <i>R</i> ̄ <i>3</i> trig, <i>R</i> ̄(2/ <i>c</i>)	340 (0.022)	4.9899 (2)		17.064							6	367.85 (5)				^t	
Ca ₁₀ (PO ₄) ₆ CO ₃ “apatite” ^l		monoc, <i>P</i> b ortho, <i>F</i> dd2	1079 (0.044)	9.557 (3)	19.114	6.872 (2)	120.36 (4)						8	1368	2.35			^u	
Na ₂ Ca(CO ₃) ₂ ·2H ₂ O (pirssonite) ^l			11.340 (4)	6.034 (5)		6.034 (2)							8	1368	2.35			^v	^w

$\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ (gaylussite) ^j	monoc, $C2/c$	2632 (0.054)	14.361 (2)	7.781 (1)	11.209 (2)	127.84 (1)	4	988	1.99	w
$\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$, (shortite) ^k	ortho, $Amm2$	684 (0.020)	4.947 (1)	11.032 (2)	7.108 (1)	2	387.9	2.629	2.620	208
$\text{K}_1\text{Ca}(\text{CO}_3)_2$, (buettschlite) ^l low temp form	trig, $R\bar{3}2/m$	5.38		18.12		3		2.61	x	
$\text{K}_2\text{Ca}(\text{CO}_3)_2$, (fairchildite) ^l high temp form	hex, $P6_3/mmc$	173 (0.052)	5.387 (2)	18.16 (1)	13.355 (2)	3	456.4 (6)		o	
$\text{MgCa}(\text{CO}_3)_2$, (dolomite) ^k	trig, $R\bar{3}$	1.97 (0.10)	5.294 (1)			3	321.06 (9)	2.86	207	209
		5.96 (0.021)	4.812 (1)		16.020 (3)					
		17.8 (0.045)	4.8033 (9)		15.984 (4)					215
$\text{MgCa}(\text{CO}_3)_2$,(dolomite) ^l	trig, $R\bar{3}$	5.01 (0.0925)	4.815	16.119		319.3 (1)			y	
	trig, $R\bar{3}$		4.8079		16.010				h	
	trig		9.505		7.821				z	
$\text{Ca}_2\text{F}_2\text{CO}_3$,(orenkite) ^k	ortho, $Pbcn$	840 (0.023)	7.650 (2)	7.550 (2)	6.548 (2)	4	378	3.10 (4)	3.126	aa
SrCO_3 , (strontianite) ^l	ortho, $P2_1cn$	5.090 (2) (0.031)	8.358 (2)	5.997 (4)		4			s	
SrCO_3 ,(strontianite) ^l	mono, $P2_1/b$	5.108	8.420	6.040					bb	
$\text{Sr}_{10}(\text{PO}_4)_6\text{CO}_3$, (wetherite) ^k	ortho, $P2_1cn$	9.88 (2) (0.033)	19.72 (5)	7.23 (9)	119.4 (3)	4			cc	
BaCO_3 ,(wetherite) ^l	mono, $P2_1/m$	5.3126 (5)	8.8958 (5)	6.4284 (5)					s	
$\text{BaMg}(\text{CO}_3)_2$,(norsethite) ^k	trig, $R\bar{3}2$	5.020 (5)	16.75 (2)			3	365.6	3.837 (5)	3.840	dd
$\text{BaMg}(\text{CO}_3)_2$,(norsethite) ^l	trig, $R\bar{3}2$	5.017 (1)	16.77 (1)			3	365.54	3.796	3.838	dd
$\text{BaCa}(\text{CO}_3)_2$,(barytocalcite) ^k	trig, $P321$	1652 (0.023)	8.092 (1)	5.2344 (6)	6.544 (1)	2	266.4	3.71	3.72	ee
$\text{BaCa}(\text{CO}_3)_2$,(paralstonite) ^k	trig, $R\bar{3}2$	7.25 (0.053)	8.692 (3)	6.148 (4)		3			ff	
$\text{Ba}_6\text{Ca}_8\text{Mg}(\text{CO}_3)_{13}$, (benstonite)	trig, $R\bar{3}$	964 (0.062)	18.289 (9)	8.652 (8)		3	3.596	3.695	gg	
$\text{NaAl}(\text{OH})_2\text{CO}_3$,(dawsonite) ^k	ortho, $Imma$	4.88 (0.058)	6.759 (1)	5.585 (1)	10.425 (1)	4	393.53	2.436 (4)	2.431	hh
$\text{NH}_4[\text{Ga}(\text{OH})_2\text{CO}_3]$	ortho, $Pbcu$	6.608	12.06	5.882		4		2.47	2.575	ii
$\text{Na}_3\text{Al}_5\text{Ge}_6\text{O}_{24}(\text{CO}_3)_2\text{H}_2\text{O}$	hex, $P6_3mc$	1.2.913 (2) [$\text{Sb}(\text{C}_6\text{H}_5)_4(\mu\text{-OCO}_2)_4$] ($\text{C}_6\text{H}_5)_4\text{Sb}]$	10.108 (5)	14.018 (7)	10.493 (3) 15.702 (8)	2	2046	1.48	1.49	\bar{J}_I, kk
Ti_2CO_3	mono, $C2/m$	655 (0.051)	12.486 (3)	5.382 (2)	7.530 (2)	4	425.4	7.25	7.32	mm
PbCO_3^l	trig, $R32$	5.176 4.924 (1)		6.137 16.56 (1)		3			bb	
$\text{PbMg}(\text{CO}_3)_2$					Transition-Metal Complexes				dd	
$[\{\text{Ti}(\text{Cp})_2\}_2(\mu\text{-CO}_3)]_2$	ortho, $Cmca$	1508 (0.058)	11.282 (1)	16.038 (1)	19.729 (2)	4			1.548	402
MnCO_3 ,(rhodochrosite) ^k	trig, $R\bar{3}(2/c)$	288 (0.015)	4.7682 (2)		15.6354 (8)	6	307.86 (4)		207	
MnCO_3 ,(rhodochrosite) ^l	trig, $R\bar{3}(2/c)$	274 (0.013)	4.7771 4.6916 (4)		15.664 15.3796 (16)	6	293.17 (8)		h	207
FeCO_3 ,(siderite) ^l	trig		4.6887		15.373 14.958				h	
CoCO_3^l	trig		4.6581		6.814 (1)	2	476.1	2.293	2.296	nn
$trans\text{-K}_1[\text{Co}^{II}(\text{H}_2\text{O})_4(\text{CO}_3)_2]$	mono, $P2_1/n$	2514 (0.024)			99.46 (1)					

TABLE XVI (Continued)

compd	space grp	cryst syst, <i>uuuu</i>	obsd ^a	<i>a</i> ₀ , Å	<i>b</i> ₀ , Å	<i>c</i> ₀ , Å	<i>β</i> , deg	<i>Z</i>	<i>d</i> , ^b g cm ⁻³		ref	
									measd	calcd		
[Co(NH ₃) ₅ CO ₃]Br·H ₂ O	ortho, <i>Pna</i> 2 ₁	956 (0.095)	12.370 (3)	12.144 (3)	6.433 (6)			4	966.4	2.08	2.075	
[Co(NH ₃) ₄ CO ₃]Br	ortho, <i>Pcmn</i>	459 (0.12)	6.760 (5)	7.629 (5)	16.886 (10)			4	870.8	2.028	2.036	
[Co(py) ₄ CO ₃]ClO ₄ ·H ₂ O	monoc, <i>P2</i> ₁ /c	3302 (0.049)	9.457 (3)	16.333 (6)	15.582 (11)	97.93 (4)		4	2384	1.547	1.540	
[Co(en) ₂ CO ₃]·2H ₂ O	monoc, <i>C2</i> /c	1485 (0.030)	8.362 (2)	15.327 (8)	10.223 (8)	93.34 (3)		4	1308 (1)	2.009	2.042	
[Co(tn) ₂ CO ₃]ClO ₄	monoc, <i>P2</i> ₁ /c	1904 (0.092)	9.51 (2)	13.22 (3)	12.03 (3)	111.17 (10)		4	1410	1.73 (1)	1.726	
[Co(phen) ₂ CO ₃]Cl·3H ₂ O	monoc, <i>P2</i> ₁ /c	1332 (0.089)	12.512 (2)	19.172 (4)	10.075 (2)	96.32 (2)		4	1.49	1.50	212	
[Co(phen) ₂ CO ₃]Br·4H ₂ O	tric, <i>P</i> ̄1	2958 (0.062)	16.411 (8)	7.858 (4)	10.601 (3)	108.3 (2), ($\alpha = 89.1$ (2), $\gamma = 76.0$ (1))		2	1253.1	1.68	ss	
Na[Co(pren)CO ₃]·3H ₂ O	monoc, <i>P2</i> ₁	2463 (0.059)	7.845 (4)	7.760 (2)	14.922 (10)	106.51 (2)		2	871 (1)	1.71 (3)	tt	
Λ(+)-cis(<i>N</i> -cis(<i>O</i> -K[Co(L-val) ₂ CO ₃] ₂ ·2H ₂ O	ortho, <i>P2</i> ₁ , <i>2</i> ₁	996 (0.087)	21.41 (4)	14.68 (3)	5.76 (1)			4	1810	1.54	1.56	
[Co(cyclen)CO ₃]ClO ₄ ·H ₂ O	ortho, <i>P2</i> ₁ , <i>2</i> ₁	940 (0.067)	13.68 (3)	13.32 (3)	8.92 (2)			4	1.69 (1)	1.669 (7)	uu	
(+)- <i>cis</i> - β -[Co(3,8-diméthienylCO ₃)ClO ₄] ⁺	ortho, <i>P2</i> ₁ , <i>2</i> ₁	1894 (0.053)	12.284 (2)	17.913 (8)	7.179 (3)			4	1579.9	1.65	1.65	
[Co(terpy)(CO ₃)]OH] ⁺ ·4H ₂ O	tric, <i>P</i> ̄1	1354 (0.075)	11.407 (6)	10.566 (6)	8.445 (4)	107.35 (5), ($\alpha = 100.21$ (5), $\gamma = 102.18$ (5))		2	917 (1)	1.60 (1)	1.60	
[(NH ₃) ₄ Co(μ -NH ₂)(μ -OH)-Co(CO ₃) ₂]·5H ₂ O	monoc, <i>P2</i> ₁ /c	3435 (0.044)	9.5572 (15)	15.8477 (29)	9.8036 (20)	90.305 (14)		4	1484.8 (5)	1.864 (13)	1.919	
{(NH ₃) ₆ Co(μ -OH) ₂ ⁺ (μ -CO ₃) ₂ SO ₄ ·5H ₂ O}	tric, <i>P</i> ̄1	2258 (0.029)	6.6914 (14)	11.2847 (18)	11.8251 (23)	99.096 (15), ($\alpha = 92.766$ (14), $\gamma = 101.496$ (15))		2	861.1 (3)	1.929	491	
Ti[Cr(CO ₃) ₂] ₂ [([9]JameN) ₂ Cr ₂ (μ -OH) ₂] ₂	monoc, <i>P2</i> ₁ /c	2545 (0.072)	19.917 (7)	8.605 (3)	19.138 (5)	104.79 (3)		4	3169.3	4.65	4.73	
(NH ₄) ₄ [H ₂ O] ₂ Cr ₂ ^{II} ₂ (μ -CO ₃) ₄]·H ₂ O	monoc, <i>P2</i> ₁ /c	1511 (0.033)	6.949 (2)	16.112 (4)	7.737 (2)	108.14 (2)		2	823.2 (7)	1.90	yy	
NiCO ₃	trig	4.5975	14.723								h	
Na ₂ [Cu(CO ₃) ₂] ₂	monoc, <i>P2</i> ₁ /a	286 (0.115)	6.092	4.493	7.030	101.34		4	188.7	4.18	4.35	
(chalconatronite) ₂ ⁺	monoc, <i>P2</i> ₁ /c	2373 (0.042)	9.961 (2)	6.091 (1)	17.111 (3)	126.40 (1)		2	256	3.1 (1)	2.98	
Rb ₂ [Cu(CO ₃) ₂]·3H ₂ O	monoc, <i>P2</i> ₁ /a	2487 (0.11)	9.696 (2)	6.101 (2)	13.779 (3)	91.83 (2)		4	813.0	2.314	2.317	
Tl ₂ [Cu(CO ₃) ₂]	monoc, <i>P2</i> ₁ /c	995 (0.112)	13.81 (2)	6.10 (1)	9.70 (1)	91.7 (2)		4	814.6	2.29 (2)	2.312	
									4	817	2.28 (2)	2.31
									4	762.4	3.06	3.24
									4	630.4	6.07	6.21

[Cu(NH ₃) ₂ CO ₃] monoc, P2 ₁ /c	934 (0.032)	5.640 (2)	10.579 (3)	7.462 (3)	97.82 (1)	4	441.32	2.35	2.372	<i>fff</i>
[Cu ₂ (OH) ₂ CO ₃] ₂ (malachite) ^k monoc, P2 ₁ /a	579 (0.063)	9.502	11.974	3.24	98.75	4				<i>ggg</i>
monoc, P2 ₁ /a monoc, P2 ₁ /c	635 (0.021)	9.502	11.974	3.240	98.75					<i>hh</i>
[Cu ₃ (OH) ₂ (CO ₃) ₂] (azurite) ^k [Cu ₈ Mg ₆ (CO ₃) ₄ (OH) _{2a}]·8H ₂ O (callaghanite) ^k monoc, C2/c	482 (0.024)	5.00 (2) 5.0109 (5)	5.85 (2) 5.8485 (6)	10.35 (2) 10.345 (2)	92.33 (33) 92.43 (3)		3.773 (3)	3.78	<i>iii</i>	<i>jjj</i>
K _{0.4} [Cu _{0.2} HCO ₃] ₂ (OH) ₂ - 1.66H ₂ O [(teed) ₂ Cu ₂ Cl ₂ (μ-CO ₃)] [(tmtm) ₂ Cu ₂ Cl ₂ (μ-CO ₃)]	466 (0.038)	8.24 (3) 11.664	11.80 (3)	10.06 (4) 9.615	107.38	4	2.71	2.65	<i>lll</i>	<i>mmm</i>
ortho, P22 ₁ 2 ₁ ortho, Iba2	2232 (0.029)	8.0832 (15)	11.6855 (14)	11.9301 (17)		2	1126.9	1.528	<i>ooo</i>	
[LCh ₂ (μ-CO ₃)L][ClO ₄] ₂ DMF ^{litt} [{Cu(pip)H ₂ O} ₃ CO ₃](NO ₃) ₄ [ZnCO ₃] ⁻ (smithonite) ^k (μ-Cl) ₂ [Cl ₄ ·7.5H ₂ O] trig, P $\bar{1}$	1230 (0.052)	16.19 (1)	16.67 (1)	15.43 (1)		4	4164	1.35 (2)	<i>ppp</i>	<i>qqq</i>
hex, P $\tilde{6}$ 2c trig, P $\bar{1}$	926 (0.054)	13.414 (3)		16.024 (2)		2	1.585	1.578	<i>rrr</i>	
ZnCO ₃ (smithonite) ^k trig, R3(2/c) trig monoc, P2 ₁ /c	4950 (0.053)	9.246 (3)	13.957 (3)	25.898 (6)	106.82 (1), ($\alpha = 121.87$ (1), $\gamma = 96.02$ (1))	2	2576.9	1.53	1.529	219
Cs ₄ [Rh ₂ (H ₂ O) ₂ (μ-CO ₃) ₂]·6H ₂ O Cs ₂ Na ₂ [Rh ₂ Cl ₆ (μ-CO ₃) ₂]·8H ₂ O [Rh(PPh ₃) ₂ Rh]·C ₆ H ₆ [Rh ₂ (PPh ₃) ₂ (μ-CO ₃) ₂] trig, P $\bar{1}$	1991 (0.052)	4.6526 (7) 4.6887	15.0257 15.373		15.0257 18.211 (2)	6	281.68 (13)		<i>207</i>	<i>h</i>
monoc, P2 ₁ /c	1409 (0.037)	7.867 (1)	7.963 (1)		91.83 (1)	2	1140.2 (3)	3.27	<i>sss</i>	
trig, P $\bar{1}$	12330 (0.079)	9.798 (2) 22.518 (9)	10.753 (2) 28.051 (12)	12.906 (3) 12.841 (7)	107.98 (2) 97.91 (3), ($\alpha = 96.12$ (3), $\gamma = 92.66$ (3))	2	1293.2 (4)	3.18	<i>sss</i>	
mono, P2 ₁ /c	5844 (0.028)	15.82 (1)	10.88 (1)	15.49 (1)	114.5 (1)	4	7972	1.39	1.38	500
[Rh {P(i-Pr) ₃ } ₂ H ₂ (CO ₃ H)] trans-[Pd(PET ₃) ₂ (CH ₃)CO ₃ H]	1308 (0.075)	7.713 (5)	9.014 (5)	15.339 (8)	94.80 (5), ($\alpha = 111.35$ (4), $\gamma = 90.77$ (5))	2	2428	1.28	1.33	403
K[AgCO ₃] CaCO ₃ CdMg ₂ (CO ₃) ₃ [Pt(PPh ₃) ₂ CO ₃] ortho, Ibca ortho, Ibca trig trig, P $\bar{1}$	1200 (0.057)	20.23 (10) 20.50 (20) 4.9204 4.7770 (9)	5.75 (3) 5.82 (6)	5.95 (3) 6.00 (6) 16.298 15.641 (3)	70.0, ($\alpha = 110.9$, $\gamma = 98.1$)	8	716	3.77 3.77	3.94 3.94	<i>uuu</i> <i>vvv</i> <i>h</i> <i>www</i>
Na[La(CO ₃) ₂] [La ₂ (CO ₃) ₃]·8H ₂ O ortho, Pccn	705 (0.061)	6.436 8.984 (4)	5.161 9.580 (4)	7.217 17.00 (1)	Lanthanide Complexes	2	239.1	3.86 2.72 (2)	3.91 2.732	<i>xxx</i>
ortho, Peen						4				2.729
ortho, Pccn						4				2.235.8
ortho, Pccn						2				250
ortho, Pccn						4				198
ortho, Pccn						6.405 6.405				250
ortho, Pccn						5.140 5.140				198
ortho, Pccn						7.163 7.163				250

TABLE XVI (Continued)

compd	cryst syst, <i>uuuu</i> space grp	obsd ^a	<i>a</i> , Å	<i>b</i> ₀ , Å	<i>c</i> ₀ , Å	<i>β</i> , deg	<i>Z</i>	vol, Å ³	<i>d</i> , ^b g cm ⁻³		
									measd	calcd	
Na ₆ [Ce(CO ₃) ₅]·12H ₂ O	tric, <i>P</i> ₁	7157 (0.051)	9.53 (2)	9.84 (2)	13.58 (3)	104.50 (21), ($\alpha = 90.46$ (18), $\gamma = 95.42$ (19))	2	1226	2.13	2.10	yyy
[Ce(NH ₂) ₃] ₆ [Ce(CO ₃) ₅]·4H ₂ O	monoc, <i>B</i> ₆	7092 (0.072)	16.05 (3)	16.63 (3)	13.14 (3)	108.10 (22)	4	3397	1.63	1.69	zzz
[Ce ₄ C] ²⁺ (OH) ₄ [CO ₃) ₄] ²⁻	hex, <i>P</i> ₆ trig, <i>R</i> 3 <i>m</i>	9.934 (7)	9.96 (2)	8.826 (9)							aaaa
[Ce ₃ Cl(CO ₃) ₄] ²⁻	ortho	6.381	5.125	7.136							aaaa
[Pb ₂ (CO ₃) ₃] ²⁻ ·8H ₂ O	ortho, <i>Pccn</i>	8.914 (5)	9.485 (5)	16.332 (9)							250
Na ₆ [Nd(CO ₃) ₂] ²⁻	ortho	6.346	5.097	7.068							198
Na ₆ [Nd(CO ₃) ₂] ²⁻ ·6H ₂ O	tetrag, <i>P</i> ₄	13.11		9.93							250
[Nd ₂ (CO ₃) ₃] ²⁻ ·7.93H ₂ O	ortho, <i>Pccn</i>	8.890 (5)	9.444 (5)	16.902 (9)							251
Na ₆ [Sm(CO ₃) ₂] ²⁻	ortho	6.324	5.079	7.026							250
Na ₆ [Sm(CO ₃) ₂] ²⁻ ·6H ₂ O	tetrag, <i>P</i> ₄	13.05		9.85							251
Na ₆ [Gd(CO ₃) ₂] ²⁻ ·6H ₂ O	tetrag, <i>P</i> ₄	12.99		9.77							251
{Gd(HCO ₃) ₃ (H ₂ O) ₄ }·H ₂ O	monoc, <i>P</i> ₂ / <i>a</i>	1906 (0.117)	6.877 (1)	9.575 (2)	18.871 (2)	102.61 (2)	4	1212.6		2.37	6666
monoc		6.268	13.186	6.169		102.89	4	497.0		4.04	250
monoc		6.238	13.146	6.151		102.82	4	491.8		4.13	250
tetrag, <i>P</i> ₄		12.93		9.69			8	1620.0			251
monoc		6.224	13.100	6.138		102.73	4	488.2		4.11	250
[Ho ₂ (CO ₃) ₃] ²⁻		6.056	9.165	6.065							cccc
Na ₆ [Y(CO ₃) ₂] ²⁻ ·2.25H ₂ O	monoc	6.222	13.106	6.140		102.70	4	488.4		3.15	250
[Ho ₂ (CO ₃) ₃] ²⁻	tetrag, <i>P</i> ₄	12.90		9.65			8	1605.8		2.31	251
ortho		9.20 (2)	11.32 (2)	7.59 (1)			4			3.2 (1)	dddd
monoc		6.206	13.065	6.124		102.68	4	484.4		4.25	250
ortho		6.05 (1)	9.13 (1)	15.00 (1)							198
monoc		6.186	13.020	6.114		102.65	4	480.5		4.31	250
monoc		6.160	12.978	6.100		102.58	4	476.0		4.41	250
monoc		6.150	12.941	6.089		102.46	4	474.2		4.46	250
---, <i>P</i> ₂ <i>m</i>		6.41 (3)	7.30 (3)	5.23 (2)							eeee
(carbocerniate) ^k											
[Na,Ca] ₃ [Ln ₃ Ca ₂ Mg] ₂ (CO ₃) ₂	hex, <i>P</i> ₆ ₃ <i>mc</i>	10.52 (4)		6.51 (2)			2	3.58			ffff
(berbankite) _k											
Actinide Complexes											
Na ₆ [Th(CO ₃) ₅]·12H ₂ O	tric, <i>P</i> ₁	4806 (0.060)	9.60 (2)	9.92 (2)	13.64 (3)	104.38 (21), ($\alpha = 90.47$ (18), $\gamma = 95.52$ (19))	2	1248		2.31	2.35
[Ce(NH ₂) ₃] ₆ [Th(CO ₃) ₅]·4H ₂ O	monoc, <i>B</i> ₆	11601 (0.062) (0.073)	16.15 (3)	16.70 (3)	13.23 (3)	108.41 (22)	4	3418		1.94	1.92
[UO ₂ (CO ₃) ₂] ²⁻	ortho, <i>Pm</i> 2 ₁ <i>n</i>										hhhh
(etherfordine) ^c											iii
[UO ₂ (CO ₃) ₂] ²⁻											jjjj
[CeNH ₂) ₃] ₄ [UO ₂ (O ₂ -O) ₂ H] ₂	ortho, <i>Pca</i> 2 ₁	1447 (0.077)	15.883 (1)	8.788 (2)	16.155 (1)		5.7	5.724			kkkk
							4	2.02			

$K_4[UO_2(CO_3)_3]$	monoc, $C2/c$	1693 (0.038)	10.247 (3)	9.202 (2)	95.11 (2)	4	3.5	3.507	III
$[NH_4]_4[UO_2(CO_3)_3]$	monoc, $C2/c$	1833 (0.076)	10.68 (1)	9.38 (1)	12.85 (1)	96.45 (8)	4	1279	
$Ca_2[UO_2(CO_3)_3 \cdot 10 \cdot 11H_2O$ (liebigite) ^c	ortho, $Bba2$	16.74	17.54	13.72		8			
$NaK_3[UO_2(CO_3)_3]$	hex, $P\bar{6}2c$	9.29		8.26		2			
$NaNa_3[NPO_2(CO_3)_2] \cdot nH_2O$	hex	3.915		17.68					
	monoc	5.070 (5)	8.78 (1)	8.00 (1)	92.5 (2)	2	356.6		
$K_3[NPO_2(CO_3)_2] \cdot nH_2O$	ortho	5.31	9.12	8.95		2	433.4	4.10	$qqqq$
	hex	5.410 (5)	9.37 (1)	9.37 (1)		2	475.0	4.71	$qqqq$
$Rb_3[NPO_2(CO_3)_2] \cdot nH_2O$	hex, $C6/mmc$	5.09 (1)		9.83 (2)		2	221	5.57	$ssss$
$KPuO_2CO_3$	hex, $C6/mmc$	5.09 (1)		10.39 (2)		2	233	4.99	$ssss$
$NH_4PuO_2CO_3$	ortho	5.29		8.90		2	428.0	4.21	$qqqq$
$RbAmO_2CO_3$	hex, $C6/mmc$	5.12 (1)		10.46 (4)		2	237	6.06	$ssss$
$K_3[AmO_2(CO_3)_2] \cdot nH_2O$	ortho	5.29	9.11	8.83		2	425.5	4.22	$qqqq$

^a Obsd. generally refers to the total number of independent reflections measured with the unweighted reliability index given in parentheses. ^b *d* is density. ^c Koo, C. H. ^d Acta Crystallogr. 1952, 5, 292. ^e Elfenberger, H.; Zemann, J. *Z. Kristallogr.* 1979, 150, 133. ^f Dubbeldam, G. C.; de Wolf, P. M. *Acta Crystallogr., Sect. B* 1969, B25, 2665. ^g De Gatchouse, B. K. M.; Lloyd, D. J. *J. Chem. Soc., Dalton Trans.* 1973, 70. ^g Kato, K.; Saalfeld, H. *Acta Crystallogr., Sect. B* 1972, B28, 3614. ^h Graf, D. L. *Am. Min.* 1961, 46, 1283. ⁱ Oh, K. M.; Morikawa, H.; Iwai, S.; Aoki, H. *Ibid.* 1973, 58, 1029. ^j Stephan, G. W.; MacGillivray, C. H. *Acta Crystallogr., Sect. B* 1972, B28, 1031. ^k Natural mineral sample. ^m Akao, M.; Iwai, S. *Acta Crystallogr., Sect. B* 1977, B33, 1273. ⁿ Pabst, A. *Am. Min.* 1973, 58, 1021. ^o Kroblach, D.; Pertlik, F.; Graf, D. L.; Arai, S. *Acta Crystallogr., Sect. B* 1977, B33, 1273. ^p Dal Negro, A.; Guisepetti, G.; Tadini, C. *Tschermaks Min. Pet. Mitt.* 1975, 22, 158. ^q Bucat, R. B.; Patrick, J. M.; White, A. H.; Willis, A. C. *Aust. J. Chem.* 1977, 30, 1379. ^r Stephan, G. W.; MacGillivray, C. H.; Koch, B. *Acta Crystallogr., Sect. B* 1972, B28, 1029. ^s de Villiers, J. P. R. *Am. Min.* 1971, 55, 758. ^t Dal Negro, A.; Ungaretti, L. *Ibid.* 1971, 56, 768. ^u Chessin, H.; Hamilton, W. C. *Acta Crystallogr., Sect. B* 1975, 18, 689. ^v Elliot, J. C.; Bonel, G.; Trombe, J. C. *J. Appl. Cryst.* 1980, 13, 618. ^w Dickens, B.; Brown, W. E. *Inorg. Chem.* 1969, 8, 2093. ^x Pabst, A. *Am. Min.* 1974, 59, 353. ^y Steinfink, H.; Sans, F. *J. Ibid.* 1959, 44, 679. ^z Leufer, U.; Tillmanns, E. *TMPM, Tschermaks Mineral. Petrogr. Mitt.* 1980, 27, 261. ^{aa} Taren, J. A. K.; Nadel, M.; Legros, J.-P.; Bonel, G.; Montel, G. C. *R. Acad. Sci., Ser. C* 1971, 272, 45. ^{bb} Dickens, B.; Bowen, J. S. *J. Res. NBS* 1971, 75A, 197. ^{cc} Effenburger, H. N. *Jb. Miner. Mh.* 1980, 353. ^{dd} L. Willms, A. C. *Bassavallung, B.; Kutty, T. R. N. J. Cryst. Growth* 1981, 55, 384. ^{ee} Dickens, B.; Bowen, J. S. *J. Res. NBS* 1971, 75A, 197. ^{ff} Effenburger, H. N. *Jb. Miner. Mh.* 1980, 353. ^{gg} Effenburger, H. N. *Jb. Miner. Abh.* 1979, 136, 326. ^{hh} Corazza, E.; Sabeli, C.; Vannucci, S. N. *Jb. Miner. Mh.* 1977, 381. ⁱⁱ Sirchenko, T. D.; Grishaeva, S. N.; Dorokhov, Yu. G. *Zh. Neorg. Khim.* 1979, 24, 1189. ^{jj} Sokolov, Yu. A.; Maksimov, B. A. *Dokl. Akad. Nauk. SSSR* 1977, 237, 585. ^{kk} Sokolov, Yu. A.; Maksimov, B. A.; Galuulin, R. V.; Marchand, R.; Piffard, Y.; Hostkins, B. F. *J. Chem. Soc.* 1974, B30, 103. ^{mm} Marchand, R.; Piffard, Y.; Hostkins, B. F. *J. Chem. Soc.* 1976, B32, 466. ^{oo} Barclay, G. A.; Hostkins, B. F. *J. Chem. Soc.* 1976, B32, 466. ^{oo} Barclay, G. A.; Pellinghelli, M. A. *Cryst. Struct. Commun.* 1980, 1, 113. ^{qq} Bigoli, F.; Lanfranchi, M.; Leporati, E.; Pellinghelli, E.; Lindqvist, O. Z. *Anorg. Allg. Chem.* 1979, 197, 1. ^{ss} Hennig, H.; Sieler, J.; Sjøen, L.; Lindqvist, O. Z. *Anorg. Allg. Chem.* 1979, 197, 1. ^{uu} Loeblin, J. H.; Fleischer, D. *J. Am. Chem. Soc.* 1970, 92, 3063. ^{vv} Kucharski, E. E. S.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* 1978, 31, 47. ^{ww} Churchill, M. R.; Harris, G. M.; Lashewycz, R. A.; Dasgupta, T. P.; Koshy, K. *Inorg. Chem.* 1979, 18, 2290. ^{xx} Ehrhardt, H.; Lemor, R.; Seidel, H. Z. *Angew. Phys. Chem.* 1981, 477, 183. ^{yy} Cotton, F. A.; Rice, G. W. *Inorg. Chem.* 1978, 17, 2004. ^{zz} Seidel, H.; Viswanathan, K.; Johannes, W.; Ehrhardt, H. Z. *Angew. Phys. Chem.* 1974, 410, 138. ^{aa} Healy, P. C.; White, A. H. *J. Chem. Soc., Dalton Trans.* 1972, 1913. ^{bb} Harlow, R. L.; Simonsen, S. J. *Acta Crystallogr., Sect. B* 1980, B36, 2033. ^{cc} Mosse, A.; Bonnet, J.-J.; Galy, J. Z. *Kristallogr.* 1978, 148, 165. ^{dd} Brotherton, P. D.; White, A. H. *J. Chem. Soc., Dalton Trans.* 1973, 2338. ^{ee} Laidoudi, A.; Ouahes, A.; Ouahes, A.; PConnor, M. F.; O'Connor, M. J. *Acta Crystallogr., Sect. B* 1975, 53, 2454. ^{ff} Meyer, M. H.; Singh, P.; Hatfield, W. E.; Hodgson, D. J. *Acta Crystallogr., Sect. B* 1972, 28, 1607. ^{gg} Suse, P. *Naturwissenschaften* 1966, 53, 80. ^{hh} Zigan, F.; Joswig, W.; Schuster, H. D. Z. *Kristallogr.* 1977, 145, 412. ⁱⁱ Gattow, G.; Zeman, J. *Acta Crystallogr.* 1958, 11, 866. ^{jj} Zigan, F.; Schuster, H. D. Z. *Kristallogr.* 1972, 135, 416. ^{kk} Brunton, G. *Am. Min.* 1973, 58, 551. ^{ll} Brunton, G.; Steinfinck, H.; Beck, C. E. W. *Acta Crystallogr.* 1958, 11, 169. ^{mm} Laidoudi, A.; Ouahes, R.; Brianno, M. C. *Rev. Chim. Miner.* 1976, 13, 290. ⁿⁿⁿ Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchison, J. P.; Rupich, M. W. *Inorg. Chem.* 1980, 19, 201. ^{ooo} Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchison, J. P.; Rupich, M. W.; Watkins, K. O. *Ibid.* 1979, 18, 2296. ^{ppp} Davis, A. R.; Einstein, F. W. B.; Curtis, N. F.; Martin, J. W. L. *J. Am. Chem. Soc.* 1978, 100, 6258. ^{qqq} Davis, A. R.; Einstein, F. W. B.; Waszcak, J. V. *J. Am. Chem. Soc.* 1980, 102, 4832. ^{sss} Cottin, F. A.; Felthouse, T. R. *Inorg. Chem.* 1980, 19, 1203. ^{ttt} Crutchley, R. J.; Powell, J.; Faggiani, R.; Locket, C. J. L. *Inorg. Chim. Acta* 1977, 24, L15. ^{uuu} Donohue, J.; Helmholz, L. J. *Am. Chem. Soc.* 1944, 66, 295. ^{vvv} Barclay, G. A.; Hoskins, B. F. *J. Chem. Soc., Chem. Commun.* 1967, 408. ^{xxx} Shinn, D. B.; Eick, J. H. A. *Inorg. Chem.* 1968, 7, 1340. ^{yyy} Voliotis, S.; Rimsky, A. *Acta Crystallogr., Sect. B* 1975, B31, 2620. ^{zzz} Voliotis, S.; Rimsky, A. *Acta Crystallogr., Sect. B* 1975, B31, 2620. ^{aaaa} Peterson, E. J.; Onstott, E. I. *J. Inorg. Nucl. Chem.* 1979, 41, 517. ^{bbbb} Furmanova, N. G.; Soboleva, L. V.; Belyaev, L. M. *Kristallografiya* 1981, 26, 312. ^{cccc} Contures, E. J. P.; Caro, P. C. R. *Hebd. Seances Acad. Sci., Ser. C* 1974, 278, 861. ^{ddaa} Wakita, H.; Nagashima, K. *Bull. Chem. Soc. Jpn.* 1972, 45, 2476. ^{eee} Voronkov, A. A.; Pyatenko, N. G. *Sov. Physic-Crystallogr.* 1968, 13, 192. ^{gggg} Voliotis, S.; Rimsky, A. *Acta Crystallogr., Sect. B* 1975, B31, 2615. ^{hhhh} Voliotis, S.; Rimsky, A. *Ibid.* 1975, B31, 2615. ⁱⁱⁱⁱ Cromer, D. T.; Harper, P. E. *Acta Crystallogr.* 1955, 8, 847. ^{jjjj} Clark, J. R.; Evans, H. T.; Anderson, A.; Chieh, C. Irish; Appelman, D. *Geol. Soc.* 1972, 2059. ^{mmmm} Grajana, B.; Bombieri, G.; Forcellini, E. J. *Chem. Soc., Dalton Trans.* 1972, 26, 718. ⁿⁿⁿⁿ Anderson, A.; Chieh, C. Irish; Appelman, D. *Geol. Soc.*

Table XVI (Continued)

Amer. Bull. 1956, 67, 1666. ^{oooo} Mazzi, F.; Rinaldi, F. *Acta Crystallogr.* 1960, 13, 1139. ^{pppp} Volkov, Yu. F.; Visyashcheva, G. I.; Kapshukov, I. I.; Kaphukov, Yu. V.; Tomilin, S. V.; Visyashcheva, G. I.; Tomilin, S. I.; Kaphukov, I. I.; Rakhov, A. G. *Ibid.* 1981, 23, 243. ^{rrrr} Volkov, Yu. F.; Visyashcheva, G. I.; Tomilin, S. I.; Kaphukov, I. I.; Rakhov, A. G. *Ibid.* 1981, 23, 237. ^{ssss} Ellinger, F. H.; Zachariasen, W. H. *J. Phys. Chem.* 1954, 58, 405. ^{tttt} L = 2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene. Abbreviations: monoc, monoclinic; ortho, orthorhombic; hex, hexagonal; trig, trigonal; isom, isometric; tric, triclinic; tetr, tetragonal.

TABLE XVII. Bond Lengths (Å) and Angles (deg) in Alkali Metal and Alkaline Earth Metal Carbonates (X-ray Diffraction)

compd	M-O (M-O _{1,2})	C ₁ -O ₁	C ₁ -O ₂	C ₁ -O ₃	O ₁ C ₁ O ₂	O ₁ C ₁ O ₃	O ₂ CO ₃	ref
NaHCO ₃	2.438 2.44 (3) 2.85 (15) 2.84 (10) 2.84 (10) 2.84 (11) 2.85 (11) 2.97 (11)	1.346 ^{dd} 1.345 ^{dd} 1.32 ^{dd} 1.274 (2) ^{dd} 1.274 (1) ^{dd} 1.266 (3) ^{dd} 1.268 (2) ^{dd} 1.33	1.263 1.275 1.33 ^{dd} 1.337 (2) ^{dd} 1.332 (1) ^{dd} 1.346 (3) ^{dd} 1.337 (2) ^{dd} 1.32	1.264 1.249 1.28 1.240 (3) 1.244 (1) 1.239 (3) 1.243 (1) 1.32	116.27 114.6 119.5 118.14 (18) 118.35 (6) 118.12 (20) 118.18 (11) 119.75	118.77 114.6 122 124.12 (17) 123.75 (6) 116.82 (19) 124.62 (12) 119.75	124.97 125.5 118.5 117.74 (16) 117.89 (6) 116.82 (19) 117.19 (12) 120.50	202, ^a ^b 203 204 203 204 205
KHCO ₃		Bicarbonates						
KDCO ₃								
RbHCO ₃								
Li ₂ CO ₃	1.96 (5) 2.48 (16) 2.85 (18) 2.46 (18) (Na) (Na)	1.270 (3) 1.299 (3) ^{dd} 1.28 (2) 1.287 (3)	1.286 (2) 1.274 (2) 1.32 (2)	1.285 (2) 1.285 (2) ^{dd} 1.28 (2)	120.0 (1) 119.6 (2) 118.0 (23)	120.1 (2) 119.2 (2) 122.0	120.0 (1) 121.2 (2) 120.1	^d 206 ^e ^f
Na ₂ CO ₃ ·H ₂ O								
K ₂ CO ₃								
KNa ₂₂ [Cl(CO ₃) ₂ (SO ₄) ₉]								
MgCO ₃	2.03 (14) (K) 2.1018 (4) 2.105 (1) 2.08 (5) 2.074 (2) (Mg) 2.63 (30) (Na) 2.073 (1) (Mg) 2.424 (12) (Na) 2.09 (3) (Mg) 2.78 (6) (K) 3.09 (20) (K)	1.2852 (4) 1.283 (1) 1.275 (13) 1.254 (4) ^{dd} 1.284 (2) 1.284 (1) 1.282 (3) ^{dd} 1.298 (3) ^{dd} 1.275 (4) (Mg)	1.273 (10) 1.262 ^{dd} 1.284 (2) 1.284 (1) 1.298 (3) 1.282 (4) 1.266 (4) 1.29 ^{dd} 1.284 (3)	1.284 (12) 1.299 (3) 1.284 (2) 1.284 (1) 1.282 (4) 1.19.6 (3) 1.18.0 (5) 1.14.4 1.284 (3) 1.287	120 122.6 (9) 118.4 (3) 121.8 (3) 120.0 (1) 120.0 (2) 120.0 (2) 120.4 (2) 123.5 (5)	114.1 (9) 123.3 (8) 119.8 (3) 121.8 (3) 120.0 (1) 120.0 (2) 120.4 (2) 122 123.5 (5)	207, ^g ^h ⁱ ^j ^k ^l ^m	
K ₂ Mg(CO ₃) ₂ ·4H ₂ O (K ₂ CO ₃ ·MgCO ₃ ·4H ₂ O) KHCO ₃ ·MgCO ₃ ·4H ₂ O	2.03 (Mg) 2.061 (Mg) 2.53 (13) 2.52 (10)	1.41 1.282 (1) 1.279 (5) 1.287	1.309 (4) 1.41 1.282 (1) 1.284 (3) 1.280	1.266 (4) 1.29 ^{dd} 1.284 (3) 1.284 (3) 1.287	118.0 (5) 114 121.3 (2) 120.19 (18) 120.70	118.3 (5) 122 119.35 (9) 120.19 (18) 120.70	122 119.35 (9) 119.55 (37) 118.47	^o ^p ^q ^t
Cu ₈ Mg ₈ (CO ₃) ₄ (OH) ₄ ·8H ₂ O ⁿ								
CaCO ₃ (aragonite)								
CaCO ₃ (calcite)	2.3598 (6) 2.46 (6) 2.47 (21) (Na) 2.47 (8) 2.43 (10) (Na)	1.2815 (6) 1.300 (12) ^{dd} 1.280 (3) ^{dd} 1.279 (5) 1.287	1.276 (14) 1.291 (2) ^{dd} 1.293 (3)	1.281 (14) 1.284 (3) 1.284 (3)	120.5 (11) 121.8 (2) 120.1 (2)	120.1 (11) 118.1 (2) 118.1 (2)	119.4 (9) 118.1 (2) 118.1 (2)	^t ^t ^t
Na ₂ Ca ₂ (CO ₃) ₂ ·2H ₂ O	2.50 (6) (Ca) 2.46 (20) (Na)	1.273 (3) 1.306 (4)	1.286 (2) 1.273 (3)	1.286 (2) 1.273 (3)	119.6 (1) 118.7 (2)	120.9 (2) 122.7 (3)	120.9 (2) 122.7 (3)	208

	<i>u</i>	<i>j</i>	<i>u</i>	<i>x</i>
$K_2Ca(CO_3)_2$ (buetschlite)	2.34 (Ca) 2.80 (K) 2.326 (3) (Ca)	1.285 (2)	1.285 (20)	
$K_2Ca(CO_3)_2$ (fairchildite)	2.91 (11) (Na) 2.76 ^b 2.61 ^v	1.29 (1) 1.31 (3) 1.2853 (4)	1.29 (1) 1.31 (3) 1.26 (1)	1.29 (1) 1.26 (2)
$MgCa(CO_3)_2$	2.3822 (5) (Ca) 2.0877 (4) (Mg) 2.378 (1) (Ca) 2.081 (1) (Mg) 2.390 (Ca) 2.095 (Mg)	1.2835 (15)	119.95 (1)	
$Mg_3Ca(CO_3)_4$	2.35 2.10 (Mg) 2.43 (9) 2.64 (12) 2.81 (11) 2.094 (2) (Mg)	1.28		
$Ca_2F_2CO_3$	2.94 (22) (Ba)	1.297 (2)	1.279 (2)	119.4 (2)
$SrCO_3$	2.39 (9) (Ca)	1.269 (10)	1.293 (6)	120.28 (40)
$BaCO_3$	2.81 (12)	1.282 (12)	1.289 (7)	120.28 (46)
$BaMg(CO_3)_2$	2.91 (13) (Ba)	1.275 (4)	1.286 (2)	120.3 (2)
$BaCa(CO_3)_2$ (barytocalcite)	2.50 (10) (Ca)	1.259 (4)	1.294 (2)	121.6 (1)
$BaCa(CO_3)_2$ (paralstonite)	2.81 (3) (Ba)	1.29 (6)	1.29 (6)	121.6 (1)
$Ba_6Ca_6Mg(CO_3)_13$	2.07 (2) (Mg) 2.48 (15) (Ca) 2.83 (12) (Ba)	1.27 (2) 1.32 (2) 1.28 (1) (Mg) 2.095 (1) (Mg) 2.67 (12) (Pb)	1.29 (2) 1.27 (3) 1.281 (1)	120.3 (2) 121.7 (12) 119.0 (14) 122.8 (16)
$PbMg(CO_3)_2$			120	120

^a Sharma, B. D. *Acta Crystallogr.* 1965, 18, 818. ^b Koo, C. H. *Ibid.* 1952, 5, 292. ^c Neutron diffraction. ^d Effenberger, H.; Zemann, J. *Z. Kristallogr.* 1979, 150, 133. ^e Gatehouse, B. M.; Lloyd, D. J. *J. Chem. Soc., Dalton Trans.* 1973, 70. ^f Kato, K.; Saalfeld, H. *Acta Crystallogr., Sect. B* 1972, B28, 3614. ^g Oh, K. D.; Morikawa, H.; Iwai, S.; Aoki, H. *Am. Min.* 1973, 58, 1029. ^h Stephan, G. W.; MacGillavry, C. H.; Tschernack, J. *Ibid.* 1972, B28, 1031. ⁱ Akao, M.; Iwai, S. *Ibid.* 1977, B33, 1275. ^j Knobloch, D.; Pertlik, F.; Zemann, J. N. *Jb. Miner. Phys.* 1980, 230. ^k Dal Negro, A.; Giuseppetti, G.; Tadini, C. *Tschernack's Min. Pet. Mitt.* 1975, 22, 158. ^l Bucat, R. B.; Patrick, J. M.; White, A. H.; Willis, A. C. *Aust. J. Chem.* 1977, 30, 1379. ^m Stephan, G. W.; MacGillavry, C. H.; Koch, B. *Acta Crystallogr.* 1972, B28, 1029. ⁿ No copper-carbonate bonds involved. ^o Brunton, G.; Steinfink, H.; Beck, C. W. *Acta Crystallogr.* 1958, II, 169. ^p Brunton, G. *Am. Min.* 1973, 58, 551. ^q De Villiers, J. P. R. *Ibid.* 1971, 56, 758. ^r De Villiers, J. P. R. *Acta Crystallogr.* 1965, I, 689. ^s Dickens, B.; Brown, W. E. *Inorg. Chem.* 1969, 8, 2093. ^t Pabst, A. *Am. Min.* 1974, 59, 353. ^v Could not distinguish between K and Ca positions. ^w Steinfink, H.; Sans, F. *J. Am. Min.* 1959, 44, 679. ^x Graf, D. L.; Bradley, W. F. *Acta Crystallogr.* 1962, 15, 238. ^y Leifer, U.; Tillmanns, E. *TMPM, Tschernack's Mineral. Petrogr. Mitt.* 1980, 27, 261. ^z Lippman, F. *Ibid.* 1968, 12, 299. ^{aa} Dickens, B.; Bowen, J. *S. J. Res. NBS* 1971, 75A, 197. ^{bb} Effenberger, H. N. *Jb. Mineral. Mh.* 1980, 353. ^{cc} Effenberger, H. N. *Jb. Mineral. Mh.* 1979, I, 36, 326. ^{dd} Protonated or hydrogen-bonded oxygen.

TABLE XVIII. Bond Lengths (\AA) and Angles (deg) for Monodentate, Mononuclear Carbonato Complexes

complex	CN ^d	M-O ₁	C-O ₁	C-O ₂	C-O ₃	M-O ₁ -C	O ₁ -C-O ₂	O ₁ -C-O ₃	O ₂ -CO ₃	O ₃ -CO ₃	ref
<i>trans</i> -[Pd ^{II} (PEI ₃) ₂ (CH ₃) ₂ CO ₃ H] ^e	4	2.13(2)	1.27(4)	1.31(3)	1.28(3)	1.31(1)	121(3)	119(2)	120(3)	89.2(1.3) ^a	b
<i>trans</i> -K ₂ [Co ^{II} (H ₂ O) ₄ (CO ₃) ₂] ^f	6	2.068(1)	1.291(1)	1.294(1)	1.291(1)	1.20(5)	119.4(1)	120.6(1)	120.1(1)	87.8(4.6) ^a	c
[Co ^{III} (NH ₃) ₆]CO ₃ Br·H ₂ O	6	1.93(3)	1.31(5)	1.29(5)	1.29(5)	1.20(5)	117.9(3.4)	122.7(3.4)	117.2(3.4)	211	

^a In these cases, the calculated mean value has a standard deviation considerably greater than the largest standard deviation in the individual values. ^b Crutchley, R. J.; Powell, H.; Faggiani, R.; Lock, C. J. L. *Inorg. Chim. Acta* 1977, 24, L15. ^c Harlow, R. L.; Simonsen, S. H. *Acta Crystallogr., Sect. B* 1976, B32, 466. ^d Coordination number.

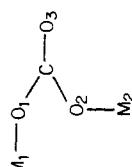
TABLE XIX. Bond Lengths (\AA) and Angles (deg) for Bidentate, Mononuclear Carbonato Complexes

complex	CN	M-O ₁	C-O ₁	C-O ₂	C-O ₃	MO ₁ C	O-MO ₂	O ₁ CO ₂	O ₁ CO ₃	O ₂ CO ₃	ref
[Pt(PPh ₃) ₂ CO ₃] ^g	4	2.07	1.28	1.28	1.28	64.0	64.0	124.3(4)	122.6(4)	122.6(4)	a
Na ₂ Cu(CO ₃) ₂ 3H ₂ O	5	1.993(10) ^b	1.302(5)	1.299(5)	1.295(5)	90.5(6)	66.0(1)	113.1(3)	123.5(4)	123.6(4)	c
5	1.999(12) ^b	1.317(5)	1.295(5)	1.251(5)	1.251(5)	90.6(10) ^b	65.9(1)	112.8(4)	123.5(4)	123.6(4)	d
5	1.99(2)	1.29(2)	1.30(2)	1.27(2)	1.27(2)	91.5(11)	65.3(4)	111.7(13)	124.2(14)	124.1(14)	e
[Rh[P(i-Pr) ₃] ₂ H ₂ (CO ₃ H)] ^h	5	2.293(16)	1.261(3)	1.284(3)	1.329(3)	57.91(7)	121.5(2)	118.7(2)	119.8(2)	403	
[Co(NH ₃) ₄ CO ₃]Br	6	1.905(11)	1.336(18)	1.336(18)	1.237(20)	89.5(8)	70.5(5)	110.4(1.3)	124.8(1.4)	124.8(1.4)	f
6	1.93(2)	1.34(3)	1.34(3)	1.24(4)	88.5(8)	70.5(6)	112.7(1.4)	123.9(1.5)	123.9(1.5)	g	
[Co(py) ₄ CO ₃]ClO ₄ ·H ₂ O	6	1.894(6)	1.330(6)	1.319(5)	1.210(3)	69.28(12)	108.7(3)	125.5(4)	125.8(4)	125.8(4)	h
[Co(en) ₂ CO ₃]H ₂ H ₂ O	6	1.907(2)	1.306(3)	1.306(3)	1.234(6)	90.9(1)	68.2(1)	109.9(2)	125.0(1)	125.0(1)	i
[Co(tn) ₂ CO ₃]ClO ₄ ^j	6	1.92(4) ^b	1.32(2)	1.32(2)	1.22(2)	90.2(2) ^b	68.8(5)	110.4(7)	122.2(1.2)	129.7(1.2)	j
[Co(phen) ₂ CO ₃]Cl·3H ₂ O	6	1.883(12)	1.331(22)	1.284(23)	1.198(21)	68.4(5)	108.1(1)	122.2(1.2)	125.0(7)	125.0(7)	k
[Co(phen) ₂ CO ₃]Br·4H ₂ O	6	1.892(7)	1.315(8)	1.332(8)	1.213(8)	69.3(2)	108.7(6)	126.3(7)	125.0(6)	124.5(6)	l
Na[Co(pren)CO ₃]·3H ₂ O	6	1.907(6)	1.305(8)	1.329(7)	1.225(8)	90.1(8)	69.1(2)	110.5(5)	125.0(6)	124.5(6)	l
6	1.914(27) ^b	1.26(3)	1.33(3)	1.29(3)	1.29(3)	90.5(9)	68.4(4)	110.0(11)	125.7(12)	123.3(12)	m
[Co(cyclen)CO ₃]ClO ₄ ·H ₂ O	6	1.917(18)	1.308(16)	1.324(15)	1.219(16)	90.5(9)	68.6(2)	111.6(5)	123.1(6)	125.3(6)	n
(+)-cis- β -[Co(3,8-dimetilen)CO ₃]ClO ₄	6	1.915(18) ^b	1.314(18)	1.296(8)	1.236(8)	89.9(1.3) ^b	68.6(2)	113(1)	123(2)	124(1)	p
[Co(terpy)(CO ₃)(OH)]·4H ₂ O	6	1.918(9)	1.29(2)	1.29(2)	1.26(2)	68.0(4)	68.0(4)	119.3(49) ^b	120.8(40) ^b	120.8(40) ^b	y
[(NH ₃) ₄ Co(μ -NH ₂) ₂ (μ -OH)Co(CO ₃) ₂]·5H ₂ O	6	1.918(5)	1.314(8)	1.314(8)	1.237(5)	90.0(1.1)	68.5(4)	117.8(72) ^b	117.5(49) ^b	123(10) ^b	z
I ₂ C(NH ₃) ₃][UO ₂ (O ₂) ₂ (CO ₃) ₂]·2H ₂ O	8	2.42(1)	1.34(3)	1.24(3)	1.24(3)	53(1)	114(2)	119(2)	127(2)	r	
I ₂ C(NH ₃) ₃][UO ₂ (O ₂) ₂ (CO ₃) ₂]·2H ₂ O	8	2.430(5)	1.32	1.23(3)	1.28(3)	52(1)	115(2)	119(2)	125(2)	s	
K ₂ [UO ₂ (CO ₃) ₂] ^g	8	2.4430(5)	1.32	1.30	1.24	95.8(6)	53.7(4)	123.2(7)	123.2(7)	t	
(NH ₄) ₄ [UO ₂ (CO ₃) ₂] ^g	8	2.45(1)	1.34(2)	1.29(2)	1.25(3)	95(1)	54.1(1.1)	115(3)	123(2)	u	
[La ₂ (CO ₃) ₃]·8H ₂ O	10	2.54(10)	1.27(2)	1.27(2)	1.27(2)	1.27(2)	119.8(46) ^b	119.4(47) ^b	120.1(48) ^b	120.5(40) ^b	v
Na ₆ [Ce(CO ₃) ₃]·12H ₂ O	10	2.437(48) ^b	1.284(24) ^b	1.283(25) ^b	1.280(30) ^b	1.280(30) ^b	117.3(62) ^b	118(4) ^b	124(6) ^b	w	
[C(NH ₃) ₃] ₆ [Ce(CO ₃) ₃]·4H ₂ O	10	2.4448(35) ^b	1.38(16) ^b	1.21(10) ^b	1.27(8) ^b	1.27(8) ^b	117.3(62) ^b	118(4) ^b	124(6) ^b	x	
[Gd(HCO ₃) ₃]·H ₂ O	10	2.54(11) ^b	1.26(3)	1.28(3)	1.30(13) ^b	1.30(13) ^b	119.3(49) ^b	119.9(52) ^b	120.8(40) ^b	y	
Na ₆ [Tb(CO ₃) ₃]·12H ₂ O	10	2.505(43) ^b	1.29(3) ^b	1.28(4) ^b	1.30(3) ^b	1.30(3) ^b	117.8(72) ^b	117.5(49) ^b	123(10) ^b	z	
[C(NH ₃) ₃] ₆ [Th(CO ₃) ₃]·4H ₂ O	10	2.493(35) ^b	1.34(8) ^b	1.26(5) ^b	1.28(5) ^b	1.28(5) ^b					

^a Cariata, F.; Mason, R.; Robertson, G. B.; Ugo, R. J. *Chem. Commun.* 1967, 408. ^b See ^a, Table XVIII. ^c Harlow, R. L.; Simonsen, S. H. *Acta Crystallogr., Sect. B* 1975, B31, 1313. ^d Mossel, A.; Bonnet, J.-J.; Galy, J. Z. *Kristallogr.* 1978, 148, 165. ^e Brotherton, P. D.; White, A. H. *J. Chem. Soc., Dalton Trans.* 1973, 2338. ^f Barclay, G. A.; Hoskins, B. F. *J. Chem. Soc.* 1962, 586. ^g Snow, M. R. *Aust. J. Chem.* 1972, 25, 1307. ^h Kaas, K.; Sørensen, A. M. *Acta Crystallogr., Sect. B* 1973, B29, 113. ⁱ Bigoli, F.; Lanfranchi, M.; Leporati, E.; Pellinghelli, M. A. *Cryst. Struct. Comm.* 1980, 9, 1261. ^j Geue, R. J.; Snow, M. R. *J. Chem. Soc. A* 1971, 2981. ^k Hennig, H.; Sieler, J.; Benedix, R.; Kaiser, J.; Sjoelin, L.; Lindqvist, O. Z. *Anorg. Allg. Chem.* 1980, 464, 151. ^l Woon, T. C.; Mackay, M. F.; O'Connor, M. J. *Acta Crystallogr., Sect. B* 1980, B36, 2033. ^m Loehlin, J. H.; Fleischer, E. B. *Ibid.* 1976, B32, 3063. ⁿ Kucharski, E. S.; Dasgupta, T. P.; Koshy, K. *Inorg. Chem.* 1979, 18, 2290. ^o Note that no carbonate bridging is involved here. ^p Churchill, M. R.; Harris, G. M.; Lashewycz, R. S.; Shchelokov, R. N.; Zh. Neorg. Khim. 1981, 26, 718. ^q Anderson, A.; Chieh, C.; Irish, D. E.; Tong, J. P. K. *Can. J. Chem.* 1980, 58, 1651. ^r Graziani, R.; Bombieri, G.; Forcellini, E. J. *Chem. Soc., Dalton Trans.* 1972, 2059. ^s Shinn, D. B.; Eick, H. A. *Inorg. Chem.* 1968, 7, 1340. ^t Furmanova, N. G.; Soboleva, L. V.; Belyaev, L. M. *Kristallogr.* 1981, 26, 312. ^u Volfiotis, S.; Rimsky, A. *Acta Crystallogr., Sect. B* 1975, B31, 2615. ^v Volfiotis, S.; Rimsky, A. *Acta Crystallogr., Sect. B* 1975, B31, 2612.

TABLE XX. Bond Lengths (\AA) and Angles (deg) for Monodentate, Binuclear Asymmetric Carbonato Complexes

complex	CN	M-O	C-O ₁	C-O ₂	C-O ₃	M,O,C	M,O,C	O,CO ₂	O,CO ₃	ref
Na ₂ Cu(CO ₃) ₂	4	1.93 (4) ^a	1.29 (2)	1.22 (2)	111.4 (5)	117.1 (5)	117.5 (16)	123.8 (16)	118.7 (16)	b
Na ₂ Cu(CO ₃) ₂ ·3H ₂ O	5	1.946 (9) ^a	1.304 (5)	1.264 (5)	107.9 (3)	78.3 (2)	115.6 (4)	121.1 (4)	123.3 (4)	c
	5	1.953 (9) ^a	1.296 (5)	1.261 (5)	107.8 (3)	88.6 (1)	115.9 (4)	121.3 (4)	122.8 (4)	d
	5	1.97 (1)	1.27 (2)	1.28 (2)	108.6 (9)	132.0 (10)	116.9 (13)	121.7 (13)	121.3 (13)	e

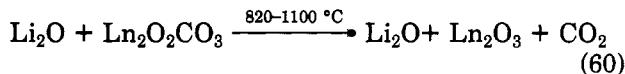
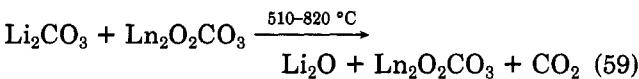
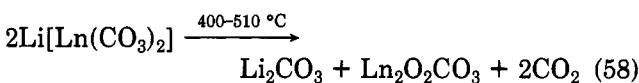
^a See ^a, Table XVIII. ^b Healy, P. C.; White, A. H. *J. Chem. Soc., Dalton Trans.* 1972, 1913. ^c Harlow, R. L.; Simonsen, S. H. *Acta Crystallogr., Sect. B* 1975, B31, 1313.^d Brotherton, P. D.; White, A. H. *J. Chem. Soc., Dalton Trans.* 1973, 2338.

cuo, air, CO₂ or N₂, the only commonly reported intermediate in the decomposition of [Ln₂(C₂O₄)₃] to Ln₂O₃ is Ln₂O₂CO₃.

Similarly, formate complexes, [M(HCO₂)₃]·xH₂O, of the rare earth elements lanthanum,²⁴⁶ europium, terbium, and lutecium²⁴⁷ first dehydrate, then decompose with increasing temperature to form the binuclear complex M₂O₂CO₃ which eventually degrades to M₂O₃. However, the route taken to yield M₂O₂CO₃ varies according to the metal. The most recent studies indicate that the bidentate intermediate EuCO₃ is formed following dehydration,²⁴⁷ while the binuclear intermediate M₂O(CO₃)₂ is formed at this stage for M = Lu²⁴⁷ and La²⁴⁶ with the lanthanum complex stemming from yet another intermediate, viz. [La₂(C₂O₄)₃]. Note also that the decomposition of EuCO₃ to Eu₂O₂CO₃ was studied separately by Dobrovolskii²⁴⁸ who observed this transition in both an oxygen and an argon atmosphere. He attributed oxidation of Eu(II) to Eu(IV) in argon to the "acid residue".

Under different conditions, the oxalato complexes, [Ln₂(C₂O₄)₃]·xH₂O, provide a source of lanthanum carbonates of a different kind, namely the lithium bis(carbonato) complexes, Li[Ln(CO₃)₂] where Ln = La to Lu. The conditions involved heating the oxalato complex to 500 °C in the presence of Li₂CO₃ under 200 MPa CO₂.²⁴⁹ These bis(carbonato) salts were well characterized and thereby shown to fall into two distinct groups. The first group includes the lanthanides, La through Gd, which exhibit the averaged properties: lattice constants, $a_0 = 8.30$, $b_0 = 7.73$, $c_0 = 6.82 \text{ \AA}$ —each decreases monotonically with increasing atomic number over a narrow range, i.e., $\leq 0.21 \text{ \AA}$; densities in the range, 3.89 to 4.50 g cm⁻³; and volumes of the unit cell, 453.0–419.2 Å³. Infrared bands were observed as follows: 1100 cm⁻¹ (symmetric valence frequency); 1410, 1505, and 1565 cm⁻¹ (asymmetric valence frequency); 660, 690, 738, and 750 (bending frequency); 860 cm⁻¹ (deformation frequency); Li–O vibrations at 385, 435, and 585 cm⁻¹; Ln–O vibrations at 280 cm⁻¹. The second group, terbium through lutetium, plus yttrium, demonstrated the corresponding properties: $a_0 = 6.63$, $b_0 = 13.63$, $c_0 = 10.37 \text{ \AA}$, with the same trend when Y follows Ho in the series, $\pm 0.21 \text{ \AA}$; densities, 4.13–4.56 g cm⁻³ (for yttrium, 3.17 g cm⁻³); and volumes 917.7–876.2 Å³.

The thermal decomposition of two examples from the first group, namely La and Nd, and one from the second, Yb, was investigated in a streaming nitrogen atmosphere.²⁴⁹ Both Li[La(CO₃)₂] and Li[Nd(CO₃)₂] behaved similarly in the following manner (presumably this is symptomatic of the whole group):



Note that Li₂O melts at $\sim 700^\circ\text{C}$ so that part of reaction 59 and all of reaction 60 take place within this melt. Moreover, the same binuclear intermediate Ln₂O₂CO₃ is observed again, but Li[LnOCO₃] was not seen (see

TABLE XXI. Bond Lengths (Å) and Angles (deg) for Monodentate, Binuclear Symmetric Carbonato Complexes

complex	CN	M-O	C-O ₁	C-O ₂	C-O ₃	M ₁ -M ₂	MOC	O ₁ CO ₂	O ₁ CO ₃	O ₂ CO ₃	ref
KAgCO ₃	2	2.09 (4)	1.33 (7)	1.24 (6)	1.26.5 (15)	121.0 (15)	119.5 (15)	119.5 (15)	119.5 (15)	119.5 (15)	a
NaAl(OH) ₂ CO ₃ (dawsonite)	6	1.939 (1) (Al)	1.308 (3)	1.250 (5)	119.79 (34)	120.91 (18)	120.91 (18)	120.91 (18)	120.91 (18)	120.91 (18)	b
[(NH ₃) ₆ Co ^{II} (μ-OH) ₂ (μ-CO ₃) ₂]SO ₄ ·5H ₂ O	6	1.901 (4)	1.286 (3)	1.262 (3)	2.817 (1)	126.9 (6) ^c	122.4 (3)	119.7 (3)	118.0 (3)	118.0 (3)	347
[(19-JaneN ₃) ₂ Cr ^{III} (μ-OH) ₂ (μ-CO ₃) ₂]H ₂ O	6	1.976 (7)	1.286 (9)	1.244 (16)	2.898 (2)	126.9 (7)	122.5 (11)	118.7 (6)	118.7 (6)	118.7 (6)	345
(NH ₄) ₂ I(H ₂ O)Cr ^{II} (μ-OH) ₂ (μ-CO ₃) ₂]·H ₂ O	6	2.012 (3)	1.297 (8)	1.292 (12) ^c	1.261 (9) ^c	2.214 (1)	120.3 (9)	119.1 (6)	120.2 (4)	120.8 (7)	d
(NH ₄) ₂ I(H ₂ O)Rh ^{II} (μ-OH) ₂ (μ-CO ₃) ₂]·6H ₂ O	6	2.033 (4)	1.276 (16)	1.283 (21) ^c	2.283 (1)	2.378 (1)	120.3 (7) ^c	122.7 (14) ^c	118.1 (15) ^c	119.3 (8)	e
Na ₂ Cs ₄ [Cl ₂ Rh ^{II} (μ-CO ₃) ₂]·8H ₂ O	6	2.043 (5)	1.31 (3)	1.28 (2)	2.380 (2)	120.2 (13) ^c	123 (2)	119 (2)	121 (3)	121 (3)	e

^a Barclay, G. A.; Hoskins, B. F. *J. Chem. Soc.* 1963, 2807. ^b Corazza, E.; Sabelli, C.; Vannucci, S. N. *Jb. Miner. Min. Phys.* 1977, 381. ^c See *a*, Table XVIII. ^d Cotton, F. A.; Rice, G. W. *Inorg. Chem.* 1978, 17, 2004. ^e Cotton, F. A.; Felthouse, T. R. *Ibid.* 1980, 19, 320.

TABLE XXII. Bond Lengths (Å) and Angles (deg) for Mono/bidentate, Binuclear Asymmetrical Carbonato Complexes

complex	CN	M-O ₁	M-O _{2,3}	C-O ₁	C-O ₂	C-O ₃	M ₁ O _{1,C}	M ₂ O _{2,C}	O ₂ M ₂ O ₃	O ₁ CO ₂	O ₁ CO ₃	O ₂ CO ₃	ref
[Cu(NH ₃) ₂ CO ₃] ₂	5	2.303 (2)	1.988 (4)	1.245 (3)	1.307 (3)	1.299 (3)	66.38 (8)	123.12 (23)	123.6 (2)	113.3 (2)	113.3 (2)	113.3 (2)	a
[(PPH ₃) ₅ Rh ₂ (μ-CO ₃) ₂ C ₆ H ₆] ₂	4	2.109	2.119	1.29 (2)	1.29 (2)	1.29 (2)	62.6 (6)	123.9 (9)	120.1 (11)	115.9 (20)	115.9 (20)	115.9 (20)	500
[(C ₆ H ₅) ₈ Sb ₂ (μ-CO ₃) ₂] ₂	5/6	2.257 (7)	2.325 (7)	1.275 (13)	1.293 (13)	1.308 (13)	121.1 (8)	90.8 (17)	120.0 (10)	116.1 (10)	116.1 (10)	116.1 (10)	b
[(Me ₂ PhP) ₆ (CO) ₂ Mo ₂ (μ-CO ₃) ₂] ^c	7	2.32 (11)	2.20 (11)	1.28 (3)	1.27 (3)	1.28 (3)	49.5 (1)	49.5 (1)	49.5 (1)	445			

Structure i

 Structure ii


^a Meyer, M. H.; Singh, P.; Hatfield, W. E.; Hodgson, D. J. *Acta Crystallogr., Sect. B* 1972, B28, 1607. ^b Harlow, R. L.; Simonsen, S. H. *Ibid.* 1975, B31, 1313. ^c Asymmetrical, with two oppositely oriented carbonate bridges.

TABLE XXIII. Bond Lengths (Å) and Angles (deg) for Bidentate, Binuclear Symmetrical Carbonato Complexes

complex	CN	M-O ₁	M-O _{2,3}	C-O ₁	C-O ₂	C-O ₃	M ₁ O _{1,M₂}	M ₂ O _{2,C}	MO _{2,C}	O ₁ MO ₂	O ₁ CO ₂	O ₁ CO ₃	O ₂ CO ₃	ref
[(dta) ₂ Cu ^{II} (μ-CO ₃)](ClO ₄) ₂ ·DMF	5	2.041 (1)	2.028 (5)	1.32 (1)	1.27 (1)	1.27 (1)	176.6 (2)	88.3 (5)	90.3 (4)	65.3 (3)	116.1 (5)	116.1 (5)	128 (1)	a
[(tmtb) ₂ Cl ₂ Cu ^{II} (μ-CO ₃) ₂] ₂	5	2.1527 (4)	1.978 (2)	1.299 (5)	1.270 (3)	1.270 (3)	85.13 (7)	170.26 (13)	63.96 (9)	117.2 (2)	117.2 (2)	125.6 (4)	c	
[(tied) ₂ Cl ₂ Cu ^{II} (μ-CO ₃) ₂] ₂	5	2.093 (2)	1.962 (16)	1.300 (4)	1.277 (4)	1.255 (4)	165.97 (13)	86.90 (20)	92.81 (21)	64.73 (10)	115.5 (3)	119.9 (3)	124.6 (3)	d

^a Davis, A. R.; Einstein, F. W. B. *Inorg. Chem.* 1980, 19, 1203. ^b Davis, A. R.; Einstein, F. W. B.; Curtis, N. F.; Martin, J. W. L. *J. Am. Chem. Soc.* 1978, 100, 6258.

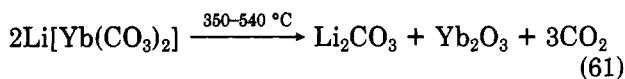
^c Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W.; Watkins, K. O. *Inorg. Chem.* 1979, 18, 2296. ^d Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W. *Ibid.* 1980, 19, 2011.

TABLE XXXV. Bond Lengths (Å) and Angles (deg) for Monodentate, Trinuclear Symmetrical (i) and Tetrานuclear Asymmetrical (ii) Carbonato Complexes

complex	CN	M-O	C-O ₁	C-O ₂	C-O ₃	M ₁ -M ₂	MO ₁ C	O ₁ CO ₂	O ₁ CO ₃	O ₂ CO ₃	ref
Cu ₃ (OH) ₂ (CO ₃) ₂	4	1.88(5)	1.30(5)	1.27(5)	1.24(5)		116.1	113.5	121.9	126.1	a
	4	1.930(1)	1.283(2)	1.286(1)	1.277(1)			119.5(1)	119.6(1)	120.9(2)	b
T ₂ Cu(CO ₃)	5(Cu)	2.01(10)	1.288	1.331	1.324	2.583		122.79	123.09	114.07	c
	7(Tl) ^d	2.94(27 ^d)	1.309	1.288	1.283	3.78(18)		122.29	117.30	120.40	
ii											
Structure i											
Cu ₂ (OH) ₂ CO ₃ ^f	4/6	2.06(5)	1.30	1.27	1.29			119.55(7)	119.00(7)	121.44(8)	e
		2.05(5)	1.308(1)	1.266(1)	1.287(1)			111.8(17)	113.4(10)	134.8(13)	219
[dpf] ₄ Cu ₄ (μ-CO ₃)(μ-Cl) ₂]Cl·7.5H ₂ O	5	2.058(21)	1.411(18)	1.237(26)	1.212(11)		111.7(8)				

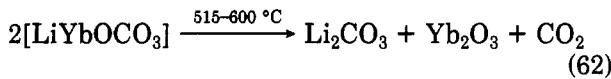
^a Gattow, G.; Zemann, J. *Acta Crystallogr.* 1958, 11, 866. ^b Zigan, F.; Schuster, H. D. *Z. Kristallogr.* 1972, 135, 416. ^c Ehrhardt, H.; Lemor, R.; Seidel, H. *Z. Anorg. Allg. Chem.* 1981, 477, 183. ^d Bonding between M₁ and O₂ exists to give resulting coordination number of 7. ^e Süss, P. *Naturwissenschaften* 1966, 53, 80. ^f Neutron diffraction.

next paragraph). Ytterbium carbonate decomposes directly to the oxide with subsequent decomposition of Li₂CO₃ to Li₂O, as shown in reaction 61.



The analogous sodium bis(carbonato) complexes Na[Ln(CO₃)₂], where Ln = La through Lu, plus Y, were similarly synthesized either by the reaction of [Ln₂(C₂O₄)₃]·xH₂O with Na₂CO₃ at 350–500 °C and 300 MPa of CO₂, or by dehydration of Na[Ln(CO₃)₂]·xH₂O.²⁵⁰ Again the same two structural groups were characterized, but all thermally decomposed by the same mechanism corresponding to eq 58. The three examples cited in the original paper²⁵⁰ are listed in Table XXV. Conflicting results were published by Mochizuki et al.²⁵¹ and Oda²⁵² who claim decomposition of Na[Nd(CO₃)₂], Na[Y(CO₃)₂]·H₂O, and Na[Gd(CO₃)₂]·H₂O yields Na[NdO(CO₃)], Na[YO(CO₃)], and Na[GdO(CO₃)] at 650–680, 580, and 400–600 °C, respectively, although the conditions are not specified. Taravel et al.²⁵³ report the direct decomposition of Na[Er(CO₃)₂] to Er₂O₃ under unspecified conditions using only TG as a monitor.

By applying about one-tenth the CO₂ pressure when heating [Ln₂(C₂O₄)₃]·H₂O, where Ln = Sm to Lu, plus Y, to 500–550 °C results in the formation of Li[LnO-CO₃] as evidenced by IR and X-ray spectroscopy.²⁴⁹ The IR spectra are all similar, consistent with a common structure. The symmetrical vibration frequency is represented by two bands at 1090 and 1120 cm⁻¹, while the asymmetrical vibration occurs at 1445 and 1515 cm⁻¹. The low energy bands in the 400–600 cm⁻¹ range increase in energy with decreasing radius of the Ln³⁺ ion (i.e., Sm through Lu). From the X-ray data the lattice parameters decrease from Sm through Lu as follows: a₀ = 3.49–3.36; b₀ = 7.71–7.44; c₀ = 7.56–7.28 Å. The densities vary systematically over the range 3.91–4.82 g cm⁻³, with the exception of Li[YOCO₃] (3.06 g cm⁻³). The TG and DTA curves, which monitored the thermal decomposition of these carbonates in a N₂ environment, are reminiscent of those obtained for the second group of LiLn(CO₃)₂ complexes. Equation 62 is given for Li[YbOCO₃].²⁴⁹



C. Actinide Complexes

The thermal decomposition of americium(III) oxalate, formate, and carbonate has been investigated in some detail.²⁵⁴ The initial dehydration of [Am₂(C₂O₄)₃]·10H₂O involved the immediate formation of the hexahydrate. Complete dehydration involved an additional four stages over the range 50–340 °C. Subsequent transformation to [Am₂(CO₃)₃] occurred at 390–430 °C. The thermolysis of this anhydrous carbonate behaved in a similar fashion to the lighter lanthanides with conversion to [Am₂O(CO₃)₂] occurring at 430–470 °C, succeeded by the familiar form Am₂O₂CO₃ at 470–520 °C. Decomposition to Am₂O₃ took place at 520–610 °C.

It is somewhat confusing, however, that following the dehydration of [Am₂(CO₃)₃]·2H₂O at 50–310 °C, only Am₂O₂CO₃ was clearly observable.²⁵⁴ The thermolysis of [Am(HCO₃)₃]·0.2H₂O also yielded Am₂O₂CO₃ directly

TABLE XXV. Representative Sample of the Data on the Thermal Decomposition of Metal Carbonato Complexes

initial complex	medium	temp., °C	products	technique ^a	ref
KHCO_3	<100 torr	145–200	$\text{K}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$	manometric	b
CaCO_3	vacuo	700 max	$\text{CaO} + \text{CO}_2$	dielectrometry	c
SrCO_3	vacuo	850 max	$\text{SrO} + \text{CO}_2$	dielectrometry	c
BaCO_3	vacuo	950 max	$\text{BaO} + \text{CO}_2$	dielectrometry	c
$\text{NaAl(OH)}_2\text{CO}_3$ (synthetic dawsonite)	air	320	$\text{Na}_2\text{O} + \text{Al}_2\text{O}_3 + \text{H}_2\text{O} + \text{CO}_2$	TG, DTA, IR, X-ray	d
$\text{Na}_3[\text{Sc}(\text{CO}_3)_4]$	air	300–650	$\text{NaAlO}_2 + \text{H}_2\text{O} + \text{CO}_2$	TG, IR	e
(Ba or Sr) $\text{V}_2\text{O}_5\text{CO}_3$	vacuo	210–400	$\text{Sc}_2\text{O}_3 + \text{Na}_2\text{CO}_3 + \text{CO}_2$	TG, DTA, IR, X-ray	253
$\text{MnCO}_3 \cdot 0.3\text{H}_2\text{O}$	air, N_2	600	(Ba or Sr) $\text{VO}_3 + \text{CO}_2$	TG, DTA, DTG, IR, X-ray	230
CoCO_3	vacuo	400	$\text{MnO} + \text{H}_2\text{O} + \text{CO}_2$	TG, DTG, TGT, DT, DTGT, DT, DTD ^f	b
	air	300–400	$\text{CoO} + \text{CO}_2$	TG	237
	air	390–480	$\text{CoO} + \text{CO}_2$	TG, magnetic susceptibility	g
$2\text{CoCO}_3 \cdot 3\text{Co}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	vacuo	200–230	$\text{Co}_3\text{O}_4 + \text{H}_2\text{O} + \text{CO}_2$	TG, GC, EGA, TM, X-ray	h
Fe CO_3 (siderite)	vacuo	480–580	FeO (wustite) + CO_2	TG, GC, EGA, TM, X-ray	h
	N_2	~400–550	Fe_3O_4 (magnetite) + CO_2	TG, GC, EGA, TM, X-ray	h
	O_2	~420–590	Fe_2O_3 (hematite) + CO_2	TG	237
$\text{Fe}_2(\text{CO}_3)_3$	vacuo	360–460	$\text{Fe}_2\text{O}_3 + \text{CO}_2$	manometric	b
NiCO_3	air	360–460	$\text{NiO} + \text{CO}_2$	TG, DTA, IR, X-ray	228
$\text{Ca}_2[\text{Zr}_2\text{O}_5\text{CO}_3]$	air	550–650	$\text{CaZrO}_3 + \text{CO}_2$	TG, DTA, IR, X-ray	228
$\text{Sr}_2[\text{Zr}_2\text{O}_5\text{CO}_3]$	air	550–725	$\text{SrZrO}_3 + \text{CO}_2$	TG, DTA, IR, X-ray	228
$\text{K}_2[\text{Zr}(\text{CO}_3)_2\text{CO}_2\text{F}_2]$	air	250–565	$\text{ZrO}_2 + \text{K}_2\text{CO}_3 + \text{KF} + \text{CO} + \text{CO}_2$	TG, IR, X-ray	i
$\text{K}_2[\text{Hf}(\text{CO}_3)_2\text{CO}_2\text{F}_2]$	air	250–565	$\text{HfO}_2 + \text{K}_2\text{CO}_3 + \text{KF} + \text{CO} + \text{CO}_2$	TE, IR, X-ray	i
$[\text{La}_2(\text{CO}_3)_3] \cdot 0.25\text{H}_2\text{O}$	vacuo	430–580	$\text{La}_2\text{O}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$	TG	240
$\text{Na}[\text{La}(\text{CO}_3)_3]$	Ar, N_2	400–540	$\text{La}_2\text{O}_2\text{CO}_3 + \text{Na}_2\text{CO}_3 + \text{CO}_2$	TG, DTA	250
$\text{La}_2\text{O}_2\text{CO}_3$	vacuo	590–760	$\text{La}_2\text{O}_3 + \text{CO}_2$	TG	240
	air	700–820	$\text{La}_2\text{O}_3 + \text{CO}_2$	TG, DTA, IR	j
	vacuo	530	$\text{La}_2\text{O}_3 \cdot 0.8\text{CO}_2$	TG, DTA, DTG	k, 243
	vacuo	600	$\text{Ce}_2\text{O}_3 + \text{CeO}_2 + \text{CO}_2 + \text{CO}$	X-ray, GC	l
	Ar, N_2	380–500	$\text{Ce}_2\text{O}_3 + \text{CeO}_2 + \text{CO}_2 + \text{CO}$	TG, DTA	250
	Ar, N_2	500–570	$\text{Ce}_2\text{O}_3 + \text{CO}_2$	TG, DTA	250
	air	500	$\text{Nd}_2\text{O}_3 \cdot 0.9\text{CO}_2$	TG, DTA, DTG	k, 243
	air	360–540	$\text{Eu}_2\text{O}_2\text{CO}_3 + \text{CO}_2$	DTA	247, 248
	Ar	600–670	$\text{Eu}_2\text{O}_2\text{CO}_3 + \text{CO}$	DTA	248
	air	610–810	$\text{Eu}_2\text{O}_2 + \text{CO}_2$	TG, IR	m
	air	490	$\text{Tb}_2\text{O}_2\text{CO}_3 + \text{CO}_2$	DTA	248
	air	560–880	$\text{Tb}_2\text{O}_7 + \text{CO}_2$	DTA	248
	air	690	$\text{Tb}_4\text{O}_7 + \text{CO}_2$	TG, IR	m
	Ar, N_2	350–480	$\text{Ho}_2\text{O}_2\text{CO}_3 + \text{Na}_2\text{CO}_3 + \text{CO}_2$	TG, DTA	250
	Ar, N_2	350–480	$\text{Ho}_2\text{O}_3 + \text{CO}_2$	TG, DTA	250
$\text{Ce}_3[\text{Cl}(\text{CO}_3)_4]$	vacuo	350–500	$\text{Er}_2\text{O}_3 + \text{Na}_2\text{CO}_3 + \text{CO}_2$	TG, IR	253
$[\text{Ce}_3\text{Cl}(\text{OH})_3(\text{CO}_3)_4]$	vacuo	200–500	$\text{Er}_2\text{O}_3 + \text{Na}_2\text{CO}_3 + \text{CO}_2$	TG, IR	253
$\text{Na}[\text{Ce}(\text{CO}_3)_2]$	vacuo	330–500	$\text{Er}_2\text{O}_3 + \text{Na}_2\text{CO}_3 + \text{CO}_2$	TG, IR	253
$\text{Ce}_2\text{O}_2\text{CO}_3$	air	460	$\text{Er}_2\text{O}_3 + \text{Na}_2\text{CO}_3 + \text{CO}_2$	TG, IR	253
$[\text{Nd}_2\text{O}(\text{CO}_3)_2] \cdot 1.5\text{H}_2\text{O}$	vacuo	640	$\text{Tm}_2\text{O}_3 + \text{Na}_2\text{CO}_3 + \text{CO}_2$	TG, IR	m
EuCO_3	air	350–360	$\text{Tm}_2\text{O}_3 + \text{CO}_2$	DTA	248
	air	440	$\text{Lu}_2\text{O}_2\text{CO}_3 + \text{CO}_2$	TG, IR	m
	air	620–800	$\text{Lu}_2\text{O}_3 + \text{CO}_2$	DTA	248
	air	610	$\text{Lu}_2\text{O}_3 + \text{CO}_2$	TG, IR	m
$\text{Tb}_2(\text{CO}_3)_3$	N ₂	503	$\text{PbCO}_3 \cdot \text{PbO} + \text{CO}_2$	calorimetry	224
$\text{Tb}_2\text{O}_2\text{CO}_3$	N ₂	588	$\text{PbO} + \text{CO}_2$	calorimetry	224
$[\text{Tb}_2\text{O}_2\text{CO}_3]_2$	CO ₂	508	$\text{PbCO}_3 \cdot \text{PbO} + \text{CO}_2$	calorimetry	224
$\text{Lu}_2\text{O}_2\text{CO}_3$					
$\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$					
$\text{PbCO}_3 \cdot \text{PbO}$					
$\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$					

$2\text{PbCO}_3 \cdot \text{PbO}$	CO ₂	200	PbCO ₃ · PbO + CO ₂	calorimetry	224
(NH ₄) ₂ [UO ₂ (cupferron)CO ₃] ^b	air	285	UO ₂ CO ₃ + ...	TG, DTA, IR	n, o
[UO ₂ CO ₃] ^b	air	620	UO ₂ + ...	TG, DTA	n, o
[Co(NH ₃) ₆]Np(CO ₃) ₃] ^c	air	100	CoCO ₃ + NpO ₂ or Np ₃ O ₈	DTA, TGA, X-ray	p

^a TG = thermogravimetric; DTA = differential thermoanalysis; DTG = derivative thermoanalysis; DTG = derivative thermodilatation; TG = thermo-gas-titrimetric; TD = thermodilatation; DTG = derivative thermo-gas-titrimetric; TM = thermogravimetric; EGA = evolved gas analysis; GC = gas chromatographic.

^b Wendlandt, W. W. *J. Chem. 1978, 52, 439.* ^c Mikheev, V. N.; Grinevich, V. N.; Brovirkov, V. N.; Grinevich, V. I. *Izv. Akad. Nauk SSSR Neorg. Mater. 1975, II, 1895.* ^d Szczepanik, M.; Budnicki, R. *Pol. Thermochim. Acta. 1974, 9, 7.* ^e Huggins, C. W.; Green, T. E. *Am. Min. 1973, 58, 548.* ^f Paulik, F.; Paulik, J. *Thermochim. Acta 1971, 3, 17.* ^g Mehandiev, D.; Nikolova, E. *Ibid.* 1978, 23, 117. ^h Gallagher, P. K.; Warne, S. J. *Ibid. 1981, 43, 253.* ⁱ Medkov, M. A.; Davidovich, R. L. *Izv. Akad. Nauk SSSR, Ser. Khim. 1978, 270.* ^j Petru, F.; Kutek, F.; Satava, J. *Coll. Czech. Chem. Commun. 1966, 31, 4459.* ^k Nagashima, K.; Wakita, H.; Mochizuki, A. *Bull. Chem. Soc. Jpn. 1973, 46, 152.* ^l Peterson, E. J.; Ostott, E. I. J. *Inorg. Nucl. Chem. 1979, 41, 517.* ^m Deineka, G. F.; Tselik, I. N.; Il'inskaya, E. P. *Zh. Neorg. Khim. 1972, 17, 1291.* ⁿ Kundu, P. C.; Roy, P. S.; Banerjee, R. K. *J. Inorg. Nucl. Chem. 1980, 42, 851.* ^o Kundu, P. C.; Roy, P. S. *Ibid. 1981, 43, 186.* ^p Saito, A.; Ueno, K. *Ibid. 1980, 42, 1301.*

at 420–540 °C with emission of CO₂, CO, H₂, and H₂O as determined by mass spectroscopy. An intermediate in this reaction was postulated to be [AmO(HCO₂)]. The apparent discrepancy in the decomposition paths of the oxalato and carbonato complexes was not rationalized.

A thermogravimetric analysis of Tl₆[Th(CO₃)₅]·2H₂O was made in an attempt to elucidate the structure of this compound.²⁵⁵ After dehydration at 50–180 °C, 2 mol of CO₂ are generated per mole of compound over the temperature range 180–380 °C, with final decomposition to Tl₂O₃ and ThO₂ at 380–510 °C. The observation of the initial loss of two-fifths of the total carbonate led Karkhanava and Daroowalla²⁵⁶ to suggest that the original complex is really the double salt 3Tl₂CO₃·[Th(CO₃)₂(H₂O)₂] with the thorium coordinated to two bidentate carbonates and two water molecules, and thus it is these two carbonates that are lost initially. A previous infrared study²⁵⁶ of the sodium analogue implied the existence of both ionic (1080 w, 865 s, 855 m, 700–705 vw) and coordinated carbonate (1055 m, 725 m) (N.B. these authors²⁵⁶ write the formula, Na₄[Th(CO₃)₄]·Na₂CO₃), in agreement with the notion of a double salt. Furthermore, Tl₂CO₃ was shown to decompose at the higher temperature range of 335–445 °C.²⁵⁵

[Th(CO₃)₂]·xH₂O can be thermolytically synthesized from aqueous Th(OH)₄ at temperatures ranging from 100–150 °C, CO₂ pressures of 182.4–344.5 MPa, and reaction times of 36–720 h.²³⁵ These conditions are inversely correlated. The partially dehydrated product, [Th(CO₃)₂]·0.5H₂O, was characterized by its IR absorption spectrum: 1085 (ν_1); 830 (ν_2); 1350, 1550 (ν_3); 680, 752 (ν_4), and 3400 cm⁻¹ (ν_5 – H₂O).

Finally, many publications have appeared in the literature dealing with the kinetics of thermal decomposition.^{257–265} However, as this information does not serve to characterize a solid in a unique sense, it will not be presented in this review.

VII. Equilibria

In this section a compilation of the available stability constants for carbonate species, complexes, and ion pairs in solution, and solubility constants for various carbonate salts is presented. A detailed discussion of the various methods employed in the determination of such stability constants was presented in the earlier review on carbonato complexes.¹ Methods used to determine the stability constants reported in Table XXVIII include spectrophotometry,^{266–272} polarography,^{273,274} potentiometry,^{275–284} pH measurements,^{285,286} solvent extraction,^{287,288} solubility measurements,^{267,289–296} ion exchange,^{297,298} ¹H NMR,²⁹⁹ and kinetic methods.^{271,300} The notation adopted in the compilation of stability and solubility constants in Table XXVIII is in agreement with that used in standard reference texts on such data.³⁰¹

The stability constants in Table XXVIII differ in some exceptional cases by as much as 3 orders of magnitude.^{282,300} In general, the agreement between the various reported constants is fairly good, and in many cases only one or two data points really fall out of the series. The scatter in the $\Delta H/\Delta S$ data is more severe and could partially be associated with the different equations adopted to fit the temperature dependencies

TABLE XXVI. Thermolysis Reactions Yielding Transition-Metal Carbonato Compounds of the Form MCO_3^{234}

starting material	temp, °C	pCO_2 , MPa	time, h	product ^a
$[MnC_2O_4] \cdot 2H_2O$	410-420	250	24	$MnCO_3$ (colorless)
$[FeC_2O_4] \cdot 2H_2O$	415-470	350	24	$FeCO_3$ (light blue)
$[CoC_2O_4] \cdot 2H_2O$	400-430	250	72	$CoCO_3$ (purple, violet)
$[NiC_2O_4] \cdot 2H_2O$	390-435	400	24	$NiCO_3$ (light gray)
$[ZnC_2O_4] \cdot 2H_2O$	400	300	24	$ZnCO_3$ (colorless)
$[CdC_2O_4] \cdot 2H_2O$	400	250	24	$CdCO_3$ (light gray)
$[CuC_2O_4] \cdot 2H_2O^b$	260-290	270-310	24	$CuCO_3$ (green)
$[VCO_3] \cdot 2H_2O$	240	350	48	$VCO_3 \cdot 0.5H_2O$ (grey brown)
	265	390	48	V_2O_3 (black)
$[Cr(CO)_6]$	280	300	48	$CrCO_3 : Cr_2O_3$ (2:3) (green)
	300	320	24	Cr_2O_3

^a Compounds were characterized from IR and X-ray diffraction. ^b Occurs only in the presence of the oxidizing agent NH_4NO_3 .

TABLE XXVII. Thermolysis Reactions in Aqueous Media Yielding Transition-Metal Carbonato Compounds²³⁵

starting material	temp, °C	pCO_2 , MPa	time, h	product	IR bands, ^a cm ⁻¹
$Mn(OH)_2$	160	243.2	40	$MnCO_3$ (pale pink)	210, 280, 360, 728, 867, 1085, 1440, 1805, 2500
$Fe(OH)_2$	150	253.3	30	$FeCO_3$ (ca. colorless)	215, 320, 370, 739, 866, -, 1425, 1820, 2520
$Co(OH)_2$	160	273.6	60	$CoCO_3$ (purple, violet)	225, 320, 360, 745, 865, 1080, 1465, 1820, 2510
$Ni(OH)_2$	160	192.5	24	$NiCO_3$ (light green)	240, 335, 370, 758, 869, 1080, 1445, 1830, 2510
$Zn(OH)_2 \cdot xH_2O$	160	283.7	30	$ZnCO_3$ (colorless)	210, 310, 370, 744, 870, -, 1430, 1820, 2500
$ZrO_2(aq)$	150	405.3	24	$ZrO_2CO_3 \cdot 2H_2O$	450, ^b 650, 840, 1050, 1350, 1410, 1545, 1625, ^c 3390

^a Cf. $CaCO_3$ (228, 310, 325, 712 (ν_4), 875 (ν_2) - (ν_1), 1430 (ν_3), 1810, 2520 cm⁻¹). ^b Zr-O. ^c ν_2 and ν_3 (H_2O).

of the stability constants. The equations used will in turn depend to a large extent on the temperature ranges over which these measurements were made. A recent review³⁰² covered the various expressions used to describe the temperature dependence of stability constants. For the data in Table XXVIII, expressions of the form

$$\log K = A + BT + CT^2 \text{ (ref 282)}$$

$$\log K = A + BT + C/T \text{ (ref 282, 284, 296)}$$

$$\log K = A + B \log T + C/T \text{ (ref 281, 282)}$$

$$\log K = A + BT + C/T + D \log T \text{ (ref 149)} \quad (63)$$

were adopted. Similar expressions have also been applied to solubility constant data.^{149,303} Some deprotonation/protonation constants of metal bicarbonato/carbonato complexes are included in Table XXVIII. A more complete series of such data is given in Table XXXIII (section VIII), which deals with kinetically determined acid dissociation constants of unstable bicarbonato complexes. The data in Table XXVIII fall within the range of values reported in section VIII and are close to the first acid dissociation constant of carbonic acid, which illustrates the similarity in the nature in the O-H bond in HCO_3^- and $MOCO_3^-$.

The data in Table XXVIII illustrate that much work has been done on the carbonate species of Mg^{2+} , Ca^{2+} , Pb^{2+} , UO_2^{2+} , and PuO_2^{2+} . In this respect it is interesting to note that $Na_4UO_2(CO_3)_3$ had been prepared and identified as early as 1842.^{304,305} The interest in the mentioned species mainly comes from biologically and environmentally orientated investigations. The modelling of biological processes, natural waters, seawater, and geochemical processes strongly depends on the availability of such data.^{272,274,306-308} In addition to the

species summarized in Table XXVIII, evidence for the formation and presence of a large number of carbonate species has been reported during the time covered by this review, and a compact summary is given in Table XXIX. These species were not included in Table XXVIII due to an absence of data on their stability or solubility constants. In some cases solubility data were reported for some of these and closely related species.³⁰⁹⁻³¹¹

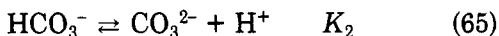
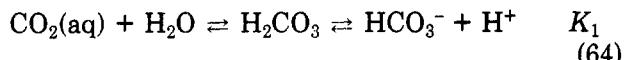
Many papers deal with thermodynamic data for various metal carbonato species. We, however, feel that a presentation and discussion of such data lies beyond the scope of this review, and therefore we only present a summary of the references where such data can be found (see Table XXX).

VIII. Kinetics and Mechanisms

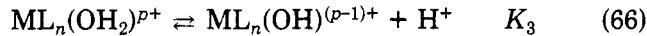
This section deals with the kinetics and mechanisms of the formation, aquation, substitution, exchange, isomerization, redox, radiochemical, and photochemical reactions of metal carbonato complexes. Significant progress has especially been made in the understanding of such processes during the period covered by this review. Our own contributions in some of these areas motivated us to present a complete and critical coverage of the appropriate subsections. The various types of reactions are treated in different subsections, and differentiation between the various bonding modes of the carbonate ligand, viz., monodentate, bidentate, or bridged, is emphasized throughout.

A. Formation Reactions

Various reaction routes exist for the formation of carbonato complexes in aqueous solution. When $CO_2(g)$ is dissolved in aqueous solution, the reactions/equilibria in eq 64 and 65 set in (see sections III and IV). As



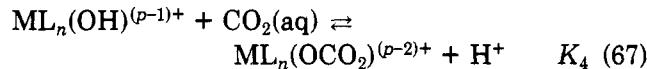
discussed in section IV, the hydration rate constant of $\text{CO}_2(\text{aq})$ and the dehydration rate constant of H_2CO_3 are such that the $\text{CO}_2(\text{aq})/\text{H}_2\text{CO}_3$ equilibrium lies to the left and more than 99% of CO_2 in water exists as dissolved CO_2 (less than 1% as true H_2CO_3).¹⁵⁵ Typical values for the overall equilibrium constants are $pK_1 = 6.03$ and $pK_2 = 9.8$ at 25 °C and ionic strength 0.5 M³¹² (see section III). It follows that there are actually four potentially reactive species in solution, viz., $\text{CO}_2(\text{aq})$, H_2CO_3 , HCO_3^- , and CO_3^{2-} , which can in principle produce carbonato complexes during their reaction with metal aquo/hydroxo species. Water coordinated to a metal ion is quite acidic such that the pK (on a molarity scale) of a typical transition-metal aquo complex ion is close to 7 as compared to a value of about 16 for solvent water molecules.³¹³ In a near neutral or weakly basic solution it is thus possible to have appreciable quantities of the hydroxo species present, which could react in a completely different manner than the corresponding aquo species (eq 66). The values of K_3 are usually



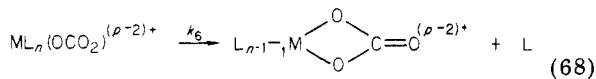
known from conventional pH or spectrophotometric titrations.

It follows that the different species present in both the carbonate and metal complex systems (eq 64–65) can result in various reaction routes for the formation of metal carbonato complexes, and these possibilities will be explored in some detail in the following subsections.

(1) **Via Carbon Dioxide Uptake.** In a series of papers (see references quoted in Table XXXI) Harris and co-workers demonstrated that metal hydroxo complexes can in general react with dissolved CO_2 to produce carbonato complexes according to the overall process shown in eq 67. This is a reversible pH-con-



trolled CO_2 uptake/decarboxylation process. The produced monodentate carbonato species may, depending on the nature of L, undergo a ring-closing reaction to produce a bidentate carbonato species.



The kinetics of CO_2 uptake reactions can be studied by following two different procedures;³¹² viz., (i) the equilibration method and (ii) acidification method. In method (i), the metal aquo complex under investigation is dissolved in an appropriate buffer solution in which the ionic strength has been adjusted to a preset value and then rapidly mixed in a stopped-flow instrument with a 0.1 M NaHCO_3 solution of similar ionic strength. The $[\text{CO}_2(\text{aq})]$ can be calculated from eq 69. At higher $[\text{CO}_2(\text{aq})]$ =

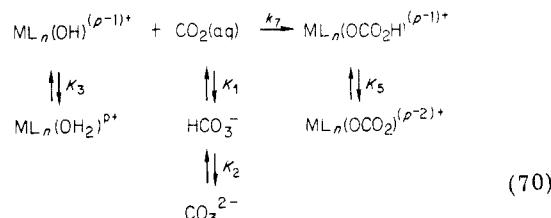
$$[\text{H}^+]^2[\text{total carbonate}] / \{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2\} \quad (69)$$

pH, where the equilibrium concentration of $\text{CO}_2(\text{aq})$ is not in considerable excess over the complex ion con-

centration, micromolar quantities of carbonic anhydrase were introduced into the complex solution in order to ensure the rapid maintenance of the $\text{CO}_2/\text{HCO}_3^-$ equilibrium (see section XIII A).

In method (ii), buffered solutions of the metal aquo species are prepared in the same way as in method (i). The second reactant is usually a 0.02 M NaHCO_3 solution (in an appropriate ionic strength controlled medium) which has been carefully acidified with HClO_4 to $\text{pH} \sim 3$ on a pH meter. After temperature equilibration, these solutions are mixed rapidly in the stopped-flow system and the final pH of the mixture measured immediately after mixing. The $[\text{CO}_2(\text{aq})]$ of such a mixture is then 0.01 M, and no carbonic anhydrase is employed in this method since CO_2 hydrolysis must be kept as slow as possible during measurements, i.e., the uncatalyzed rate of CO_2 hydrolysis is considerably slower than the rate of reaction under investigation. In most of the quoted studies (Table XXXI), method (ii) was employed.

The CO_2 uptake reactions were all found to proceed according to the general mechanism:³¹²



Protons are omitted from this scheme for the sake of simplicity, k_7 is the rate-determining CO_2 uptake rate constant, and K_1 , K_2 , K_3 , and K_5 are acid-dissociation constants. An important aspect of this mechanism is the fact that only the metal hydroxo species are capable of taking up CO_2 . This was verified by an analysis of the kinetic data. For the mechanism outlined in (70)

$$k_{\text{obsd}} = k_7 \left[\frac{K_3}{[\text{H}^+] + K_3} \right] [\text{CO}_2(\text{aq})] \quad (71)$$

and substituting for $[\text{CO}_2(\text{aq})]$ from eq 69 results in

$$k_{\text{obsd}} = \frac{k_7 K_3 [\text{H}^+]^2 [\text{total carbonate}]}{([\text{H}^+] + K_3)([\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2)} \quad (72)$$

During the kinetic measurements k_{obsd} was studied as a function of pH and $[\text{CO}_2(\text{aq})]$ (acidification method) or $[\text{total carbonate}]$ (equilibration method). The validity of the suggested mechanism required a pH and $[\text{CO}_2(\text{aq})]$ or $[\text{total carbonate}]$ independent value for k_7 . This was found to be the case for all the uptake reactions studied.

A summary of the available rate and activation parameters for a series of CO_2 uptake reactions along with the pK_3 values of the corresponding aquo complexes is given in Table XXXI. It was found^{313–315} that $\log k_7$ increases linearly with pK_3 as shown in Figure 3. This correlation is in agreement with the suggestion that the rate of CO_2 uptake depends on the nucleophilicity of the bound hydroxide ion which in turn depends on the strength of the O–H bond of the corresponding aquo complex as reflected by the pK_3 value. The plot in Figure 3 has a slope of 0.15 ± 0.04 and an intercept of 1.2 ± 0.3 ,³¹⁵ which is in close agreement with that reported for a limited number of systems.³¹⁴ The very

TABLE XXVIII. Equilibrium Constants for Metal Bicarbonate and Carbonate Species,
 $\text{HL} = \text{HCO}_3^-$; $\text{L} = \text{CO}_3^{2-}$; M = Metal Ion

metal ion	equilibrium	temp, °C	ionic strength, M	log K	ΔH , kJ mol ⁻¹	ΔS , J K ⁻¹ mol ⁻¹	ref
Mg^{2+}	ML/M·L	25	1.0	0.544			271
		25	-	3.11 ± 0.22^a			b
		25	-	2.98 ± 0.03	8.44	85.5	b
		90	-	3.41 ± 0.07			b
		20	0	3.26			280
		25	-	2.88 ± 0.05	13.5		284
		25	0.72	2.05			c
		25	-	3.20 ± 0.22^a			306
		20	0.1	2.18 ± 0.05			279
		25	0	5.30	28.4	196	271
	MHL/M·HL	25	0	2.88	12.5	84	301
		25	-	1.07	3.26		281
		25	-	1.07			d
		25	-	1.27			e
		25	-	1.05 ± 0.18^a			d
		25	-	1.07 ± 0.03	4.99	37.2	d
		90	-	1.34 ± 0.03			d
		20	0	0.84			280
		25	0.72	0.21			c
		25	-	1.01 ± 0.19^a			f
Ca^{2+}	M ₂ L/M ² ·L	25	-	1.07			f
		25	-	1.14 ± 0.13 ^a			306
		22	0.15	0.77			285
		25	0	4.85	28.0	186	271
		25	0	0.95			301
		25	0.72	2.59			c
		25	0.15	8.5			285
		20	0	7.99			280
		25	0	-7.46	20.9	-84	301
		25	-	-8.1			290
	ML/M·L	25	-	3.22 ± 0.14			149
		25	-	3.2			559
		25	-	3.15 ± 0.08	16.8	-	284
		25	0.72	2.21			c
		25	-	3.34 ± 0.39^a			306
		25	0	3.15 ± 0.05	16.7	125	301
		22	0.15	3.00			301
		25	0	3.10			g
		25	-	1.23	0.89		289
		25	-		2.63		h
Sr^{2+}	MHL/M·HL	25	-	1.17 ± 0.11^a			i
		25	-	1.11 ± 0.07			149
		0	-	0.7			559
		25	-	1.0			559
		50	-	1.35			559
		25	0.72	0.29			c
		25	-	1.08 ± 0.17^a			f
		25	-	1.23	1.96		f
		25	-	1.19 ± 0.11^a			306
		22	0.15	0.79			285
	MHL/ML·H	25	0	1.0 ± 0.0			301
		25	0	1.24			g
		22	0.15	7.9			285
		22	0.15	-8.01			285
		25	0	-8.33			g
		25	-	-8.48 ± 0.02			149
		25	0	-8.35 ± 0.1	8.4	-125	301
		25	-	-8.42	-10.1	-195	559
		25	-	-8.47	-10.8	-198	559
		25	-	-8.34			149
Ba^{2+}	M ₂ L/M ² ·L	25	-	-7.91			149
		25	-	-7.91			306
		25	-	1.25			306
		25	-	3.92			306
		25	0	-9.03			301
		25	0	2.78			301
Cr(en)_3^{3+}	ML/M·L	25	-	3.78			j
		25	0	-8.30 ± 0.01			301
		25	0.01	-5.48			j
		25	3	-0.046	19.2	63.5	289
		25	3	-0.071	13.8	45.0	289
		25	0	4.90			k
Mn^{2+}	ML/M·L	25	0	1.95			k
		25	0	1.80			301
		25	-	1.28			281
		25	-				

TABLE XXVIII (Continued)

metal ion	equilibrium	temp, °C	ionic strength, M	log K	ΔH , kJ mol ⁻¹	ΔS , J K ⁻¹ mol ⁻¹	ref
Mn^{2+}	$M(HL)_2/MHL \cdot HL$	25		1.27	4.1	38.1	282
		25		1.04			300
	$M \cdot L/ML(s)$	25	-	0.57			300
		25	0	-9.8			301
Fe^{2+}	$MHL/M \cdot HL$	25	-	-10.4			g
		25	0	1-1.5			283
	$M \cdot L/ML(s)$	25	0	-10.7			301
Co^{2+}	$M \cdot L/ML(s)$	25	0	-9.98			301
Co^{3+}	$ML_3/M \cdot L^3$	25	1	29			277
$Co(en)_3^{3+}$	$ML/M \cdot L$	25	0	3.33 ± 0.05			l
		25	0-0.5	-	1.05	57.3	m
	$ML_2/M \cdot L^2$	25	0	5.1 ± 0.2			l
		25	0-0.5	-	-2.9	21	m
$Co(pn)_3^{3+}$	$ML_3/M \cdot L^3$	25	0-0.5	-	0.4	17	m
		25	0	3.27 ± 0.05			l
	$ML_2/M \cdot L^2$	25	0	4.9 ± 0.2			l
		25	0	4.8 ± 0.2			l
$Co(NH_3)_6^{3+}$	$ML/M \cdot L$	25	0	3.47 ± 0.05			l
		25	0	3.3 ± 0.2			l
	$ML_2/M \cdot L^2$	25	3	-	4.0	21	n
		25	3	-	5.8	29	n
$Co(NH_3)_5NO_2^{2+}$	$ML_3/M \cdot L^3$	25	3	-	6.5	33	n
		25	3	-	4.8	33	n
	$ML_4/M \cdot L^4$	25	3	-	8.4	46	n
		25	3	-			o
$Co(NH_3)_5Cl^{2+}$	$ML_5/M \cdot L^5$	25	0	2.88			o
		25	0	3.9			o
	$ML_3/M \cdot L^3$	25	0	3.6			o
		25	0	2.6			o
$cis\text{-}Co(en)_2(NH_3)Cl^{2+}$	$ML_2/M \cdot L^2$	25	0	3.9			o
		25	0	3.6			o
	$ML_3/M \cdot L^3$	25	0	2.6			o
		25	0	3.9			o
$trans\text{-}Co(en)_2(NH_3)Cl^{2+}$	$ML/M \cdot L$	25	0	3.6			o
		25	0	2.5			o
	$ML_2/M \cdot L^2$	25	0	4.1			o
		25	0	4.0			o
Ni^{2+}	$M \cdot L/ML(s)$	25	0	-6.87			301
		25	0.1	6.8			298
	$ML/M \cdot L$	25	0	6.78			278
		25	0	6.75 ± 0.02			301
Cu^{2+}	$ML_2/M \cdot L^2$	25	0	10.24			278
		25	0	9.92 ± 0.09			301
	$MHL/M \cdot HL$	18	1.7	8.6			301
		25	-	2.08	23.4		281
Zn^{2+}	$M \cdot L/ML(s)$	25	-	-	20.9		p
		25	0	-9.63			301
	$ML/M \cdot L$	25	0	5.3			k
		25	0	2.1			k
$M \cdot L/ML(s)$	$MHL/M \cdot HL$	25	-	1.4			281
		25	-	-	7.3		q
	$M \cdot L/ML(s)$	25	-	1.4	3.5	39	q
		25	-	1.4			f
$M^5 \cdot OH^6 \cdot L^2/M_5OH_6L_2(s)$	$M^2 \cdot L/M_2L(s)$	25	0	-9.84			t
		25	0.2	-10.79			t
	$M^5 \cdot OH^6 \cdot L^2/M_5OH_6L_2(s)$	25	0	-10.00			301
		25	0	-14.01			q
Ag^+	$M^2 \cdot L/M_2L(s)$	25	0	-14.86			q
		25	0	-11.09			301
	$ML/M \cdot L$	25	0	5.4			s
		25	3	2.1			g
Hg_2^{2+}	$M \cdot L/ML(s)$	25	0	-13.74			301
		25	0	-16.05			301
	$ML/M \cdot L$	25	-	7			296
		200	-	10.9			296
Pb^{2+}	$ML_2/M \cdot L^2$	25	0.7	5.36			76
		25	0	5.59			76
	$ML_2/M \cdot L^2$	25	seawater	5.62			76
		25	0.1-1.0	6.4 ^a			303
$ML_2/M \cdot L^2$	$ML_2/M \cdot L^2$	25	0.3	5.4 ± 0.1			292
		25	0	7.5			s
	$ML_2/M \cdot L^2$	18	1.7	8.2			301
		25	0.1-1.0	9.4 ^a			303
$ML_2/M \cdot L^2$	$ML_2/M \cdot L^2$	25	-	9.0			296
		200	-	12.3			296
	$ML_2/M \cdot L^2$	25	0.7	8.6			76
		25	0	9.08			76
$ML_2/M \cdot L^2$	$ML_2/M \cdot L^2$	25	seawater	8.8			t
		25	0.3	8.86 ± 0.1			292
	$ML_2/M \cdot L^2$	25	0	2.9			s
		25	-				
$MHL/M \cdot HL$	$MHL/M \cdot HL$	25	-				

TABLE XXVIII (Continued)

metal ion	equilibrium	temp, °C	ionic strength, M	log K	ΔH , kJ mol ⁻¹	ΔS , J K ⁻¹ mol ⁻¹	ref
	M·L/ML(s)	25	0	-13.1			303
		25	0	-13.1			301
		25	1	-11.0			301
		25	0.3	-12.1			292
	M ³⁺ ·L ²⁻ OH ²⁻ /ML-MOH ₂ (s)	25	0.3	-44.1 ± 0.06			292
		25	0.1	-44.8 ± 0.2			292
Pb(CH ₃) ₃ ⁺	ML/ML(s)	25	0.3	-6.4 ± 0.1			292
Y ³⁺	ML ₂ /ML(s)·L	25	0.3	-3.1 ± 0.2			292
La ³⁺	ML/M·L	25	0.3	2.6 ± 0.1			299
	ML ₄ /M·L ⁴⁻	25	2.5	13.24 ± 0.11			288
Ce ⁴⁺	M·L ⁵⁻ /ML ₅	25	2.25-3	-0.02			u, v
Pr ³⁺	ML ₄ /M·L ⁴⁻	25	2.5	13.78 ± 0.06			288
Nd ³⁺	ML ₄ /M·L ⁴⁻	25	2.5	14.03 ± 0.08			288
Sm ³⁺	M ²⁻ ·L ³⁻ /M ₂ L ₃ (s)	25	0	-33.0			301
	ML ₄ /M·L ⁴⁻	25	2.5	14.20 ± 0.01			288
	M ²⁻ ·L ³⁻ /M ₂ L ₃ (s)	25	0	-32.5			301
Eu ³⁺	ML ₄ /M·L ⁴⁻	25	2.5	14.33 ± 0.09			288
Gd ³⁺	ML ₄ /M·L ⁴⁻	25	2.5	14.31 ± 0.10			288
Tb ³⁺	M ²⁻ ·L ³⁻ /M ₂ L ₃ (s)	25	0	-32.2			301
Dy ³⁺	ML ₄ /M·L ⁴⁻	25	2.5	15.03 ± 0.12			288
	ML ₄ /M·L ⁴⁻	25	2.5	15.32 ± 0.16			288
	M ²⁻ ·L ³⁻ /M ₂ L ₃ (s)	25	0	-31.5			301
Ho ³⁺	ML ₄ /M·L ⁴⁻	25	2.5	15.55 ± 0.11			288
Er ³⁺	ML ₄ /M·L ⁴⁻	25	2.5	15.69 ± 0.08			288
Tm ³⁺	ML ₄ /M·L ⁴⁻	25	2.5	15.71 ± 0.09			288
Yb ³⁺	ML ₄ /M·L ⁴⁻	25	2.5	15.84 ± 0.09			288
Lu ³⁺	M ²⁻ ·L ³⁻ /M ₂ L ₃ (s)	25	0	-31.1			301
Th ⁴⁺	ML ₄ /M·L ⁴⁻	2.25-3		0.14			u, v
UO ₂ ²⁺	ML/M·L	25	0.22-0.36	2.78			273
		25	0.40-0.53	2.23			273
		25	-	9.87			w
		25	3	9.02			275
	ML ₂ /M·L ²	25	0.03-0.18	4.03			373
		25	0.2	15.57			293
		20	0.1	16.2			268
		25	-	14.7; 16.7			w
		25	0	14.6			269
		25	0.1	16.16			286
	ML ₃ /ML ³	25	0.1-0.29	7.71			373
		20	0.1	21.54			287
		25	0.2	20.7			293
		25	-	18.3			267, 269
		25	0.5	23.0			297
		25	1	22.8			294
		20	-	21.4			w
		25	0.1	21.57			286
	ML ₂ /ML·HL	25	0	1.4			269
	ML ₃ /ML ₂ ·L	25	2	3.5			266
		25	-	3.77			267
		20	0.1	5.48			268
	ML ₃ /ML ₂ ·HL	25	0	1.8			269
	MOHL·H/M·L	25	0.1	4.1			286
	M ₃ OH ₃ ·L/M ³ ·OH ³ ·L	25	3	16.34			275
	(ML ₃) ³ /M ₃ OH ₃ ·L ⁹	25	-	80.4			z
	(ML ₃) ³ H ⁶ /M ₃ L ₆ ·(CO ₂) ³	25	3	-41.5 ± 0.1			270
	(ML ₃) ³ (CO ₂) ³ /M ₃ L ₆ ·(HL) ⁶	25	3	6.4 ± 0.1			276
	M·L ³ /ML ₃ (s)	26	1	-1.16			266
Pu ²⁺	ML/M·L	20	10	47			g
Pu(VI)	ML ₃ /M·L ³	25	0.15	6.24			y
PuO ₂ ²⁺	ML/M·L	25	0	23.0			291
		25	0	23.8			291
		25	1	12.0			g
	ML ₂ /M·L ²	25	0	15.1			291
		25	0	15.04			z
		25	0.1	13.1			272
	ML ₃ /M·L ³	25	1	2.09			h
	MLOH/M·L·OH	25	0	23.85			z, aa
	MLOH ₂ /M·L·OH ²	25	0	23.0			z
	MHL/M·HL	25	0.1	2.7 ± 0.1		6	272
	M(HL) ₂ /M·HL ²	25	0.1	4.36			272
	M·L/ML(s)	25	1	-12.77			g
	M·L ² /ML ₂ (s)	25	1	-1.33			g

^a Mean value of quoted literature data in this reference. ^b Siebert, R. M.; Hostetler, P. B. *Am. J. Sci.* 1977, 277, 716. ^c Pytkowicz, R. M.; Hawley, J. E. *Limnol. Oceanogr.* 1974, 19, 223. ^d Siebert, R. M.; Hostetler, P. B. *Am. J. Sci.* 1977, 277, 697. ^e Lesht, D., M.A. Thesis, University of Missouri—Columbia, 1977. ^f Bauman, J. E., Jr.; Siebert, R. M.; Almon, W. R.; Hostetler, P. B. *Chem. Phys. Aqueous Gas Solutions [Proc. Symp.]* 1975, 77. ^g Sillen, L. G.; Martell, A. E. "Stability Constants of Metal Ion Complexes", 2nd ed.; Chemical Society: London, 1967; Spec. Publ. 17, p 754. ^h Almon, W. R., M.A. Thesis, University of Missouri—Columbia, 1973. ⁱ Plummer, L. N.; Sundquist, E. T. *Geochim. Cosmochim. Acta* 1982, 46, 247. ^j Benes, P.; Selecká, H. *Radiochim. Radioanal. Lett.* 1973, 13, 339. ^k Zirino, A.; Yamamoto, S. *Limnol. Oceanogr.* 1972, 17, 661. ^l Pyartman, A. K.; Kolobov, N. P.; Merkul'eva, L. E.; Mironov, V. E. *Zh. Neorg. Khim.* 1974, 19, 2217. ^m Mironov, V. E.; Pyartman, A. K.; Kolobov, N. P. *Zh. Fiz. Khim.* 1976, 50, 1967. ⁿ Mironov, V. E.; Kolobov, N. P.; Komarova, A. V.; Mavrin, I. F. *Ibid.* 1974, 48, 1645. ^o Pyartman, A. K.; Kolobov, N. P.; Merkul'eva, L. E.; Solov'ev, Yu. B.; Mironov, V. E. *Zh. Neorg. Khim.* 1975, 20, 141. ^p Rages, D., M.A. Thesis, University of Missouri—Columbia, 1978. ^q Ryan, M. P.; Bauman, J. E., Jr. *Inorg. Chem.* 1978, 17, 3329. ^r Schindler, P.; Reinert, M.; Gamsjaeger, H. *Helv. Chim. Acta* 1969, 52, 2327. ^s Zirino, A.; Yamamoto, S. *Limnol. Oceanogr.* 1972, 17, 661. ^t Balko, B.; Bowen, P.; Berger, R. L.; Anderson, K. J. *Biochem. Biophys. Methods* 1981, 4, 1. ^u Dervin, J.; Faucherre, J. *Bull. Soc. Chim. Fr.* 1973, 2926. ^v Dervin, J.; Faucherre, J. *Ibid.* 1973, 2930. ^w Babinec, A. E.; Zhorov, V. A.; Mitropol'skii, A. Yu; Bezborkov, A. A. *Geol. Zh.* 1977, 37, 109. ^x Doughty, D. T.; Stewart, R. P., Jr.; Gordon G. *J. Am. Chem. Soc.* 1981, 103, 3388. ^y Woods, M.; Mitchell, M. L.; Sullivan, J. C. *Inorg. Nucl. Chem. Lett.* 1978, 14, 465. ^z Cleveland, J. M. "The Chemistry of Plutonium"; Gordon and Breach: New York, 1970. ^{aa} Rhai, D.; Serne, R. J. *J. Environ. Qual.* 1977, 6, 89.

long extrapolation of this line to the pK value of H_2O (15.7) predicts a satisfactory value for the magnitude of the rate constant for the CO_2/OH^- reaction, viz., $\log k_7 = 3.6$ in comparison with $\log k_{\text{obsd}} = 3.9^{313}$ at 25°C .

It is also known (see section B) that the decarboxylation reaction occurs with retention of the M—O bond, such that the principle of microscopic reversibility dictates that retention of this bond should also occur during CO_2 uptake. This is in line with the much higher rate of CO_2 uptake than normal substitution reactions involving M—O bond breakage. In addition, the kinetic data in Table XXXI and the tendency in Figure 4 illustrate that the rates of CO_2 uptake are only moderately sensitive to the nature of the central metal ion, the nonparticipating ligands, effects resulting from substitution in the trans position, and the overall charge on the metal hydroxo complex. These observations emphasize the secondary bond formation character of the CO_2 uptake process.

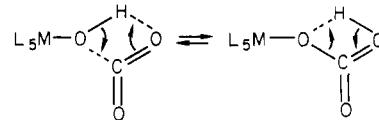
The activation parameters for k_7 are presented as an isokinetic plot in Figure 4. The significance of such a plot has been emphasized elsewhere.^{315–318} The linear relationship stems from eq 73 where ΔG_0^* is the in-

$$\Delta H^* = \Delta G_0^* + \beta_0 \Delta S^* \quad (73)$$

trinsic free energy of activation and β_0 is the isokinetic temperature. From a linear least-squares fit of the data in Figure 4 it follows that $\Delta G_0^* = 59.8 \pm 0.5 \text{ kJ mol}^{-1}$ and $\beta_0 = 318 \pm 6 \text{ K}$. Since no significant deviation from the line is observed for any of the data points, it was concluded³¹⁵ that a common mechanism is operative. Furthermore, the process does not involve the formation or breakage of any metal-ligand bonds since, if this were the case, different isokinetic plots of similar slope, but varying intercepts, would have been expected for different metal ions.^{315,316} This is considered as further confirmation³¹⁵ of the assumption that all CO_2 uptake reactions proceed via secondary oxygen-carbon bond formation.

The pressure dependence of k_7 for CO_2 uptake by $\text{M}(\text{NH}_3)_5\text{OH}^{2+}$ ($\text{M} = \text{Co(III)}, \text{Rh(III)}, \text{Ir(III)}$) was studied¹⁰³ under conditions where $K_3 \gg [\text{H}^+]$, such that eq 71 simplified to $k_{\text{obsd}} = k_7[\text{CO}_2(\text{aq})]$. Kinetic data were obtained using a high pressure stopped-flow apparatus³¹⁹ and plots of $\ln k_7$ vs. pressure were found to be linear within the experimental error limits concerned. The volumes of activation were reported¹⁰³ to be -10.1 ± 0.6 ($\text{M} = \text{Co(III)})$, -4.7 ± 0.8 ($\text{M} = \text{Rh(III)})$ and -4.0 ± 1.0 ($\text{M} = \text{Ir(III)}) \text{ cm}^3 \text{ mol}^{-1}$ at 25°C and an ionic strength of 0.5 M. These values are in agreement with

a bond formation process in which the volume decrease is ascribed to intrinsic volume changes since no major contribution from changes in solvation is expected to occur during the CO_2 uptake process. These and other arguments^{103,313} led to the suggestion that the intimate mechanism of a CO_2 uptake reaction may be visualized in terms of the transition state:



During CO_2 uptake the MO—H and C—O bonds are broken, whereas these are formed during the reverse aquation process (see section B). This involves nucleophilic attack by the OH ligand on CO_2 , accompanied by a concerted transfer of the OH proton to one of the CO_2 oxygens.

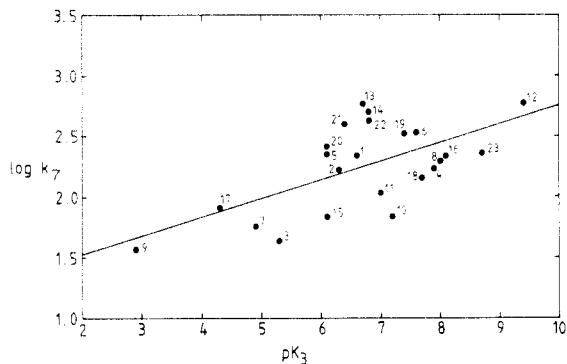
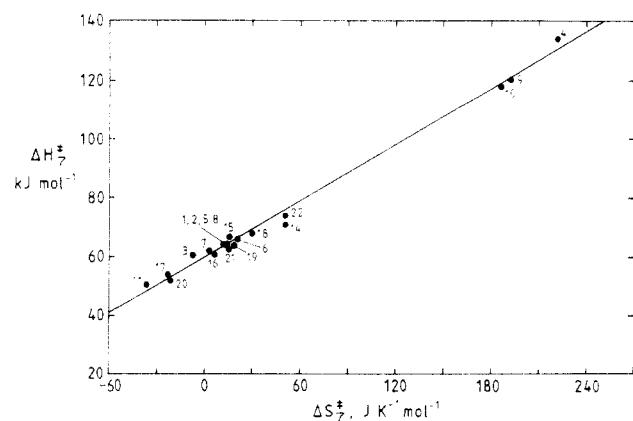
A number of *cis*-aquo carbonato complexes can undergo ring closure to produce bidentate carbonato species as outlined in eq 68. These reactions are usually slow since they are controlled by the rate of metal-oxygen bond breakage for the aquo/hydroxo ligand *cis* to the monodentate carbonato ligand. A summary of the rate and activation parameters for this step is given in Table XXXII. In two cases^{320,321} it was found that ring closure of a hydroxo-carbonato species is significantly slower than for the corresponding aquo-carbonato species. This can be ascribed to the greater strength of the metal-hydroxo bond.

At this stage it is appropriate to comment on the chosen notation³²² for some aquo-carbonato species in Table XXXII. Although the two possible forms, viz., $-(\text{OH})\text{OCO}_2$ and $-(\text{OH})\text{OCO}_2\text{H}$, are kinetically indistinguishable, the former notation is preferred due to the following arguments. On the basis of the considerable amount of kinetic data available on the decarboxylation of monodentate carbonato species (see section B), it is apparent that once a monodentate carbonato species is protonated, carbon dioxide is liberated at a rate which is virtually independent of the nature of the metal center and the surrounding ligands. Therefore, it seems unlikely that a $-(\text{OH})\text{OCO}_2\text{H}$ species would not also be equally reactive and, therefore, cannot be considered as a stable intermediate. Furthermore, our formulation is also in good agreement with the observation that for a series of trans carbonato complexes the aquo ligand is indeed more basic than the carbonato ligand.³²²

(2) **Via Anation by Bicarbonate/Carbonate Ion.** According to the general reaction system outlined in eq

TABLE XXIX. Evidence for Carbonato Complex Formation

metal ion	identified complexes	method	ref
UO_2^{2+}	$\text{UO}_2(\text{CO}_3)_3(\text{CDMBA})_4$, $\text{UO}_2(\text{CO}_3)_2(\text{CDMBA})_2$, $\text{UO}_2(\text{CO}_3)(\text{OH})_2(\text{CDMBA})_2$, $(\text{UO}_2)_2\text{CO}_3^+$, $(\text{UO}_2)_3(\text{CO}_3)_2^{2+}$, $(\text{UO}_2)_6(\text{CO}_3)_5^{2+}$, $(\text{UO}_2)_6(\text{CO}_3)_6$, $(\text{UO}_2)_6(\text{CO}_3)_7^{2-}$, $(\text{UO}_2)_6(\text{CO}_3)_6^{8-}$, $(\text{UO}_2)_6(\text{CO}_3)_5(\text{OH})_2 \cdot n\text{H}_2\text{O}(\text{S})$, $(\text{UO}_2)_6(\text{CO}_3)_6(\text{S})$, $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3(\text{S})$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, $(\text{UO}_2)_2(\text{CO}_3)(\text{OH})_3^-$, $(\text{UO}_2)_2(\text{CO}_3)(\text{OH})_3^-$, $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$, $(\text{UO}_2)_2(\text{CO}_3)(\text{OH})_3^-$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, $(\text{UO}_2)_3(\text{OH})_3\text{CO}_3^+$, $\{(\text{UO}_2)_{11}(\text{OH})_{24}(\text{CO}_3)_6^{2-}\}$	IR, TG emf chem. anal.	a, b c c
Sc^{3+}	$\text{Sc}(\text{CO}_3)_2$, $\text{Sc}(\text{CO}_3)_3^{3-}$, $\text{Sc}(\text{CO}_3)_4^{5-}$, $\text{Sc}(\text{CO}_3)_6^{9-}$	^{13}C NMR Raman Raman polarogr. emf pH	356 d d e 275 f
Y^{3+}	$\text{Y}_2(\text{CO}_3)_3 \cdot 5\text{H}_2\text{O}$, $(\text{NH}_4)\text{Y}(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$	chem. anal., emf	g
Zr^{4+}	$\text{Zr}(\text{CO}_3)_3^{2-}$, $\text{ZrO}(\text{CO}_3)_2^{2-}$, $\text{Na}[\text{Zr}(\text{OH})_3\text{CO}_3]$, $(\text{NH}_4)\text{H}\text{ZrO}(\text{CO}_3)_3$	chem. anal.	h
La^{3+}	$\text{La}_2(\text{CO}_3)_3 \cdot 5\text{H}_2\text{O}$, $(\text{NH}_4)\text{La}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$	chem. anal.	g
Nd^{3+}	$(\text{NH}_4)_2\text{CO}_3 \cdot 8\text{Nd}_2(\text{CO}_3)_3 \cdot 32\text{H}_2\text{O}$, $(\text{NH}_4)\text{Nd}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$	chem. anal.	g
Eu^{3+}	$\text{Eu}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$, $\text{Eu}(\text{OH})\text{CO}_3 \cdot 0.25\text{H}_2\text{O}$	emf	311
Gd^{3+}	$\text{Gd}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$, $(\text{NH}_4)\text{Gd}(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$	emf	g
Dy^{3+}	$\text{Dy}_2(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$, $2(\text{NH}_4)_2\text{CO}_3 \cdot 3\text{Dy}_2(\text{CO}_3)_3 \cdot 15\text{H}_2\text{O}$	emf	g
Er^{3+}	$(\text{NH}_4)\text{Er}(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$	emf	g
Yb^{3+}	$\text{Yb}(\text{OH})\text{CO}_3 \cdot 0.7\text{H}_2\text{O}$, $\text{Yb}(\text{OH})\text{CO}_3 \cdot \text{H}_2\text{O}$, $\text{Yb}_2(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O}$	emf	311
Hf^{4+}	$\text{Hf}(\text{CO}_3)_4^{4-}$	sorption on $\text{Fe}(\text{OH})_3$	h
Th^{4+}	$\text{Th}(\text{CO}_3)_4^{4-}$	sorption on $\text{Fe}(\text{OH})_3$	h

^a Vera, P. J.; Galiano, S. J. A.; Parellada, B. R.; Bellido, G. A. *Junta Energ. Nucl.*, 1975, Rep. JEN (Spain) 305, 1.^b Vera, P.; Galiano, S. J. A.; Parellada, B. R.; Bellido, G. A. *Ibid.* 1975, JEN 306, 1. ^c Double, G.; Pongi, N. K.; Hurwic, J. *Bull. Soc. Chim. Fr.* 1980, 354. ^d Maya, L.; Begun, G. M. *J. Inorg. Nucl. Chem.* 1981, 43, 2827. ^e Maya, L. *Inorg. Chim. Acta*. 1982, 65, L13. ^f Komissarova, L. N.; Shatskii, V. M.; Zhorov, V. A. *Zh. Neorg. Khim.* 1971, 16, 2347.^g Tselik, I. N.; Deineka, G. F.; Fedorenko, V. D.; Shvartsman, V. Ya. *Ibid.* 1968, 14, 2356. ^h Upor, E.; Nagy, G. *Acta. Chim. (Budapest)* 1973, 78, 47.Figure 3. Plot of $\log k_7$ vs. $p\text{K}_3$ for various CO_2 uptake reactions at 25 °C. (See Table XXXI for the data numbering system.)Figure 4. Plot of ΔH_7^* vs. ΔS_7^* for various CO_2 uptake reactions. (See Table XXXI for the data numbering system.)

64–66 it should be possible to form carbonato complexes via anation reactions of the metal aquo/hydroxo species with bicarbonate/carbonate ion. Such substitution reactions are expected to be significantly slower than CO_2 uptake since they involve, and are usually governed by, the breaking of the metal–oxygen bond. Typical water exchange rate constants for complexes of the type $\text{M}(\text{NH}_3)_5\text{OH}_2^{3+}$ ($\text{M} = \text{Co(III)}, \text{Rh(III)}$), are of the order of $1 \times 10^{-6} \text{ s}^{-1}$ at 25 °C.^{323,324} To our knowledge only one such system was investigated in detail,³²⁵ viz., the formation of $\text{Co}(\text{tren})\text{CO}_3^+$ via anation by HCO_3^- and CO_3^{2-} . The $\text{Co}(\text{tren})(\text{OH})_2^+$ species is stable in basic medium and does not undergo any cis to trans isomerization.^{320,325–328} It is therefore an ideal system to study such an anation process. At $\text{pH} > 10.5$ no interference of the competing reaction with $\text{CO}_2(\text{aq})$ was detected, and the kinetic data exhibit a linear dependence on [total carbonate]. A detailed analysis of the kinetic data produces the rate constants $(4.0 \pm 1.5) \times 10^{-4}$ and $(4.7 \pm 0.1) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for the anation by CO_3^{2-} and HCO_3^- at 50 °C, respectively. A surprising feature is that the anation by HCO_3^- is significantly faster than the anation by CO_3^{2-} . It was suggested³²⁵ that partial proton transfer from bicarbonate to $\text{Co}(\text{tren})(\text{OH})_2^+$ could result in the formation of an aquohydroxo species such that the subsequent substitution reaction closely parallels the substitution of an aquo instead of hydroxo ligand, and so accounts for the difference in reactivity. At high pH, the major reaction path is anation by CO_3^{2-} , for which $\Delta H^\ddagger = 100 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 8 \text{ JK}^{-1} \text{ mol}^{-1}$. This reaction probably follows the normal I_d mode of substitution (i.e., a dissociative interchange process) for Co(III) complexes.^{329,330} The

TABLE XXX. Thermodynamic Quantities for Metal Carbonato Species

metal ion	carbonate species	thermodynamic quantity	ref
Mg ²⁺	MgCO ₃	ΔG _f [°] , S [°] , C _p [°]	290, a
Ca ²⁺	CaCO ₃ , CaMg(CO ₃)CO ₂ , CaMn(CO ₃) ₂ , CaFe(CO ₃) ₂ , CaCo(CO ₃) ₂ , CaNi(CO ₃) ₂ , CaCu(CO ₃) ₂ , CaZn(CO ₃) ₂	ΔG _f [°]	a
Mn ²⁺	MnCO ₃	ΔG _f [°]	a
Fe ²⁺	FeCO ₃	ΔG _f [°]	a, b
Co ²⁺	CoCO ₃	ΔG _f [°]	a
Ni ²⁺	NiCO ₃	ΔG _f [°]	a
Cu ²⁺	CuCO ₃	ΔG _f [°]	a, b
	Cu ₂ (CO ₃)(OH) ₂	ΔH _f [°]	c
Zn ²⁺	ZnCO ₃ , Zn ₅ (OH) ₆ (CO ₃) ₂	ΔG _f [°]	a, d
Hg ⁺	Hg ₂ CO ₃	ΔH _f [°] , S [°]	e
Hg ²⁺	HgCO ₃ , HgHCO ₃ ⁺ , Hg(OH)CO ₃ ⁻ , HgCO ₃ ·2HgO	ΔH _f [°] , S [°]	e
Pb ²⁺	PbCO ₃	ΔH _{spl} [°] , ΔS _{spl} [°] , ΔC _p [°] sol, ΔH _f [°] , S [°] , C _p [°]	296
Cs ²⁺	CsCO ₃	ΔH _f [°] , S [°] , C _p [°]	f
Cs ⁺	Cs ₂ CO ₃ , CsHCO ₃ , Cs ₂ CO ₃ ·0.5H ₂ O, ·1.5H ₂ O, ·3H ₂ O, ·5H ₂ O, ·8H ₂ O	ΔH _{spl} [°] , ΔH _f [°]	g
Rb ⁺	Rb ₂ CO ₃ , RbHCO ₃ , Rb ₂ CO ₃ ·0.5H ₂ O, ·1.5H ₂ O, ·3H ₂ O, ·8H ₂ O, ·9H ₂ O	ΔH _{spl} [°] , ΔH _f [°]	g
		ΔH _f [°]	g
Y ³⁺	Y ₂ (CO ₃) ₃ , ·3H ₂ O	ΔH _{sol} [°] , ΔH _f [°] , ΔG _f [°] , ΔS _f [°]	h-j
La ³⁺	La ₂ (CO ₃) ₃ ·0.5H ₂ O, ·3H ₂ O, ·6H ₂ O, ·8H ₂ O	ΔH _{sol} [°] , ΔH _f [°] , ΔG _f [°] , ΔS _f [°]	h-j
Ce ³⁺	Ce ₂ (CO ₃) ₃ , ·0.5H ₂ O, ·3H ₂ O, ·8H ₂ O	ΔH _{sol} [°] , ΔH _f [°] , ΔG _f [°] , ΔS _f [°]	h-k
Pr ³⁺	Pr ₂ (CO ₃) ₃ , ·0.5H ₂ O, ·H ₂ O, ·3H ₂ O, ·8H ₂ O	ΔH _{sol} [°] , ΔH _f [°] , ΔG _f [°] , ΔS _f [°]	h-k
Nd ³⁺	Nd ₂ (CO ₃) ₃ , ·H ₂ O, ·3H ₂ O, ·4H ₂ O	ΔH _{sol} [°] , ΔH _f [°] , ΔG _f [°] , ΔS _f [°]	h-k
Sm ³⁺	Sm ₂ (CO ₃) ₃ , ·3H ₂ O	ΔH _{sol} [°] , ΔH _f [°] , ΔG _f [°] , ΔS _f [°]	h-k
Eu ³⁺	Eu ₂ (CO ₃) ₃ , ·3H ₂ O	ΔH _{sol} [°] , ΔH _f [°] , ΔG _f [°] , ΔS _f [°]	h, i
Gd ³⁺	Gd ₂ (CO ₃) ₃ , ·3H ₂ O	ΔH _{sol} [°] , ΔH _f [°] , ΔG _f [°] , ΔS _f [°]	h-k
Tb ³⁺	Tb ₂ (CO ₃) ₃ , ·1.3H ₂ O, ·2.3H ₂ O, ·3H ₂ O	ΔH _{sol} [°] , ΔH _f [°] , ΔG _f [°] , ΔS _f [°]	h, i
Dy ³⁺	Dy ₂ (CO ₃) ₃ , ·H ₂ O, ·3H ₂ O	ΔH _{sol} [°] , ΔH _f [°] , ΔG _f [°] , ΔS _f [°]	h, i
Ho ³⁺	Ho ₂ (CO ₃) ₃ , ·2H ₂ O, ·3H ₂ O	ΔH _{sol} [°] , ΔH _f [°] , ΔG _f [°] , ΔS _f [°]	h, i
Er ³⁺	Er ₂ (CO ₃) ₃ , ·3H ₂ O	ΔH _{sol} [°] , ΔH _f [°] , ΔG _f [°] , ΔS _f [°]	h-k
Tm ³⁺	Tm ₂ (CO ₃) ₃ , ·3H ₂ O	ΔH _{sol} [°] , ΔH _f [°] , ΔG _f [°] , ΔS _f [°]	h, i
Yb ³⁺	Yb ₂ (CO ₃) ₃ , ·H ₂ O, ·2H ₂ O, ·3H ₂ O, ·6H ₂ O	ΔH _{sol} [°] , ΔH _f [°] , ΔG _f [°] , ΔS _f [°]	h-k
Lu ³⁺	Lu ₂ (CO ₃) ₃ , ·H ₂ O, ·3H ₂ O, ·6H ₂ O	ΔH _{sol} [°] , ΔH _f [°] , ΔG _f [°] , ΔS _f [°]	h, i

^a Roosenberg, P. E.; Foit, F. F., Jr. *Geochim. Cosmochim. Acta* 1979, 43, 951. ^b Reiterer, F.; Johannes, W.; Gamsjaeger, H. *Mikrochim. Acta* 1981, 1, 63. ^c Richardson, D. W.; Brown, R. R. *Rep. Invest.-U.S. Bur. Mines*, 1974, 5, RI-7851. ^d Schinder, P.; Reinert, M.; Gamsjaeger, H. *Helv. Chim. Acta* 1969, 52, 2327. ^e Khodakovskii, I. L.; Shikima, N. D. *Geokhimiya* 1981, 671. ^f Paukov, I. E.; Rakhamenkulov, F. S.; Luk'yanova, I. G. *Zh. Fiz. Khim.* 1970, 44, 256. ^g Raffelini; F.; My Le V. C. *R. Hebd. Seances Acad. Sci., Ser. C* 1971, 273, 92. ^h Maier, A. I.; Bas'kova, N. A. *Izv. Akad. Nauk SSSR, Neorg. Mater.* 1977, 13, 1055. ⁱ Karapet'yants, M. Kh.; Maier, A. I.; Bas'kova, N. A. *Ibid.* 1977, 13, 1279. ^j Bas'kova, N. A.; Maier, A. I.; Karapet'yants, M. Kh. *Tr. Mosk. Khim.-Tekhnol. Inst.* 1974, 81, 8. ^k Batkibekova, M.; Usubaliev, D.; *Zh. Fiz. Khim.* 1974, 48, 1615.

TABLE XXXI. Rate and Activation Parameters for CO₂ Uptake Reactions^h

complex ion	pK _a ^a	k _η , M ⁻¹ s ⁻¹	ΔH _η [‡] , kJ mol ⁻¹	ΔS _η [‡] , J K ⁻¹ mol ⁻¹	ref
(1) Co(NH ₃) ₅ OH ²⁺	6.6	220 ± 40	64 ± 4	15 ± 12	312
(2) (αβS)-Co(tetren)OH ²⁺	6.3	166 ± 15	64 ± 5	14 ± 17	327
(3) cis-Co(tren)(OH) ₂ OH ²⁺	5.3	44 ± 2	61 ± 1	-8 ± 1	320
(4) cis-Co(tren)(OH) ₂ ⁺	7.9	170 ± 10	134 ± 25	222 ± 92	320
(5) cis-Co(en) ₂ (OH) ₂ OH ²⁺	6.1	225 ± 15	64 ± 4	14 ± 13	b
(6) trans-Co(NH ₃) ₄ (CN)OH ⁺	7.6	338 ± 32	66 ± 6	21 ± 21	c
(7) cis-Co(cyclam)(OH) ₂ OH ²⁺	4.9	57 ± 4	62 ± 4	3 ± 15	314
(8) cis-Co(cyclam)(OH) ₂ ⁺	8.0	196 ± 24	64 ± 2	12 ± 8	314
(9) trans-Co(cyclam)(OH) ₂ OH ²⁺	2.9	37 ± 0.1	121 ± 1	193 ± 2	314
(10) trans-Co(cyclam)(OH) ₂ ⁺	7.2	70 ± 0.2	118 ± 3	186 ± 8	314
(11) cis-Cr(C ₂ O ₄) ₂ (OH) ₂ OH ²⁺	7.0	170 ± 10	51 ± 1	-36 ± 5	350
(12) Cu(gly) ₂ OH	9.4	590 ± 30			314
(13) Ir(NH ₃) ₅ OH ²⁺	6.7	590 ± 30			d
(14) Rh(NH ₃) ₅ OH ²⁺	6.8	490 ± 120	71 ± 4	50 ± 13	d
(15) cis-Rh(en) ₂ (OH) ₂ OH ²⁺	6.1	69 ± 18	67 ± 2	16 ± 7	e
(16) cis-Rh(en) ₂ (OH) ₂ ⁺	8.1	215 ± 29	61 ± 1	5 ± 3	e
(17) trans-Rh(en) ₂ (OH) ₂ OH ²⁺	4.3	81 ± 3	54 ± 4	-23 ± 13	322
(18) trans-Rh(en) ₂ (OH) ₂ ⁺ ^f	7.7	140 ± 20	68 ± 4	30 ± 12	322
(19) trans-Rh(en) ₂ (OCO ₂)OH	7.4	330 ± 80	64 ± 3	19 ± 10	322
(20) trans-Rh(en) ₂ (Cl)OH ⁺	6.1	260 ± 12	52 ± 5	-22 ± 18	315
(21) trans-Rh(en) ₂ (Br)OH ⁺	6.4	395 ± 33	63 ± 5	16 ± 16	315
(22) trans-Rh(en) ₂ (I)OH ⁺	6.8	422 ± 43	74 ± 3	50 ± 11	315
(23) Zn(CR)OH ⁺	8.7	225 ± 23			g

^a Acid dissociation constant of corresponding aquo complex ion (see eq 66). ^b Wan, W. K., Ph. D. Thesis, SUNY, Buffalo, NY 1978. ^c Krishnamoorthy, C. R.; Palmer, D. A.; van Eldik, R.; Harris, G. M. *Inorg. Chim. Acta* 1979, 35, L361. ^d Palmer, D. A.; Harris, G. M. *Inorg. Chem.* 1974, 13, 965. ^e Palmer, D. A.; van Eldik, R.; Kelm, H.; Harris, G. M. *Ibid.* 1980, 19, 1009. ^f The rate constant for CO₂ uptake for this species is third order. For comparison purposes it is represented here as k(CO₂), with (CO₂) = 0.01 M, a typical value in a large proportion of the data reported. ^g Woolley, P. *Nature (London)* 1975, 258, 677. ^h Temperature 25 °C; ionic strength 0.5 M.

TABLE XXXII. Rate and Activation Parameters for Ring-Closure Reactions of Monodentate Carbonato Complexes at 25 °C

complex ion	$k_6, \text{ s}^{-1}$	$\Delta H_6^\ddagger, \text{ kJ mol}^{-1}$	$\Delta S_6^\ddagger, \text{ J K}^{-1} \text{ mol}^{-1}$	ref
cis-Co(tren)(OH ₂)OCO ₂ ⁺ ^a	5×10^{-2}	52 ± 2	-95 ± 7	320
cis-Co(tren)(OH)OCO ₂	$\sim 1 \times 10^{-4}$ ^b			320
cis-Co(cyclam)(OH ₂)OCO ₂ ⁺ ^a	2.8×10^{-2}	57 ± 7	-87 ± 24	314
cis-Co(en) ₂ (OH ₂)OCO ₂ ⁺ ^a	1.1×10^{-1} ^c	58 ± 8	-67 ± 21	320, 321
cis-Co(en) ₂ (OH)OCO ₂	6×10^{-5}	117 ± 13	71 ± 38	321
cis-Cr(C ₂ O ₄) ₂ (OH ₂)OCO ₂ ³⁻	$\sim 2.4 \times 10^{-2}$ ^d			350
cis-Rh(en) ₂ (OH ₂)OCO ₂ ⁺	very slow ^e			f

^a These species are reported in the literature as hydroxobicarbonate complexes, we however prefer the given notation (see discussion), data at 20 °C only available. ^b Extrapolated from quoted activation parameters. ^c Mean value of data reported in the acidity range 7.09 < pH < 9.18. ^d Reaction is complete when heated under reflux for 1 h at pH ~ 7.

^e Palmer, D. A.; van Eldik, R.; Kelm, H.; Harris, G. M. *Inorg. Chem.* 1980, 19, 1009.

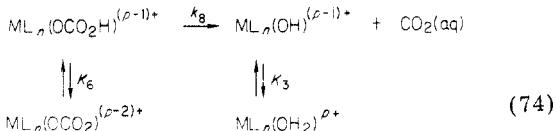
so-formed carbonato-hydroxo species can undergo slow ring closure as referred to before.^{320,325}

B. Aquation Reactions

Various reaction routes exist for the aquation of carbonato complexes in aqueous solution since such processes can in general occur via acid- and base-catalyzed aquation. Furthermore, the nature of the carbonato complex, i.e., whether carbonate acts as a monodentate, bidentate, or bridged ligand, will determine the detailed mechanism of the aquation process. We have, therefore, further subdivided this subsection to treat the various aspects separately.

(1) Acid-Catalyzed Aquation of Monodentate Carbonato Complexes. On treating monodentate carbonato complexes of the type ML_n(OCO₂)⁽ⁿ⁻²⁾⁺ with acid, CO₂(aq) is released and the corresponding aquo complex is formed (see eq 67). These reactions are in general rapid (stopped-flow rate), which suggests that no M-O bond breakage occurs during aquation. Indeed, isotope labeling experiments^{331,332} have proved conclusively that acid-catalyzed aquation takes place without metal-oxygen bond breakage. The rate-determining step is, therefore, not the substitution of a water molecule for the carbonate/bicarbonate ion, but rather a decarboxylation reaction involving O-C bond breakage in the carbonate group.

Acid-catalyzed decarboxylation of a series of monodentate carbonato complexes was found to proceed according to the general mechanism³³³ shown in eq 74



(reverse of eq 70). Protons have been omitted from this scheme and k_8 is the rate-determining decarboxylation rate constant, and K_3 and K_6 are acid-dissociation constants. According to this mechanism only the protonated bicarbonate species is capable of undergoing decarboxylation. For the above mechanism,

$$k_{\text{obsd}} = k_8[\text{H}^+]/[K_6 + [\text{H}^+]] \quad (75)$$

such that k_{obsd} exhibits the expected sigmoid pH dependence (for an example see Figure 5) for all the systems quoted in Table XXXIII. Under conditions where $[\text{H}^+] \gg K_6$ (usually at pH < 5), eq 75 simplifies to $k_{\text{obsd}} = k_8$. Furthermore, the pH dependence of k_{obsd} enables one to estimate the value of K_6 , which is in general of the same order of magnitude as the first

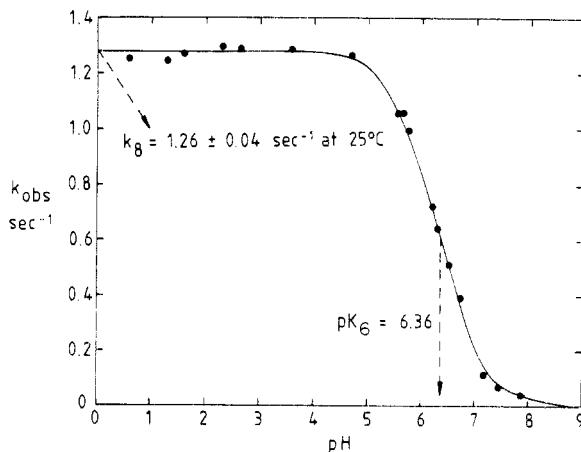


Figure 5. Plot of k_{obsd} vs. pH for the reaction $\text{trans-Rh}(\text{en})_2(\text{Cl})\text{OCO}_2 + \text{H}^+ \rightarrow \text{trans-Rh}(\text{en})_2(\text{Cl})\text{OH}^+ + \text{CO}_2$ at 25 °C and an ionic strength of 0.5 M. Data taken from ref 315.

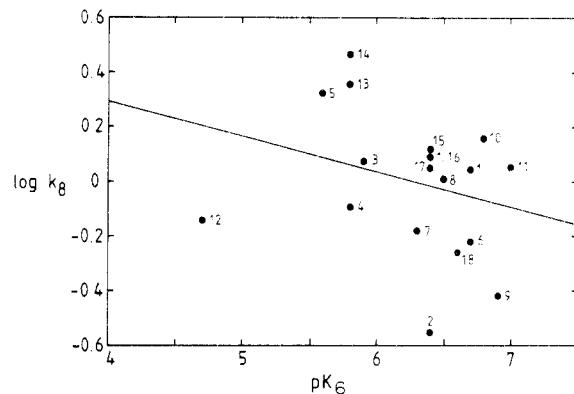


Figure 6. Plot of $\log k_8$ vs. pK_6 for various decarboxylation reactions of monodentate carbonato complexes. (See Table XXXIII for the data numbering system.)

dissociation constant of carbonic acid (K_1).

The results in Table XXXIII illustrate that the nature of the central metal ion and surrounding ligands has a minor influence on the magnitudes of K_6 and k_8 . The acid dissociation constant (K_6) of the bicarbonate species should reflect the strength of the M-O bond and indirectly that of the O-C bond, which determines the magnitude of k_8 . Figure 6 illustrates that k_8 decreases approximately with decreasing K_6 (increasing pK_6). The two species which are most markedly deviant are Co(tetren)OCO₂H²⁺ and cis-Rh(en)₂(OH₂)OCO₂H²⁺; however, reasonable explanations have been offered for their behavior.³¹⁵ Notwithstanding the scatter in Figure 6, the correlation between the acidity of the parent

TABLE XXXIII. Rate and Activation Parameters for Decarboxylation Reactions of Monodentate Carbonato Complexes^f

complex ion	pK_6	$k_s, \text{ s}^{-1}$	$\Delta H_s^\ddagger, \text{ kJ mol}^{-1}$	$\Delta S_s^\ddagger, \text{ J K}^{-1} \text{ mol}^{-1}$	ref
(1) $\text{Co}(\text{NH}_3)_5\text{OCO}_2\text{H}^{2+}$	6.4	1.25 ± 0.06	71 ± 2	-2 ± 4	333
	6.7	1.10 ± 0.05	70 ± 1	-8 ± 4	a
(2) $(\alpha\beta S)\text{-Co}(\text{tetren})\text{OCO}_2\text{H}^{2+}$	6.4	0.28 ± 0.03	65 ± 8	-36 ± 18	327
(3) $cis\text{-Co}(\text{tren})(\text{OH}_2)\text{OCO}_2\text{H}^{2+}$	5.9	1.19 ± 0.06	60 ± 2	-43 ± 5	352
(4) $cis\text{-Co}(\text{en})_2(\text{OH}_2)\text{OCO}_2\text{H}^{2+}$	5.8	0.81 ± 0.04	60 ± 3	-46 ± 12	b
(5) $trans\text{-Co}(\text{en})_2(\text{OH}_2)\text{OCO}_2\text{H}^{2+}$	5.6	2.1 ± 0.1	58 ± 7	-42 ± 25	b
(6) $cis\text{-Co}(\text{en})_2(\text{NH}_3)\text{OCO}_2\text{H}^{2+}$	6.7	0.60 ± 0.02	68 ± 2	-17 ± 7	c
(7) $trans\text{-Co}(\text{en})_2(\text{NH}_3)\text{OCO}_2\text{H}^{2+}$	6.3	0.66 ± 0.02	70 ± 4	-13 ± 12	c
(8) $trans\text{-Co}(\text{en})_2(\text{Cl})\text{OCO}_2\text{H}^{2+}$	6.5	1.02 ± 0.05	73 ± 5	0 ± 17	353
(9) $trans\text{-Co}(\text{NH}_3)_4(\text{CN})\text{OCO}_2\text{H}^{2+}$	6.9	0.38 ± 0.01	90 ± 4	46 ± 12	d
(10) $\text{Ir}(\text{NH}_3)_5\text{OCO}_2\text{H}^{2+}$	6.8	1.45 ± 0.07	79 ± 2	25 ± 4	a
(11) $\text{Rh}(\text{NH}_3)_5\text{OCO}_2\text{H}^{2+}$	7.0	1.13 ± 0.06	71 ± 2	-4 ± 4	a
(12) $cis\text{-Rh}(\text{en})_2(\text{OH}_2)\text{OCO}_2\text{H}^{2+}$	4.7	0.72 ± 0.02	81 ± 1	24 ± 4	e
(13) $trans\text{-Rh}(\text{en})_2(\text{OH}_2)\text{OCO}_2\text{H}^{2+}$	5.8	2.92 ± 0.08	46 ± 1	-82 ± 2	322
(14) $trans\text{-Rh}(\text{en})_2(\text{OCO}_2\text{H}_2)^+$	5.8	2.26 ± 0.05	68 ± 1	-9 ± 3	322
(15) $trans\text{-Rh}(\text{en})_2(\text{OCO}_2)^-\text{OCO}_2\text{H}$	6.4	1.3 ± 0.1			322
(16) $trans\text{-Rh}(\text{en})_2(\text{Cl})\text{OCO}_2\text{H}^+$	6.4	1.26 ± 0.04	73 ± 2	-1 ± 7	315
(17) $trans\text{-Rh}(\text{en})_2(\text{Br})\text{OCO}_2\text{H}^+$	6.4	1.12 ± 0.03	76 ± 1	11 ± 3	315
(18) $trans\text{-Rh}(\text{en})_2(\text{I})\text{OCO}_2\text{H}^+$	6.6	0.55 ± 0.04	72 ± 1	-10 ± 5	315

^a Palmer, D. A.; Harris, G. M. *Inorg. Chem.* 1974, 13, 965. ^b Wan, W. K. Ph.D. Thesis, State University of New York at Buffalo, New York, 1978. ^c Ficner, S. A. Ph.D. Thesis, State University of New York at Buffalo, New York, 1980.

^d Krishnamoorthy, C. R.; Palmer, D. A.; van Eldik, R.; Harris, G. M. *Inorg. Chim. Acta* 1979, 35, L361. ^e Palmer, D. A.; van Eldik, R.; Kelm, H.; Harris, G. M. *Inorg. Chem.* 1980, 19, 1009. ^f Temperature of 25 °C; ionic strength of 0.5 M.

species and its rate of decarboxylation is obvious. As for the various *trans* Rh(III) species, it is clear that the labilizing effect of the ligand *trans* to the bicarbonate group decreases in the order $\text{H}_2\text{O} > \text{OCO}_2\text{H}^- > \text{OCO}_2^{2-} > \text{Cl}^- > \text{Br}^- \sim \text{NH}_3 > \text{I}^-$, although the magnitude of this effect is diminished as it operates on the more remote C–O bond.³¹⁵ Certainly crystallographic studies are not sensitive enough to register a *trans* effect on the C–O bond lengths (see Table XVIII).

The activation parameters for k_s exhibit a good isokinetic relationship (Figure 7), from which it follows that $\Delta G_0^\ddagger = 73.2 \pm 0.4 \text{ kJ mol}^{-1}$ and $\beta_0 = 318 \pm 13 \text{ K}$. These are indeed very close to those reported for the reverse CO_2 uptake process in Figure 4. This illustrates that a common mechanism is operative, viz., the formation or breakage of secondary oxygen–carbon bonds. The pressure dependence of k_s for the decarboxylation of $\text{M}(\text{NH}_3)_5\text{OCO}_2^+$ ($\text{M} = \text{Co}(\text{III}), \text{Rh}(\text{III}), \text{Ir}(\text{III})$) was studied¹⁰³ at high $[\text{H}^+]$, i.e., where $[\text{H}^+] \gg K_6$, such that $k_{\text{obsd}} = k_s$. The volumes of activation were reported¹⁰³ to be $+6.8 \pm 0.3$ ($\text{M} = \text{Co}(\text{III})$), $+5.2 \pm 0.3$ ($\text{M} = \text{Rh}(\text{III})$), and $+2.5 \pm 0.4$ ($\text{M} = \text{Ir}(\text{III})$) $\text{cm}^3 \text{ mol}^{-1}$ at 25 °C and an ionic strength of 0.5 M. Although the magnitude of ΔV^\ddagger is rather small, it can be assigned to intrinsic volume changes during the release of CO_2 . A combination of the above values and those found¹⁰³ for the corresponding formation reactions, along with partial molar volume measurements, enabled the construction of reaction volume profiles.¹⁰³ These indicate that the transition state has a volume approximately halfway between that of the reactant and product species.

(2) Acid-Catalyzed Aquation of Bidentate Carbonato Complexes. The aquation of $\text{Co}(\text{NH}_3)_5\text{CO}_3^{2+}$ is one of the earliest investigated bidentate systems.³³⁴ With the aid of ^{18}O tracer experiments, Posey and Taube³³⁵ demonstrated that the acidification proceeds via a rate-determining acid-catalyzed ring-opening step (the reverse of reaction 68), followed by a fast decarboxylation step of the monodentate bicarbonate species as discussed in the previous section. Similar findings were reported for a series of such complexes as sum-

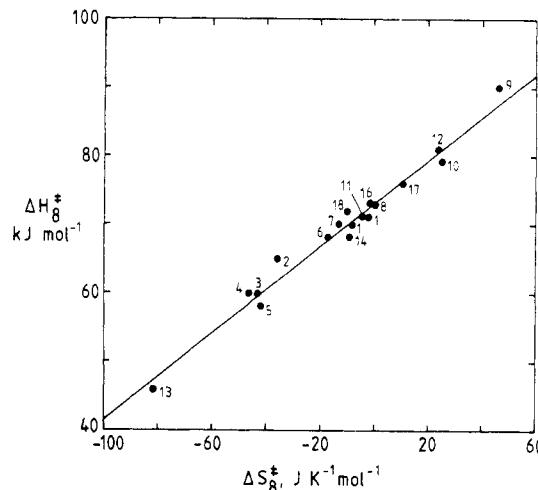
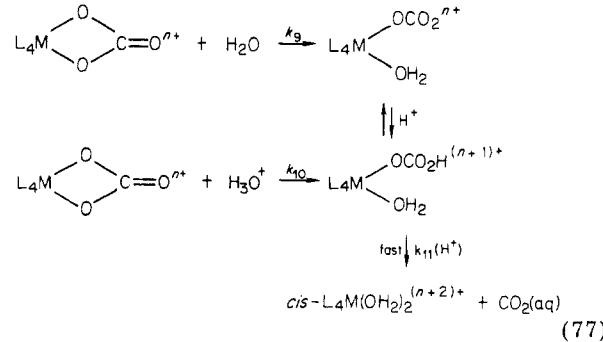


Figure 7. Plot of ΔH_s^\ddagger vs. ΔS_s^\ddagger for various decarboxylation reactions of monodentate carbonato complexes. (See Table XXXIII for the data numbering system.)

marized in Tables XXXIV and XXXV. The ring-opening process obeys the rate law

$$k_{\text{obsd}} = k_9 + k_{10}[\text{H}^+] \quad (76)$$

where k_9 and k_{10} represent the rate constants for the “water”- and acid-catalyzed ring-opening reactions as illustrated in reaction 77. Here k_{11} represents the



decarboxylation rate constant of the ring-opened monodentate carbonato intermediate, which is usually a fast

TABLE XXXIV. Rate and Activation Parameters for "Water-Catalyzed" Ring-Opening Reactionsⁱ

complex ion	<i>I</i> , M	<i>k</i> ₉ , s ⁻¹	ΔH_9^\ddagger , kJ mol ⁻¹	ΔS_9^\ddagger , J K ⁻¹ mol ⁻¹	ref
(1) Co(NH ₃) ₄ CO ₃ ⁺	0.5	(1.3 ± 0.2) × 10 ⁻⁴	50 ± 21	-155 ± 79	334
(2) Co(en) ₂ CO ₃ ⁺		(1.2 ± 0.2) × 10 ⁻⁴	75 ± 13	-63 ± 38	^a
(3) Co(pn) ₂ CO ₃ ⁺		(1.0 ± 0.2) × 10 ⁻⁴	75 ± 13	-63 ± 38	^a
(4) Co(tn) ₂ CO ₃ ⁺		(0.8 ± 0.2) × 10 ⁻⁴	67 ± 13	-88 ± 38	^a
(5) Co(tren)CO ₃ ⁺	0.5	(1.7 ± 0.2) × 10 ⁻⁴	63 ± 8	-105 ± 21	326
(6) <i>cis</i> -Co(en)(NH ₃) ₂ CO ₃ ⁺	0.5	(0.8 ± 0.1) × 10 ⁻⁴	71 ± 21	-100 ± 50	326
(7) <i>cis</i> -Co(en)(H ₂ O) ₂ CO ₃ ⁺ ^b	1.0	7.1 × 10 ⁻²	169 ± 34	+300 ± 122	^c
(8) <i>trans</i> -Co(en)(NH ₃) ₂ CO ₃ ⁺	0.5	(1.1 ± 0.6) × 10 ⁻⁴	79 ± 21	-59 ± 50	326
(9) α -Co(trien)CO ₃ ⁺	0.5	(1.5 ± 1.2) × 10 ⁻⁴	84 ± 13	-29 ± 29	326
(10) β -Co(trien)CO ₃ ⁺	0.5	(0.1 ± 0.1) × 10 ⁻⁴	71 ± 13	-96 ± 38	326
(11) α -Co(Me ₂ trien)CO ₃ ⁺	1.0	~3 × 10 ⁻⁴	64 ± 13	-100 ± 42	339
(12) Co(Me ₂ [14]dieneN ₄)CO ₃ ⁺	0.5	7.5 × 10 ⁻⁵	115 ± 28	+65 ± 89	338
(13) Co(py) ₄ CO ₃ ⁺	1.0	(1.3 ± 0.1) × 10 ⁻⁶	138 ± 4	+109 ± 8	342
(14) <i>cis</i> -Co(py) ₂ (H ₂ O) ₂ CO ₃ ⁺	1.0	(7.5 ± 1.6) × 10 ⁻⁵	111 ± 1	+49 ± 4	^d
(15) <i>cis</i> -Co(py) ₂ (CO ₃) ₂ ⁻	0.5	(5.2 ± 0.5) × 10 ⁻⁵	96 ± 4	-4 ± 17	^e
(16) α -Co(edda)CO ₃ ⁺	2.0	(2.9 ± 0.2) × 10 ⁻³	71 ± 8	-59 ± 29	341
	0.5	2.2 × 10 ⁻³	88 ± 13	0 ± 50	^f
(17) β -Co(edda)CO ₃ ⁺	2.0	(9.8 ± 4.3) × 10 ⁻⁴	88 ± 25	-8 ± 84	341
	0.5	3.8 × 10 ⁻⁴	88 ± 13	+8 ± 50	^f
(18) Co(nta)CO ₃ ²⁻	2.0	(3.0 ± 0.8) × 10 ⁻³	53 ± 11	-117 ± 38	^g
(19) <i>cis</i> -Rh(en) ₂ CO ₃ ⁺	0.5	(9.5 ± 1.0) × 10 ⁻⁶	95 ± 6	-21 ± 21	^h
(20) Cr ₂ ((9)aneN ₃) ₂ (OH) ₂ CO ₃ ²⁺	1.0	(1.7 ± 0.1) × 10 ⁻⁵	86 ± 10	-48 ± 34	345

^a Sastri, V. S.; Harris, G. M. *J. Am. Chem. Soc.* 1970, 92, 2943. ^b A clear distinction cannot be made between this species or Co(en)(CO₃)₂⁻ as the reactant. ^c Coddington, P. M.; Hyde, K. E. *Inorg. Chem.* 1983, 22, 2211. ^d Glenister, J. F.; Hyde, K. E.; Davies, G. *Ibid.* 1982, 21, 2331. ^e Hyde, K. E.; Hyde, E. W.; Moryl, J.; Baltus, B.; Harris, G. M. *Ibid.* 1980, 19, 1603. ^f Garnett, P. J.; Watts, D. W. *Inorg. Chim. Acta* 1974, 8, 313. ^g Dasgupta, T. P.; Harris, G. M. *Inorg. Chem.* 1974, 13, 1275. ^h Palmer, D. A.; van Eldik, R.; Kelm, H.; Harris, G. M. *Ibid.* 1980, 19, 1009.

ⁱ Temperature, 25 °C. ^j Palmer, D. A.; van Eldik, R.; Kelm, H.; Harris, G. M. *Ibid.* 1980, 19, 1009. ^k Temperature, 25 °C.

TABLE XXXV. Rate and Activation Parameters for "Acid-Catalyzed" Ring-Opening Reactionsⁱ

complex ion	<i>I</i> , M	<i>k</i> ₁₀ , ^a M ⁻¹ s ⁻¹	ΔH_{10}^\ddagger , kJ mol ⁻¹	ΔS_{10}^\ddagger , J K ⁻¹ mol ⁻¹	ref
(1) Co(NH ₃) ₄ CO ₃ ⁺	0.5	(1.5 ± 0.1)	64 ± 4	-26 ± 16	334
(2) Co(en) ₂ CO ₃ ⁺		(0.6 ± 0.05)	59 ± 13	-54 ± 38	^b
(3) Co(pn) ₂ CO ₃ ⁺		(0.5 ± 0.05)	59 ± 13	-54 ± 38	^b
(4) Co(tn) ₂ CO ₃ ⁺		(0.8 ± 0.05)	50 ± 13	-79 ± 38	^b
(5) Co(bpy) ₂ CO ₃ ⁺	1.0	2.2 × 10 ⁻⁴	93 ± 7	-6 ± 20	340
(6) Co(phen) ₂ CO ₃ ⁺	1.0	1.5 × 10 ⁻⁴	85 ± 8	-36 ± 21	340
(7) Co(tren)CO ₃ ⁺	0.5	(2.0 ± 0.05)	46 ± 4	-84 ± 17	326
(8) Co(cyclam)CO ₃ ⁺	0.5	1.8 × 10 ⁻³	86 ± 2	-11 ± 5	344
(9) Co(cyclen)CO ₃ ⁺	0.5	7.0 × 10 ⁻³	100 ± 3	+51 ± 10	337
(10) <i>cis</i> -Co(en)(NH ₃) ₂ CO ₃ ⁺	0.5	(0.9 ± 0.05)	67 ± 4	-17 ± 13	326
(11) <i>cis</i> -Co(en)(H ₂ O) ₂ CO ₃ ⁺ ^c	1.0	2.2 × 10 ⁻¹	51 ± 9	-87 ± 32	^d
(12) <i>trans</i> -Co(en)(NH ₃) ₂ CO ₃ ⁺	0.5	(8.9 ± 0.8)	42 ± 4	-84 ± 13	326
(13) α -Co(trien)CO ₃ ⁺	0.5	(5.2 ± 0.1)	63 ± 4	-21 ± 13	326
(14) β -Co(trien)CO ₃ ⁺	0.5	(0.2 ± 0.02)	71 ± 4	-21 ± 13	326
(15) α -Co(Me ₂ trien)CO ₃ ⁺	1.0	2 × 10 ⁻²	92 ± 5	+32 ± 17	339
(16) β -Co(Me ₂ trien)CO ₃ ⁺	1.0	5.5 × 10 ⁻⁴	87 ± 2	-16 ± 6	339
(17) Co(Me ₂ (14)dieneN ₄)CO ₃ ⁺	0.5	1.5 × 10 ⁻²	81 ± 1	-6 ± 2	338
(18) Co(Me ₂ (14)dieneN ₄)CO ₃ ⁺	0.25	8.0 × 10 ⁻³	70 ± 21	-42 ± 71	^e
(19) α -Co(dmtr)CO ₃ ⁺	1.0	1.8 × 10 ⁻²			343
(20) β -Co(dmtr)CO ₃ ⁺	1.0	5.6 × 10 ⁻⁴			343
(21) Co(py) ₄ CO ₃ ⁺	5.0	(8.0 ± 0.5) × 10 ⁻⁶	97 ± 4	-17 ± 13	342
(22) <i>cis</i> -Co(py) ₂ (H ₂ O) ₂ CO ₃ ⁺	1.0	(3.4 ± 0.2) × 10 ⁻⁴	82 ± 5	-36 ± 18	^f
(23) Co(py) ₃ (H ₂ O)CO ₃ ⁺	1.0	4 × 10 ⁻⁴			^{f, g}
(24) <i>cis</i> -Co(py) ₂ (CO ₃) ₂ ⁻	0.5	(5.9 ± 0.6)	71 ± 4	+8 ± 17	^h
(25) Co(gly) ₂ CO ₃ ⁺	2.0	8	92	+84	350
(26) α -Co(edda)CO ₃ ⁺	2.0	(118 ± 1)	50 ± 4	-33 ± 33	341
	0.5	83	67 ± 4	+21 ± 13	ⁱ
(27) β -Co(edda)CO ₃ ⁺	2.0	(2.4 ± 0.1)	45 ± 1	-84 ± 4	341
	0.5	3.0	71 ± 4	+8 ± 13	ⁱ
(28) Co(nta)CO ₃ ²⁻	2.0	(41.9 ± 0.8)	66 ± 2	-6 ± 6	^j
(29) <i>cis</i> -Rh(en) ₂ CO ₃ ⁺	0.5	(7.8 ± 1.0) × 10 ⁻⁶	104 ± 15	+8 ± 46	^k
(30) Rh ₂ ((9)aneN ₃) ₂ (OH) ₂ CO ₃ ²⁺	1.0	(1.7 ± 0.1) × 10 ⁻⁴	63 ± 1	-106 ± 2	345
(31) Cr ₂ ((9)aneN ₃) ₂ (OH) ₂ CO ₃ ²⁺	1.0	(3.8 ± 0.8) × 10 ⁻⁵	66 ± 2	-106 ± 8	345
(32) Cr(C ₂ O ₄) ₂ CO ₃ ³⁻	2.0	(2.0 ± 0.2)	61 ± 2	-33 ± 8	350

^a $k_{10} = k_{12}K_7$ (see discussion). ^b Sastri, V. S.; Harris, G. M. *J. Am. Chem. Soc.* 1970, 92, 2943. ^c A clear distinction could not be made between this species and Co(en)(CO₃)₂⁻ as the reactant. ^d Coddington, P. M.; Hyde, K. E. *Inorg. Chem.* 1983, 22, 2211. ^e Kernohan, J. A.; Endicott, J. F. *J. Am. Chem. Soc.* 1969, 91, 6977. ^f Glenister, J. F.; Hyde, K. E.; Davies, G. *Inorg. Chem.* 1982, 21, 2331. ^g Laier, T.; Schaffer, C. E.; Springborg, J. *Acta Chem. Scand., Ser. A* 1980, A34, 343. ^h Hyde, K. E.; Hyde, E. W.; Moryl, J.; Baltus, R.; Harris, G. M. *Inorg. Chem.* 1980, 19, 1603. ⁱ Garnett, P. J.; Watts, D. W. *Inorg. Chim. Acta* 1974, 8, 313. ^j Dasgupta, T. P.; Harris, G. M. *Inorg. Chem.* 1974, 13, 1275. ^k Palmer, D. A.; van Eldik, R.; Kelm, H.; Harris, G. M. *Ibid.* 1980, 19, 1009. ^l Temperature, 25 °C.

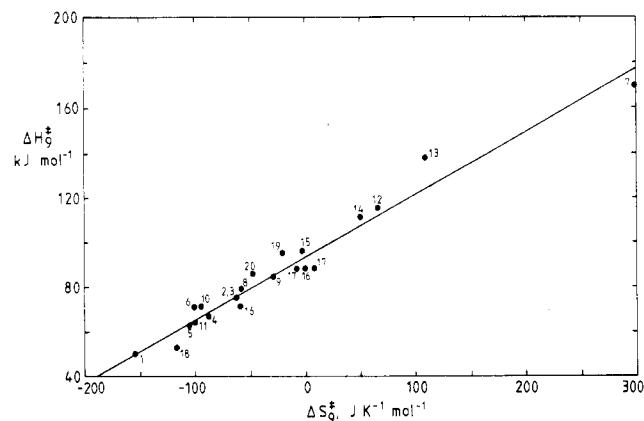
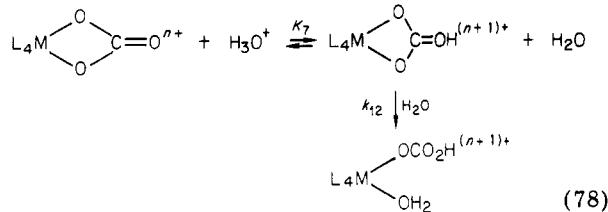


Figure 8. Plot of ΔH_9^* vs. ΔS_9^* for various “water-catalyzed” ring-opening reactions of bidentate carbonato complexes. (See Table XXXIV for the data numbering system.)

step (see subsection B1 and further discussion), such that this step is not rate determining.

Solvent isotope effects³³⁶⁻³³⁹ led to the suggestion that the acid-catalyzed ring-opening step (k_{10}) actually consists of a rapid preprotonation equilibrium followed by a rate-determining ring-opening reaction.



As a result, eq 76 modifies to

$$k_{\text{obsd}} = \frac{k_9 + k_{12}K_7[\text{H}^+]}{1 + K_7[\text{H}^+]} \quad (79)$$

which can be further simplified to

$$k_{\text{obsed}} = k_9 + k_{12} K_7 [\text{H}^+] \quad (80)$$

since it is known that K_7 for the protonation of a carbonyl group is very small.³³⁶ If this were not the case, the simplification that $1 + K_7[H^+] \sim 1$ would have been invalid, and k_{obsd} vs. $[H^+]$ should have been nonlinear. It follows that k_{10} is replaced by the product $k_{12}K_7$. The values of k_9 and k_{10} (i.e., $k_{12}K_7$), and their corresponding activation parameters, are summarized in Tables XXXIV and XXXV, respectively.

The values of k_9 in Table XXXIV vary within 4 orders of magnitude. Furthermore, the nature of the central metal atom, the surrounding nonparticipating ligands and the overall charge on the complex influence the magnitude of k_9 and its corresponding activation parameters, as expected for a metal-oxygen bond breakage process. The activation parameters exhibit a good isokinetic relationship (Figure 8), which demonstrates the common nature of the processes involved. The values of k_{10} in Table XXXV vary within 6 orders of magnitude, which once again emphasizes the influence of the nonparticipating ligands and the charge of the complex on the strength of the metal-oxygen bond. The factors that govern the relative magnitudes of k_{10} obviously include a stereochemical component. The influence of the electronic structure of the ligand, however, is not clearly delineated for this type of reaction. Francis and Jordan³⁴⁰ proposed a correlation

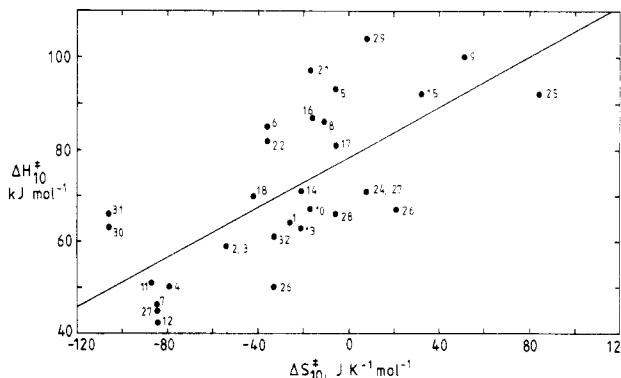


Figure 9. Plot of ΔH_{10}^* vs. ΔS_{10}^* for various acid-catalyzed ring-opening reactions of bidentate carbonato complexes. (See Table XXXV for the data numbering system.)

TABLE XXXVI. Rate and Activation Parameters for the Decarboxylation of Some Ring-Opened Carbonato Complexes^a

complex ^b	k_{11} , s ⁻¹	ΔH_{11}^{\ddagger} , kJ mol ⁻¹	ΔS_{11}^{\ddagger} , J K ⁻¹ mol ⁻¹	ref
Co(nta)CO ₃ ²⁻	57.1 ± 2.5	64 ± 4	-3 ± 13	c
α -Co(edda)CO ₃ ⁻	55.0 ± 4.6	46 ± 3	-54 ± 8	341
β -Co(edda)CO ₃ ⁻	2.3 ± 0.1	68 ± 6	-8 ± 21	341
Co(en) ₂ CO ₃ ⁺	0.37			336
Co(tren)CO ₃ ⁺	1.5			326

^a Ionic strength of 2.0M and a temperature of 25 °C.

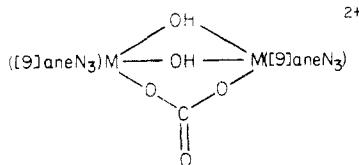
^b Complex prior to acidification. ^c Dasgupta, T. P.; Harris, G. M. *Inorg. Chem.* 1974, 13, 1275.

between the value of k_{10} and pK_a of the amine ligands for a series of $\text{CoN}_4\text{CO}_3^+$ complexes.³⁴¹⁻³⁴⁴ Obviously the more acidic the ligands are, then the stronger will be the Co-O bond. However, this correlation is only valid for a limited number of systems, and steric arguments must also be taken into account.³⁴¹ A further complication in the interpretation of k_{10} arises from the fact that k_{10} is actually a combination of two constants, viz., k_{12} and K_7 . These constants may in fact behave very differently towards stereochemical and other effects. The overall activation parameters ΔH_{10}^\ddagger and ΔS_{10}^\ddagger result in a poor isokinetic plot (Figure 9). This demonstrates the significant role played by the nature of the central metal atom and the nonparticipating ligands during the acid-catalyzed ring-opening process. Furthermore, the complex nature of k_{10} could partially account for the large scatter in Figure 9 since the overall activation parameters are indeed composite quantities, viz., $\Delta H_{10}^\ddagger = \Delta H_7^\circ + \Delta H_{12}^\ddagger$ and $\Delta S_{10}^\ddagger = \Delta S_7^\circ + \Delta S_{12}^\ddagger$.

In a few cases (see Table XXXVI), plots of k_{obsd} vs. $[\text{H}^+]$ tend to reach a limiting value at high $[\text{H}^+]$. Under such conditions the rate of the ring-opening reaction ($k_{10}[\text{H}^+]$ or $k_{12}K_7[\text{H}^+]$) is enhanced to such an extent that the decarboxylation step (k_{11} , which is independent of $[\text{H}^+]$) becomes rate determining (see eq 77). The values of k_{11} are within the expected range and in good agreement with corresponding data in Table XXXIII. The activation parameters for β -Co(edda) CO_3^{2-} fall on the isokinetic plot in Figure 7, but those for Co(nta)- CO_3^{2-} and α -Co(edda) CO_3^{2-} do not fit this relationship. In the latter cases, k_{11} is very large indeed, which indicates that some form of specific interaction, probably involving the amido group cis to the bicarbonato ligand, which hinders the decarboxylation process in the majority of cases but does not occur in these systems.³⁴¹

(3) Acid-Catalyzed Aquation of Bridged Carbonato Complexes. The examples in the previous two subsections clearly illustrate that mono- and bidentate carbonato complexes exhibit completely different acid-catalyzed aquation kinetics (compare eq 74 and 75). The question remains, how do bridged carbonato complexes behave under such conditions?

Wieghardt and co-workers^{345,346} recently reported the syntheses and X-ray analyses of two carbonato-bridged complexes, viz. (see Table XXI)

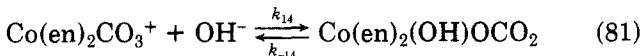
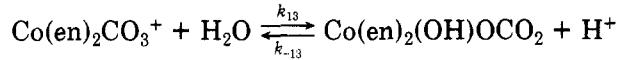


M = Cr(III), Rh(III)

The acid-catalyzed aquation of these complexes was studied³⁴⁵ to clarify their structural habit in aqueous solution. The data underline the typical bidentate character of the carbonate ligand and the results are included in Tables XXXIV and XXXV. The Cr(III) complex exhibits a strong contribution from the "water-catalyzed" reaction path.

Dasgupta and co-workers³⁴⁷ recently reported the isolation and structure of two binuclear Co(III) complexes containing carbonate as a bridging group. The acid-catalyzed aquation of (NH3)5Co(μ-CO3)Co(NH3)5⁴⁺ produces kinetic data³⁴⁸ identical to that for Co(NH3)5OCO2⁺.³⁴⁸ These results are in disagreement with those reported above for the Rh(III) and Cr(III) bridged species,³⁴⁵ so that it is doubtful whether the Co(III) bridged species really exists in this form in aqueous solution. Preliminary measurements³⁴⁹ on the acid-catalyzed aquation of (NH3)3Co(μ-OH)2(μ-CO3)-Co(NH3)3²⁺ gave kinetic data similar to that reported for the Rh(III) and Cr(III) bridged species,³⁵⁰ thus emphasizing the bidentate character of the carbonato ligand.

(4) Base-Catalyzed Aquation of Carbonato Complexes. In contrast to acid-catalyzed aquation studies, relatively little has been reported on the base-catalyzed aquation reactions of carbonato complexes. In one of the first studies Francis and Jordan³²¹ suggested that Co(en)₂CO₃⁺ undergoes hydrolysis according to a two-step process in which first the intermediate Co(en)₂-(OH)OCO₂ is produced, followed by loss of carbonate to form Co(en)₂(OH)₂⁺. Their kinetic data suggested a mechanism as outlined in eq 81 for which $k_{\text{obsd}} = k_{-14}$



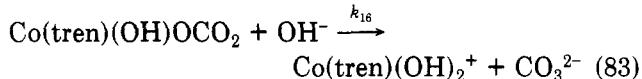
+ $k_{-13}[\text{H}^+] + k_{13}[\text{H}_2\text{O}] + k_{14}[\text{OH}^-]$. The magnitude of the various rate constants in (81) and their activation parameters could be estimated³²¹ from the pH dependence of k_{obsd} . Typical values for k_{14} and k_{-14} are $3.2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ and $6.5 \times 10^{-5} \text{ s}^{-1}$ at 26°C , respectively.³²¹ An ¹⁸O tracer study showed that the k_{14} path proceeds with Co-O bond cleavage. Endicott and co-workers³⁵¹ reported a similar finding for the base-catalyzed aquation of Co(Me₆[14]dieneN₄)CO₃⁺ and three different isomeric Co(Me₆[14]aneN₄)CO₃⁺ species. Both the

ring-opening and subsequent decarboxylation reactions were studied in detail³⁵¹ and exhibit an $[\text{OH}^-]$ dependence of the general form:

$$k_{\text{obsd}} = k_{15}' + k_{15}''[\text{OH}^-] + k_{15}'''[\text{OH}^-]^2 \quad (82)$$

The authors offer a thorough discussion of various possible reaction routes, including the role of ligand stereochemistry in determining the net reactivity in terms of nucleophilic scavenging of the five-coordinate ring-opened intermediate.

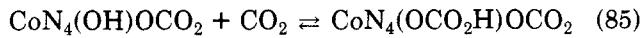
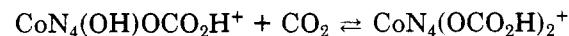
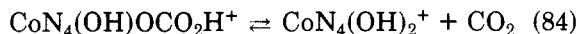
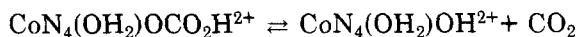
Base-catalyzed aquation of Co(tren)CO₃⁺ was reported³⁵² to include two ring-opening (Co-O bond breakage) reactions, similar to those outlined in (81), followed by



The reported values of k_{13} for this complex are in very good agreement with those measured during the acid-catalyzed aquation reaction.³²⁶ The rate and activation parameters for the base-catalyzed reactions were reported³⁵² to be $k_{14} = 3.6 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 25°C ($\Delta H^\ddagger = 72 \pm 8 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -50 \pm 25 \text{ J K}^{-1} \text{ mol}^{-1}$) and $k_{16} = 6 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ at 40°C ($\Delta H^\ddagger = 103 \pm 5 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -4 \pm 17 \text{ J K}^{-1} \text{ mol}^{-1}$). The authors conclude that reaction 83 includes the complete substitution of CO₃²⁻ by OH⁻, i.e., Co-O bond breakage. In a subsequent study,³²⁵ the [OH⁻] dependence of k_{16} was investigated in more detail, and a "water-path" was detected kinetically for the substitution of carbonate in the Co(tren)(OH)OCO₂ species ($k = 1 \times 10^{-4} \text{ s}^{-1}$ at 50°C). Finally, no substitution of carbonate or loss of CO₂ was found in the base hydrolysis of trans-Co(en)₂(Cl)-OCO₂.³⁵³ The reaction product was trans-Co(en)₂-(OH)OCO₂ under all conditions, and the kinetic data correlate well with those usually observed³⁵⁴ for the hydrolysis of complexes of the type trans-Co(en)₂(Cl)Lⁿ⁺. Finally, it should be noted that all the mentioned base-catalyzed aquation reactions are thought to proceed via a conjugate base mechanism.

C. Exchange, Substitution, and Isomerization Reactions

The previous review on the chemistry of metal carbonato complexes¹ included a detailed discussion on ligand and isotope exchange reactions in which deuterium, ¹⁴C, and ¹⁸O labeling was employed. Following a series of earlier studies, Harris et al.³⁵⁵ reported a revised general mechanism for carbonate exchange reactions of complexes of the type CoN₄CO₃⁺. In this they modified their earlier suggestion of a dual mechanism, partly dissociative and partly associative, to a dual dissociative path consisting of decarboxylation of the ring-opened monodentate carbonato species (reaction 84) and a dual associative path consisting of CO₂ uptake by the monodentates (reaction 85). In reference



to our earlier remarks³²² concerning the stability of protonated carbonato species, it is obvious that the bicarbonato products in (85) can only exist in the de-

TABLE XXXVII. Rate and Activation Parameters for Ring Closure in (Carbonato)diaminecobalt(III) Systems^a

ligand	$10^5 C, s^{-1}$	$10^5 D, M^{-1} s^{-1}$	$\Delta H_C^\ddagger, kJ mol^{-1}$	$\Delta S_C^\ddagger, J K^{-1} mol^{-1}$	$\Delta H_D^\ddagger, kJ mol^{-1}$	$\Delta S_D^\ddagger, J K^{-1} mol^{-1}$
en	92 ± 3	208 ± 8	138 ± 8	159 ± 33	89 ± 3	0 ± 8
pn	30 ± 13	300 ± 30	196 ± 33	351 ± 125	49 ± 8	-130 ± 25
tn	19 ± 0.5	71 ± 3				

^a At 25 °C taken from ref 365.

TABLE XXXVIII. Characteristic IR Absorption Bands for Metal-Carbon Dioxide Complexes

compound	ν_{CO_2}, cm^{-1}	ref
[Ti(<i>n</i> ⁵ -C ₅ H ₅) ₂] ₂ CO ₂	1440, 1360	407
Mo(PMe ₂ Ph) ₃ (CO ₂) ₂	1760, 1510, 1335	445
Fe(PMe ₃) ₃ (H)(PMe ₂ CH ₂ CO ₂)	1610, 1592, 1328	415
Co(pr-salen)(CO ₂)(K)(THF) ^a	1650 s, 1280 ms, 1215 s, 745 s	431
Co(pr-salen)(CO ₂)(Na)	1680, 1278, 1213	470
Co(pr-salen)(py)(CO ₂)(Na)	1700, 1273, 1208	470
Rh ₂ (PPh ₃) ₅ (Cl) ₂ CO ₂	1630	408
Rh(CO)(OH)(PPh ₃) ₂ CO ₂	1966 vs, 1620 s, 1351 s, 821 s	452
Rh ₂ (PPh ₃) ₅ (H) ₂ (Cl) ₃ (CHCl ₂)CO ₂ ·CHCl ₃	1602, 1351, 821 1480, 1430, 1380, 1270, 1175, 1090, 1000, 975 857, 765, 745, 725, 705, 695	453 409
Rh ₂ (PPh ₃) ₅ (Me)(H)(Cl) ₃ CO ₂	1480, 1430, 1380, 850, 760, 740, 690	409
Rh(diphos)(Cl)CO ₂ ^b	1712	c, d
Rh(Cl)(PNP)CO ₂ ^e	1660 vs, 1628 s	428, 455
Rh(Cl)(PBu- <i>n</i> ₃) ₂ CO ₂	1668, 1630, 1165, 1120	447
Rh(Cl)(PET ₂ Ph) ₂ CO ₂	1670 vs, 1635 sh, 1255 m, 963 m, 780 m	447
Rh(Cl)(PET ₂ Ph) ₂ CO ₂	1658 vs, 1620 vs, 1238 m, 827 m	447
Rh(Cl)(PMe ₂ Ph) ₂ CO ₂	1657 vs, 1627 vs, 1217 m, 996 m, 823 m	447
Rh(Cl)(PMePh ₂) ₂ CO ₂	1673 vs, 1635 sh, 1290 m, 1000 m, 822 m, 760 m	447
Rh ₂ (PPh ₃) ₅ (CO) ₂ (CO ₂) ₂ ·C ₆ H ₆	1600, 1355, 825	456
Rh ₂ (PPh ₃) ₅ (CO) ₂ CO ₂ ·C ₆ H ₆	1498, 1368, 813	429
Rh ₂ (H) ₂ (PPh ₃) ₆ CO ₂ ·C ₆ H ₅ CH ₃	1460, 1300	443, 457
Ir(CO)(OH)(PPh ₃) ₂ CO ₂	1636 m, 1310 s, 815 m	452, 453
Ir(dmpe) ₂ (Cl)CO ₂ ^f	1550, 1230	405
Ni ₂ [P(C ₆ H ₁₁) ₃] ₄ CO ₂	1735	467
Ni[P(C ₆ H ₁₁) ₃] ₂ CO ₂ ·0.75 C ₆ H ₅ CH ₃	1740 vs, 1698 vw, 1150 s, 1094 ms, 845 s	430
Ni(PET ₃) ₂ CO ₂	1660 vs, 1635 vs, 1203 vs, 1009 s, 828 s	426
Ni(PBu- <i>n</i> ₃) ₂ CO ₂	1660 vs, 1632 vs, 1200 vs, 1008 s, 825 s	426
Pt(PPh ₃) ₂ CO ₂	1640 s, 1370 s, 1320 s	408
Pd(CH ₃)(PET ₃)CO ₂	2610 w, 1610 s, 1350 s, 825 m	g
Pd(CH ₃)(PMPh ₂)CO ₂ ·(CH ₃) ₂ CO	2605 w, 1605 s, 1405 s, 1350 s, 835 m	g
Pd(C ₂ H ₄)(PET ₃) ₂ CO ₂	2600 w, 1630 s, 1350 s, 830 m	g
Pd(C ₂ H ₄)(PMPh ₂) ₂ CO ₂	2600 w, 1605 s, 1400 s, 1360 s, 832 m	g
Cu(CH ₃ COO)[P(C ₆ H ₁₁) ₃]CO ₂	2600 m, 1610 s, 1420 m, 1380 s, 830 m, 650 m	424
Cu(CH ₃ COO)(PPh ₃) ₂ CO ₂	2620 w, 1600 vs, 1320 s, 821 m, 648 w	489
Cu ₂ (PPh ₃) ₄ CO ₂ ^h	1475 s, 1330 m, 835 w	406
Cu(eph)CO ₂ ^h	2350 m, 2380 s	461
Cu(eph)CO ₂ ^h	1549, 1344, 800	463
[(C ₆ H ₅)Ag(CO ₂)Ag] _n	1496 s, 1326 s, 828 s	471

^a pr-salen = *N,N'*-ethylenebis(salicylideneiminoato). ^b diphos = (Ph)₂PCH₂CH₂P(Ph)₂. ^c Albano, P.; Aresta, M.; Manassero, M. *Inorg. Chem.* 1980, 19, 1069. ^d Albano, P.; Aresta, M.; Manassero, M. *Cong. Naz. Chem. Inorg.* 1979, 83. ^e PNP = 2,6-bis((diphenylphosphino)methyl)pyridine. ^f dmpe = (CH₃)₂PCH₂CH₂P(CH₃)₂. ^g Ito, T.; Tsuchiya, H.; Yamamoto, A. *Chem. Lett.* 1976, 851. ^h eph = C₆H₅CH(OH)CH(NHCH₃)CH₃.

protonated form. Analysis of the available kinetic data illustrated³⁵⁵ that the above mechanism is valid for N₄ = (NH₃)₄, (en)₂, (pn)₂, (tn)₂, *cis*-(NH₃)₂en, *trans*-(NH₃)₂en, and *trans*-(NH₃)₂tn. Furthermore, this mechanism is also in line with the general mechanistic feature of metal carbonato complexes as discussed in parts A and B of this section.

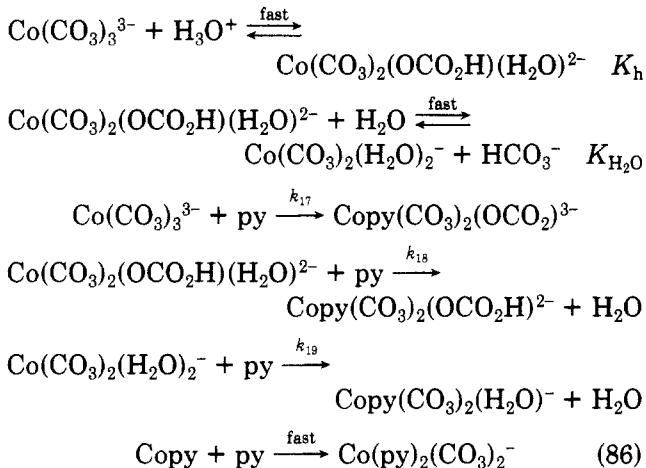
In a later study, Francis and Jordan³⁴⁰ compared the oxygen exchange kinetics of HCO₃⁻ and Co(NH₃)₅OCO₂⁺. Their findings underline the earlier suggestion of Dasgupta and Harris³³³ that the rates of oxygen exchange are controlled by the hydration of CO₂. Recently,³⁵⁶ ¹³C NMR techniques were employed to determine activation parameters for the carbonate exchange on the uranyl tris(carbonato) complex.

Relatively few studies have been reported on substitution reactions of metal carbonato complexes that involve replacement of the carbonato ligand itself. In some cases evidence for the occurrence of such reactions

has been observed in the form of intermediate steps in substitution reactions of other complexes. For example, Sastri and Ramam³⁵⁷ found that the rate of substitution of Cr(C₂O₄)₃³⁻ by edta depended on the bicarbonate ion concentration. They suggested the formation of Cr(C₂O₄)₃HCO₃⁴⁻ and Cr(C₂O₄)₂HCO₃²⁻ intermediates, which can react with edta to give the observed reaction product. The remaining studies concerning the substitution amenability of Co(CO₃)₃³⁻, a species whose complex chemical nature has been discussed before.^{1,2,358} The stability of this species depends markedly on the temperature and bicarbonate concentration^{359,360} and the occurrence of dimeric species has been suggested.³⁶¹ In the reaction of Co(CO₃)₃³⁻ with ammonia, a blue *cis*-Co(NH₃)₂(CO₃)₂⁻ species is produced, which was then believed to isomerize to the *trans* species.³⁵⁹ However, a later study³⁶² confirmed that the *trans* solution is a mixture of the *cis* species and Co(NH₃)₄⁻(CO₃)⁺. In a similar way, the complexes Co(DH)₂CO₃⁻

and $\text{Co}(\text{DH})_2\text{C}_2\text{O}_4^-$ were prepared by substitution of $\text{Co}(\text{CO}_3)_3^{3-}$ with dimethylglyoxime (DH_2), producing the first complex, followed by reaction with oxalate to produce the second species.³⁶³

Davies and Hung^{364,365} reported kinetic data for a series of substitution reactions of $\text{Co}(\text{CO}_3)_3^{3-}$ with py, en, pn, and tn. They found that solutions of $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$ in 0.1–1.0 M sodium bicarbonate are stable under ordinary laboratory conditions, and used the latter for their mechanistic studies. This solution reacts with py³⁶⁴ to produce *cis*- $\text{Co}(\text{py})_2(\text{CO}_3)_2^-$ and no evidence for the formation of the trans isomer³⁶⁶ could be found. The suggested mechanism includes two rapid equilibrations in which HCO_3^- stabilizes the $\text{Co}(\text{CO}_3)_3^{3-}$ species³⁵⁸

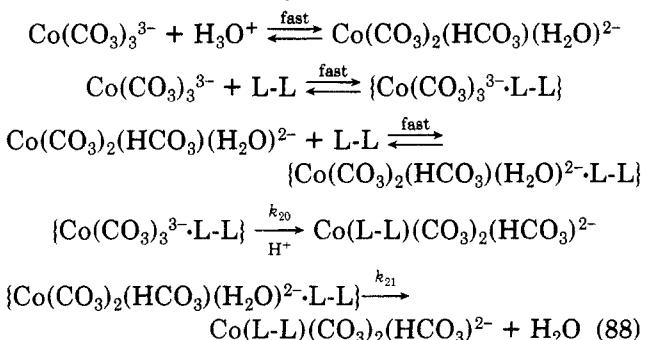


where Copy represents all the monosubstituted pyridine species. This mechanism is in line with the empirical rate law

$$k_{\text{obsd}} = \left[\frac{A[\text{H}^+] + B[\text{H}^+]/[\text{HCO}_3^-]}{1 + C[\text{H}^+]} \right] [\text{py}] \quad (87)$$

from which it follows that $k_{17} \leq 7 \times 10^{-3}$, $k_{18} = A/C = (2.2 \pm 0.3) \times 10^{-2}$, $k_{19} \geq 0.17 \text{ M}^{-1} \text{ s}^{-1}$, $K_h = (1.3 \pm 0.1) \times 10^9 \text{ M}^{-1}$, and $K_{\text{H}_2\text{O}} \leq 6 \times 10^{-2} \text{ M}$ at 25°C and an ionic strength of 1.0 M . The ratio $[\text{Co}(\text{CO}_3)_2 \cdot (\text{HCO}_3)(\text{H}_2\text{O})^{2-}] / [\text{Co}(\text{CO}_3)_3^{3-}]$ varied from 0.2 to 12.4 over the range of experimental conditions. The indication that $k_{19} >> k_{18}$ suggests that the aquo ligands are more readily replaced by pyridine than is coordinated carbonate.

In their subsequent study,³⁶⁶ the formation of chelated $\text{Co}(\text{diamine})(\text{CO}_3)_2^-$ complexes was found to proceed via unusually stable, half-bonded diamine species. The formation of these intermediates was suggested to occur via an associative interchange mechanism for en or pn as the diamine ligand.



The kinetic data fit the empirical rate law

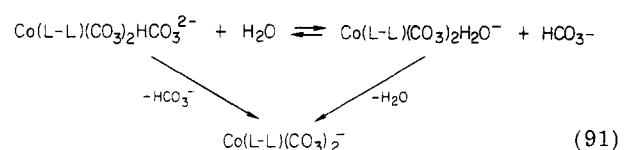
$$k_{\text{obsd}} = A[\text{H}^+]/(1 + B[\text{H}^+]) \quad (89)$$

from which it follows that the precursor complex formation constants are of the order of $2 \times 10^3 \text{ M}^{-1}$, $k_{20} \leq 0.1$, and $k_{21} = 6 \text{ s}^{-1}$ at 25°C and an ionic strength of 1.0 M. Alternatively, the $[\text{L-L}]$ independence of k_{obsd} could point to a dissociative mechanism in which a five-coordinate intermediate $\text{Co}(\text{CO}_3)_2(\text{HCO}_3)^2$ reacts with the diamine.

The subsequent ring-closure reactions follow the rate law

$$k_{\text{obsd}} = C + D[\text{HCO}_3^-] \quad (90)$$

for which the rate and activation parameters are summarized in Table XXXVII. The suggested mechanism consists of the reactions:



In the case of L-L = en or pn, evidence for higher order ammine complex formation was presented.³⁶⁶

More recently³⁶⁷ it was reported that sulfite reacts with $\text{Co}(\text{CO}_3)_3^{3-}$ to produce two products, viz., either $\text{Co}(\text{CO}_3)_2(\text{OH}_2)\text{SO}_3^{3-}$ or $\text{Co}(\text{CO}_3)_2(\text{HCO}_3)\text{SO}_3^{4-}$, and subsequently a bis(sulfito) species. The rate of the first step ($k = (1.6 \pm 0.2) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ at 25°C , $\text{pH} = 9.52$ and an ionic strength of 1.75 M) is in good agreement with the value of k_{18} (reactions 86) reported for the substitution by py,³⁶⁴ such that a similar type of mechanism is probably operative. The rate of the second step is independent of $[\text{SO}_3^{2-}]$, and therefore requires either ring opening trans to the first sulfite group or loss of H_2O or HCO_3^- cis to it to be rate determining.

A number of studies have reported kinetic data on isomerization reactions of carbonato complexes that involve the geometrical rearrangement of a chelated ligand present in such systems. Dasgupta and Harris³⁶⁸ reported data for the α to β isomerization of $\text{Co}(\text{trien})\text{CO}_3^+$. The pH dependence of the process suggests that the α complex produces the ring-opened species $\alpha\text{-cis-}\text{Co}(\text{trien})(\text{OH}_2)\text{OCO}_2^+$ that can either isomerize directly or via its hydroxo form to the ring-opened β analogue, followed by ring closure. The observed rate constants vary between 1×10^{-4} and 3×10^{-4} s^{-1} at 55 °C depending on the pH (7 and 10, respectively) of the solution. A similar α to β isomerization process was found to occur for the $\text{Co}(\text{edda})\text{CO}_3^-$ species,^{341,369} with rate constants of the order of 3×10^{-4} s^{-1} at 30 °C. This reaction presumably also includes the formation of a ring-opened carbonate species prior to the isomerization step.

D. Miscellaneous Reactions

In this section we cover photochemical, radiochemical, redox, and catalytic reactions of metal carbonato complexes.

Hoffman and co-workers³⁷⁰⁻³⁷⁸ have reported a series of papers on the continuous and flash photolysis of some carbonato-ammine Co(III) complexes. Continuous irradiation³⁷³ at 254 nm of solutions of $\text{Co}(\text{NH}_3)_5\text{OCO}_2^+$, $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$, and $\text{Co}(\text{en})_2\text{CO}_3^+$ resulted in partial photoaquation and photoredox reactions. For irradiation of the $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$ complex, $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$ was identified as the aquation product, and $\Phi_{\text{aq}} = 0.11 \pm 0.03$ and $\Phi_{\text{Co}^{2+}} = 0.07$ at pH 6.4 and 25 °C. This observation added ring opening, followed by aquation, to the list of processes that can result from charge-transfer excitation of Co(III) complexes. It was further reported³⁷³ that the presence of O_2 had no effect on the values of $\Phi_{\text{Co}^{2+}}$, but that 1 M 2-propanol in the absence of O_2 caused the quantum yield to double. This was considered as evidence that the CO_3^- radical is scavenged to generate the $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ radical, since the latter is known to be a good reducing agent³⁷⁹ capable of converting Co(III) complexes to $\text{Co}^{2+}(\text{aq})$ with rate constants in the order of 10^7 – $10^9 \text{ M}^{-1} \text{ s}^{-1}$.^{19,380} In this way the oxidizing CO_3^- radical is converted into a reducing radical and $\Phi_{\text{Co}^{2+}}$ is doubled.

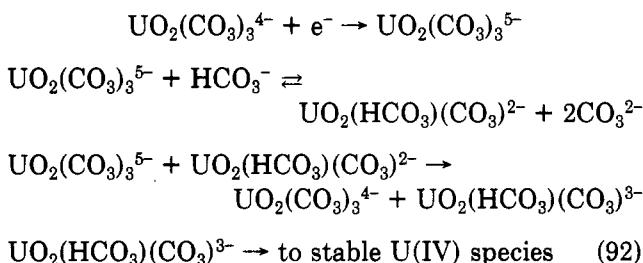
The flash photolysis³⁷³ of the above-mentioned complexes generated the CO_3^- radical, and a long-lived transient species in the case of $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$ and $\text{Co}(\text{en})_2\text{CO}_3^+$. This was shown to be an aquo-carbonato species produced during ring opening of the carbonate ligand. $\text{Co}(\text{NH}_3)_5\text{OCO}_2^+$ did not yield this intermediate and there was no evidence to indicate that photoaquation occurs. In general the authors³⁷³ reported a good correlation with the ground-state aquation reactions of metal carbonato complexes (subsection B). They propose that excitation of the complexes produces a charge-transfer singlet state, which generates, via radiationless transition, the charge-transfer triplet state and a ligand excited state. The charge-transfer triplet state is the precursor to the redox reaction, whereas protonation of the carbonato ligand in the ligand excited state is viewed as causing ring opening and aquation.

One study³⁸¹ has come to our attention in which $\text{Pt}(\text{PPh}_3)_2\text{CO}_3$ reacts either thermally or photochemically in alcoholic solvents to produce $\text{Pt}(\text{PPh}_3)_2$ in situ and the release of an equimolar amount of CO_2 , whereas another study³⁸² reports the reaction between $\text{Pt}(\text{PPhMe}_2)_2\text{CO}_3$ and triorganotin hydrides.

It has, in general, been shown that Co(II) is produced during γ irradiation of Co(III) complexes. An ESR study³⁸³ demonstrated that this is also true for the γ irradiation of $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$. In a pulse radiolysis study,³⁸⁴ aquated electrons (e_{aq}^-) were allowed to react with $\text{NpO}_2(\text{CO}_3)_3^{4-}$, $\text{NpO}_2(\text{CO}_3)_2^{3-}$, $\text{Np}(\text{CO}_3)_5^{6-}$, and $\text{PuO}_2(\text{CO}_3)_3^{4-}$, and rate constants between 2×10^9 and $2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ were reported. Calculations indicated that the reaction of e_{aq}^- with the $\text{MO}_2(\text{CO}_3)_3^{4-}$ species ($\text{M} = \text{Np(VI), Pu(VI)}$) is diffusion controlled. Similarly, the rate constant for the reaction of e_{aq}^- with $\text{UO}_2(\text{CO}_3)_3^{4-}$ ³⁸⁵ was reported³⁸⁶ to be $(1.32 \pm 0.01) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

Redox reactions of metal carbonato species were induced either electrochemically or photochemically. Cyclic chronopotentiometry³⁸⁷ was used to elucidate the complex reaction sequence of uranium(V) in bicarbonate-carbonate solutions. The following reaction

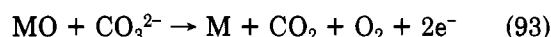
scheme was suggested for the reduction of $\text{UO}_2(\text{CO}_3)_3^{4-}$:



With the aid of ac polarography, Matusinovic and Smith³⁸⁸ obtained rate constants for the homogeneous reduction of pentaamminecobalt(III) complexes by Eu(III), and reported a value of $4.5 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C for the reduction of $\text{Co}(\text{NH}_3)_5\text{OCO}_2^+$. Keenan and co-workers^{389,390} have studied a series of $\text{M}/\text{MO}/\text{CO}_3^{2-}/\text{CO}_2$ electrodes at 350 °C in fused KNO_3 . Two types of reactions were found:



$\text{M} = \text{Co, Ni, Pd, Pt}$

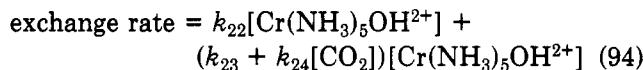


$\text{M} = \text{Fe, Zn, Ag, Ta, Cu}$

The authors³⁹⁰ find a direct correlation between the crystal field stabilization energies of the metal carbonato complexes and the above classification (93) of the metals into the two distinct types of reactions. This supports their hypothesis that metal carbonato complexes are the critical species in these electrode reactions. Photinduced electron transfer was found³⁹¹ to occur between $\text{Os}(\text{bpy})_3^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{OCO}_2^+$ at a rate of $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, which was estimated using the lifetime of the osmium species as 19.2 ns.

A few studies have been reported in which metal carbonato species exhibit catalytic effects. It was found³⁹² that $\text{Mn}(\text{HCO}_3)^+$ and $\text{Co}(\text{HCO}_3)^+$ catalyze the decomposition of hydrogen peroxide. The catalytic activity of such complexes can be arranged in the sequence $\text{Mn(II)} > \text{Co(II)} > \text{Ni(II)} > \text{Cu(II)}$. Das and De³⁹³ reported that complexes of the type $\text{Co}(\text{N}_4)\text{CO}_3^+$ catalyze the reduction of nitrobenzene by NaBH_4 , and this activity was ascribed to the different oxidation state in which cobalt is capable of existing.

Many systems have been reported in which CO_2 or CO_3^{2-} exhibit catalytic properties in a variety of reactions. For instance, CO_2 was found to catalyze the exchange of oxygen with $\text{Cr}(\text{NH}_3)_5\text{OH}^{2+}$ in aqueous solutions,³⁹⁴ and the rate law was of the form



At 25 °C and an ionic strength of 0.1 M, $k_{22} = 6.3 \times 10^{-5} \text{ s}^{-1}$, $k_{23} = 17 \times 10^{-5} \text{ s}^{-1}$, and $k_{24} = 7 \text{ M}^{-1} \text{ s}^{-1}$. A mechanism involving the formation of a carbonato-Cr(III) complex followed by quite rapid scrambling of the oxygen atoms was suggested to account for the obtained data. Similarly, substitution of $\text{Cr}(\text{ox})_3^{3-}$ by edta was found³⁹⁵ to be catalyzed by HCO_3^- , and the formation of intermediate carbonato complexes was suggested (see subsection C).

The ability of HCO_3^- to donate or accept protons has been considered to be responsible for its catalytic effects

in a number of reactions. For instance, the reaction between Cr(III) and edta is suggested³⁹⁶ to involve proton acceptance by HCO_3^- ; the catalytic effect of HCO_3^- during the complexation of Cr(III) with some aminopolycarboxylic acids was ascribed³⁹⁷ to the enhancement of the deprotonation rate of the ion-pair intermediate, since HCO_3^- is a more effective Lewis base; the transfer of a proton from HCO_3^- to Ni(H₂DGEN) is considered to account for the catalytic effect during the substitution reaction of the Ni(II) complex with edta (DGEN = *N,N'*-diglycylethylenediamine).³⁹⁸ Ion-pair formation, in addition to the proton donation/acceptance phenomenon, was suggested to account for the catalytic effects of HCO_3^- and CO_3^{2-} in the intramolecular hydrolysis of glycinamide and glycine dipeptides coordinated to Co(III).³⁹⁹ In one study, such ion-pair formation was found to retard the base hydrolysis of $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}^{2+}$.⁴⁰⁰

It is apparent from the overall discussion and data presented in this section that the kinetic systems discussed are well understood and there is little need to pursue such investigations much further. Unresolved questions do remain in the application of similar processes in the geochemical and biochemical fields (see sections XII and XIII).

The Chemistry of Metal-Carbon Dioxide Complexes

In the previous sections we have dealt with the chemistry of metal carbonato complexes. These were mainly produced via CO_2 uptake by metal hydroxo species, during which the metal-oxygen bond remained intact. In this section we summarize the chemistry of metal-carbon dioxide complexes in which CO_2 interacts directly with the metal center during either a fixation or insertion process.

It is generally accepted that little is known about the reactions of CO_2 with transition-metal compounds, and their role in the reduction of CO_2 .⁴⁰¹⁻⁴⁰⁴ The interest in the potential chemistry of CO_2 has been stimulated by the search for alternative petrochemical feedstocks,⁴⁰⁵⁻⁴⁰⁷ and the investigation of the water-gas shift reaction.⁴⁰⁴ In this respect CO_2 is the largest carbon source in the world:^{401,408} ca. 330 ppm, i.e., 2.3×10^{12} tons in the atmosphere,⁴⁰⁹ which is expected to increase during the coming years.^{6,8,410-412} CO_2 has some important functional properties⁴⁰¹ (carbon is a Lewis acid and oxygen a Lewis base) that influence its coordination to metal centers.^{408,413-415} In general, coordination activates ligands and creates favorable steric conditions for ligand interactions and numerous catalytic processes (ref 401, 404, 405, 408, 415-418). Questions that arise⁴⁰¹ are: does CO_2 coordination agree with real activation; what bonding modes are possible; what reaction routes do the different bonding modes prefer; are these influenced by the nature of the metal complex?

Some excellent reviews (ref 3, 401, 406, 408, 413, 414, 419, 420) have appeared in the literature, describing the reactions of transition-metal- CO_2 complexes. We, therefore, do not intend to give a complete survey of this topic, but rather to summarize those aspects of this field that bear on the chemistry of metal carbonato complexes. In the coming sections we will differentiate between fixation and insertion processes, although it is not always possible to distinguish between them

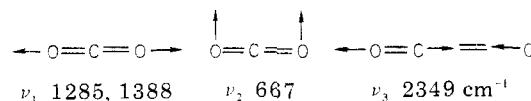
completely since many insertion reactions proceed via a "fixation" intermediate. Furthermore, many systems are described as fixation processes, but really involve insertion reactions.^{416,421-423} It follows that this differentiation is somewhat artificial, and we therefore classify all processes in which CO_2 is bound directly to the metal center as fixation, and those in which CO_2 is bound via the breakage of a metal-ligand or internal ligand bond, as insertion. In this sense CO_2 uptake by metal hydroxo complexes, as described in the previous section, can also be classified as an insertion reaction. However, for such uptake processes it was illustrated that the metal-oxygen bond remains intact, in contrast to the reactions reported in the forthcoming subsection on insertion processes.

IX. Preparation and Characterization

When reviewing the literature on metal- CO_2 complexes, one immediately realizes that fairly simple synthetic procedures are usually employed. These vary from bubbling CO_2 into a solution of the metal compound^{403,413,424} to heating the complex in an autoclave under a CO_2 pressure of 10–15 atm.^{405,425} Usually a CO_2 atmosphere^{402,415,426} or a solvent saturated with CO_2 ^{405,427,428} satisfies the required conditions for effective synthetic work. In some cases^{413,429} metal- CO_2 complexes are prepared via the oxidation of a carbonyl ligand by oxygen. Alternatively, CO can sometimes be used to synthesize CO_2 complexes.

Characterization of metal- CO_2 complexes and CO_2 insertion products is usually done with IR and NMR spectroscopy. For some crystalline species, X-ray structure analyses were performed. To our knowledge the structures of two metal- CO_2 complexes have been resolved, viz. $[\text{Ni}(\text{CO}_2)\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2] \cdot 0.75\text{MePh}$ ⁴³⁰ and $[\text{Co}(\text{pr-salen})(\text{CO}_2)\text{K}(\text{THF})]_n$ ⁴³¹ (pr-salen = *N,N'*-ethylenabis(salicylideneaminato)). In the former, CO_2 is coordinated to the metal center in a η^2 mode, whereas in the latter species CO_2 is coordinated via the carbon atom to the Co(I) center. Numerous structures of CO_2 insertion products have been determined,^{402,403,432-440} and these will be referred to in more detail in the section on CO_2 insertion reactions.

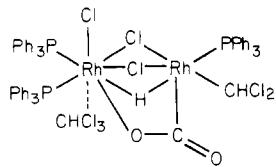
IR data have contributed significantly towards the characterization of metal- CO_2 complexes, and a summary of typical CO_2 vibrations in such complexes is given in Table XXXVIII. These can generally³ be ascribed to $1500-1700\text{ cm}^{-1}$ for $\nu_{\text{OCO}}^{\text{as}}$; $1200-1400\text{ cm}^{-1}$ for $\nu_{\text{OCO}}^{\text{s}}$; around 1750 cm^{-1} for $\nu_{\text{C=O}}$; around 1150 cm^{-1} for $\nu_{\text{C-O}}^{\text{as}}$; $1750-1900\text{ cm}^{-1}$ for $\text{M}-\pi(\text{CO}_2)$; and around 820 cm^{-1} for $\nu_{\text{C-O}}^{\text{s}}$. In comparison, it should be kept in mind that gaseous CO_2 is a linear $D_{\infty h}$ triatomic molecule with three fundamental modes of vibration⁴⁴¹



These are referred to as symmetric (ν_1) and asymmetric (ν_3) CO stretching modes, and ν_2 as the degenerate CO deformational mode (see section IIA).

In some cases NMR spectroscopy could be applied with success to elucidate the structure of metal- CO_2 complexes. Karsch⁴¹⁵ reported the application of ¹H and ³¹P NMR to determine the structure of $\text{Fe}(\text{PMe}_3)_4\text{CO}_2$ and $\text{Fe}(\text{PMe}_3)_3(\text{PMe}_2\text{CH}_2\text{CO}_2)$. In another

study, Yamaguchi⁴⁰⁹ reported the ¹H NMR signals for the complex.

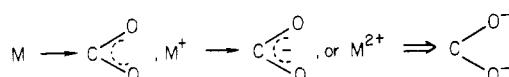


NMR spectroscopy has been used for the characterization of numerous CO₂ insertion products, and these will be referred to in more detail in the appropriate subsection.

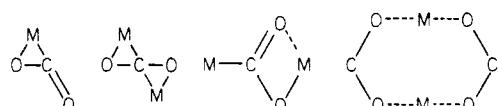
X. Carbon Dioxide Fixation Reactions

In general there is a paucity of information concerning CO₂ fixation reactions and other metal-promoted transformations,^{402,442} although simple CO₂ addition is assumed to be the first step in a number of reactions.^{408,413,414,427,443-446} Metal basicity is an important prerequisite to M-CO₂ formation.⁴³¹ Highly basic Ir(I),^{405,427} Rh(I),⁴⁴⁷ and Ni(0)^{426,430} complexes have been found to cause CO₂ activation. In several cases, CO₂ seems to require a bifunctional system, i.e., acid-base, for its fixation and activation.^{402,448} Therefore, in addition to the basic metal center, the assistance of an acidic partner is required.⁴³¹ A new class of CO₂ reversible carriers, which contain CO₂ intact and closely approach the requirements of a bifunctional system was recently discovered.^{402,431} In addition to the above-quoted examples, reactions of CO₂ with transition-metal complexes have resulted⁴⁰⁸ in the formation of metal CO₂ species,^{406,414,449,450} which will be discussed in more detail in this section.

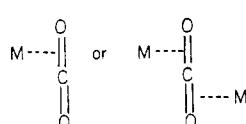
Various bonding modes of CO₂ to the metal M must be considered:^{3,406,409,413,419} M-C bonding through electron donation from the metal,



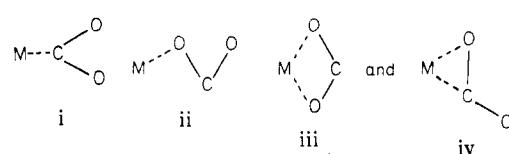
M-O bonding through transfer of the oxygen p electrons to the metal, M ← :O=C=O, M ← :O=C=O:→ M,



or complex formation.



In a theoretical study,⁴⁵¹ four models for M-CO₂ bonding modes were considered.



MO LCAO calculations in the CNDO/2 approximation illustrate that model ii is least favorable and that model iv is most favorable. This prediction is in good agree-

ment with the recent structural observations on two metal-CO₂ complexes.^{430,431}

We now turn to a detailed discussion of CO₂ fixation reactions, and will subdivide the following subsections according to the central metal atoms. By far the most CO₂ fixation studies were performed on Rh and Ir complexes, with fewer on Cu and Ni, and very few on the remaining metals.

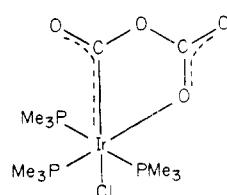
A. Rh-CO₂ Complexes

In the solid phase *trans*-Rh(PPh₃)₂(OH)(CO) reacts with CO₂ gas to form Rh(PPh₃)₂(OH)(CO)CO₂, which loses CO₂ at reduced pressures.^{452,453} Although the exact mode of coordination of CO₂ was not known at that stage, the investigators⁴⁵² found that on dissolution in methanol or acetone a bicarbonato species is produced, viz., Rh(PPh₃)₂(CO)OCO₂H. Later investigators⁴⁵⁴ believed that the suggested change in coordination number (from 4 to 5) during the CO₂ fixation process is unreal and argue in favor of the direct formation of a bicarbonato complex, which would then be a typical insertion product. However, very recent studies report the formation of five-coordinate Rh-CO₂ complexes of the type Rh(Cl)L₃CO₂ and Rh(X)L₄CO₂ (L = phosphine or arsine, X = Cl or Br),⁴⁰¹ and Rh(Cl)(PNP)CO₂ (PNP = 2,6-bis((diphenylphosphino)methyl)pyridine).^{428,455}

Evidence for the formation of bridged CO₂ complexes has also been reported. Iwashita and Hayata⁴²⁹ found that Rh₂(CO)₄(PPh₃)₄ is easily oxidized by molecular oxygen to form Rh₂(CO)₂(CO₂)(PPh₃)₃L_n (L = benzene, toluene, *o*-, *m*-, and *p*-xylene or mesitylene). Similar products were found by Vol'pin and co-workers,⁴⁵⁶ where [(PPh₃)Rh(CO)₂]₂·C₆H₆ was found to react with CO₂ in the presence of PPh₃ in benzene to produce (PPh₃)₃Rh₂(CO)₂(CO₂)₂C₆H₆. When air was passed through a benzene solution of this complex, CO₂ was released and (PPh₃)₃Rh₂(CO)₂(CO₂)C₆H₆ was produced, in agreement with the above species proposed by Vol'pin et al.⁴²⁹ In another study,⁴⁵⁷ it was found that CO₂ reacted with Rh(H)(PPh₃)₄ in toluene to produce Rh₂(H)₂(PPh₃)₆(CO₂)·toluene, which released CO₂ when heated to 200 °C. Finally, Yamaguchi⁴⁰⁹ showed that (PPh₃)₃RhCl reacted with CO₂ in CHCl₃ to produce (PPh₃)₃Rh₂(Cl)(μ-Cl)₂(μ-H)(μ-CO₂)·CHCl₃, which could easily be converted to (PPh₃)₃Rh₂(Me)(Cl)₃(μ-Cl)₂(μ-H)(μ-CO₂).

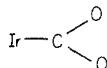
B. Ir-CO₂ Complexes

A series of Ir-CO₂ complexes have been reported in the literature that were prepared and characterized in a similar way as the corresponding rhodium complexes. These include Ir(PPh₃)₂(OH)(CO)CO₂^{452,453} or Ir(PPh₃)₂(CO)OCO₂H,⁴⁵⁴ and a series of complexes of the type Ir(Cl)L₃CO₂ and Ir(X)L₄CO₂⁴⁰¹ (see Rh-CO₂ section for abbreviations). A very interesting CO₂ fixation reaction was reported⁴²⁷ for the species Ir(Cl)(PM₃)₃(C₈H₁₄), which produces a novel CO₂ adduct with the structure:



It was suggested that stepwise uptake of CO₂ occurred and that Ir(Cl)(PMe₃)₃CO₂ is the reaction intermediate. Thermal decomposition of Ir(Cl)(PMe₃)₃(C₂O₄) resulted in the formation of a carbonyl complex and a 1:1 Ir:CO₂ adduct. It was further suggested⁴²⁷ that the formation of Mo₂(PMe₂Ph)₆(CO)₂(CO₃)₂ from *cis*-Mo(N₂)₂(PMe₂Ph)₄ and CO₂⁴⁴⁵ may involve a similar mechanism as outlined above.

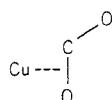
The importance of the basicity of the metal center was stressed by Bianco et al.,⁴⁵⁸ who investigated the reaction of a series of Ir(I) and Ir(III) complexes with CO₂. They found that neither five- nor six-coordinated complexes reacted with CO₂, but that the more basic four-coordinated Ir(I) species produced CO₂ adducts from the species Ir(OH)(CO)(PPh₃)₂,⁴²⁷ Ir(L-L)₂Cl (L-L = Me₂PCH₂CH₂PMe₂, Et₂PCH₂CH₂PEt₂)⁴⁰⁵ and Ir(Cl)(PMe₃)₃(C₅H₁₄).^{427,459} Herskovitz⁴⁰⁵ also reported a series of CO₂ adducts with Ir(I) complexes of the type Ir(dmpe)₂Cl·CO₂ (dmpe = Me₂PCH₂CH₂PMe₂) and Ir(diars)₂Cl·CO₂ (diars = *o*-phenylenebis(dimethylarsine)). The dmpe complex was found to dissolve in acetonitrile, acetone, and methylene chloride with liberation of CO₂. IR data are such that they favor an



bonding mode. Recently, the possible formation of complexes with CO₂ by the action of Lewis acids on Ir(PPh₃)₂(CO)₂COOCH₃ was reported.⁴⁶⁰

C. Cu-CO₂ Complexes

Quite some interest has been shown for the reversible CO₂ fixation by amino complexes of Cu(II). In earlier publications,^{461,462} the formation of Cu(Eph)₂CO₂ (Eph = ephedrine) was reported. Later work⁴⁶³ demonstrated that CO₂ formed an adduct with ephedrine, viz. (Eph)CO₂. IR and X-ray photoelectronic spectra⁴⁶³ suggested that CO₂ entered into the coordination sphere of copper, that it was present in the bent form, probably



and that it formed an intramolecular hydrogen bond with the protons on Eph. A later ESR study⁴⁶⁴ indicated that unstable carbamato structures are formed with reversible binding of CO₂. It attaches to Eph⁻ via the N-H bond to form a carbamate structure,⁴⁶⁵ in contrast to the earlier claim^{461,466} that CO₂ binds to the copper center.

For the reaction of CH₃Cu^IP(C₆H₁₁)₃ with CO₂,⁴²⁴ the formation of an insertion product CH₃COOCuP(C₆H₁₁)₃ and an adduct CH₃COOCu(CO₂)P(C₆H₁₁)₃ was reported. The latter species released CO₂ when heated to 150 °C. In another study,⁴⁵⁰ RCu(PPh₃)₂ (R = Me, Et, *n*-Pr, *i*-Bu) was observed to react with CO₂ to produce an insertion/adduct product (RCOO)Cu(CO₂)(PPh₃)₂. Evidence for the formation of Cu₂(CO₂)(PPh₃)₄, where CO₂ is the bridging ligand, was also reported.⁴⁵⁰

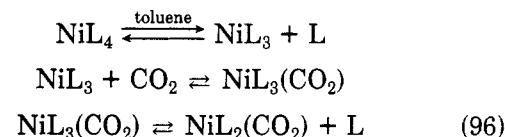
D. Ni-CO₂ Complexes

It is generally known that Ni(0) forms stable CO₂ complexes.^{434,467} The first structure ever to be reported for a metal-CO₂ complex was for Ni(PCy₃)₂(η²-CO₂).⁴³⁰

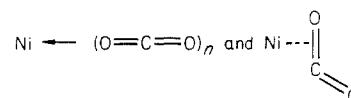
Later work⁴²⁶ established that a common reaction could account for their formation, viz.



for L = PEt₃, PBu-*n*₃ and P(C₆H₁₁)₃.⁴³⁰ The suggested mechanism⁴²⁶ is



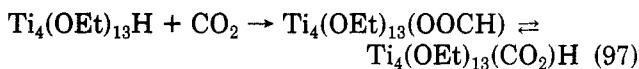
Some matrix isolation experiments⁴¹⁶ demonstrated that two types of Ni-CO₂ complexes could be detected, viz.



Other studies indicated the possibility that CO₂ could act as a bridging ligand in Ni complexes.^{450,467}

E. Other Metal-CO₂ Complexes

We will now present some information on the interaction of CO₂ with a wide range of metal clusters. Complexes of the type M(CH₂Ph)₄ (M = Ti, Zr) were found⁴²⁵ to absorb 2 mol of CO₂ per mole of complex. Such fixation of CO₂ can proceed via an insertion process as found for

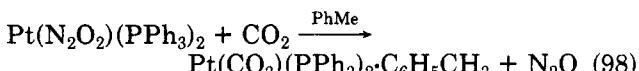


The latter equilibrium has also been suggested for the formation of Ru(H)(CO₂H)(PPh₃)₃^{408,443,468} and Re(H)(CO₂)(Ph₂PCH₂CH₂PPh₂)₂.⁴⁶⁹

The Na(C₅H₅)Fe(CO)₂ complex was found to undergo rapid CO₂ uptake in THF, followed by conversion (oxidation) to produce [(C₅H₅)Fe(CO)₂]₂, with the possibility that an adduct of the type (C₅H₅)Fe(CO)₂CO₂ is produced as an intermediate. A solution of Co(pr-salen)Na (see Table XXXVIII) was found⁴⁷⁰ to react with CO₂ in THF to produce Co(pr-salen)(CO₂)Na, which loses CO₂ in vacuo. In the presence of pyridine a substance (py)Co(pr-salen)(CO₂)Na is produced. The X-ray structure of a very similar Co species was reported⁴³¹ (see earlier discussion). In these reactions it is possible that Na⁺ acts as a Lewis acid in a concerted acid-base attack on CO₂ with Co(I) as the other partner.

One example exists in the literature⁴⁷¹ where a Ag complex, viz., C₆H₅Ag·nAgNO₃, reacts with CO₂ in EtOH to produce C₆H₅Ag(CO₂)Ag. In another study⁴⁷² silver atoms were found to react with CO₂ at 10–25 K to produce Ag(CO₂). Infrared, Raman, UV-visible spectroscopy and various molecular orbital calculations are in favor of an asymmetrically side-on bonded CO₂ complex, similar in nature to that reported⁴³⁰ for the Ni(CO₂)₂{P(C₆H₁₁)₃}₂ complex.

The Pt(N₂O₂)(CO₂)(PPh₃)₂ complex was suggested⁴⁷³ to be the intermediate in the reaction

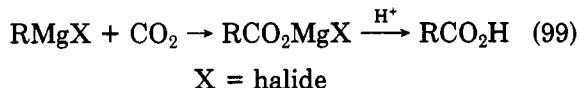


Theoretical predictions by Sakaki et al.⁴⁷⁴ employing a CNDO-type semiempirical SCF-MO method lead to the conclusion that for Pt(0) complexes of the type Pt(PPh₃)₂L (L = C₂H₂, C₂H₄, CS₂, CO₂) the s orbital

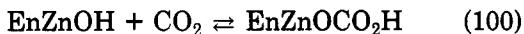
of L contributes substantially to the Pt-L interaction, which suggests a large three-membered-ring type of interaction between Pt and L.

XI. Carbon Dioxide Insertion Reactions

In contrast to N₂, CO₂ is rather reactive and can undergo insertion into a series of metal-ligand bonds.^{413,414,442} The most common insertion reaction is found in the preparation of organic acids via the Grignard reagent (eq 99).⁴⁷⁵ In this reaction the metal-

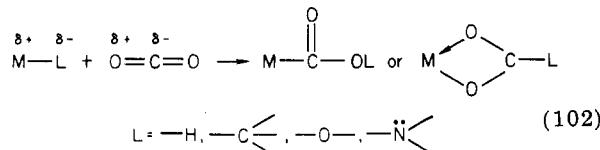
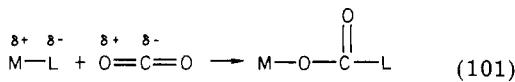


carbon bond ($Mg-R$) is broken and CO_2 is inserted. Similar results have been observed with SO_2 . Such insertion reactions play an important role in various catalytic processes. By analogy, the catalysis of CO_2 hydration⁴⁰¹ by the enzyme carbonic anhydrase, which is postulated to involve eq 100 (see section XIII) may

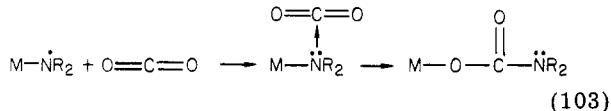


be considered as a CO₂ insertion reaction, at least superficially.

In general, two possible insertion reactions can occur, depending on the nature of the metal-ligand bond^{3,406,419}



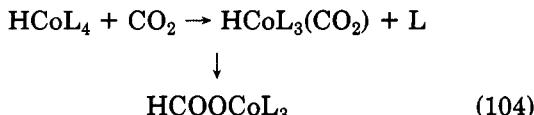
In many systems insertion is preceded by a fixation step, e.g.



The following presentation is subdivided according to the type of metal-ligand bond involved in the insertion reaction.

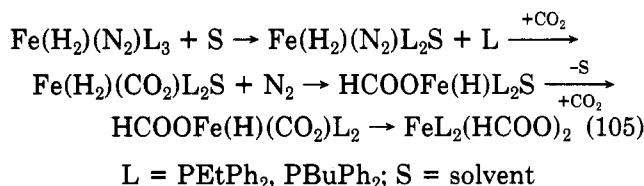
A. Insertion into M-H Bonds

A large number of papers has been published in recent years (ref 271, 403, 415, 419, 435, 442, 444, 476, 477) that stress the significance of CO₂ insertion reactions into M-H bonds. This aspect has also been covered by a number of review articles.^{406,408,413,414,449} A summary of the different insertion reactions for various metal centers is given in Table XXXIX. The formation of cobalt-formato complexes has been suggested⁴²¹ to involve a CO₂ fixation step for different ligands L.

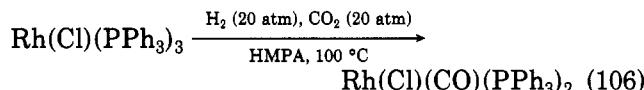


The species $\text{HM}(\text{CO})_5^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) are the most prominent intermediates in the water-gas shift reaction. These react with CO_2 to produce formate species,⁴⁰⁴ and therefore compete with bicarbonate complex formation.

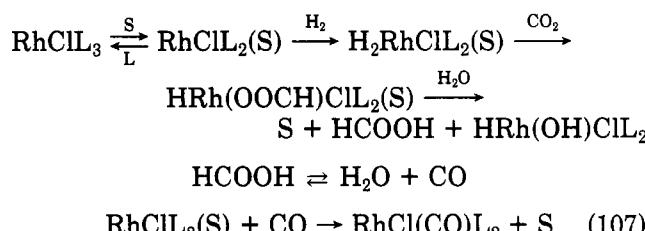
Insertion of CO₂ into the Fe-H bond was suggested²⁷¹ to occur via a fixation step:



It was reported⁴⁸⁰ that a rhodium-carbonyl complex is formed via CO₂ insertion into a Rh-H bond. The overall reaction is

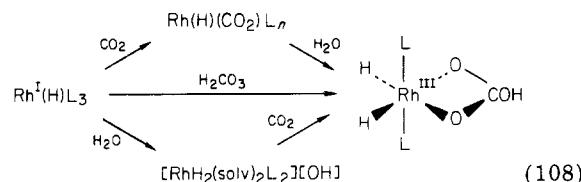


and the suggested generalized mechanism can be formulated as



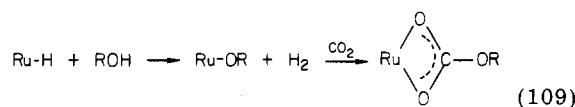
L = PPh₃; S = HMPA = hexamethylphosphoramide

Ibers et al.⁴⁰³ could not detect any formato product (insertion of CO₂) during the reaction of Rh(H)L₃ (L = P(i-Pr)₃, PPh(t-Bu)₂, P(C₆H₁₁)₃) with CO₂. A bi-carbonato product was isolated, viz., (H)₂RhL₂(O₂COH), and the structure was determined for L = P(i-Pr)₃. Three possible reaction routes were suggested.



Which route dominates will depend on the experimental conditions. It was found⁴⁰³ that the product is stable towards reductive elimination, and instead reduces CO₂ to give Rh^I(CO)(O₂COH)L₂. This step probably proceeds by CO₂ insertion leading to either Rh(H)(CO₂-H)(O₂COH)L₂ or Rh(H)(O₂CH)(O₂COH)L₂, after which elimination of H₂O completes the reaction. The authors⁴⁰³ stress the fact that no reaction between Rh(I)-hydride complexes and CO₂ occurs when H₂O is excluded.

Ashworth and Singleton⁴⁸¹ reported the formation of a bidentate carbonato complex $[\text{Ru}(\text{O}_2\text{COR})_2(\text{PMe}_2\text{Ph})_4]\text{PF}_6$ in the reaction of $[\text{Ru}(\text{H})(\text{PMe}_2\text{Ph})_5]\text{PF}_6$ with CO_2 in MeOH or EtOH. They suggest the following mechanism based on NMR and IR data.



B. Insertion into $M-C$ Bonds

Various review papers (ref 406, 408, 413, 414, 419, 449) have treated typical CO₂ insertion reactions into

TABLE XXXIX. Insertion of CO₂ into M-H Bonds

metal center	reactant	product (P)	comments	ref
Co	H(N ₂)Co(PPPh ₃) ₃	P $\xrightarrow{\text{CH}_3\text{I}}$ HCOOCH ₃	408, 413, 414, 421, 478, 479	
	H(N ₂)Co(PPPh ₃) ₃	P $\xrightarrow{\text{CH}_3\text{I}}$ CH ₃ COOH + CH ₃ COOCH ₃	408, 413, 414	
	H ₃ Co(PPPh ₃) ₃	P $\xrightarrow{\text{CH}_3\text{I}}$ HCOOCH ₃	408, 421, 479	
	HCOOC ₂ Co(PPPh ₃) ₃	IR absorptions at 1610 and 1370 cm ⁻¹ for coordinated formate	421	
	HCOOC ₂ Co(PPh ₂ Et) ₃		421	
	HCOOC ₂ Co(PPh ₂ Et) ₃		421	
	HCOOC ₂ Co(PPh ₂ Et) ₃		421	
	HCOOC ₂ Co(PPh ₂ Et) ₃		421	
	HCOOC ₂ Cr(CO) ₅	IR and NMR evidence for formate species	404	
Cu	(HCluPPPh ₃) ₂	same product from Cu/formic acid reaction	a	
Fe	Fe(H ₂)L' L, L' = H ₂ , N ₂ , L = PEtPh ₂	(HCOO) ₂ FeL ₂	b	
	Fe(H ₂)L' L, L' = PEtPh ₂ , PBuPh ₂	(HCOO) ₂ FeL ₂	c	
	Rh(H)(PPPh ₃) _n , n = 3, 4	Rh ₂ (O ₂ CO)(PPPh ₃) ₅	do not react with CO ₂	
Rh	Ru(H ₂)(PPPh ₃) ₄ or Ru(N ₂)(H ₂)(PPPh ₃) ₃ or Ru(H ₂)(PPPh ₃) ₃	Ru(CO ₂ H)(H)(PPPh ₃) ₃	H ₂ O participates in the reaction	500
Ru	RuH ₂ (PPPh ₃) ₄ [Ru(H)(PMc ₂ Ph) ₅]PF ₆ HSiMeEt ₂	(HCOO)Ru(H)(PPPh ₃) ₃ ·C ₆ H ₅ CH ₃ [Ru(O ₂ COR)(PMc ₂ Ph) ₄]PF ₆ , R = Me, Et	IR evidence for formato species	433
Si		reaction in toluene reaction in MeOH or EtOH in the presence of RuCl ₂ (PPh ₃) ₃ , RuH ₂ (PPh ₃) ₃ , or Pd(PPh ₃) ₄ as catalyst	443, 457, d 481 e	

^a Beguin, B.; Denise, B.; Sneeden, R. P. A. *J. Organomet. Chem.* 1981, 208, C18. ^b Bianco, V. D.; Doronzo, S.; Rossi, M. J. *Inorganomet. Chem.* 1972, 35, 337. ^c Bianco, V. D.; Doronzo, S.; Gallo, N. *Inorg. Nucl. Chem. Lett.* 1980, 16, 97. ^d Komiya, S.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* 1976, 49, 784. ^e Koinuma, H.; Kawakami, F.; Kato, H.; Hirai, H. *J. Chem. Soc., Chem. Commun.* 1981, 213.

TABLE XL. Insertion of CO₂ into M-C Bonds

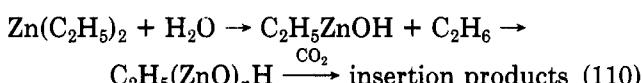
metal center	reactant	product (P)	comments	ref
Al Co	AlEt ₃ (PPh ₃) ₂ Co(CO)·C ₂ H ₅ (PPh ₃) ₃ Co(N ₂)H + H ₂ C = CHCHO CH ₃ Cu(PPh ₃) ₂ ·0.5Et ₂ O CH ₃ CuP(C ₆ H ₁₁) ₃ PhC≡CCu·(PBu-n ₃) ₂ RCuL _n	Et ₂ AlO ₂ CET (Ph ₃ P) ₂ Co(CO ₃) _n (COOC ₂ H ₅) _n (Ph ₃ P) ₂ Co(OCOC ₂ H ₅) ₂ (Ph ₃ P) ₂ Co(CO ₃) _n (COOC ₂ H ₅) _n (Ph ₃ P) ₂ Co(OCOC ₂ H ₅) ₂ (CH ₃ COO) ₂ Cu(PPh ₃) ₂ (CH ₃ COO) ₂ CuP(C ₆ H ₁₁) ₃ PhC≡CCO ₂ Cu·(PBu-n ₃) ₂ (RCOO) ₂ Cu(PPh ₃) ₂	P $\xrightarrow{\text{AlEt}_3}$ Et ₂ AlOAlEt ₂ + Et ₃ COAlEt ₂ CO ₂ is released upon acidification	475 488
Cu	L _n = (PPh ₃) ₃ ; (PPh ₃) ₂ ·0.5Et ₂ O; R = Me L _n = (PPh ₃) ₃ ; R = Et L _n = (PPh ₃) ₂ ; R = n-Pr, i-Bu	IR spectra characteristic for formulated products	487	
Fe	NCCH ₂ Cu·(PBu-n ₃) _x HFeCH ₂ CN(dmpe) ₂ , dmpe = Me ₂ PCH ₂ CH ₂ PM ₂	NCCH ₂ CO ₂ Cu·(PBu-n ₃) _x HFe(OOCCH ₂ CN)(dmpe) ₂	IR typical of acetate complex P obtained along with CO ₂ adduct process is reversible all species identified as Cu(I) carboxylates from IR and NMR data	489 424 422 450
Ir Mn	[Ir(PMe ₃) ₄]Cl Ph ₂ MnPCy ₃	[Ir(H)(O ₂ CCH ₂ CN)(PMe ₃) ₄]Cl (PhCOO) ₂ MnPCy ₃	process is reversible reaction performed in CH ₃ CN P $\xrightarrow[\text{BF}_3]{\text{CH}_3\text{OH}}$ NCCH ₂ COOME	490 485
Ni	Ni(C ₂ H ₅) ₂ bpy (bpy)Ni(C ₂ H ₅) ₂ (O ₂ CC ₂ H ₅) Ni(<i>n</i> ³ -2-CH ₃ C ₃ H ₄) ₂	(bpy)Ni(C ₂ H ₅) ₂ (O ₂ CC ₂ H ₅) Ni(bpy)(O ₂ CC ₂ H ₅) ₂ <i>n</i> ³ -2-CH ₃ C ₃ H ₄ Ni(OCOC ₄ H ₇)PR ₃	P $\xrightarrow{\text{CO}_2}$ Ni(bpy)CO ₃	482 482
Pd	(<i>n</i> ¹ , <i>n</i> ³ -C ₃ H ₅) ₂ Pd(PR ₃), R = CH ₃ , C ₆ H ₁₁	dimer and tetramer of (C ₆ H ₁₁) ₂ PNiC ₈ H ₁₂ CO ₂	X-ray structure determined for both products	434
Rh	(Ph ₃ P) ₃ RhPh	(Ph ₃ P) ₃ RhOOCPh	crystals of (Ph ₃ P) ₃ RhOOCPh·0.5C ₆ H ₆ were isolated	439
	(C ₆ H ₅)Rh(L-L), L-L = Ph ₂ PCH ₂ CH ₂ PPh ₂	(L-L)Rh(O ₂ C-C ₆ H ₅)	IR data suggest that the benzoate group is bidentate	d, e
Ti	(C ₅ H ₅) ₂ Ti (C ₅ H ₅) ₂ Ti	(C ₅ H ₅) ₂ Ti (C ₅ H ₅) ₂ Ti	structure confirmed by x-ray analysis ⁴³⁷	413, 437
		(C ₅ H ₅) ₂ Ti (C ₅ H ₅) ₂ Ti	formed in excess CO ₂	408, 413
	Ti(CH ₂ Ph) ₄	(CH ₂ Ph) ₃ Ti(O ₂ CCH ₂ Ph)	P $\xrightarrow{\text{H}^+}$ PhCH ₂ COOH	408, 425
	(C ₅ H ₅) ₂ Ti(CH ₃) ₂	(C ₅ H ₅) ₂ (CH ₃)Ti(O ₂ CCH ₃)	P $\xrightarrow[\text{HCl}]{\text{CH}_3\text{OH}}$ CH ₃ COOCH ₃	408, 425
Zn	(<i>n</i> ⁵ -C ₅ H ₅) ₂ Ti(<i>n</i> ³ -C ₄ H ₇) ₂ CH ₃ OZnOCH ₃	(<i>n</i> ⁵ -C ₅ H ₅) ₂ Ti(O ₂ C-2-C ₄ H ₇) ₂ CH ₃ OZnOCO ₂ CH ₃	P $\xrightarrow{\text{HCl}}$ 2-methyl-3-butenoic acid	f 491

^a English, A. D.; Herskovitz, T. *J. Am. Chem. Soc.* 1977, 99, 1648. ^b Maruyama, K.; Ito, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* 1979, 52, 849. ^c Hung, T.; Jolly, P. W.; Wilke, G. *J. Organomet. Chem.* 1980, 190, C5. ^d Albano, P.; Aresta, M.; Manassero, M. *Inorg. Chem.* 1980, 19, 1069. ^e Albano, P.; Aresta, M.; Manassero, M. *Cong. Naz. Chem. Inorg.* 1979, 83. ^f Sato, F.; Igima, S.; Sato, M. *J. Chem. Soc., Chem. Commun.* 1981, 180.

M-C bonds. Other authors (ref 403, 415, 419, 435, 442, 476, 477, 482) have especially stressed the significance of such reactions, which sometimes only occur as intermediate steps.^{425,483} In a number of cases the reactions involve preliminary coordination of CO₂, followed by insertion^{450,471,484,485} to produce a variety of products.⁴⁸⁶ We summarize examples of these reactions in Table XL and make some comments concerning the chemistry involved.

Insertion of CO₂ into Co-C bonds follows two modes in which carboxylate and M-COOR fragments are formed.^{487,488} By far the most M-C insertion reactions have been reported for copper complexes (see Table XL). The formation of acetate complexes via CO₂ insertion could be indicated by the isolation of similar products in the reaction with acetic acid.⁴⁸⁹ In two cases, reversible insertion reactions occur with Cu complexes.^{422,490} Similar reactions to those reported for

Ni(C₂H₅)₂bpy⁴⁸² were found for the corresponding dimethyl complex. During the copolymerization of CO₂, the reaction of the Zn catalyst with CO₂ occurred in the following manner.⁴⁹¹



C. Insertion into M-N Bonds

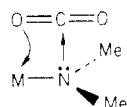
Relatively few systems have been presented where CO₂ insertion into M-N bonds occurs.^{403,406,414,435,442,449} Representative examples are summarized in Table XLI. The most significant contribution in this area comes from Chisholm and Extine.^{423,438,440,492-494} They isolated a series of carbamato complexes and determined the structure of some with X-ray diffraction data.^{438,440,493} An interesting aspect reported by these authors is that

TABLE XLI. Insertion of CO₂ into M-N Bonds^a

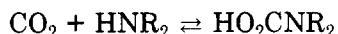
metal center	reactant	product (P)	comments	ref
Ti, V, Zr	M(NMe ₂) ₄	M(O ₂ CNMe ₂) ₄		423, 492, a
Ti	Ti(NMe ₂) ₄	Ti(NMe ₂) _n (O ₂ CNMe ₂) _{4-n}	X-ray structure of P for n = 2	493
Nb, Ta	M(NMe ₂) ₅	M(O ₂ CNMe ₂) ₅	X-ray structure of Nb(O ₂ CNMe ₂) ₅	423, 440, 492
W	W(NMe ₂) ₆	W(NMe ₂) ₃ (O ₂ CNMe ₂) ₃	X-ray structure of P	438
	W ₂ (NMe ₂) ₆	W ₂ (O ₂ CNMe ₂) ₆		494
	W ₂ (NMeEt) ₆	W ₂ (O ₂ CNMeEt) ₆		494
Mo	Mo ₂ (NMe ₂) ₆	Mo ₂ (NMe ₂) ₂ (O ₂ CNMe ₂) ₄	based on NMR evidence	b
	Mo ₂ (NMe ₂) ₂ (CH ₂ SiMe ₃) ₄	(Me ₂ N)(Me ₂ NCO ₂)Mo ₂ (CH ₂ SiMe ₃) ₄	based on NMR evidence	c
Hf	Me ₂ Hf[N(SiMe ₃) ₂] ₂	Me ₂ Hf[O ₂ CN(SiMe ₃) ₂]	based on IR and NMR evidence	d
Mg	(THF) ₃ Cl ₂ Mg ₂ MN, M = Ti, V	(THF) ₃ Cl ₂ Mg ₂ OM(NCO)	reaction in THF	495, e
Pd	PdMe ₂ L ₂ , L = PET ₃ , PMePh ₂ , PPh ₃	PdMe(O ₂ CNR ¹)L ₂ , R = H, Et; R ¹ = Ph, Et, n-Bu, CH ₂ Ph	Pd ₂ Me ₂ (μ-CO ₂)(PPh ₃) ₃ was isolated on heating corresponding P in toluene	f
P	P(NMe ₂) _n X _{3-n} , X = Cl, F	P(O ₂ CNMe ₂) _n X _{3-n}	characterized by IR and NMR	496
U	(C ₅ H ₅) ₂ UIV(NEt ₂) ₂	(C ₅ H ₅) ₂ U(O ₂ CNET ₂) ₂	characterized by IR and NMR	497

^a See footnotes in Table XLII.

all the observed species are labile towards CO₂ exchange.^{423,494} The complexes ML_n* (n = 4, 5—see Table XLI), W₂L₆*, and W(NMe₂)₃L₃* (L = O₂¹²CNMe₂, L* = O₂¹³CNMe₂) react with ¹²CO₂ to give ML_n, W₂L₆, and W(NMe₂)₃L₃. It was found that mixtures of ML_n and ML_n* scramble CO₂ in the presence of a CO₂ atmosphere.^{423,492} A plausible mechanism was suggested to be^{423,440} M(O₂CNMe₂)_n ⇌ M(O₂CNMe₂)_{n-1}(NMe₂) + CO₂ for which NMR evidence was presented for M = Nb.⁴⁴⁰ Further evidence comes from mechanistic studies⁴⁹³ in which the stepwise formation of such carbamato complexes could be observed and various models for CO₂ exchange were suggested. These insertion reactions differ from the other types discussed so far in that they are catalyzed by the presence of HNR₂. Insertion can therefore follow the normal mode⁴³⁸

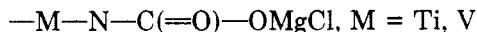


or proceed according to⁴⁹³



It should be mentioned that similar reactions were also observed for the insertion of COS and CS₂.^{492,494}

Evidence has been presented⁴⁹⁵ for the attack of CO₂ on N during insertion of CO₂ into the Mg-N bond, probably involving the intermediate



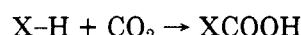
The insertion of CO₂ into P-N bonds of a series of species containing NMe₂ and CH₃NCH₂CH₂NCH₃ as ligands was also found to occur for COS and CS₂.⁴⁹⁶ A similar result was obtained for the insertion into the U-N bond.⁴⁹⁷

D. Insertion into M-O Bonds

Insertion of CO₂ into M-O bonds results in the formation of carbonato or similar type complexes (ref 426, 427, 430, 445, 498–500). In section VIIIA the formation of carbonato complexes via CO₂ uptake by hydroxo ligands was discussed in detail. The latter reactions all proceed with retention of the M-O bond and therefore

differ in principle from insertion type processes, although very similar reaction products may be formed.^{501,502} Various papers have stressed the significance of CO₂ insertion reactions into M-O bonds (ref 403, 406, 408, 413–415, 435, 442, 449). A summary of such reactions is given in Table XLII.

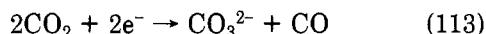
Cupric methoxide exhibits reversible CO₂ fixation through insertion into the Cu-O bond.^{503,504} Stability of the carbonato complexes can be controlled by the number of other ligands coordinated to the metal center. Insertion of CO₂ into Ir-O and Rh-O bonds⁴¹⁶ produces monodentate bicarbonato complexes, but it is uncertain whether this process involves M-O or O-H bond rupture, and whether CO₂ initially attacks the metal or the OH ligand. Such bicarbonato complexes have been shown to be unstable in an aqueous medium (see section VIIIB). A series of Mo complexes^{435,505} exhibit completely reversible CO₂ insertion; the mechanism in the solid state proceeds via a direct attack on either M or OR, while the mechanism in solution is suggested to be



X-H = organic molecule



Identification of Rh-bicarbonato complexes^{403,416} suggests that the previously supposed⁴⁵² CO₂ complex, viz., Rh(PPH₃)₂(OH)(CO)(CO₂), is more in line with a bicarbonato complex (see Table XLII). The formation of the Ti-CO₃ species⁴⁰² is suggested to follow a route that corresponds to CO₂ disproportionation.^{445,498,499}



E. Other Insertion Reactions

It was recently reported⁴³⁶ that reversible CO₂ insertion into a Pd(II) complex occurred via carbon-carbon bond formation. This is the first example where reversible CO₂ fixation has been fully characterized by X-ray diffraction for C-N = 8-methylquinoline.

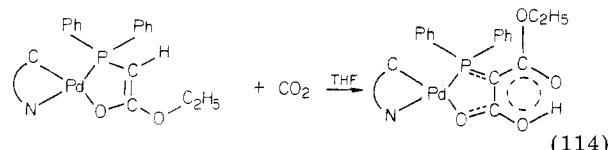


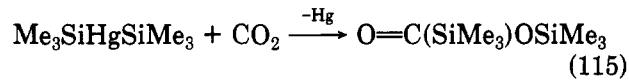
TABLE XLII. Insertion of CO₂ into M-O Bonds

metal center	reactant	product (P)	comments	ref
Fe, Ti, Nb, Zr, <i>n</i> = 3, 4, 5, 4, resp.	M(OR) _n	M(OR) _{n-1} (O ₂ COR)	analysis of P by IR	<i>g</i>
Cu	Cu(OCH ₃) ₂	Cu(O ₂ COCH ₃) ₂	in pyridine as solvent, reversible process	503
	(<i>t</i> -BuO)Cu(CN- <i>t</i> -Bu)	(<i>t</i> -BuOCO ₂)Cu(CN- <i>t</i> -Bu) ₃	in C ₆ H ₆ as solvent, and in the presence of <i>t</i> -BuNC, reversible process	504
Ir Mo	C ₆ H ₅ OCu(PPh ₃) ₂ (Ph ₃ P) ₂ (CO)Ir(OH)	[HOOC ₂ Cu(PPh ₃) ₂] _n	reaction performed in moist THF	<i>h</i>
	Mo ₂ (OCH ₂ CHMe ₃) ₆	(Ph ₃ P) ₂ (CO)Ir(OOC ₂ H) ₂	in C ₂ H ₅ OH as solvent	418
Mo	Mo ₂ (OR) ₆ , R = Me ₃ Si, Me ₃ C, Me ₂ CH, Me ₃ CCH ₂	Mo ₂ (OR) ₄ (O ₂ COR) ₂	in hydrocarbon solvents, reaction is completely reversible	505
			reaction occurs in solid state or in solution, IR and NMR characterization, X-ray structure for R = Me ₃ C	435
Rh	Rh(CO)(OH)L ₃ , L = P(C ₆ H ₁₁) ₃ , PPh ₃	L ₃ Rh(OCO ₂ H)(CO)	IR characterization	403, 418, 501
Ti W	(C ₅ H ₅) ₂ Ti(CO) ₂ W ₂ (O- <i>t</i> -Bu) ₆	[(C ₅ H ₅) ₂ Ti] ₂ CO ₃] ₂ W ₂ (O- <i>t</i> -Bu) ₄ (O ₂ CO- <i>t</i> -Bu) ₂	process is reversible, toluene as solvent	402 494

^a Muetterties, E. L. *Inorg. Chem.* 1974, 12, 1963. ^b Chisholm, M. H.; Reichert, W. W. *Ibid.* 1978, 17, 767. ^c Chisholm, M. H.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun.* 1980, 985. ^d Andersen, R. A. *Inorg. Chem.* 1979, 18, 2928.

^e Sabota, P.; Trzebiatowska, B. J.; Janas, Z. *J. Organomet. Chem.* 1976, 118, 253. ^f Ozawa, F.; Ito, T.; Yamamoto, A. *Chem. Lett.* 1979, 735. ^g Hidai, M.; Hikita, T.; Uchida, Y. *Chem. Lett.* 1972, 521. ^h Yamamoto, T.; Kubota, M.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* 1980, 53, 680.

Insertion into C-H bonds has also been reported for some Pd complexes, and a series of carboxylic acids could be prepared in this fashion.⁵⁰⁶ Indirect insertion into Si-Si bonds seems to occur in eq 115.⁵⁰⁷ A similar



reaction was reported for the insertion of CS₂.

Finally, it should be mentioned that a series of processes has been discussed in the literature that at some stage may involve CO₂ insertion reactions of the types discussed so far. These include CO₂ attack on an inorganic ligand,^{508,509} insertion into M-Si bonds,⁵¹⁰ insertion into an organic molecule in the presence of a metal,^{482,511,512} the formation of an intermediate CO₂ complex.⁵¹³ The role played by CO₂ insertion reactions in general during the water-gas shift has been emphasized in detail elsewhere.⁵¹⁴

As a final comment in the section on the chemistry of metal CO₂ complexes, we would like to draw attention to the wide range of reactions involved in typical fixation and insertion processes. The similarity in the reactions with CO₂, COS, and CS₂ is striking, and could be of significant interest in future developments. Many questions remain unanswered and future studies should include⁴⁰¹ synthetic and spectroscopic investigations of metal CO₂ and related complexes, mechanistic investigations of fixation and insertion reactions, the study of CO₂ coupling reactions with itself and other organic substrates, probably catalyzed by metal centers, and the role of such processes in pollution related areas.

Applied Metal Carbonate Chemistry

XII. Geochemistry and Oceanography

As mentioned in the Introduction, this section is meant to provide the chemist with an insight into the role of carbon dioxide and carbonates in natural systems. Emphasis is given to those systems which involve

interaction with metals or metal-containing species. We do not attempt to provide a complete review of these two topics as would satisfy either the geochemist or oceanographer. Moreover, some information relevant to this section has been included in prior sections, such as the effect of salinity, or chlorinity, on carbonate equilibria (section III), or the structures of naturally occurring minerals (section V). In some instances, isolated examples have been chosen to represent applied aspects of carbonate chemistry and are therefore not meant to indicate that they are unique in this sense.

A. Mineralization and Transport

The equilibria treated in section III are fundamental to modeling the chemistry of most complex natural water systems,⁵¹⁵ be they groundwaters, hydrothermal solutions, rivers, lakes, or oceans. Helgeson⁵¹⁶ stressed the importance of aqueous phase chemistry in applying constraints on phase relationships in geological systems and allowing for mass transfer among mineral assemblages. The aqueous phase is directly involved in many geological processes such as weathering, sedimentation, diagenesis, metamorphism, hydrothermal metasomatism, ore deposition, volcanism and igneous intrusions. Although Helgeson refers mainly to chloride salts as being the dominant constituent of the aqueous phases in these processes, carbonates and sulfates also play important roles, e.g., pH control, precipitation, complexation, Eh control, mineral replacement, etc.

The economic impact at a local level is exemplified by the case where the activity of CO₂(aq) was modeled for a particular flowing geothermal well in which other salts (e.g., NaCl, CaCl₂, etc.) are present. These calculations led to quantitative predictions for scaling and gas evolution.⁵¹⁷

Calcite, CaCO₃, is the most common form of carbonate and much is known about its crystallization behavior. The rapid rate of crystallization was discussed briefly in section IV. The solubility of calcite decreases with temperature at any given CO₂ pressure.⁵¹⁸ For

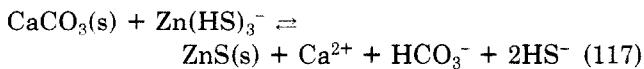
conditions generally associated with natural solutions, calcite can be precipitated by release of CO_2 , but not by cooling. The solubility of CaCO_3 as calcite, aragonite, and vaterite has recently been measured and modeled over the temperature range 0–90 °C.¹⁴⁹ At constant p_{CO_2} , the ratio of calcite solubilities in NaCl solutions and pure water increases with increasing salt concentration, particularly at higher temperatures. However, addition of CaCl_2 or NaHCO_3 gives rise to two competing effects, viz., the same ionic strength effect as in the NaCl case and the counteracting common ion effect. The complexing of carbonate by other cations at higher temperatures has an unknown effect on CaCO_3 solubility. Nonetheless, as a general rule, boiling of natural waters containing Ca^{2+} and HCO_3^- ions (i.e., the applied pressure falls below the vapor pressure) can cause deposition of CaCO_3 . The composition of adjacent fluid inclusions in hydrothermal minerals provides strong evidence that boiling has taken place in at least some hydrothermal systems, although it may not be the most common event in the formation of such deposits.⁵¹⁸ As a direct consequence of this finding, the chemistry of flashing of geothermal waters could be explained in terms of eq 116. Thus the release of CO_2

$$\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3(\downarrow) + \text{CO}_2(\uparrow) + \text{H}_2\text{O} \quad (116)$$

is responsible for the observed deposition of calcite. A further consequence of reaction 116 is to raise the concentration of carbonate that results in further hydrolysis to produce more HCO_3^- and OH^- , particularly prior to calcite precipitation. This accounts for the initial sharp increase in pH to 9.2 at this particular well,⁵¹⁹ compared to 6.5 as would be expected if the original groundwater were just allowed to cool slowly from the reservoir temperature of ca. 165 ± 8 °C to ambient temperature.

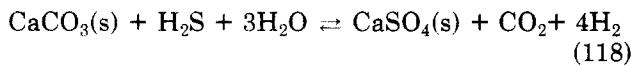
Note that the formation of insoluble carbonate scales, mainly of calcium, is economically important not only because it tends to reduce the porosity of the host rock in oil wells, but also because it reduces the efficiency of heat exchangers in power generating plants. Some of the commercially available scale inhibitors function by reducing the rate of the second-order reaction shown in eq 116; however, the main effect is to reduce the rate of nucleation of CaCO_3 , which occurs as a second stage to reaction 116, by passivating the surface crystallization sites.⁵²⁰

Replacement reactions, such as the substitution of wall rock calcite by sulfide minerals, are also important mineralization processes.⁵¹⁸ One such example involves the localization of Zn as sphalerite from its transporting complex by means of eq 117. The reaction is assumed



to be favored by decreasing temperature that would provide a mechanism for replacing limestone with sphalerite.⁵¹⁸

It may also be suggested that anhydrite, CaSO_4 , is formed in a similar reaction



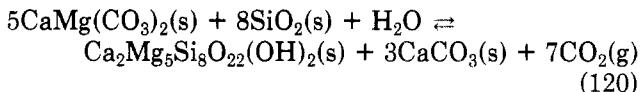
in an oxidizing region adjacent to a rising column of thermal fluid which comes into contact with aerated, nonthermal ground water. However, thermodynamic

calculations show that the concentration of H_2S is far too low with respect to $[\text{H}_2]$ to allow anhydrite to coexist as a stable phase.⁵²¹

Dolomite, $\text{CaMg}(\text{CO}_3)_2$, is the next most important mineral and in solutions saturated with respect to both calcite and dolomite, the following replacement equilibrium can be considered



with the ratio of $a_{\text{Ca}^{2+}}/a_{\text{Mg}^{2+}} \sim 1$ at room temperature. Thus, for normal seawater, for which this ratio is ca. 0.19, calcite should be converted to dolomite, but if the $m(\text{Ca})/m(\text{Mg})$ ratio is increased to ca. 0.5, dolomitization will cease. Existing solubility measurements at low temperatures can be unreliable because the rates of reaction are very slow below 200 °C; although the stability of dolomite relative to calcite apparently decreases with increasing temperature.⁵¹⁸ Therefore, whether calcite, dolomite, or magnesite is precipitated depends on the $a_{\text{Ca}^{2+}}/a_{\text{Mg}^{2+}}$ at a given temperature so that, for example, a hydrothermal solution rich in magnesium will react with (dolomitize) calcite until this ratio reaches the equilibrium value. Again it should be stressed that this reaction is very sluggish at lower temperatures. Furthermore, unless the CO_2 content is sufficiently high the phase precipitated may well be brucite, $\text{Mg}(\text{OH})_2$, or a silicate mineral. In fact, Holland⁵¹⁸ suggests that the formation of tremolite, eq 120,

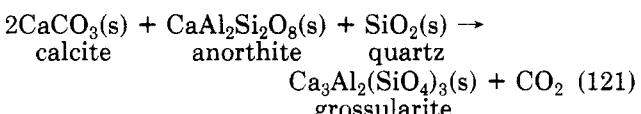


may have considerable influence on the CO_2 content of rising hydrothermal solutions.

Although strontianite, SrCO_3 , is only one-tenth as soluble as calcite at 25 °C, it becomes increasingly more soluble than calcite above 200 °C so that coupled with the relative low activity of Sr^{2+} in most ground waters, $a_{\text{Sr}^{2+}}/a_{\text{Ca}^{2+}} < 0.01$, it is not surprising that calcite is more commonly precipitated than strontianite in hydrothermal systems. Most strontianite is apparently precipitated at or below 100 °C for the above reasons.

Witherite, BaCO_3 , follows a similar pattern to strontianite, although its solubility is close to that of calcite at 25 °C. In the absence of CO_2 the solubility of witherite increases with added salt concentration ($\text{LiCl} > \text{NaCl} > \text{KCl}$), but this effect is a composite of the individual contributions from ionic strength; complexing of Ba^{2+} with Cl^- ; Li^+ , Na^+ , and K^+ interactions with HCO_3^- and CO_3^{2-} ; plus interaction of these cations with OH^- .⁵¹⁸ Witherite is less abundant than barite, BaSO_4 . Ratios of $a_{\text{Ba}^{2+}}/a_{\text{Ca}^{2+}}$ needed for the preferential precipitation of BaCO_3 over CaCO_3 are ca. 0.4 at 25 °C and 15.3 at 225 °C, whereas general natural solutions exhibit ratios $\ll 0.4$.

Many other, more complex, phase rearrangements occur in nature resulting in multicomponent systems such as, for example, the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{CO}_2$ system. Under certain conditions of temperature, pressure, and CO_2 concentration the following equilibrium can be studied.⁵²²



To quote more examples of this type would add little to the concept of this section, which is more aimed at creating an awareness of general behavior.

Complexation of metal ions by carbonate to form more soluble species which may then be transported by ground waters is an important aspect both in waste disposal⁵²³ and in the formation of mineral deposits. However, complexation resulting in the formation of insoluble carbonates is an equally important consideration and the more probable of the two processes. Vuceta and Morgan⁵²⁴ modeled the complexing of the transition-metal ions Cu, Pb, Cd, Co, Ni, Zn, Hg, Mn, and Fe by a variety of anions CO_3^{2-} , SO_4^{2-} , Cl^- , F^- , Br^- , PO_4^{3-} , OH^- , and neutral ligands such as NH_3 , edta, citric acid, etc. in the presence of potential solid adsorbates, SiO_2 , Fe(OH)_3 , and MnO_2 over the pH range 6.2–8 in oxic fresh water. These results show that both CuCO_3 and CdCO_3 precipitate at the higher pH end of the scale and that, depending on the choice of the stability constant for $\text{Cu}(\text{OH})_2$, solid malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$) is either formed as the dominant species at high pH or it is totally absent from the speciation diagram. Copper is also readily removed from solution by adsorption on SiO_2 . The speciation of the Zn and Pb systems is strongly pH dependent with $\text{Zn}^{2+}/\text{ZnCO}_3$, and $\text{PbCO}_3/\text{Pb}^{2+}$ being the most abundant species at high pH. For the mercury system, the hydroxide and halide (Cl^- , Br^-) forms are significantly more stable than the carbonate complex.

Complexation of Ge, W, Ga, and Mo was judged⁵²⁵ to be strongest by HCO_3^- , CO_3^{2-} , and SO_4^{2-} compared to Cl^- , F^- , S^{2-} , and organic anions. Elenbogena⁵²⁶ gauged the general ability of anions to form complexes to be in the order $\text{CO}_3^{2-} \gg \text{SO}_4^{2-} > \text{HCO}_3^- \gg \text{Cl}^-$, but obviously specific interactions alluded to earlier⁵²⁴ modify and even reverse such general trends in certain cases. Pittwell⁵²⁷ tabulates a vast range of metal ions in terms of their interactions with aqueous anionic species. Based on absorption spectra, ability to dissolve the metal oxide, carbonate, or sulfide, and on stability constant data, this formulation indicates that carbonate has the most widely applicable coordinating powers. However, factors such as temperature, ionic strength, redox control, valence state, etc. are not discussed.

The solubility of CO_2 in molten rocks is of interest. For example, in granitic and basaltic melts, CO_2 is substantially less soluble than water, amounting to 0.2–0.3% by weight at 101 MPa total pressure and 0.4–0.5% at 304 MPa (where $p_{\text{CO}_2} \sim 0.6 \times$ total pressure).⁵²⁸

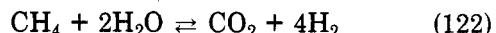
Another facet of this topic involves the utilization of the unit cell parameters of a mineral to provide geological information as to the history of a given deposit. In the case of the mineral francolite, $\text{Ca}_{10-x-y}\text{Na}_x\text{Mg}_y(\text{PO}_4)_{6-z}(\text{CO}_3)_3\text{F}_{0.43}\text{F}_2$, the a parameter shows variations of ca. 9.32–9.37 Å when taken from deposits throughout the world.⁵²⁹ Francolite is generally metastable with respect to fluorapatite and effects of weathering, metamorphism, and geological time cause systematic changes in the composition of francolite (N.B., $a = 9.36$ Å for fluorapatite).

B. Isotopic Exchange Reactions

An estimation of the natural abundances of the carbon isotope ^{12}C and ^{13}C in petroleum, gas, and other

organic deposits is central to an understanding of the origins and subsequent history of such deposits. The origin may be either biogenic in low temperature zones (i.e., near surface regions), or abiogenic where higher temperatures were encountered ($>80^\circ\text{C}$). Carbon dioxide and methane are often found together as a result of bacterial decomposition of organic matter. The observed fractionation factors between these two gases are relatively large and favor a higher ^{13}C content in CO_2 as compared to CH_4 . The magnitude of this discrepancy decreases with temperature and therefore reflects the temperature to which the system was subjected.

Bottinga,⁵³⁰ for one, has calculated the $^{13}\text{C}:\text{C}^{12}$ distribution ratio between CH_4 and CO_2 , as well as the ratios for CO_2 :graphite and graphite:methane, using spectroscopic data over the temperature range, 0–700 °C. One path for carbon exchange is provided by the equation



which involves the water-gas shift reaction, and is also known as the steam-reformation reaction of methane. In the absence of concrete experimental data, confirmation of these calculations is not available. In addition, other authors⁵³¹ have predicted different fractionation factors, particularly at higher temperatures, based on similar calculations. Bottinga⁵³⁰ also stated that isotopic ratios calculated by these methods indicate that tropospheric CO_2 and CH_4 cannot be in isotopic equilibrium because the current ratio corresponds to an estimated temperature at 200 °C.

To our knowledge, only one positive set of experimental results exist on the kinetics of this isotopic exchange reaction via eq 122,⁵³² although a study published 1 year earlier did indicate that no exchange occurred after heating the gaseous mixture to 500 °C for 10.5 days.⁵³³ This is in keeping with the second study's findings⁵³² that equilibrium would only be achieved at 400 °C after 8×10^4 years. These results would therefore suggest that under normal geothermal conditions with temperatures of ca. 200 °C, isotopic exchange does not reach equilibrium. In other words, for natural gas deposits which do not experience higher interim temperatures, the isotopic ratio reflects that of the source.^{534,535} On the other hand, at much higher temperatures that may result from, say, a magmatic intrusion, isotopic equilibrium may be approached, and the value of the ratio at that higher temperature would then be "frozen in" after subsequent cooling.

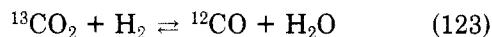
A further complication is the effect of surface catalysis.^{536–541} Even the walls of the glass ampules used in the above-mentioned experiments may provide catalytic input. Certain metal oxides, including those likely to be found in nature, are very effective catalysts. Nonetheless, Giggenbach⁵⁴² has processed these kinetic data⁵³² in terms of the known isotopic ratios found in different natural gas wells throughout the world. He also points out that in view of the slow rate of chemical and isotopic equilibration, isotopic ratios only serve as an accurate geothermometer for very deep wells and that the results may otherwise be biased by secondary reactions or by a net flux of methane or carbon dioxide with incongruent isotopic compositions. An example of such a secondary reaction is the dilution of the ^{13}C content of CO_2 by the decomposition of more ^{12}C -rich carbonates within a sample of montmorillonite during

an experiment to determine the catalytic effect of this clay on the $\text{CH}_4\text{:CO}_2$ exchange reaction at 400 °C.⁵³²

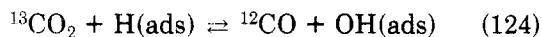
The $\delta^{13}\text{C}$ value for dissolved HCO_3^- associated with oil and natural gas wells can also be valuable as an indicator of the history of the deposit. Carothers and Kharaka⁵⁴³ have discussed their experimental findings for some 15 oil and gas fields in the light of the conclusions of previous workers concerning the possible mechanisms for producing various $\delta^{13}\text{C}$ values. Perhaps the simplest of these mechanisms pertains to shallow ground waters where equilibration with atmospheric CO_2 , with its present value of -7‰, should lead to a similar isotopic value for the dissolved carbonates. Bacteria known as methanogens can operate at 50 °C to produce methane by the reverse reaction of eq 122, thereby depleting the ^{13}C in the CH_4 by ca. 60‰ while enriching the remaining CO_2 . Other bacteria aid in the reduction of SO_4^{2-} present in the ground water by degradation of organic matter to form HCO_3^- and HS^- . By this process organic matter with $\delta^{13}\text{C}$ values of ca. -25‰ produce typical $\delta^{13}\text{C}$ values in HCO_3^- of ca. -20‰. The concentration of SO_4^{2-} determines the final $\delta^{13}\text{C}$ value.

For deeper deposits, thermal decomposition of organic matter is probably an important source of aqueous HCO_3^- , which may precipitate to form secondary carbonate cements often associated with such fields. The constraints of CH_4/CO_2 carbon exchange discussed above then control further changes in the $\delta^{13}\text{C}$ content of the HCO_3^- .

Another important exchange reaction is that between CO_2 and CO, especially at high temperatures where CO becomes relatively more stable. Brander and Urey⁵⁴⁴ showed very early that this process is catalyzed on the surfaces of quartz, gold, and silver. They reported an activation energy of ca. 472 kJ mol⁻¹ and noted that hydrogen and water increase the rate of exchange in keeping with the reaction



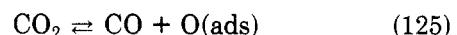
which is known to be operative at 800 °C. As water and hydrogen are known to be strongly adsorbed by quartz at these temperatures, the equivalent surface reaction (eq 124) was proposed. This mechanism was more



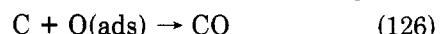
difficult to visualize as taking place on a gold or silver surface and is obviously different in the absence of water vapor and hydrogen. Subsequent work⁵⁴⁵ in quartz tubes ($^{14}\text{CO}_2$, ^{12}CO) established that although the same activation energy is obtained at high temperatures, 900–870 °C, it decreases dramatically to ca. 46 kJ mol⁻¹ at 550–650 °C. It was reasoned that at the higher temperature region the reaction is more homogeneous, whereas at lower temperatures exchange occurs exclusively on a limited number of active sites on the vessel walls. However, even above 900 °C the reaction appears complex due to the fact that it is first order with respect to CO_2 and only a half with respect to CO.

Over various carbon surfaces the kinetics of CO_2/CO exchange, referred to in this case as an oxygen transfer reaction, can be described by a general rate expression, which is also valid for metal and metal oxide surfaces.⁵⁴⁶ However, under most conditions (in this study temperatures were varied from 500 to 1000 °C), reaction

125 can be considered as a "preequilibrium step" which



establishes the oxygen activity. The rate of the second step (eq 126) is then determined by the simple ex-



pression, $k_2 p_{\text{CO}_2}/p_{\text{CO}}$. Strong oxygen adsorption was observed, although not of the Langmuir type, with rapid surface diffusion establishing equilibrium between adsorbed oxygen at different sites. Contrary to some previous claims, these authors⁵⁴⁶ found that reactions 125 and 126 can occur at different sites.

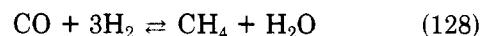
Carbon dioxide and monoxide are believed to exchange carbon via eq 123 over an iron catalyst with a different mechanism for much faster oxygen exchange involving only water and CO at 170 °C.⁵⁴⁷ Sakata et al.⁵⁴⁸ rationalized the oxygen exchange mechanism over $\gamma\text{-Fe}_2\text{O}_3$ in terms of the migration of Fe^{3+} to bound CO sites, followed by oxidation/reduction to CO_2 and Fe^{2+} . Lattice oxygen diffusion rate is too slow to contribute to this step, although it can participate in the subsequent rapid and irreversible reoxidation of Fe^{2+} to Fe^{3+} . Adsorbed molecular oxygen serves to increase the rate of exchange by participating in both steps of the redox process.

In the case of ZnO , CO_2 and CO are both adsorbed over the temperature range 25–300 °C and exchange oxygen atoms with the metal oxide.⁵⁴⁹ Carbon exchange is again far slower and is postulated to occur when a uniquely bound CO molecule is oxidized by the surface to then be released as CO_2 .

Another surface mechanism is proposed for the steam reforming of ethane over a $\text{Ni-Al}_2\text{O}_3$ catalyst at 217 °C.⁵⁵⁰ Here methane is formed by hydrogenation of surface carbon formed as an intermediate in the steam re-forming reaction (i.e., reverse Fisher-Tropsch reaction)



rather than by the reaction



The proof for this hypothesis was obtained from experiments in which ^{13}CO was added to the reaction mixture and yet no appreciable $^{13}\text{CH}_4$ was detected. Although this reaction scheme does not involve CO_2 , it seems worthy of mention as adsorbed carbon may well play an important role in exchange reactions of the type discussed above.

A brief mention should also be made of the use of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in determining the probable origin, or sequence of formation, of carbonate containing minerals. For example, a carbonate-fluorapatite (francolite) with the approximate composition, $(\text{Ca-NaMgSr})_{10}(\text{PO}_4\text{CO}_3\text{SO}_4)_6\text{F}_{2-3}$, may be of diagenetic origin (i.e., formed by replacement of carbonate within existing sediments), or authigenic (i.e., formed by precipitation, in this case, within anoxic sediments).⁵⁵¹ In the former case, the carbon isotopic composition would reflect that of the precursor and the water as well as being sensitive to temperature. Authigenic francolite may contain either light or heavy carbon depending on the environment during the organic degradation process which was responsible for the formation of the carbonate originally.

Finally, as a general comment on isotopic fractionation, it becomes apparent that a knowledge of such values provides a powerful tool in determining the origin of mineral and oil/gas formations, but only when combined with other pertinent information. Moreover, as stressed above, the use of $\delta^{13}\text{C}/\delta^{12}\text{C}$ ratios for methane and carbon dioxide as a geothermometer should apparently be restricted to very high temperature regions due to the kinetic restrictions of the equilibration reaction, although catalysis still may account for the near equilibrium ratios found in lower temperature regions.

C. Oceanography

Estimates of the total current release of CO₂ to the atmosphere indicate that approximately one-half (1.5 ppm) is being continuously removed.^{552,553} The most obvious carbon sinks are the oceans and the biosphere. As it has been proposed^{554,555} that the land biota reservoir is decreasing at a rate comparable to fossil fuel combustion, the role of CO₂ uptake by the waters of the world has probably been underestimated in earlier studies. In other words, if no yet unknown sink for carbon exists, the oceans must be the major scavenger for atmospheric CO₂.^{552,553,556}

The pH of most bodies of exposed water, typically 7.6–8.3 for ocean waters, is governed mainly by the carbonate buffering system, which involves the hydrolysis equilibria (section III) as a function of temperature, depth, and salinity (or chlorinity).^{119,134,141,557} Other contributions to this system are found in the solubility equilibria of principally CaCO₃ and Mg(OH)₂, and the exchange of CO₂ between the atmosphere and the water surface. The first dissociation constant for boric acid should also be included in any rigorous model for the pH of seawater.

In section IV it was stressed that the rates of CO₂ hydrolysis in "pure" water at pH values normally encountered in sea water are such that equilibrium is obtained within several minutes. The recent kinetic data of Johnson⁵⁵⁸ show that the same time periods apply to sea water. Given effective agitation, which one may expect for surface waters extending to an average of 70 m in oceans, the rate of transfer of CO₂ from the atmosphere to the surface water is far more rapid than either the rate of CO₂ hydrolysis, which occurs within minutes, or the rate of mixing, which may take hours.¹⁸¹ Thus, the surface waters in nature should be very near equilibrium with the adjacent atmosphere with respect to CO₂.

Takahashi and co-workers⁵⁵² have reviewed the "Carbonate Chemistry of the Surface Waters of the World Oceans". The main parameters used in their discussion are: the Revelle factor $\{(dp_{\text{CO}_2}/p_{\text{CO}_2})/(dT\text{C}/\text{TC})\}_{\text{TA,T,S}}$, where p_{CO_2} is the partial pressure of CO₂ and TC is the total "carbonate" = [CO₃²⁻(aq) + HCO₃⁻ + CO₃²⁻]; and the titration alkalinity, TA, which is defined as the equivalent amount of acid required to bring the pH of a liter of sea water to the bicarbonate/carbonic acid end point and can be approximated as follows:

$$\text{TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{HPO}_4^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (129)$$

The mean value for the Revelle factor for the world's

ocean surfaces was estimated at 10.0 ± 0.5 ,⁵⁵² while the alkalinity, temperature, and salinity generally fall in the ranges 2.2–2.4 mequiv/kg, –1 to 27 °C, and 33–37‰, respectively. At the time of their review, 1980,⁵⁵² the partial pressure of CO₂ was ca. 33.4 mPa. In very general terms, the alkalinity values were considered to follow two major trends: the warm water and Antarctic trends, which mainly owe their differences to the differences in calcium ion concentration.

Baes⁵⁵⁶ pointed out that precipitation of CaCO₃, as well as photosynthesis and decay are biogenically controlled in the ocean. Photosynthesis accounts for a lowering of the total carbon budget of surface waters leading to a supersaturation of CaCO₃ where this process is particularly active. Thus, these biological processes must be included in models of CO₂ absorption by surface waters.⁵⁵⁶

It should be noted that mixing of waters in the ocean is sluggish beyond the surface region. Circulation is commonly expressed in terms of two processes, namely, advection along layers of similar density (isopycnals) and turbulent mixing which occurs vertically across these density gradients.⁵⁵⁶

From the above discussion it is obvious that the solubility of CaCO₃ is important to sea-water chemistry. Edmond and Gieskes¹¹⁹ have critically reviewed these data for sea water and have derived eq 130 and 131 for

$$K_{\text{sp}}' \text{ (calcite)} = (0.1614 + 0.02892\text{Cl} - 0.0063t)10^{-6} \quad (130)$$

$$K_{\text{sp}}' \text{ (aragonite)} = (0.5115 + 0.02892\text{Cl} - 0.0063t)10^{-6} \quad (131)$$

the apparent solubility products for CaCO₃ in its calcite and aragonite forms to within an estimated uncertainty of $\pm 5\%$. Jacobson and Langmuir⁵⁵⁹ determined a value for $pK_{\text{sp}}(\text{calcite})$ of 8.42 at 25 °C which compares closely with 8.41 obtained from eq 130 at 25 °C and Cl = 0, i.e., at infinite dilution. However, when these authors took ion pairing of Ca(HCO₃)⁺ and CaCO₃[°] into account they arrived at a value for K_{sp} of 8.47, which emphasizes that until a better model for 2:1 and 2:2 electrolytes is found, these ion pairs can be neglected.

In order to assess the effect of pressure on the apparent solubility constants, the temperature dependence of the apparent volume changes were estimated⁵⁶⁰ to within $\pm 1 \text{ cm}^3 \text{ mol}^{-1}$ (eq 132 and 133). Bradshaw⁵⁶⁰

$$\Delta V' \text{ (calcite)} = -(35.4 - 0.23t) \quad (132)$$

$$\Delta V' \text{ (aragonite)} = -(32.8 - 0.23t) \quad (133)$$

determined the apparent molar volume of carbon dioxide in sea water (Sl = 35‰ and 23 °C) to be 33.4 cm³ mol⁻¹ which is well within the range of partial molar volumes quoted for CO₂(aq) in water (see sections II and III). Under the same conditions, he derived a value for the difference between the apparent molar volumes of HCO₃⁻ and CO₃²⁻ in artificial sea water (i.e., it contained no boric acid) of 22.5 cm³ mol⁻¹. This compares favorably with 20.37 cm³ mol⁻¹ obtained¹⁰⁹ at 25 °C in 0.725 m NaCl for the sodium salts. Note that $\phi_v(\text{HCO}_3^-) - \phi_v(\text{CO}_3^{2-})$ in pure water at 25 °C is 23.9 cm³ mol⁻¹,¹⁰⁹ assuming $\phi(\text{Na}^+) = -5.7 \text{ cm}^3 \text{ mol}^{-1}$.

As in the case of natural ground waters, trace metals can be complexed in sea water by such anions as chloride, hydroxide, bicarbonate, carbonate, sulfate, etc.

Identification of such species is difficult due to the low concentrations involved against the high background of salt concentrations. To quote but one example, examination of deposits accumulated in the Black Sea led to the identification of many of the trace metals present, so that by using known stability constant data estimates could be made in this indirect manner of their original concentrations in the sea.⁵⁶¹ Bicarbonato and carbonato complexes were postulated to exist in the relative amounts depending on the pH of such metals as Cu, Zn, Ni, Co, Be, and Sr in their +2 oxidation states. The uranium species, UO_2CO_3^0 , $\text{UO}_2(\text{CO}_3)_2^{2-}$, and $\text{UO}_2^{2-}(\text{CO}_3)_3^{4-}$ apparently exist in relatively high abundances, with the latter species becoming the dominant uranium form at high pH.⁵⁶¹ In regards to uranium, this behavior parallels that observed in natural ground waters,^{562,563} where the mobility of uranium is enhanced by the presence of aqueous carbonate. Extraction of uranium from sea water onto $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ columns⁵⁶⁴ and the formation of "hydrothermal ematite" in certain uranium deposits⁵⁶³ both appear to rely on the adsorption of the negatively charged uranium carbonates, particularly $\text{UO}_2(\text{CO}_3)_3^{4-}$, on grains or colloidal particles, in the latter case, of metal oxides.

XIII. Biochemistry

In this section we discuss the interaction of $\text{CO}_2/\text{HCO}_3^-/\text{CO}_3^{2-}$ with metalloenzymes and other bioinorganic species. Since the earlier review on metal carbonato complexes by Krishnamurthy et al.,¹ much work has been done in this area and a more complete coverage can now be presented. The enzyme within this field that has attracted the most attention over the past 10 years is certainly carbonic anhydrase. A recent extensive review⁵⁶⁵ dealt with its structure and activity, and some aspects related to metal carbonato chemistry will be treated in subsection A. All other bioinorganic species that show significant interaction with $\text{CO}_2/\text{HCO}_3^-$ will be treated in subsection B.

A. Carbonic Anhydrase

Quite some time ago it was realized that the dehydration of HCO_3^- to form CO_2 in the human lung, and the hydration of CO_2 as it passes into the bloodstream, must proceed with the aid of a catalyst. In the early sixties, biochemists succeeded in isolating various forms of carbonic anhydrase which were shown to be responsible for the catalytic action in the $\text{CO}_2-\text{HCO}_3^-$ system.⁵⁶⁶ Carbonic anhydrase is one of the most efficient biocatalysts known and is of obvious physiological importance in rapidly maintaining the $\text{CO}_2-\text{HCO}_3^-$ equilibrium,⁵⁶⁷ particularly in view of the fact that hydration of CO_2 and dehydration of HCO_3^- are indeed relatively slow processes under normal conditions (see section IV). Carbonic anhydrase is a zinc metalloenzyme made up of one polypeptide chain with a molecular weight of about 29 000 and occurs in various forms: one of high specific activity designated carbonic anhydrase C and two of low activity designated A and B.⁵⁶⁸ Most mammals have forms B and C.⁵⁶⁹ A main question focuses on the mode of binding of CO_2 at the active site of the enzyme, since this knowledge would be of much value in understanding the catalysis mechanism. It is quite certain that CO_2 does not coordinate directly to the Zn metal.⁵⁶⁸ Numerous studies have been undertaken in

TABLE XLIII. Activation Parameters

enzyme	substrate	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , J K ⁻¹ mol ⁻¹
none	CO_2^a	72.3	30.9 ± 0.4
	$\text{HCO}_3^- b$	62.7	81.1 ± 0.8
HCAC ^c	CO_2^a	31.6 ± 0.6	25.4 ± 0.7
	$\text{HCO}_3^- b$	30.5 ± 0.7	39.5 ± 1.1
HCAB ^d	CO_2^a	15.8 ± 0.9	101 ± 0.6
	$\text{HCO}_3^- b$	18.7 ± 1.5	105 ± 0.9

^a Hydration at pH 7.5. ^b Dehydration at pH 7.2.

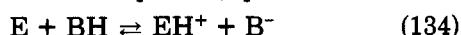
^c Human carbonic anhydrase C. ^d Human carbonic anhydrase B.

efforts to elucidate the fundamental mechanism involved. It is generally accepted that Zn^{2+} must be coordinated to three imidazoles of histidines and a water molecule in order to achieve its catalytic activity.⁵⁷⁰

The pH dependence of the catalytic activity is characterized by a pK_a near 7.^{569,570} Human carbonic anhydrase C has a maximum turnover number of $1 \times 10^6 \text{ s}^{-1}$ at 25 °C, compared to a value of $2 \times 10^5 \text{ s}^{-1}$ for carbonic anhydrase B.^{569,571} The corresponding activation parameters are shown in Table XLIII.⁵⁷¹ In the case of bovine carbonic anhydrase, it was found^{567,570} that the Michael's constant (K_m) for CO_2 hydration is essentially constant at pH 5.9–10.2; pK_a values of 6.85 and 7.35 in H_2O and D_2O , respectively; $k_{\text{cat}} = 8.3 \times 10^5 \text{ s}^{-1}$ at 25 °C in the basic form during CO_2 hydration; $k_{\text{cat}} = 3.8 \times 10^5 \text{ s}^{-1}$ at 25 °C in the acidic form during dehydration of HCO_3^- ; $K_m^{\text{H}_2\text{O}}/K_m^{\text{D}_2\text{O}} = 3.3$; $K_m^{\text{HCO}_3^-}/K_m^{\text{DCO}_3^-} = 2.6$; $k_{\text{cat}}^{\text{H}_2\text{O}}/k_{\text{cat}}^{\text{D}_2\text{O}} = 3.3$ for hydration; $k_{\text{cat}}^{\text{H}_2\text{O}}/k_{\text{cat}}^{\text{D}_2\text{O}} = 4.3$ for dehydration. From these tendencies, the authors⁵⁶⁷ conclude that only mechanisms which utilize proton transfer as part of the rate-determining step can be correct. Very similar results were reported for spinach carbonic anhydrase.⁵⁷² It follows that the basic form of the enzyme is active towards CO_2 hydration, whereas the acidic form is active towards HCO_3^- dehydration.⁵⁷⁰ Two models have been proposed^{569,570} concerning the chemical nature of the catalytic group that has a pK_a around 7. This group might be a histidine side chain linked to the metal ion indirectly via one or more water molecules, or it may involve ionization of a metal-coordinated water molecule to produce a Zn-OH species. In the case of the latter possibility, the activity of the enzyme cannot be ascribed to the nucleophilicity of the hydroxo ligand only, since a rate constant for CO_2 uptake (see Figure 3—section VIIIA) of ca. $300 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C would then be expected, which is much slower than the observed value. Other factors must therefore play a significant role in such a process.

X-ray studies⁵⁷³ have demonstrated that human carbonic anhydrase C has an ellipsoidal molecular shape and that the Zn atom is positioned in the center of the molecule at the bottom of a crevice, constituting the active site. Infrared studies by Wang⁵⁷⁴ have illustrated that the binding site of carbonic anhydrase is a hydrophobic surface or cavity which loosely binds CO_2 . A detailed mechanism was presented^{70,568,570} in which the Zn-bound water molecule provides both donor and acceptor functions, and it was suggested⁷⁰ that rapid proton transfer occurs between the water molecules in the cavity. The participation of a basic imidazole group in the proton transfer process has also been stressed.^{405,575} Attention was drawn^{70,569} to a serious

dilemma, originating when rates exceeding diffusion-controlled processes are obtained. However, this probably could be solved⁵⁷⁶ when proton transfer between enzyme and buffer species (eq 134) is taken into



account. It follows⁵⁶⁹ that CO_2 and HCO_3^- can combine with the enzyme at diffusion-controlled rates, and that proton exchange can occur very rapidly through buffer mediation.

Silverman and co-workers⁵⁷⁷ developed an ^{18}O exchange technique to study exchange between H_2O and HCO_3^- catalyzed by human carbonic anhydrase C. They presented results that supported the hypothesis that there is a proton-transfer step in the mechanism involving the enzyme and buffers in solution.⁵⁷⁸ They found⁵⁷⁹ that as the buffer concentration is increased a change in rate-determining step occurs. In the absence of buffers, the rate is determined by alternating hydration-dehydration steps at equilibrium which do not require proton transfer to the enzyme. At low buffer concentrations, proton transfer is rate limiting and the catalytic exchange rate increases with buffer concentration. Further studies by this group illustrate similar results for the exchange of ^{18}O between CO_2 and H_2O catalyzed by bovine carbonic anhydrase,⁵⁸⁰ human carbonic anhydrase,⁵⁸¹ brush-border carbonic anhydrase from dog kidney,⁵⁸² and red cell suspensions.⁵⁸³

^{13}C NMR techniques have also been used to study the $\text{CO}_2/\text{HCO}_3^-$ system in the presence of various carbonic anhydrases.⁵⁸⁴⁻⁵⁸⁶ The results are in accord with mechanisms that suggest metal-bonded OH adds directly to the carbon of enzyme-bound CO_2 so that dehydration proceeds via HCO_3^- coordinated directly to the metal.⁵⁸⁵ The CO_2 could be bound close to the metal through an interaction with the protein part of the enzyme active site. However, HCO_3^- binds directly to the metal. Very recently⁵⁸⁷ a model was suggested in which the enzyme has a water molecule on the metal ion at the active site and this results in a rate of water exchange independent of pH.

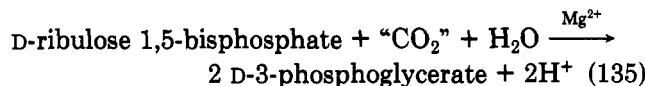
A number of theoretical studies have computed the nature of the CO_2 hydration process.⁵⁸⁸⁻⁵⁹⁰ In one study only the schemes with a direct reaction between buffer and enzyme gave consistent data.⁵⁹¹ Monte Carlo calculations demonstrate⁵⁹² that the field of Zn^{2+} dominates the carbonic anhydrase reaction, and four steps could be identified: CO_2 approaches $\text{Zn}-\text{OH}_2$ and forms a precursor complex in which both reactants maintain original geometry; a complex is formed between CO_2 and H_2O ; removal of the complex by sandwiching a molecule of water between Zn^{2+} and the complex; deprotonation at one side of the complex and protonation of an oxygen atom at a different side.

Finally, it is significant that carbonic anhydrase will affect the absorption characteristics of carbon dioxide.⁵⁹³ Tsao⁵⁹⁴ proposed a two-zone model to describe the phenomena at the gas-liquid interface during CO_2 absorption in the presence of carbonic anhydrase. In a later study by Alper et al.,⁵⁹⁵ the absorption data were found to be compatible with classical mass transfer models and suggest that the carbonic anhydrase distribution in the liquid is probably uniform. These findings contradict the earlier observations made by Tsao,⁵⁹⁴ but the discrepancies were rationalized.⁵⁹⁶ Deckwer and co-workers published a series of pa-

pers⁵⁹⁶⁻⁵⁹⁸ on various aspects of the absorption of CO_2 under the influence of carbonic anhydrase. At high pH (9.6–11.1), the reaction is first order in CO_2 and the rate constant is proportional to the enzyme concentration with an activation energy of 38 kJ mol⁻¹.^{596,597} At low pH (~6.5), the catalytic power of the enzyme is considerably reduced and the results do not fit a simple first-order process.⁵⁹⁷

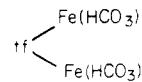
B. Other Enzymes

Another series of enzymes that has received considerable attention over the past 10 years are the carboxylases. Various studies^{599,600} were launched to identify the active species of "CO₂", i.e., CO₂ or HCO₃⁻, utilized in the ribulose bisphosphate carboxylase reaction



Earlier suggestions include the formation of a Mg²⁺-CO₂ complex prior to the carboxylation of ribulose bisphosphate. ¹⁴C labeling experiments^{599,600} demonstrated that the obtained data could all be explained in terms of CO₂ being the active species. In another study,⁶⁰¹ it was concluded that it is rather the HCO₃⁻ species that is utilized in the reactions of pyruvate and phosphoenolpyruvate carboxylases. Certainly the role of bound metal ions in CO₂ fixation by carboxylases is very important⁶⁰² and should exhibit a close correlation with the carbonic anhydrase system. In this respect, several lines of evidence were reported⁶⁰² to indicate that Mn²⁺ is a constitutive component of pyruvate carboxylase, and is involved in the carboxylation process.⁶⁰³ The role of adenosine triphosphate (ATP) in such reactions has been considered in terms of the coupling of ATP hydrolysis and CO₂ fixation.⁶⁰⁴ Kinetic evidence indicates that the first step involves the fixation of CO₂ with concurrent hydrolysis of ATP, for which various possible reaction mechanisms were considered.⁶⁰⁴ In general,⁶⁰⁵ the enzyme must first be activated by preincubation with a divalent cation (Mg²⁺, Mn²⁺, Ni²⁺, or Co²⁺) and CO₂, for maximum catalytic activity.⁶⁰⁶⁻⁶⁰⁸

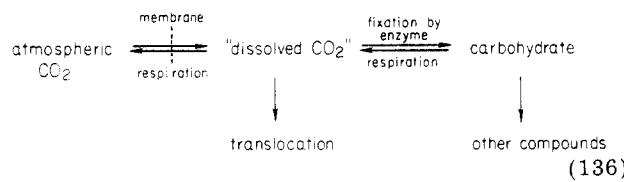
Various aspects of the binding of metal ions and anions like HCO₃⁻ to the enzyme transferrin have been investigated. Apotransferrin was found⁶⁰⁹ to bind simultaneously to Fe³⁺ and HCO₃⁻ to produce a complex (HCO₃)₂-Fe₂-transferrin with the suggested structure.



Competitive binding experiments showed that oxalate displaced the bound bicarbonate to produce an oxalato complex. In an effort to study the role of bound bicarbonate in the metal-complexing function of transferrin, NMR experiments were performed on copper transferrin and copper transferrin-HCO₃⁻.⁶¹⁰ It turns out that at least one rapidly exchanging water molecule is located so close to the metal in copper transferrin that it can be considered as one of its ligands. Binding of HCO₃⁻ alters the exchange rate and may be due to direct steric hindrance by HCO₃⁻ bound near the metal ion or conformational changes induced in transferrin by the binding of HCO₃⁻.⁶¹⁰ Other interesting reactions reported in the literature include the formation of an

intermediate nta-Fe(III)-tf species during the reaction of Fe^{III}nta with transferrin, which subsequently decomposes to nta and Fe(III)-transferrin.^{611,612} In the presence of HCO₃⁻, the complex transferrin [Fe^{III}HCO₃]₂ is formed in the above reaction.⁶¹² Later studies have found that carbonate must be bound to Fe(III) prior to the binding of the metal to transferrin.^{613,614} Kojima and Bates⁶¹⁵ reported the formation of Fe²⁺-transferrin-CO₃²⁻ which was subsequently oxidized by O₂ to yield Fe³⁺-transferrin-CO₃²⁻ at a rate of 4 × 10⁻³ M⁻¹ s⁻¹. In an earlier study, they⁶¹⁶ reported the reductive release of iron from Fe³⁺-transferrin-CO₃²⁻, and the kinetic data suggested a mechanism that includes the protonation of two groups during the release of iron.

Similar studies have been performed on the reaction of CO₂/HCO₃⁻ with other biologically important species such as chloroplasts^{617,618} and phytoplankton.⁶¹⁹ These interactions, and those referred to above, stress the biochemical significance of the distribution of carbon isotopes.⁶²⁰ Along these lines a model could be suggested to explain the isotopic fractionation associated with photosynthesis.⁶²⁰



Finally, we would like to draw attention to a series of studies that involves the the reaction of CO₂/HCO₃⁻ with hemoglobin,^{621,622} red cells, and plasma,^{623,624} and the role played by the CO₂-HCO₃⁻ equilibrium during the process of breathing.⁶²⁵⁻⁶²⁸

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List of Abbreviations

acac	Ligands	bpy	bipyridine
adao	acetylacetone	CDMBA	cetyltrimethylbenzylammonium radical
L-ala	8-amino-3,6-diazaoctanoate	cupferron	N-nitroso-N-phenylhydroxylamine
[9]aneN ₃	L-alaninate	cy	cyclopentadiene
[12]aneN ₄ = cyclen	1,4,7-triazacyclononane	DH	dimethylglyoxime
[13]aneN ₄	1,4,7,10-tetraazacyclododecane	diars	o-phenylenebis(dimethylarsine)
[14]aneN ₄ = cyclam	1,4,8,11-tetraazacyclotridecane	Me ₂ [14]dieneN ₄	5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene
C(5,14)-meso-Me ₆ -[14]aneN ₄ = tett	1,4,8,11-tetraazacyclotetradecane	Me ₄ [14]dieneN ₄	5,6,12,13-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene
C(5,12)-rac-Me ₆ -[14]aneN ₄ = tetr	C(5,14)-meso-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane	trans-Me ₆ [14]dieneN ₄	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene
[15]aneN ₄	C(5,12)-rac-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane	diphos	1,2-bis(diphenylphosphino)ethane
[16]aneN ₄	1,5,9,12-tetraazacyclopentadecane	dmpe	1,2-bis(dimethylphosphino)ethane
	1,5,9,13-tetraazacyclohexadecane	dmtr	4,7-dimethyltriethylenetetramine
		dpt	dipropyltriamine = 4-azahexane-1,7-diamine
		i-dtma	N,N-bis(2-aminoethyl)glycine
		dtnd	3,7-dithianonane-1,9-diamine
		edda	ethylenediaminediacetate
		en	ethylenediamine
		Me ₄ [12]eneN ₃ = dla	2,4,4,9-tetramethyl-1,5,9-triaza-cyclododec-1-ene
		fars	o-phenylenebis[[γ-(dimethylarsino)propyl]methylarsine]
		gly	glycinate
		HDPA	2,2'-bipyridylamine
		mal	malinate
		mda	(methylimino)dacetate
		mdpt	4-methyl-4-azahexane-1,7-diamine
		nta	nitrilotriacetate
		ox	oxalate
		phen	o-phenanthroline
		S,S-pyhn	1,6-bis[2(S)-pyrrolidyl]-2,5-diazahexane
		picol	2-pyridinecarboxylate
		pip	2-[[2-(2-pyridyl)ethyl]imino]ethylpyridine
		pn	propylenediamine
		S-praH	(S)-2-amino-1-propanol
		pren	(2S,2'S)-1,1'-ethylenedi-2-pyrrolidinecarboxylate
		py	pyridine
		qars	o-phenylenebis[[o-(dimethylarsino)phenyl]methylarsine]
		teed	N,N,N',N'-tetraethylethylene-diamine
		terpy	2,2':6',2''-terpyridine
		3,2,3-tet	4,7-diaza-1,10-decanediamine
		5,7-Me ₂ -2,3,2-tet	4,6-dimethyl-3,7-diaza-1,9-nanediamine
		1,5,7,11-Me ₄ -2,3,2-tet	6,8-dimethyl-2,5,9,12-tetraazatricane
		tetars	ethylenediaminebis[[γ-(dimethylarsino)propyl]phenylarsine]

tetren	($\alpha\beta S$)tetraethylenepentamine ($\alpha S, \beta S$)
tmtd = tmpd	N,N,N',N' -tetramethyl-1,3-propanediamine
tn	trimethylenediamine
tpam	tris(2-pyridyl)amine
tren	N,N',N'' -triaminotriethylamine
trien	triethylenetetramine
3,8-Me ₂ trien	3(S),8(S)-dimethyltriethylene-tetramine
L-val	L-valinate
br	Spectral
m	broad
sh	medium
s	shoulder
vs	strong
vw	very strong
w	very weak
	weak

References

- (1) Krishnamurthy, K. V.; Harris, G. M.; Sastri, V. S. *Chem. Rev.* 1970, 70, 171.
- (2) Piriz MacColl, C. R. *Coord. Chem. Rev.* 1969, 4, 147.
- (3) Sobota, P. *Wiad. Chem.* 1977, 31, 101.
- (4) Cramer, J.; Myers, A. L. *Atmos. Environ.* 1972, 6, 563.
- (5) Pearman, G. I.; Garratt, J. R. *Search* 1972, 3, 67.
- (6) Baes, C. F., Jr.; Goeller, H. E.; Olson, J. S.; Rotty, R. M. *Am. J. Sci.* 1977, 265, 310.
- (7) Sakai, H. *Kagaku to Kogyo (Tokyo)* 1978, 31, 949.
- (8) Woodwell, G. M. *Sci. Am.* 1978, 238, 34.
- (9) Baes, C. F., Jr.; Beall, S. E.; Lee, D. W.; Marland, G. "Interactions of Energy and Climate"; Bach, W., Pankrath, J., Williams, J., Eds.; Reidel: Dordrecht, 1980; p 495.
- (10) Moses, H. *Proc., Annu. Meet.—Air Pollut. Control Assoc.* 1980, 73, 1.
- (11) Kolthoff, I. M.; Meehan, E. J.; Kimura, M. *J. Phys. Chem.* 1971, 75, 3343.
- (12) Kolthoff, I. M.; Meehan, E. J.; Kimura, M. *Talanta* 1972, 19, 1179.
- (13) Kolthoff, I. M.; Meehan, E. J.; Kimura, M. *Talanta* 1973, 20, 81.
- (14) Rehorek, D.; Hennig, H. Z. *Chem.* 1980, 20, 109.
- (15) Mentzen, B. F.; Sautereau, H. J. *Photochem.* 1981, 15, 169.
- (16) Bennett, J. E.; Graham, S. C.; Mile, B. *Spectrochim. Acta, Part A* 1973, 29A, 375.
- (17) Hoffman, M. Z.; Simic, M. *Inorg. Chem.* 1973, 12, 2471.
- (18) Natarajan, P.; Raghavan, N. V. J. *Phys. Chem.* 1981, 85, 188.
- (19) Hoffman, M. Z.; Simic, M. J. *Am. Chem. Soc.* 1972, 94, 1757.
- (20) Tait, A. M.; Hoffman, M. Z.; Hayon, E. *Int. J. Radiat. Phys. Chem.* 1976, 8, 691.
- (21) Tait, A. M.; Hoffman, M. Z.; Hayon, E. *J. Am. Chem. Soc.* 1976, 98, 86.
- (22) Simic, M. G.; Hoffman, M. Z.; Brezniak, N. V. *J. Am. Chem. Soc.* 1977, 99, 2166.
- (23) Cheney, R. P.; Hoffman, M. Z.; Lust, J. A. *Inorg. Chem.* 1978, 17, 1177.
- (24) Dougherty, P. L.; Gottschall, W. C. *Radiat. Phys. Chem.* 1977, 10, 17.
- (25) Heidt, L. J.; Tregay, G. W.; Middleton, F. A., Jr. *J. Phys. Chem.* 1970, 74, 1876.
- (26) Brits, A. G.; van Eldik, R.; van den Berg, J. A. Z. *Phys. Chem. (Wiesbaden)* 1976, 102, 203, 213.
- (27) Brits, A. G.; van Eldik, R.; van den Berg, J. A. *J. Inorg. Nucl. Chem.* 1977, 39, 1195.
- (28) Brits, A. G.; van Eldik, R.; van den Berg, J. A. *Inorg. Chim. Acta* 1980, 39, 47.
- (29) Reiche, H.; Dunn, W. W.; Bard, A. J. *J. Phys. Chem.* 1979, 83, 2248.
- (30) Poznyak, A. L.; Stel'mashok, V. E. *Koord. Khim.* 1979, 5, 1670.
- (31) Brezniak, N. V.; Hoffman, M. Z. *Inorg. Chem.* 1979, 18, 2935.
- (32) Slanger, T. G. *JGR, J. Geophys. Res., A* 1981, 86, 7795.
- (33) Chan, W. H.; Uselman, W. M.; Calvert, J. G.; Shaw, J. H. *Chem. Phys. Lett.* 197, 45, 240.
- (34) Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* 1980, 102, 7604.
- (35) Akermark, B.; Eklund-Westlin, U.; Backstrom, P. *Acta Chem. Scand., Ser. B* 1980, B34, 27.
- (36) Sieck, L. W. *Int. J. Chem. Kinet.* 1978, 10, 335.
- (37) Ikezoe, Y.; Sato, S.; Shimizu, S.; Matsuoka, S. *Radiat. Phys. Chem.* 1981, 17, 69.
- (38) Hanson, R. C.; Jones, L. H. *J. Chem. Phys.* 1981, 75, 1102.
- (39) Petrov, S. B.; Podkladenko, M. V. *Zh. Prikl. Spektrosk.* 1971, 15, 510.
- (40) Moskalenko, N. I.; Zotov, O. V.; Mirumyants, S. O. *Zh. Prikl. Spektrosk.* 1974, 21, 893.
- (41) Moskalenko, N. I.; Il'm, Y. A.; Pokotilo, N. K.; Sementsov, S. A.; Pushkin, V. T. *Zh. Prikl. Spektrosk.* 1981, 34, 475.
- (42) Kudryavtsev, N. N.; Novikov, S. S. *Rev. Phys. Appl.* 1981, 16, 49.
- (43) Hamada, K.; Morishita, H. *Nagasaki Daigaku Kyoikugakubu Shizen Kagaku Kenkyu Hokoku* 1974, 25, 55.
- (44) Sze, Y.-K.; Adams, W. A.; Davis, A. R. "Chemical Physics Aqueous Gas Solutions"; Adams, W. A., Ed.; The Electrochemical Society: Princeton, NJ, 1975; p 42.
- (45) Mekjavić, I. *Vestn. Slov. Kem. Drus.* 1979, 26, 283; *Chem. Abstr.* 1981, 94, 55307b.
- (46) Davis, A. R.; Oliver, B. G. *J. Sol. Chem.* 1972, 1, 329.
- (47) Anderson, G. R. *J. Phys. Chem.* 1977, 81, 273.
- (48) Kruse, R.; Franck, E. U. *Ber. Bunsenges. Phys. Chem.* 1982, 86, 1036.
- (49) Oliver, B. G.; Davis, A. R. *Can. J. Chem.* 1973, 51, 698.
- (50) Sterzel, W.; Schnee, W. D. Z. *Anorg. Allg. Chem.* 1970, 376, 134.
- (51) Becher, H. J.; Friedrich, F.; Willner, H. Z. *Anorg. Allg. Chem.* 1973, 395, 134.
- (52) Sterzel, W.; Schnee, W. D. Z. *Anorg. Allg. Chem.* 1972, 392, 173.
- (53) Pidzirailo, M. S.; Khalimonova, I. M. *Ukr. Fiz. Zh.* 1967, 12, 1063.
- (54) Abbott, T. M.; Buchanan, G. W.; Kruus, P.; Lee, K. C. *Can. J. Chem.* 1982, 60, 1000.
- (55) Shemansky, D. E. *J. Chem. Phys.* 1972, 56, 1582.
- (56) Underwood, A. L.; Howe, L. H. *Anal. Chem.* 1962, 34, 692.
- (57) McGlynn, S. P.; Rabalaïs, J. W.; McDonald, J. R.; Scheer, V. M. *Chem. Rev.* 1971, 71, 73.
- (58) Bar, R.; Sasson, Y. *Anal. Chim. Acta* 1982, 142, 345.
- (59) Poplett, I. J. F.; Smith, J. A. S. *J. Chem. Soc., Faraday Trans. I* 1981, 77, 761.
- (60) Cabane, M.; Playe, P. *J. Aerosol. Sci.* 1980, 11, 475.
- (61) Kraus, B.; Breth, A.; Dobrozemsky, R. *Contrib.—Symp. At. Surf. Phys.* 1980, 129.
- (62) Borel, J. P.; Faes, F.; Pittet, A. *J. Chem. Phys.* 1981, 74, 2120.
- (63) von Burg, K.; Delahay, P. *Chem. Phys. Lett.* 1981, 78, 287.
- (64) Zemann, J. *Fortschr. Mineral.* 1981, 59, 95.
- (65) Herman, H. B.; Rechnitz, G. A. *Anal. Chim. Acta* 1975, 76, 155.
- (66) Krasov, V. I.; Maleiko, L. V.; Tsvetkov, V. A. *Tr. Gl. Geofiz. Obs.* 1979, 42, 18; *Chem. Abstr.* 1981, 94, 70425g.
- (67) Funck, R. J. J.; Morf, W. E.; Schultheiss, P.; Amman, D.; Simon, W. *Anal. Chem.* 1982, 54, 423.
- (68) Greenberg, J.; Meyerhoff, M. E. *Anal. Chim. Acta* 1982, 141, 57.
- (69) Edsall, J. T. *NASA [Spec. Publ.] SP* 1968, *NASA SP-188, 1972*, 15.
- (70) Edsall, J. T.; Khalifah, R. G. *Alfred Benzon Symp.* 1972, 4, 393.
- (71) Wilhelm, E.; Battino, R.; Wilcock, R. *Chem. Rev.* 1977, 77, 219.
- (72) Malinin, S. D. *Geochem. Int.* 1979, 15, 108.
- (73) Cargill, R. W.; MacPhee, D. E. *J. Chem. Res.* 1981, 232.
- (74) Takahashi, M.; Kobayashi, Y.; Takeuchi, H. *J. Chem. Eng. Data* 1982, 27, 328.
- (75) Reddy, M. M.; Gaillard, W. D. *J. Colloid Interface Sci.* 1981, 80, 171.
- (76) Laddha, S. S.; Diaz, J. M.; Danckwerts, P. V. *Chem. Eng. Sci.* 1981, 36, 228.
- (77) Annesini, M. C.; Fumasoni, S.; Pochetti, F. *Chim. Ind. (Milan)* 1979, 61, 898.
- (78) Chai, C.-P.; Paulaitis, M. E. *J. Chem. Eng. Data* 1981, 26, 277.
- (79) Robinson, R. A.; Macaskill, J. B. *J. Sol. Chem.* 1979, 8, 35.
- (80) Bottinga, Y.; Richet, P. *Am. J. Sci.* 1981, 281, 615.
- (81) Cox, J. D. *CODATA Spec. Rep.* 1980, 8, 51.
- (82) Vanderzee, C. E. *J. Chem. Thermodyn.* 1982, 14, 1051.
- (83) Sarbar, M.; Covington, A. K.; Nuttal, R. L.; Goldberg, R. N. *J. Chem. Thermodyn.* 1982, 14, 695.
- (84) Sarbar, M.; Covington, A. K.; Nuttal, R. L.; Goldberg, R. N. *J. Chem. Thermodyn.* 1982, 14, 967.
- (85) Onda, K.; Sada, E.; Kobayashi, T.; Ando, N.; Kito, S. *Kagaku Kogaku* 1970, 34, 603.
- (86) Le Neindre, B.; Bury, P.; Tufeu, R.; Johannin, P.; Vodar, B. *Therm. Conduct.* 1969, 9, 69.
- (87) Besserer, G. J.; Robinson, D. B. *J. Chem. Eng. Data* 1973, 18, 137.
- (88) Kurin, V. I.; Golubev, I. F. *Teploenergetika* 1974, 84.
- (89) van Huff, N. E.; Houghton, G.; Coull, J. J. *Chem. Eng. Data* 1963, 8, 336.
- (90) Greenwood, H. J. *Am. J. Sci.* 1969, 267, 191.

- (91) Butler, J. N.; Huston, R. *J. Phys. Chem.* 1970, 74, 2976.
 (92) Tolkachev, A. M.; Manzhelii, V. G.; Azarenkov, V. P.; Je-
 zowski, A.; Kosobutskaya, E. A. *Fiz. Nizk. Temp. (Kiev)*
 1980, 6, 1533; *Chem. Abstr.* 1981, 94, 112768d.
 (93) Moldover, M. R. *J. Chem. Phys.* 1974, 61, 1766.
 (94) Takenouchi, S.; Kennedy, G. C. *Am. J. Sci.* 1961, 262, 1055.
 (95) "IUPAC International Thermodynamic Tables of the Fluid
 State Carbon Dioxide"; Angus, S., Armstrong, B., de Reuck,
 K. M., Eds.; Pergamon Press: Oxford, 1973.
 (96) Tsiklis, D. S.; Linshits, L. R.; Tsimerman, S. S. *Tr. Nau-
 chno-Issled. Proektn. Inst. Azotn. Prom. Prod. Org. Sin.*
 1971, 133; *Chem. Abstr.* 1973, 78, 20902j.
 (97) Douville, J. A. *Chemistry* 1970, 43, 25.
 (98) Tsiklis, D. S.; Linshits, L. R.; Tsimerman, S. S. *Zh. Fiz.
 Khim.* 1969, 43, 1919.
 (99) Ellis, A. *Chem. Commun.* 1966, 802.
 (100) Millero, F. J. "Water and Aqueous Solutions: Structure,
 Thermodynamics and Transport Properties"; Horne, R. A.,
 Ed.; Wiley-Interscience: London, 1972; Chapter 13.
 (101) Ellis, A. J.; McFadden, I. M. *Geochim. Cosmochim. Acta*
 1972, 36, 413.
 (102) Read, A. J. *J. Sol. Chem.* 1975, 4, 53.
 (103) Spitzer, U.; van Eldik, R.; Kelm, H. *Inorg. Chem.* 1982, 21,
 2821.
 (104) Parkinson, W. J.; de Nevers, N. *Ind. Eng. Chem., Fundam.*
 1969, 8, 709.
 (105) Gibbs, R. E.; van Ness, H. C. *Ind. Eng. Chem., Fundam.*
 1971, 10, 312.
 (106) Ellis, A. J.; McFadden, I. M. *Geochim. Cosmochim. Acta*
 1972, 36, 413.
 (107) Tsiklis, D. S.; Linshits, L. R.; Tsimerman, S. S. *Teplofig.
 Svoistva, Veshestv Mater.* 1971, 130.
 (108) Perron, G.; Desnoyers, J. E.; Millero, F. J. *Can. J. Chem.*
 1975, 53, 1134.
 (109) Millero, F. J.; Laferriere, A. L.; Chetirkin, P. V. *J. Phys.
 Chem.* 1977, 81, 1737.
 (110) Olszewski, H. A.; Troe, J.; Wagner, H. G. *Ber. Bunsenges.
 Phys. Chem.* 1966, 70, 1060.
 (111) Wagner, H. G.; Zabel, F. *Ber. Bunsenges. Phys. Chem.* 1974,
 78, 705.
 (112) Yau, A. W.; Pritchard, H. O. *Can. J. Chem.* 1979, 57, 1731.
 (113) DeMore, W. B. *J. Phys. Chem.* 1972, 76, 3527.
 (114) Lietzke, M. H.; Mullins, C. J. *Inorg. Nucl. Chem.* 1981, 43,
 1769.
 (115) Berg, R. L.; Vanderzee, C. E. *J. Chem. Thermodyn.* 1978, 10,
 1113.
 (116) Hu, A. T.; Sinke, G. C.; Masson, M.; Ringner, B. *J. Chem.
 Thermodyn.* 1972, 4, 283.
 (117) Berg, R. L.; Vanderzee, C. E. *J. Chem. Thermodyn.* 1978, 10,
 1049.
 (118) Drummond, S. E., Jr. Ph.D. Thesis, The Pennsylvania State
 University, 1981.
 (119) Edmond, J. M.; Gieskes, J. M. T. M. *Geochim. Cosmochim.
 Acta* 1970, 34, 1261.
 (120) Harned, H. S.; Davis, R., Jr. *J. Am. Chem. Soc.* 1943, 65,
 2030.
 (121) Lyman, J. Ph.D. Thesis, University of California, 1957.
 (122) Wissburn, K. F.; French, D. M.; Patterson, A., Jr. *J. Phys.
 Chem.* 1954, 58, 693.
 (123) Berg, D.; Patterson, A., Jr. *J. Am. Chem. Soc.* 1953, 75, 5197.
 (124) Boe, R. J. Ph.D. Thesis, University of Maryland, 1970.
 (125) Roughton, F. J. W. *J. Am. Chem. Soc.* 1941, 63, 2930.
 (126) Patterson, C. S.; Slocum, G. H.; Busey, R. H.; Mesmer, R. E.
Geochim. Cosmochim. Acta 1982, 46, 1653.
 (127) Nakayama, T. S. *J. Inorg. Nucl. Chem.* 1971, 33, 1287.
 (128) Frydman, M.; Nilsson, G.; Rengemo, T.; Sillen, L. G. *Acta
 Chem. Scand.* 1958, 12, 878.
 (129) Distèche, A.; Distèche, S. *J. Electrochem. Soc.* 1967, 114, 330.
 (130) Harned, H. S.; Bonner, F. T. *J. Am. Chem. Soc.* 1945, 67,
 1026.
 (131) MacInnes, D. A.; Belcher, D. *J. Am. Chem. Soc.* 1933, 55,
 2630.
 (132) Roy, R. N.; Gibbons, J. J.; Trower, J. K.; Lee, G. A.; Hartley,
 J. J.; Mack, J. G. *J. Chem. Thermodyn.* 1982, 14, 473.
 (133) Peiperl, J. C.; Pitzer, K. S. *J. Chem. Thermodyn.* 1982, 14,
 613.
 (134) Millero, F. J. *Geochim. Cosmochim. Acta* 1979, 43, 1651.
 (135) Ryzhenko, R. N. *Geokhimiya* 1963, 151.
 (136) Stretenskaya, N. G. *Metody Eksp. Issled. Gidroterm. Rav-
 novesii (Dokl. Soveshch.)* 1977, 46; *Chem. Abstr.* 1981, 94,
 21234k.
 (137) Owen, B. B.; Brinkley, S. R., Jr. *Chem. Rev.* 1941, 29, 461.
 (138) Ellis, A. J. *J. Chem. Soc.* 1959, 3689.
 (139) Lown, D. A.; Thirsk, H. R.; Wynne-Jones, L. *Trans. Faraday
 Soc.* 1970, 66, 51.
 (140) Millero, F. J.; Berner, R. A. *Geochim. Cosmochim. Acta* 1972,
 36, 92.
 (141) Mehrbach, C.; Culberson, C. H.; Hawley, J. E.; Pytkowicz, R.
 M. *Limnol. Oceanogr.* 1973, 18, 897.
 (142) Hansson, I. *Acta Chem. Scand.* 1973, 27, 931.
 (143) Hansson, I. *Deep-Sea Res. Oceanogr. Abstr.* 1973, 20, 461.
 (144) Buch, K.; Harvey, H. W.; Wattenberg, H.; Gripenberg, S.
Rapp. Pr.-V. Reun. Cons. Int. Explor. Mer 1932, 79, 1.
 (145) Culberson, C. D.; Pytkowicz, R. M. *Limnol. Oceanogr.* 1968,
 13, 403.
 (146) Nakayama, F. S. *J. Phys. Chem.* 1970, 74, 2726.
 (147) Larson, J. W.; Zeeb, K. G.; Hepler, L. G. *Can. J. Chem.* 1982,
 60, 2141.
 (148) Harned, H. S.; Scholes, S. R., Jr. *J. Am. Chem. Soc.* 1941, 63,
 1706.
 (149) Plummer, L. N.; Busenberg, E. *Geochim. Cosmochim. Acta*,
 1982, 46, 1011.
 (150) Larson, J. W.; Hepler, L. G. "Solute-Solvent Interactions";
 Coetzee, F. J., Ritchie, C. D., Eds.; Marcel Dekker: New
 York, 1969; p 1.
 (151) Lietzke, M. H.; Stoughton, R. W. *J. Tenn. Acad. Sci.* 1974,
 49, 130.
 (152) Hamann, S. D. "Modern Aspects of Electrochemistry No. 9";
 Conway, B. E., Brockris, J. O.'M., Eds.; Plenum Press: New
 York, 1974; Chapter 2.
 (153) Paabo, M.; Bates, R. G. *J. Phys. Chem.* 1969, 73, 3014.
 (154) Kern, D. M. *J. Chem. Ed.* 1960, 37, 14.
 (155) Patel, R. C.; Boe, R. J.; Atkinson, G. *J. Sol. Chem.* 1973, 2,
 357.
 (156) Knoche, W. *Biophys. Physiol. Carbon Dioxide, Symp.* 1979
 1980, 3.
 (157) Eigen, M. *Angew. Chem.* 1963, 75, 489.
 (158) Faurholt, C. *J. Chim. Phys.* 1924, 21, 400.
 (159) Poulton, D. J.; Baldwin, H. W. *Can. J. Chem.* 1967, 45, 1045.
 (160) Dennard, A. E.; Williams, R. J. P. *J. Chem. Soc.* 1966, 812.
 (161) Pocker, Y.; Davison, B. L.; Deits, T. L. *J. Am. Chem. Soc.*
 1978, 100, 3564.
 (162) Pocker, Y.; Bjorkquist, D. W. *J. Am. Chem. Soc.* 1977, 99,
 6537.
 (163) van Eldik, R.; Palmer, D. A. *J. Sol. Chem.* 1982, 11, 339.
 (164) Atkinson, G.; Patel, R. C.; Boe, R. J. *Chem. Phys. Aqueous
 Gas Solutions [Proc. Symp.]* 1975, 85.
 (165) Pinsent, B. R. W.; Pearson, L.; Roughton, F. J. W. *Trans.
 Faraday Soc.* 1956, 52, 1512.
 (166) Pinsent, B. R. W.; Roughton, F. J. W. *Trans. Faraday Soc.*
 1951, 47, 263.
 (167) Welch, M. J.; Lifton, J. F.; Seck, J. A. *J. Phys. Chem.* 1969,
 73, 3351.
 (168) Roughton, F. J. W.; Booth, V. *Biochem. J.* 1938, 32, 2049.
 (169) Tu, C. K.; Silverman, D. N. *J. Phys. Chem.* 1975, 79, 1647.
 (170) Gerster, R. H.; Maren, M. H.; Silverman, D. N. *Proc. Int.
 Conf. Stable Isot. Chem., Biol., Med., 1st* 1973, 219.
 (171) Da Silva, A. T.; Danckwerts, P. V. *Chem. Eng. Sci.* 1973, 28,
 847.
 (172) McLachlan, C. N. S. N. Z. *J. Sci.* 1971, 14, 634.
 (173) Staschewski, D. *Chem.-Ing.-Tech.* 1969, 41, 1111.
 (174) Sharma, M. M.; Danckwerts, P. V. *Trans. Faraday Soc.* 1963,
 59, 386.
 (175) Roberts, D.; Danckwerts, P. V. *Chem. Eng. Sci.* 1962, 17, 961.
 (176) Danckwerts, P. V.; Kennedy, A. M. *Chem. Eng. Sci.* 1958, 8,
 201.
 (177) Nysing, R. A. T. O.; Kramers, H. *Chem. Eng. Sci.* 1958, 8, 81.
 (178) Goodridge, F.; Taylor, M. D. *Trans. Faraday Soc.* 1963, 59,
 2868.
 (179) Onda, K.; Sada, E.; Maeda, Y. *Kagaku Kogaku* 1971, 35, 345.
 (180) Onda, K.; Kobayashi, T.; Fujine, M. *Kogyo Kagaku Zasshi*
 1971, 74, 547.
 (181) Miller, R. F.; Berkshire, D. C.; Kelley, J. J.; Hood, D. W.
Environ. Sci. Technol. 1971, 5, 127.
 (182) Pohorecki, R. *Inz. Chem.* 1972, 2, 383.
 (183) Sokolov, V. E.; Zel'venskii, Ya. D.; Kirilina, L. A. *Tr. Nau-
 chno-Issled. Proektn. Inst. Azotn. Prom. Prod. Org. Sin.*
 1971, 219; *Chem. Abstr.* 1973, 78, 48404x.
 (184) Popa, T. M. *Poverkh. Yavleniya Adsorbsiya, Koord.
 Vzaimodeistviye* 1972, 63; *Chem. Abstr.* 1974, 80, 64241p.
 (185) Szaran, J.; Zuk, W. *ZfI-Mitt.* 1980, 29, 48.
 (186) Mook, W. G.; Bommerson, J. C.; Staverman, W. H. *Earth
 Planet. Sci. Lett.* 1974, 22, 169.
 (187) Constantinescu, I. G. *Bul. Inst. Politeh. "Gheorghe Gheor-
 giu-Dej" Bucuresti* 1971, 33, 61.
 (188) House, W. A. *J. Chem. Soc., Faraday Trans. 1* 1981, 77, 341.
 (189) Ficner, S.; Palmer, D. A.; Dasgupta, T. P.; Harris, G. M.
Inorg. Synth. 1977, 17, 152.
 (190) Bauer, H. F.; Drinkard, W. C. *J. Am. Chem. Soc.* 1960, 82,
 5031.
 (191) Bates, J. B.; Brooker, M. H.; Quist, A. S.; Boyd, G. E. *J. Phys.
 Chem.* 1972, 76, 1565.
 (192) Donoghue, M.; Hepburn, P. H.; Ross, S. D. *Spectrochim.
 Acta, Part A* 1971, 27A, 1065.
 (193) Sterzel, W. Z. *Anorg. Allg. Chem.* 1969, 368, 308.
 (194) Gatehouse, B. M.; Livingstone, S. E.; Nyholm, R. S. *J. Chem.
 Soc.* 1958, 1279.
 (195) Fujita, J.; Martell, A. E.; Nakamoto, K. *J. Chem. Phys.* 1962,
 36, 339.

- (196) Jolivet, J. P.; Thomas, Y.; Taravel, B.; Lorenzelli, V. *J. Mol. Struct.* 1980, 60, 93.
- (197) Baylis, B. K. W.; Bailar, J. C., Jr. *Inorg. Chem.* 1970, 9, 641.
- (198) Caro, P. E.; Sawyer, J. O.; Eyring, L. *Spectrochim. Acta, Part A* 1972, 28A, 1167.
- (199) Kharitonov, Y. Y.; Molodkin, A. K.; Balakaeva, T. A. *Zh. Neorg. Khim.* 1969, 14, 2761.
- (200) Rulmont, A. *Spectrochim. Acta, Part A* 1978, 34A, 1117.
- (201) Ogden, J. S.; Williams, S. J. *J. Chem. Soc., Dalton Trans.* 1981, 456.
- (202) Sass, R. L.; Scheuerman, R. F. *Acta Crystallogr.* 1962, 15, 77.
- (203) Thomas, J. O.; Tellgren, R.; Olovsson, I. *Acta Crystallogr., Sect. B* 1974, B30, 1155.
- (204) Thomas, J. O.; Tellgren, R.; Olovsson, I. *Acta Crystallogr., Sect. B* 1974, B30, 2540.
- (205) Kim, M. Il. *Taehan Hwahakhoe Chi.* 1969, 13, 131.
- (206) Dickens, B.; Mauer, F. A.; Brown, W. E. *J. Res. Nat. Bur. Stand., Sect. A* 1970, 74A, 319.
- (207) Effenberger, H.; Mereiter, K.; Zemann, J. Z. *Kristallogr.* 1981, 156, 233.
- (208) Dickens, B.; Hyman, A.; Brown, W. E. *J. Res. Nat. Bur. Stand., Sect. A* 1971, 75A, 129.
- (209) Pertlik, F. Z. *Krystallogr.* 1981, 157, 199.
- (210) Pauling, L. Z. *Krystallogr.* 1979, 150, 155.
- (211) Freeman, H. C.; Robinson, G. J. *Chem. Soc.* 1965, 3194.
- (212) Guild, B. C.; Hayden, T.; Brennan, T. F. *Cryst. Struct. Commun.* 1980, 9, 371.
- (213) Price, M. G.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* 1981, 1067.
- (214) Toriumi, K.; Saito, Y. *Acta Crystallogr., Sect. B* 1975, B31, 1247.
- (215) Althoff, P. L. *Am. Min.* 1977, 62, 772.
- (216) Cotton, F. A.; DeBoer, B. G.; LaPrade, M. D.; Pipal, J. R.; Ucko, D. A. *Acta Crystallogr., Sect. B* 1971, B27, 1664.
- (217) Norman, J. G., Jr.; Kolari, H. J. *J. Am. Chem. Soc.* 1978, 100, 791.
- (218) Cotton, F. A.; Extine, M.; Rice, G. W. *Inorg. Chem.* 1978, 17, 176.
- (219) Einstein, F. W. B.; Willis, A. C. *Inorg. Chem.* 1981, 20, 609.
- (220) Rowan, N. S.; Storm, C. B.; Hunt, J. B. *Inorg. Chem.* 1978, 17, 2853.
- (221) Veselkov, E. A. *Zh. Prikl. Khim.* 1980, 53, 2427.
- (222) Bakhramova, N. P.; Bois, G. V.; Gindin, E. I.; Zhukovskii, V. I.; Kostikov, Y. P.; Martynov, V. B.; Prokhvatilov, V. G. *Izv. Akad. Nauk SSSR, Neorg. Mater.* 1977, 13, 1275.
- (223) Yamaguchi, J.; Sawada, Y.; Sakurai, O.; Uematsu, K.; Mizutani, N.; Kato, M. *Thermochim. Acta* 1980, 35, 307.
- (224) Ball, M. C.; Casson, M. J. *J. Inorg. Nucl. Chem.* 1977, 39, 1456.
- (225) Ball, M. C.; Casson, M. J. *J. Inorg. Nucl. Chem.* 1975, 37, 2253.
- (226) Kato, M.; Mizutani, N. *Kobutsugaku Zasshi* 1980, 14, 15. (a) Singh, N. B.; Singh, R. P.; Singh, J.; Singh, H. C. *J. Solid State Chem.* 1980, 33, 391.
- (227) Arkhangelskii, I. V.; Zhorov, V. A.; Komissarova, L. N.; Teterin, E. G.; Shatskii, V. M. *Zh. Neorg. Khim.* 1971, 16, 636.
- (228) Gangadevi, T.; Subba Rao, M.; Kutty, T. R. N. *Indian J. Chem., Sect. A* 1980, 19A, 309.
- (229) Reddy, V. B.; Mehrotra, P. N. *Thermochim. Acta* 1979, 31, 349.
- (230) Murthy, H. S. G. K.; Subba Rao, M.; Kutty, T. R. N. *Indian J. Chem., Sect. A* 1977, 15A, 863.
- (231) Schwendt, P.; Uskert, D. *Chem. Zvesti* 1981, 35, 229.
- (232) Schwendt, P.; Petrovic, P.; Uskert, D. Z. *Anorg. Allg. Chem.* 1980, 466, 232.
- (233) Nagase, K. *Bull. Chem. Soc. Jpn.* 1973, 46, 144.
- (234) Ehrhardt, H.; Schober, H.-Chr.; Seidel, H. Z. *Anorg. Allg. Chem.* 1980, 465, 83.
- (235) Ehrhardt, H.; Schweer, H.; Seidel, H. Z. *Anorg. Allg. Chem.* 1980, 462, 185.
- (236) Moreau, R. *Bull. Soc. R. Sci. Liege* 1967, 36, 673.
- (237) Varma, R. P.; Bhargava, H. K. *Rev. Roum. Chim.* 1979, 24, 537.
- (238) Grassini-Strazza, G.; Polcaro, C. M.; Carunchio, V.; Messina, A. *Inorg. Chim. Acta* 1978, 29, L265.
- (239) Rastogi, R. P.; Dubey, B. L.; Das, L.; Das, I. *J. Inorg. Nucl. Chem.* 1977, 39, 2179.
- (240) Samuskevich, V. V.; Prodán, E. A.; Pavlyuchenko, M. M. *Zh. Neorg. Khim.* 1972, 17, 2067.
- (241) Prodán, E. A.; Pavlyuchenko, M. M.; Samuskevich, V. V. *Kinet. Katal.* 1973, 14, 252.
- (242) Sharov, V. A.; Bezdezhnykh, G. V. *Usp. Khim.* 1981, 50, 1197.
- (243) Mochizuki, A. *Numazu Kogyo Koto Semmon Gakko Kenkyu Hokoku* 1974, 9, 57; *Chem. Abstr.* 1978, 88, 97530a.
- (244) Peterson, E. J.; Onstott, E. I.; Johnson, M. R.; Bowman, M. G. *J. Inorg. Nucl. Chem.* 1978, 40, 1357.
- (245) Chai, B. H. T.; Mroczkowski, S. J. *Cryst. Growth* 1978, 44, 84.
- (246) Dharwadkar, S. R.; Kumbhar, M. S.; Chandrasekharaiah, M. S.; Karkhanavala, M. D. *J. Inorg. Nucl. Chem.* 1980, 42, 1621.
- (247) Dabkowska, M. *Ann. Univ. Mariae Curie-Skłodowska, Sect. AA: Phys. Chem.* 1976-1977, 31-32, 111; *Chem. Abstr.* 1981, 94, 40685z.
- (248) Dobrovolskii, K. A. *Zh. Neorg. Khim.* 1970, 15, 1999.
- (249) Kalz, H. J.; Seidel, H. Z. *Anorg. Allg. Chem.* 1980, 465, 92.
- (250) Schweer, H.; Seidel, H. Z. *Anorg. Allg. Chem.* 1981, 477, 196.
- (251) Mochizuki, A.; Nagashima, K.; Wakita, H. *Bull. Chem. Soc. Jpn.* 1974, 47, 755.
- (252) Oda, T. *Oita Daigaku Kyoikugakubu Kenkyu Kiyo, Shizen Kagaku* 1975, 4, 1; *Chem. Abstr.* 1977, 87, 161013t.
- (253) Taravel, B.; Fromage, F.; Delorme, P.; Lorenzelli, V. *J. Mol. Struct.* 1973, 16, 483.
- (254) Weigel, F.; Ter Meer, N. Z. *Naturforsch. B* 1971, 26B, 504.
- (255) Karkhanavala, M. D.; Daroowalla, S. H. *J. Indian Chem. Soc.* 1969, 46, 729.
- (256) Karyakin, A. V.; Volynets, M. P. *Zh. Struct. Khim.* 1962, 3, 714.
- (257) Dollimore, D.; Taylor, T. J. *Thermochim. Acta* 1980, 40, 297.
- (258) Criado, J. M.; González, M. *Thermochim. Acta* 1981, 46, 201.
- (259) Zivkovic, Z. D. *Rud.-Metall. Zb.* 1980, 27, 469.
- (260) Zubovskii, V. M.; Veksler, S. F. *Kinet. Katal.* 1973, 14, 248.
- (261) Orewczyk, J. *Pr. Mineral. (Pol. Akad. Nauk, Oddzial Krakowkie, Kom. Nauk Mineral.)* 1976, 44, 19.
- (262) Dollimore, D.; France, J. A.; Krupay, B. W.; Whitehead, R. *Thermochim. Acta* 1980, 36, 343.
- (263) Kubas, Z.; Orewczyk, J. *J. Therm. Anal., Proc. Int. Conf.*, 4th 1974 1975, 1, 517.
- (264) Kokhanovskii, V. V.; Pavlyuchenko, M. M.; Prodán, E. A. *Vestn. Akad. Nauk BSSR, Ser. Khim. Nauk* 1970, 34; *Chem. Abstr.* 1970, 73, 70255t.
- (265) Arora, B. R.; Banerjee, R. K.; Rao, T. S. R. P.; Mandal, N. K.; Ganguli, N. C.; Sen, S. P. *Thermochim. Acta* 1973, 7, 25.
- (266) Blake, C. A.; Colman, C. F.; Brown, K. B.; Hill, D. G.; Lowie, R. S.; Schmitt, J. M. *J. Am. Chem. Soc.* 1956, 78, 5978.
- (267) Bullwinkel, E. P. USAEC Report RMO-2614, 1954.
- (268) Scanlan, J. P. *J. Inorg. Nucl. Chem.* 1977, 39, 635.
- (269) McClaine, L. A.; Bullwinkel, E. P.; Huggins, J. C. *Actes. Conf. Int. Geneve* 1955, 8, 29.
- (270) Ferri, D.; Grenthe, I.; Salvatore, F. *Acta Chem. Scand., Ser. A* 1981, 35A, 165.
- (271) Patel, R. C.; Garland, F.; Atkinson, G. *J. Sol. Chem.* 1975, 4, 161.
- (272) Sullivan, J. C.; Woods, M.; Bertrand, P. A.; Choppin, G. R. *Radiochim. Acta* 1982, 31, 45.
- (273) Almagro, V.; Garcia, F. S.; Suncho, J. *An. Quim.* 1973, 69, 709.
- (274) Sipos, L.; Valenta, P.; Nuernberg, H. W.; Branica, M. *Lead Mar. Environ., Proc. Int. Experts Discuss.* 1977 1980, 61.
- (275) Ciavatta, L.; Ferri, D.; Grimaldi, M.; Palombari, R.; Salvatore, F. *J. Inorg. Nucl. Chem.* 1979, 41, 1175.
- (276) Ciavatta, L.; Ferri, D.; Grenthe, I.; Salvatore, F. *Inorg. Chem.* 1981, 20, 463.
- (277) Al-Obadie, M. S. *Inorg. Chem.* 1980, 19, 2897.
- (278) Sunda, W. G.; Hanson, P. J. *ACS Symp. Ser.* 1979, No. 93, 147.
- (279) Raaflaub, J. *Fasciculus* 1960, 43, 629.
- (280) Lin, C.-T.; Atkingas Son, G. *Chem. Phys. Aqueous Solutions, [Proc. Symp.]* 1975, 257.
- (281) Bauman, J. E., Jr. *Inf. Circ. -U.S., Bur. Mines* 1981, No. 8853, 268.
- (282) Lesht, D.; Bauman, J. E., Jr. *Inorg. Chem.* 1978, 17, 3332.
- (283) Johnson, G. K.; Bauman, J. E., Jr. *Inorg. Chem.* 1978, 17, 2774.
- (284) Reardon, E. J.; Langmuir, D. *Am. J. Sci.* 1974, 274, 599.
- (285) Greenwald, I. *J. Biol. Chem.* 1941, 141, 789.
- (286) Tsymball, C. *Commis. Energ. At. (Fr.), Rapp.* 1969, CEAR-3476; *Chem. Abstr.* 1970, 72, 6684j.
- (287) Cinneide, S. O.; Scanlan, J. P.; Hynes, M. J. *J. Inorg. Nucl. Chem.* 1975, 37, 1013.
- (288) Dumonceau, J.; Bigot, S.; Treuil, M.; Faucherre, J.; Fromage, F. *C. R. Hebd. Seances Acad. Sci., Ser. C* 1978, 287, 325.
- (289) Umova, I. E.; Lobov, B. I.; Rutkovskii, Y. I.; Mironov, V. E. *Zh. Neorg. Khim.* 1973, 18, 836.
- (290) Christ, C. L.; Hostetler, P. B. *Am. J. Sci.* 1970, 268, 439.
- (291) Gel'man, A. D.; Moskvin, A. I.; Zaitseva, V. P. *Radiokhimiya* 1962, 4, 154.
- (292) Bilinski, H.; Schindler, P. *Geochim. Cosmochim. Acta* 1982, 46, 921.
- (293) Babko, A. K.; Kodenskaya, V. S. *Russ. J. Inorg. Chem. (Engl. Transl.)* 1960, 5, 1241.
- (294) Klygin, A. E.; Smirnova, Y. D. *Russ. J. Inorg. Chem. (Engl. Transl.)* 1959, 4, 16.
- (295) Sergeyeva, E. I.; Nikitin, A. A.; Khodakovskii, I. L.; Naumov, G. B. *Geokhimiya* 1972, 11, 1340.
- (296) Baranova, N. N. *Zh. Neorg. Khim.* 1969, 14, 3257.
- (297) Paramonova, V. I.; Nikolaeva, M. N. *Radiokhimiya* 1962, 4, 84.

- (298) van den Berg, C. M. G.; Kramer, J. R. *Anal. Chim. Acta* 1979, 106, 113.
- (299) Millar, E. K.; Evans, C. A.; Rabenstein, D. L. *Can. J. Chem.* 1978, 56, 3104.
- (300) Sychev, A. Ya.; Pfannmller, W.; Isak, V. G. *Zh. Fiz. Khim.* 1981, 55, 365.
- (301) Smith, R. M.; Martell, A. E. "Critical Stability Constants, Volume 4: Inorganic Complexes"; Plenum Press: New York, 1976.
- (302) Blandamer, M. J.; Burgess, J.; Robertson, R. E.; Scott, J. M. *W. Chem. Rev.* 1982, 82, 259.
- (303) Lawrence, C. H.; Johnston, F. J. *J. Phys. Chem. Ref. Data* 1980, 9, 751.
- (304) Ebelman, M. *Ann. Physik* 1842, 43, 302.
- (305) Ebelman, M. *Ann. Chim. Phys.* 1842, 5, 206.
- (306) Millero, F. J.; Schreiber, D. R. *Am. J. Sci.* 1982, 282, 1508.
- (307) Dickson, A. G.; Whitfield, M. *Mar. Chem.* 1981, 10, 315.
- (308) O'Shea, T. A.; Mancy, K. H. *Water Res.* 1978, 12, 703.
- (309) Klets, V. E.; Tertyshnaya, N. A. *Zh. Prikl. Khim. (Leningrad)* 1977, 50, 1215.
- (310) Caro, P. E.; Lemaitre-Blaise, M. *Proc. Rare Earth Res. Conf., 7th, 1968 1969*, 1, 187.
- (311) Sklyarenko, Y. S.; Ruzaikina, L. V. *Zh. Neorg. Khim.* 1970, 15, 778.
- (312) Chaffee, E.; Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* 1973, 95, 4169.
- (313) Harris, G. M.; Dasgupta, T. P. *J. Indian Chem. Soc.* 1977, 54, 62.
- (314) Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* 1977, 99, 2490.
- (315) van Eldik, R.; Palmer, D. A.; Kelm, H.; Harris, G. M. *Inorg. Chem.* 1980, 19, 3679.
- (316) Bennetto, H. P.; Caldin, E. F. *J. Chem. Soc. A* 1971, 2198, 2207.
- (317) Brown, R. F. *J. Org. Chem.* 1962, 27, 3015.
- (318) Leffler, J. E. *J. Org. Chem.* 1955, 20, 1202.
- (319) van Eldik, R.; Palmer, D. A.; Schmidt, R.; Kelm, H. *Inorg. Chim. Acta* 1981, 50, 131.
- (320) Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* 1975, 97, 1733.
- (321) Francis, D. J.; Jordan, R. B. *J. Am. Chem. Soc.* 1969, 91, 6626.
- (322) van Eldik, R.; Palmer, D. A.; Harris, G. M. *Inorg. Chem.* 1980, 19, 3673.
- (323) Hunt, H. R.; Taube, H. *J. Am. Chem. Soc.* 1958, 80, 2642.
- (324) Swaddle, T. W.; Stranks, D. R. *J. Am. Chem. Soc.* 1972, 94, 8357.
- (325) van Eldik, R.; Harris, G. M. *Inorg. Chem.* 1980, 19, 3684.
- (326) Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* 1971, 93, 91.
- (327) Dasgupta, T. P.; Harris, G. M. *Inorg. Chem.* 1978, 17, 3304.
- (328) Scheidegger, H. A. Ph.D. Thesis, ETH (Zurich), 1966.
- (329) van Eldik, R.; Harris, G. M. *Inorg. Chem.* 1975, 14, 10.
- (330) Joubert, P. R.; van Eldik, R. *Int. J. Chem. Kinet.* 1976, 8, 411.
- (331) Hunt, J. P.; Rutenberg, A. C.; Taube, H. *J. Am. Chem. Soc.* 1952, 74, 268.
- (332) Bunton, C. A.; Llewellyn, D. R. *J. Chem. Soc.* 1953, 1692.
- (333) Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* 1968, 90, 6360.
- (334) Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* 1969, 91, 3207.
- (335) Posey, F. A.; Taube, H. *J. Am. Chem. Soc.* 1953, 75, 4099.
- (336) Harris, G. M.; Hyde, K. E. *Inorg. Chem.* 1978, 17, 1892.
- (337) Hay, R. W.; Jeragh, B. *Transition Metal Chem. (Weinheim, Ger.)* 1979, 4, 288.
- (338) Hay, R. W.; Jeragh, B. *J. Chem. Soc., Dalton Trans.* 1979, 1343.
- (339) Hay, R. W.; Jeragh, B. *Transition Metal Chem. (Weinheim, Ger.)* 1980, 5, 252.
- (340) Francis, D. J.; Jordan, R. B. *Inorg. Chem.* 1972, 11, 1170.
- (341) van Eldik, R.; Dasgupta, T. P.; Harris, G. M. *Inorg. Chem.* 1975, 14, 2573.
- (342) Hyde, K. E.; Fairchild, G. H.; Harris, G. M. *Inorg. Chem.* 1976, 15, 2631.
- (343) Francis, D. J.; Searle, G. H. *Aust. J. Chem.* 1974, 27, 269.
- (344) Dasgupta, T. P. *Inorg. Chim. Acta* 1976, 20, 33.
- (345) Wieghardt, K.; Schmidt, W.; van Eldik, R.; Nuber, B.; Weiss, J. *Inorg. Chem.* 1980, 19, 2922.
- (346) Wieghardt, K.; Schmidt, W.; Nuber, B.; Prikner, B.; Weiss, J. *J. Chem. Ber.* 1980, 113, 36.
- (347) Churchill, M. R.; Laszewycz, R. A.; Koshy, K.; Dasgupta, T. P. *Inorg. Chem.* 1981, 20, 376.
- (348) Koshy, K.; Dasgupta, T. P. *Inorg. Chim. Acta* 1982, 61, 207.
- (349) van Eldik, R.; Dasgupta, T. P., unpublished results.
- (350) Palmer, D. A.; Dasgupta, T. P.; Kelm, H. *Inorg. Chem.* 1978, 17, 1173.
- (351) Endicott, J. F.; Kane-Maguire, N. A. P.; Rillema, D. P.; Roche, T. S. *Inorg. Chem.* 1973, 12, 1818.
- (352) Dasgupta, T. P.; Harris, G. M. *Inorg. Chem.* 1978, 17, 3123.
- (353) Inoue, T.; Harris, G. M. *Inorg. Chem.* 1980, 19, 1091.
- (354) Edwards, J. O.; Monacelli, F.; Orttaggi, G. *Inorg. Chim. Acta* 1974, 11, 47.
- (355) Dobbins, R. J.; Harris, G. M. *J. Am. Chem. Soc.* 1970, 92, 5104.
- (356) Strom, E. T.; Woessner, D. E.; Smith, W. B. *J. Am. Chem. Soc.* 1981, 103, 1255.
- (357) Sastri, M. N.; Raman, V. A. *Z. Phys. Chem. (Leipzig)* 1975, 6, 993.
- (358) Gillard, R. D.; Mitchell, P. G.; Price, M. G. *J. Chem. Soc., Dalton Trans.* 1972, 1211.
- (359) Mori, M.; Shibata, M.; Kyuno, E.; Hoshiyama, K. *Bull. Chem. Soc. Jpn.* 1958, 31, 291.
- (360) Shibata, M.; Mori, M.; Kyuno, E. *Inorg. Chem.* 1964, 3, 1573.
- (361) Bodek, I.; Davies, G.; Ferguson, J. H. *Inorg. Chem.* 1975, 14, 1708.
- (362) Hyodo, O.; Archer, R. D. *Inorg. Chem.* 1969, 8, 2510.
- (363) Ripan, R.; Varhelyi, C. *Rev. Roum. Chim.* 1972, 17, 259.
- (364) Davies, G.; Hung, Y.-W. *Inorg. Chem.* 1976, 15, 704.
- (365) Davies, G.; Hung, Y.-W. *Inorg. Chem.* 1976, 15, 1358.
- (366) Ida, Y.; Kobayashi, K.; Shibata, M. *Chem. Lett.* 1974, 1299.
- (367) Rosseinsky, D. R.; Jaurequi, G. A. *J. Chem. Soc., Dalton Trans.* 1979, 805.
- (368) Dasgupta, T. P.; Harris, G. M. *Inorg. Chem.* 1973, 12, 488.
- (369) Garnett, P. J.; Watts, D. W., private communication, see ref 341.
- (370) Cope, V. W.; Hoffman, M. Z. *J. Chem. Soc., Chem. Commun.* 1972, 227.
- (371) Chen, S.-N.; Hoffman, M. Z. *J. Chem. Soc., Chem. Commun.* 1972, 991.
- (372) Chen, S.-N.; Cope, V. W.; Hoffman, M. Z. *J. Phys. Chem.* 1973, 77, 1111.
- (373) Cope, V. W.; Chen, S.-N.; Hoffman, M. Z. *J. Am. Chem. Soc.* 1973, 95, 3116.
- (374) Chen, S.-N.; Hoffman, M. Z. *Radiat. Res.* 1973, 56, 40.
- (375) Chen, S.-N.; Hoffman, M. Z. *J. Phys. Chem.* 1974, 78, 2099.
- (376) Chen, S.-N.; Hoffman, M. Z. *Radiat. Res.* 1975, 62, 18.
- (377) Chen, S.-N.; Hoffman, M. Z.; Parsons, G. H., Jr. *J. Phys. Chem.* 1975, 79, 1911.
- (378) Cope, V. W.; Hoffman, M. Z.; Chen, S.-N. *J. Phys. Chem.* 1978, 82, 2665.
- (379) Lillie, J.; Beck, G.; Henglein, A. *Ber. Bunsenges. Phys. Chem.* 1971, 75, 458.
- (380) Cohen, H.; Meyerstein, D. *J. Am. Chem. Soc.* 1972, 94, 6944.
- (381) Blake, D. M.; Mersecchi, R. *J. Chem. Soc., Chem. Commun.* 1971, 1045.
- (382) Eaborn, C.; Pidcock, A.; Steele, B. R. *J. Chem. Soc., Dalton Trans.* 1975, 809.
- (383) Fujiwana, S.; Watanabe, T.; Tadano, H. *J. Coord. Chem.* 1971, 1, 195.
- (384) Pikaev, A. K.; Ershov, B. G.; Makarov, I. E. *J. Phys. Chem.* 1975, 79, 3025.
- (385) Basile, L. J.; Ferraro, J. R.; Mitchell, M. L.; Sullivan, J. C. *Appl. Spectrosc.* 1978, 32, 535.
- (386) Nash, K.; Mulac, W.; Noon, M.; Fried, S.; Sullivan, J. C. *J. Inorg. Nucl. Chem.* 1981, 43, 897.
- (387) Vukovic, M.; Cukman, D.; Pravdic, V. J. *Electroanal. Chem. Interfacial Electrochem.* 1974, 54, 209.
- (388) Matusinovic, T.; Smith, D. E. *J. Electroanal. Chem. Interfacial Electrochem.* 1979, 98, 133.
- (389) Keenan, A. G.; Williamson, T. R. *J. Phys. Chem.* 1978, 82, 46.
- (390) Keenan, A. G.; Ferrer-Vinent, I. J. *J. Phys. Chem.* 1979, 83, 358.
- (391) Finkenberg, E.; Fisher, P.; Huang, S.-M. Y.; Gafney, H. D. *J. Phys. Chem.* 1978, 82, 526.
- (392) Sychev, A. Ya.; Isak, V. G.; Lap, D. V. *Zh. Fiz. Khim.* 1977, 51, 363.
- (393) Das, P. K.; De, A. K. *J. Indian Chem. Soc.* 1979, 56, 562.
- (394) Early, J. E.; Alexander, W. *J. Am. Chem. Soc.* 1970, 92, 2294.
- (395) Sastri, M. N.; Raman, V. A. *Z. Phys. Chem. (Leipzig)* 1975, 256, 993.
- (396) Phatak, G. M.; Bhat, T. R.; Shankar, J. *J. Inorg. Nucl. Chem.* 1970, 32, 1305.
- (397) Phatak, G. M.; Rao, K. V. S. R.; Shankar, J. *Proc. Indian Acad. Sci., Sect. A* 1976, 83A, 243.
- (398) Pearson, R.; Pagenkopf, G. K. *Inorg. Chem.* 1978, 17, 1799.
- (399) Boreham, C. J.; Buckingham, D. A.; Keene, F. R. *J. Am. Chem. Soc.* 1979, 101, 1409.
- (400) Dash, A. C.; Nanda, R. K. *J. Indian Chem. Soc.* 1975, 52, 298.
- (401) Braunstein, P. *Nachr. Chem. Tech. Lab.* 1981, 29, 695.
- (402) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* 1979, 101, 1767.
- (403) Yoshida, T.; Thorn, D. L.; Okano, T.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* 1979, 101, 4212.
- (404) Darendsbourg, D. J.; Rokicki, A.; Darendsbourg, M. Y. *J. Am. Chem. Soc.* 1981, 103, 3223.
- (405) Herskovitz, T. *J. Am. Chem. Soc.* 1977, 99, 2391.
- (406) Ito, T.; Yamamoto, A. *Yuki Gosei Kagaku Kyokaishi* 1976, 34, 308; *Chem. Abstr.* 1976, 85, 136305r.

- (407) Yamamoto, A. *Kagaku Sosetsu* 1973, 3, 45.
- (408) Vol'pin, M. E.; Kolomnikov, I. S. *Pure Appl. Chem.* 1973, 33, 567.
- (409) Yamaguchi, I. *Tokyo Kasei Daigaku Kenkyu Kiyo* 1980, 20, 43; *Chem. Abstr.* 1981, 95, 25247k.
- (410) Lepkowski, W. *Chem. Eng. News* 1977, 55 (Oct. 17), 26.
- (411) Lepkowski, W. *Chem. Eng. News* 1977, 55 (Aug. 1), 18.
- (412) Stuiver, M. *Science (Washington, D.C.)* 1978, 199, 253.
- (413) Vol'pin, M. E. *Pure Appl. Chem.* 1972, 30, 607.
- (414) Vol'pin, M. E.; Kolomnikov, I. S. *Organomet. React.* 1975, 5, 313.
- (415) Karsch, H. H. *Chem. Ber.* 1977, 110, 2213.
- (416) Huber, H.; Moskovits, M.; Ozin, G. A. *Nature (London)*, *Phys. Sci.* 1972, 236, 127.
- (417) Kohnle, J. F.; Slaugh, L. H.; Nakamaye, K. L. *J. Am. Chem. Soc.* 1969, 91, 5904.
- (418) Flynn, B. R.; Vaska, L. *J. Am. Chem. Soc.* 1973, 95, 5081.
- (419) Kolomnikov, I. S.; Grigoryan, M. Kh. *Usp. Khim.* 1978, 47, 603.
- (420) Vol'pin, M. E. *Zh. Vses. Khim. Obshchest.* 1972, 17, 396.
- (421) Bianco, V. D.; Doronzo, S.; Gallo, N. *Inorg. Nucl. Chem. Lett.* 1981, 17, 75.
- (422) Tsuda, T.; Chujo, Y.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* 1975, 963.
- (423) Chisholm, M. H.; Extine, M. *J. Chem. Soc., Chem. Commun.* 1975, 438.
- (424) Ikariya, T.; Yamamoto, A. *J. Organomet. Chem.* 1974, 72, 145.
- (425) Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* 1971, 26, 357.
- (426) Aresta, M.; Nobile, C. F. *J. Chem. Soc., Dalton Trans.* 1977, 708.
- (427) Herskovitz, T.; Guggenberger, L. *J. J. Am. Chem. Soc.* 1976, 98, 1615.
- (428) Vasapollo, G.; Giannoccaro, P.; Nobile, C. F.; Sacco, A. *Inorg. Chim. Acta* 1981, 48, 125.
- (429) Iwashita, Y.; Hayata, A. *J. Am. Chem. Soc.* 1969, 91, 2525.
- (430) Aresta, M.; Nobile, C. F.; Albano, V. G. *J. Chem. Soc., Chem. Commun.* 1975, 636.
- (431) Fachinetto, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* 1978, 100, 7405.
- (432) Ibers, J. A.; Krogssrud, S.; Yamamoto, A.; Komiya, S., unpublished results.
- (433) Kolomnikov, I. S.; Gusev, A. I.; Aleksandrov, G. G.; Lobeeva, T. S.; Struchkov, Yu. T.; Vol'pin, M. E. *J. Organomet. Chem.* 1973, 59, 349.
- (434) Jolly, P. W.; Stobbe, S.; Wilke, G.; Goddard, R.; Kruger, C.; Sekutowski, J. C.; Tsay, Y.-H. *Angew. Chem.* 1978, 90, 144.
- (435) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *J. Am. Chem. Soc.* 1978, 100, 1727.
- (436) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J.; Mitschler, A.; Ricard, L. *J. Am. Chem. Soc.* 1981, 103, 5115.
- (437) Kolomnikov, I. S.; Lobeeva, T. S.; Gorbachevskaya, V. V.; Aleksandrov, G. G.; Struchkov, Yu. T.; Vol'pin, M. E. *J. Chem. Soc., Chem. Commun.* 1971, 972.
- (438) Chisholm, M. H.; Extine, M. *J. Am. Chem. Soc.* 1974, 96, 6214.
- (439) Kolomnikov, I. S.; Gusev, A. I.; Belopotapova, T. S.; Grigoryan, M. Kh.; Lysyak, T. V.; Struchkov, Yu. T.; Vol'pin, M. E. *J. Organomet. Chem.* 1974, 69, C10.
- (440) Chisholm, M. H.; Extine, M. *J. Am. Chem. Soc.* 1975, 97, 1623.
- (441) Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed.; Wiley-Interscience: New York, 1970.
- (442) Hidai, M.; Uchida, Y. *Kagaku Sosetsu* 1981, 32, 261.
- (443) Komiya, S.; Yamamoto, A. *J. Organomet. Chem.* 1972, 46, C58.
- (444) Kolomnikov, I. S.; Belopotapova, T. S.; Vol'pin, M. E. *J. Gen. Chem. USSR (Engl. Transl.)* 1976, 45, 1958.
- (445) Chatt, J.; Kubota, M.; Leigh, G. J.; March, F. C.; Mason, R.; Yarrow, D. J. *J. Chem. Soc., Chem. Commun.* 1974, 1033.
- (446) Inoue, Y.; Sasaki, Y.; Hasimoto, H. *J. Chem. Soc., Chem. Commun.* 1975, 718.
- (447) Aresta, M.; Nobile, C. F. *Inorg. Chim. Acta* 1977, 24, L49.
- (448) Dennard, A. E.; Williams, R. J. P. *Transition Met. Chem.* 1966, 2, 123.
- (449) Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* 1979, 28, 79.
- (450) Miyashita, A.; Yamamoto, A. *J. Organomet. Chem.* 1976, 113, 187.
- (451) Vinogradova, S. M.; Gutsev, G. L. *Koord. Khim.* 1978, 4, 992.
- (452) Flynn, B. R.; Vaska, L. *J. Chem. Soc., Chem. Commun.* 1974, 703.
- (453) Saegusa, T.; Tsuda, T. *Kagaku Kogyo* 1975, 26, 562.
- (454) Jewsbury, R. A. *Inorg. Chim. Acta* 1981, 49, 141.
- (455) Vasapollo, G.; Giannoccaro, P.; Nobile, C. F.; Sacco, A. *Congr. Naz. Chim. Inorg. [Atti]*, 13th 1980, 312.
- (456) Kolomnikov, I. S.; Belopotopova, T. S.; Lysyak, T. V.; Vol'pin, M. E. *J. Organomet. Chem.* 1974, 67, C25.
- (457) Komiya, S.; Yamamoto, A. *Asahi Garasu Kogyo Gijutsu Shoreikai Kenkyu Hokoku* 1973, 23, 429.
- (458) Bianco, V. D.; Doronzo, S.; Gallo, N. *Inorg. Nucl. Chem. Lett.* 1979, 15, 187.
- (459) Bianco, V. D.; Doronzo, S.; Gallo, N. *J. Inorg. Nucl. Chem.* 1978, 40, 1820.
- (460) Djaoued, Y.; Lysyak, T. V.; Kolomnikov, I. S.; Kharitonov, Yu. Ya. *Koord. Khim.* 1981, 7, 1432.
- (461) Ivckova, J.; Barton, J. J. *Chem. Soc., Chem. Commun.* 1973, 306.
- (462) Savel'ev, M. M.; Kolomnikov, I. S.; Vitt, S. V.; Vol'pin, M. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1975, 486.
- (463) Kachapina, L. M.; Shul'ga, Yu. M.; Echmaev, S. B.; Kolomnikov, I. S.; Vinogradova, S. M.; Borod'ko, Yu. G. *Koord. Khim.* 1977, 3, 435.
- (464) Boguslavskii, E. G.; Shklyaev, A. A.; Maksimov, N. G.; Alaudinova, Z. M.; Kolomnikov, I. S.; Anufrienko, V. F. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1980, 1231.
- (465) Beck, M. T.; Joo, F. *J. Chem. Soc., Chem. Commun.* 1975, 230.
- (466) Kachapina, L. M.; Shul'ga, Yu. M.; Ermaev, S. B.; Kolomnikov, I. S.; Vinogradova, S. M.; Borod'ko, Yu. G. *Koord. Khim.* 1977, 3, 435.
- (467) Jolly, P. W.; Jonas, K.; Kruger, C.; Tsay, Y.-H. *J. Organomet. Chem.* 1971, 33, 109.
- (468) Vol'pin, M. E.; Kolomnikov, I. S.; Lobeeva, T. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1972, 211.
- (469) Roberts, D. R.; Geoffroy, G. L.; Bradley, M. G. *J. Organomet. Chem.* 1980, 198, C75.
- (470) Floriani, C.; Fachinetto, G. *J. Chem. Soc., Chem. Commun.* 1974, 615.
- (471) Beverwijk, C. D. M.; van der Kerk, G. J. M. *J. Organomet. Chem.* 1973, 49, C59.
- (472) Ozin, G. A.; Huber, H.; McIntosh, D. *Inorg. Chem.* 1978, 17, 1472.
- (473) Johnson, B. F. G.; Khair, A. *J. Bangladesh Acad. Sci.* 1977, 1, 123.
- (474) Sakaki, S.; Kudou, N.; Ohyoshi, A. *Inorg. Chem.* 1977, 16, 202.
- (475) Weidlein, J. *Z. Anorg. Allg. Chem.* 1970, 378, 245.
- (476) Kolomnikov, I. S.; Novotortsev, V. M.; Lysyak, T. V.; Grigoryan, M. Kh.; Kalinnikov, V. T.; Lodzhevskii, V. L. *Koord. Khim.* 1979, 5, 1759.
- (477) Stankevich, I. V.; Lysyak, T. V.; Aleksandrov, G. G.; Kolomnikov, I. S. *Zh. Strukt. Khim.* 1978, 19, 908.
- (478) Pu, L. S.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* 1968, 90, 3896.
- (479) Misono, A.; Uchida, Y.; Hidai, M.; Kuse, T. *J. Chem. Soc., Chem. Commun.* 1968, 981.
- (480) Koinuma, H.; Yoshida, Y.; Hirai, H. *Chem. Lett.* 1975, 1223.
- (481) Ashworth, T. V.; Singleton, E. *J. Chem. Soc., Chem. Commun.* 1976, 204.
- (482) Yamamoto, T.; Yamamoto, A. *Chem. Lett.* 1978, 615.
- (483) Tsuda, T.; Ueda, K.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* 1974, 380.
- (484) Yashita, A. M.; Yamamoto, A. *J. Organomet. Chem.* 1973, 49, C57.
- (485) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* 1978, 100, 7577.
- (486) Normant, J. F.; Cahiez, G.; Chuit, C.; Villieras, J. *J. Organometal. Chem.* 1973, 54, C53.
- (487) Kolomnikov, I. S.; Stepovska, H.; Tyrluk, S.; Vol'pin, M. E. *Zh. Obshch. Khim.* 1974, 44, 1743.
- (488) Kolomnikov, I. S.; Stepovska, G.; Tyrluk, S.; Vol'pin, M. E. *Zh. Obshch. Khim.* 1972, 42, 1652.
- (489) Miyashita, A.; Yamamoto, A. *J. Organomet. Chem.* 1973, 49, C57.
- (490) Tsuda, T.; Chujo, Y.; Saegusa, T. *J. Am. Chem. Soc.* 1978, 100, 630.
- (491) Inoue, S.; Kobayashi, M.; Koinuma, H.; Tsuruta, T. *Makromol. Chem.* 1972, 155, 61.
- (492) Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* 1977, 99, 782.
- (493) Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* 1977, 99, 792.
- (494) Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* 1975, 97, 5625.
- (495) Sobota, P.; Jezowska-Trzebiatowska, B.; Kaczurba, E. *Chem. Stosow.* 1980, 24, 11.
- (496) Light, R. W.; Hutchins, L. D.; Paine, R. T.; Campana, C. F. *Inorg. Chem.* 1980, 19, 3597.
- (497) Arduini, A. L.; Jamerson, J. D.; Takats, J. *Inorg. Chem.* 1981, 20, 2474.
- (498) Ito, T.; Yamamoto, A. *J. Chem. Soc., Dalton Trans.* 1975, 1398.
- (499) Evans, G. O.; Walter, W. F.; Mills, D. R.; Streit, C. A. *J. Organomet. Chem.* 1978, 144, C34.
- (500) Krogssrud, S.; Komiya, S.; Ito, T.; Ibers, J. A.; Yamamoto, A. *Inorg. Chem.* 1976, 15, 2798.

- (501) Crutchley, R. J.; Powell, J.; Faggiani, R.; Lock, C. J. *Inorg. Chim. Acta* 1977, 24, L15.
- (502) Hayward, P. J.; Blake, D. M.; Wilkinson, G.; Nyman, C. J. *J. Am. Chem. Soc.* 1970, 92, 5873.
- (503) Tsuda, T.; Saegusa, T. *Inorg. Chem.* 1972, 11, 2561.
- (504) Tsuda, T.; Sanada, S.; Ueda, K.; Saegusa, T. *Inorg. Chem.* 1976, 15, 2329.
- (505) Chisholm, M. H.; Reichert, W. W.; Cotton, F. A.; Murillo, C. A. *J. Am. Chem. Soc.* 1977, 99, 1652.
- (506) Ito, T.; Kindaichi, Y.; Takami, Y. *Chem. Ind. (London)* 1980, 83.
- (507) Neumann, G.; Neumann, W. P. *J. Organomet. Chem.* 1972, 42, 293.
- (508) Calderazzo, F.; d'Aminco, G.; Netti, R.; Pasquali, M. *Inorg. Chem.* 1978, 17, 471.
- (509) Roman, E.; Dabard, R.; Moinet, C.; Astruc, D. *Tetrahedron Lett.* 1979, 1433.
- (510) Svoboda, P.; Hetflejs, J. *Collect. Czech. Chem. Commun.* 1975, 40, 1746.
- (511) Giannoccaro, P.; Rossi, M.; Sacco, A. *Coord. Chem. Rev.* 1972, 8, 77.
- (512) Luppold, E.; Mueller, E.; Winter, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1976, 31B, 1654.
- (513) Bottomley, F.; Lin, I. J. B. *J. Chem. Soc., Dalton Trans.* 1981, 271.
- (514) Yoshida, T.; Okano, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* 1981, 103, 3411.
- (515) Schoeller, H. *Bull. Bur. Rech. Geol. Min., Sect. 2: Geol. Gites Miner. (Fr.)* 1969, 1.
- (516) Helgeson, H. C. *Am. J. Sci.* 1970, 268, 415.
- (517) Ross, L. W. *Trans.—Geotherm. Resour. Councl.* 1979, 3, 597.
- (518) Holland, H. D.; Malinin, S. D. "Geochemistry of Hydrothermal Metal Ore Deposits", 2nd ed.; Barnes, H. L., Ed.; Wiley-Interscience: New York, 1979, p 461.
- (519) Michels, D. E. *Trans.—Geotherm. Resour. Councl.* 1979, 3, 457.
- (520) Mikhailovskii, V. Ya.; Ivanov, A. M.; Chervinskii, K. A. *J. Appl. Chem. USSR (Engl. Transl.)* 1980, 53, 363.
- (521) Giggenbach, W. F. *Geochim. Cosmochim. Acta* 1980, 44, 2021.
- (522) Gordon, T. M.; Greenwood, H. *J. Am. Mineral.* 1971, 56, 1674.
- (523) Jensen, B. S. *Risoe Rep.* 1980, 430, 53.
- (524) Vuceta, J.; Morgan, J. *J. Environ. Sci. Technol.* 1978, 12, 1302.
- (525) Pencheva, E. *Inzh. Geol. Khidrogeol.* 1976, 4, 17; *Chem. Abstr.* 1976, 85, 163828v.
- (526) Elenbogena, R. N. *Tr., Vses. Nauch.-Issled. Inst. Vodosnabzh., Kanaliz., Gidrotekh. Sooruzhenii Inzh. Gidrogeol.* 1970, 113; *Chem. Abstr.* 1970, 73, 69650m.
- (527) Pittwell, L. R. *J. Hydrol. (Amsterdam)* 1974, 21, 301.
- (528) Kadik, A. A.; Lukanin, O. A.; Lebedev, E. B.; Korovushkina, E. E. *Geokhimiya* 1972, 1549.
- (529) McClellan, G. H. *J. Geol. Soc., London* 1980, 137, 675.
- (530) Bottzinga, Y. *Geochim. Cosmochim. Acta* 1969, 33, 49.
- (531) Stefanik, Yu. V. *Geol. Geokhim. Goryuch. Iskop.* 1973, 12.
- (532) Harting, P.; Maass, I. *ZfH-Mitt.* 1980, 30, 13.
- (533) Sackett, W. M.; Moses Chung, H. *Geochim. Cosmochim. Acta* 1979, 43, 273.
- (534) Gutsalo, L. K.; Plotnikov, A. M. *8-I Vses. Simpoz. po Stabil'n. Izotopov v Geokhimi, Moskva* 1980, 241; *Chem. Abstr.* 1981, 94, 177640a.
- (535) Gutsalo, L. K.; Plotnikov, A. M. *Dokl. Akad. Nauk SSSR* 1981, 259, 470.
- (536) Russell, T. W. *Report EMD-77-1420*, 1980.
- (537) Kasida, Y.; Ishii, T. *Radioisotopes* 1969, 18, 205.
- (538) Li, S.-F.; Gao, W.-X.; Liao, H. *Hua Kung Hsueh Pao* 1981, 51; *Chem. Abstr.* 1981, 95, 45592x.
- (539) Naumov, V. A.; Krylov, O. V. *Kinet. Katal.* 1979, 20, 1347.
- (540) Gryaznov, V. M.; Gul'yanova, S. G.; Serov, Yu. M.; Yagodovskii, V. D. *Zh. Fiz. Khim.* 1981, 55, 1306.
- (541) Barrett, D. *Ind. Eng. Chem. Process Des. Dev.* 1972, 11, 415.
- (542) Giggenbach, W. F. *Geochim. Cosmochim. Acta* 1982, 46, 159.
- (543) Carothers, W. W.; Kharaka, Y. K. *Geochim. Cosmochim. Acta* 1980, 44, 323.
- (544) Brandner, J. D.; Urey, H. C. *J. Chem. Phys.* 1945, 13, 351.
- (545) Zielinski, M.; Wawer, A.; Tabaka, A. *Nukleonika* 1970, 15, 165.
- (546) Grabke, H. J. *Carbon* 1972, 10, 587.
- (547) Kryukov, Yu. B.; Bashkirov, A. N.; Liberov, L. G.; Smirnova, R. M.; Fridman, R. A. *Kinet. Katal.* 1970, 11, 1069.
- (548) Sakata, K.; Ueda, F.; Misono, M.; Yoneda, Y. *Bull. Chem. Soc. Jpn.* 1980, 53, 324.
- (549) Nekipelov, V. N.; Kasatkina, L. A. *Kinet. Katal.* 1970, 11, 910.
- (550) Kneale, B.; Ross, J. R. H. *J. Chem. Soc., Chem. Commun.* 1981, 751.
- (551) McArthur, J. M.; Coleman, M. L.; Bremner, J. M. *J. Geol. Soc., London* 1980, 137, 669.
- (552) Takahashi, T.; Broecker, W. S.; Werner, S. R.; Bainbridge, A. E. *Isot. Mar. Chem.* 1980, 291.
- (553) Kohlmaier, G. H.; Sire, E. O.; Kratz, G.; Fischbach, U.; Broehl, H. *Ber. Bunsenges. Phys. Chem.* 1980, 84, 1076.
- (554) Bolin, B. *Science (Washington D.C.)* 1977, 196, 613.
- (555) Woodwell, G.; Whittaker, R. H.; Reiners, W. A.; Likens, G. E.; Delwiche, C. C.; Botkin, D. B. *Science (Washington D.C.)* 1978, 199, 141.
- (556) Baes, C. F., Jr. *Carbon Dioxide Rev.* 1982.
- (557) Pytkowicz, R. M.; Atlas, E. *Limnol. Oceanogr.* 1975, 20, 222.
- (558) Johnson, K. S. *Limnol. Oceanogr.* 1982, 27, 849.
- (559) Jacobson, R. L.; Langmuir, D. *Geochim. Cosmochim. Acta* 1974, 38, 301.
- (560) Bradshaw, A. *Limnol. Oceanogr.* 1973, 18, 95.
- (561) Bezdrodov, A. A.; Zhorov, V. A.; Komissarova, L. N. *Dokl. Akad. Nauk SSSR* 1976, 229, 618.
- (562) Langmuir, D. *Geochim. Cosmochim. Acta* 1978, 42, 547.
- (563) Giblin, A. M.; Batts, B. D.; Swaine, D. J. *Geochim. Cosmochim. Acta* 1981, 45, 699.
- (564) Kanno, M.; Ozawa, Y.; Mukai, T. *Nippon Genshiryoku Gakkaishi* 1970, 12, 708.
- (565) Pocker, Y.; Sarkany, S. *Adv. Enzymol. Relat. Areas, Mol. Biol.* 1978, 47, 149.
- (566) Edsall, J. T. *NASA [Spec. Publ.] SP 1968, NASA SP-188*, 87.
- (567) Pocker, Y.; Bjorkquist, D. W. *Biochemistry* 1977, 16, 5698.
- (568) Khalifah, R. G. *J. Biol. Chem.* 1971, 246, 2561.
- (569) Lindskog, S. *Chimia* 1975, 29, 65.
- (570) Pocker, Y.; Deits, T. L.; Tanaka, N. *Adv. Solution Chem., Int. Symp. Solute-Solute-Solvent Interact., 5th* 1980 1981, 253.
- (571) Sanyal, G.; Maren, T. H. *J. Biol. Chem.* 1981, 256, 608.
- (572) Pocker, Y.; Mitsch, R. R. *Biochemistry* 1978, 17, 1119.
- (573) Strandberg, B.; Waara, I. *NASA [Spec. Publ.] SP 1968, NASA SP-188*, 89.
- (574) Riepe, M. E.; Wang, J. H. *J. Biol. Chem.* 1968, 243, 2779.
- (575) Wang, J. H. *Proc. Nat. Acad. Sci. U.S.A.* 1970, 66, 874.
- (576) Khalifah, R. G. *Proc. Nat. Acad. Sci. U.S.A.* 1973, 70, 1986.
- (577) Silverman, D. N. *Arch. Biochem. Biophys.* 1973, 155, 452.
- (578) Tu, C. K.; Silverman, D. N. *J. Am. Chem. Soc.* 1975, 97, 5935.
- (579) Silverman, D. N.; Tu, C. K. *J. Am. Chem. Soc.* 1975, 97, 2263.
- (580) Silverman, D. N.; Tu, C. K. *J. Am. Chem. Soc.* 1976, 98, 978.
- (581) Silverman, D. N.; Tu, C. K.; Lindskog, S.; Wynns, G. C. *J. Am. Chem. Soc.* 1979, 101, 6734.
- (582) Vincent, S. H.; Silverman, D. N. *Arch. Biochem. Biophys.* 1980, 205, 51.
- (583) Silverman, D. N.; Tu, C. K.; Roessler, N. *Respir. Physiol.* 1981, 44, 285.
- (584) Koenig, S. H.; Brown, R. D.; London, R. E.; Needham, T. E.; Matwioff, N. A. *Pure Appl. Chem.* 1974, 40, 103.
- (585) Stein, P. J.; Merrill, S. P.; Henkens, R. W. *J. Am. Chem. Soc.* 1977, 99, 3194.
- (586) Bertini, I.; Borghi, E.; Luchinat, C. *Congr. Naz. Chim. Inorg., [Atti], 12th* 1979, 301.
- (587) Koenig, S. H.; Brown, R. D. *Biophys. J.* 1981, 35, 59.
- (588) Demoulin, D.; Pullman, A. *Jerusalem Symp. Quantum Chem. Biochem.* 1979, 12, 51.
- (589) Sawaryn, A.; Sokalski, W. A. *Int. J. Quantum Chem.* 1979, 16, 293.
- (590) Sokalski, W. A. *Int. J. Quantum Chem.* 1981, 20, 231.
- (591) Jonsson, B.; Wennerstrom, H. *Biophys. Chem.* 1978, 7, 285.
- (592) Clementi, E.; Corongiu, G.; Jonsson, B.; Romano, S. *Gazz. Chim. Ital.* 1979, 109, 669.
- (593) Berger, R.; Libby, W. F. *Science (Washington D.C.)* 1969, 164, 1395.
- (594) Tsao, G. T. *Chem. Eng. Sci.* 1972, 27, 1593.
- (595) Alper, E.; Lohse, M.; Deckwer, W. D. *Chem. Eng. Sci.* 1980, 35, 2147.
- (596) Alper, E.; Lohse, M.; Deckwer, W. D. *Chem. Ing. Tech.* 1979, 51, 980.
- (597) Alper, E.; Deckwer, W. D. *Chem. Eng. Sci.* 1980, 35, 549.
- (598) Lohse, M.; Alper, E.; Deckwer, W. D. *VDI-Ber.* 1979, 391, 367.
- (599) Cooper, T. G.; Filmer, D.; Wishnick, M.; Lane, M. D. *J. Biol. Chem.* 1969, 244, 1081.
- (600) Filmer, D.; Cooper, T. G. *J. Theor. Biol.* 1970, 29, 131.
- (601) Cooper, T. G.; Wood, H. G. *J. Biol. Chem.* 1971, 246, 5488.
- (602) Scruton, M. C.; Mildvan, A. S. *NASA [Spec. Publ.] SP 1968, NASA SP-188*, 207.
- (603) Scruton, M. C.; White, M. D. *Biochem. Biophys. Res. Commun.* 1972, 48, 85.
- (604) Ashman, L. K.; Keech, B. D. *J. Biol. Chem.* 1975, 250, 14.
- (605) Robinson, P. D.; Tabita, F. R. *FEBS Lett.* 1980, 111, 369.
- (606) Lorimer, G. H.; Badger, M. R.; Andrews, T. J. *Biochemistry* 1976, 15, 529.
- (607) Laing, W. A.; Christeller, J. T. *Biochem. J.* 1976, 159, 563.
- (608) Wildner, G. F.; Henkel, J. *Planta* 1979, 146, 223.
- (609) Young, W.; Perkins, D. J. *Eur. J. Biochem.* 1968, 4, 385.
- (610) Gaber, B. P.; Schillinger, W. E.; Koenig, S. H.; Aisen, A. P. *J. Biol. Chem.* 1970, 245, 4251.
- (611) Honda, K.; Nishikata, I.; Sasakawa, S. *Chem. Lett.* 1980, 21.

- (612) Binford, J. S.; Foster, J. C. *J. Biol. Chem.* 1974, 249, 407.
(613) Rogers, T. B.; Feeney, R. E.; Meares, C. F. *J. Biol. Chem.* 1977, 252, 8108.
(614) Bates, G. W.; Graham, G. *Adv. Exp. Med. Biol.* 1976, 74, 400.
(615) Kojima, N.; Bates, G. W. *J. Biol. Chem.* 1981, 256, 12034.
(616) Kojima, N.; Bates, G. W. *J. Biol. Chem.* 1979, 254, 8847.
(617) Akbaev, A. *Zh. Prikl. Khim. (Leningrad)* 1973, 46, 648.
(618) Everson, R. G. *Nature (London)* 1969, 222, 876.
(619) Gavis, J.; Ferguson, J. F. *Limnol. Oceanogr.* 1975, 20, 211.
(620) Epstein, S. NASA Spec. Publ. 1968 (Pub. 1969) NASA SP-188, 5.
(621) Forster, R. E. NASA Spec. Publ. 1968 (Pub. 1969), NASA SP-188, 55.
(622) Arnone, A. *Nature (London)* 1974, 247, 143.
(623) Forster, R. E. NASA [Spec. Publ.] SP 1968, NASA SP-188, 275.
(624) Piiper, J. NASA [Spec. Publ.] SP 1968, NASA SP-188, 267.
(625) Gurtner, G. H. NASA [Spec. Publ.] SP 1968, NASA SP-188, 233.
(626) Jones, N. L.; Campbell, E. J. M. NASA [Spec. Publ.] SP 1968, NASA SP188, 229.
(627) Winchell, H. S.; Stahelin, H. B.; Kusubov, N.; Slanger, B. H.; Fish, M. B.; Pollycove, M.; Lawrence, J. H. *J. Nucl. Med.* 1970, 11, 711.
(628) Slanger, B. H.; Kusubov, N.; Winchell, H. S. *J. Nucl. Med.* 1970, 11, 716.