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The Pulse Radiolysis of Deaerated Aqueous Carbonate Solutions. I. Transient Optical Spectrum and Mechanism. II. pK for OH Radicals¹

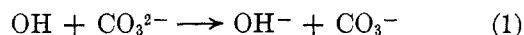
by James L. Weeks and Joseph Rabani

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The pulse radiolysis of deaerated aqueous carbonate solutions in the neutral and alkaline pH was studied. A mechanism is presented, and several rate constants have been determined (all are in units of $M^{-1} \text{ sec}^{-1}$): $k(\text{OH} + \text{CO}_3^{2-}) = 4.2 \times 10^8$, $k(\text{O}^- + \text{CO}_3^{2-}) < 10^7$, $2k(\text{CO}_3^- + \text{CO}_3^-) = 1.25 \times 10^7$ (zero ionic strength), and $k(\text{OH} + \text{HCO}_3^-) = 1.5 \times 10^7$. In the pulse radiolysis of carbonate solutions a transient optical absorption appears which is identified as the carbonate radical ion (CO_3^-). Its spectrum is reported and has a maximum extinction coefficient of $1860 \pm 160 M^{-1} \text{ cm}^{-1}$ at 6000 Å. There is a pH dependency of the rate of CO_3^- formation, from which the pK for the ionic dissociation of OH radicals has been determined as 11.8 ± 0.2 , where pK is defined as $-\log \{ [\text{H}^+][\text{O}^-]/[\text{OH}] \}$. The results are compared with earlier work.

Introduction

A transient optical absorption at 5780 Å was reported by Gordon, *et al.*,² who assumed that carbonate radical ions, CO_3^- , are formed by



Adams and Boag³ used the absorption of CO_3^- to get relative rate constants of hydroxyl radicals with various solutes in aqueous solution. Adams, Boag, and Michael,⁴ using photographic plates, obtained the CO_3^- spectrum and reported a maximum absorption at 6000 Å, with an extinction coefficient, ϵ , equal to $1880 M^{-1} \text{ cm}^{-1}$.

In the present work it seemed desirable to (a) extend the previous spectroscopic work to obtain a more precise spectrum of CO_3^- over a wider wavelength region, (b) study kinetics of the formation and decay of CO_3^- under various conditions, and (c) use the CO_3^- absorption to discriminate between OH and O_{aq}^- and the determination of the pK for the ionic dissociation of OH.

Experimental Section

The experimental procedure used in this work has been described previously.⁵ The preparation and handling of the solutions made use of a syringe technique.^{6,7} A multiple-reflection cell⁵ with a 4 cm long

optical cell gave an 80-cm light path. The formation and decay of CO_3^- was followed at 6000 Å using a 450-w xenon lamp, a Bausch and Lomb monochromator, a 1P28 photomultiplier, and a Tektronix oscilloscope with a Polaroid camera. A 0.4- μsec , 15-Mev electron pulse from a linear accelerator was used. Unless otherwise stated or indicated by the maximum optical density, the dose was about $2.5 \times 10^{19} \text{ ev l.}^{-1}$ per pulse.

Using the above apparatus and varying the wavelength of the monochromator, the spectrum of CO_3^- was determined. No attempt was made to monitor the pulse intensity for the data taken between 2600 and 3300 Å. However, from 3250 to 6400 Å, the light beam was split, after passing through the cell, by means of a partially aluminized mirror. The reflected beam was used to obtain the relative pulse intensity at con-

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *J. Am. Chem. Soc.*, **85**, 1375 (1963).

(3) G. E. Adams and J. W. Boag, *Proc. Chem. Soc.*, 112 (1964).

(4) G. E. Adams, J. W. Boag, and B. D. Michael, *Trans. Faraday Soc.*, **61**, 1674 (1965).

(5) J. Rabani, W. A. Mulac, and M. S. Matheson, *J. Phys. Chem.*, **69**, 53 (1965), and references cited therein.

(6) C. B. Senvar and E. J. Hart, *Proc. Intern. Conf. Peaceful Uses At. Energy, 2nd, Geneva*, **29**, 19 (1958).

(7) E. J. Hart, S. Gordon, and J. K. Thomas, *J. Phys. Chem.*, **68**, 1271 (1964).

stant wavelength, since the optical density of the pulsed solution is proportional to the pulse intensity. The data for the calculation of the extinction coefficient of CO_3^{2-} at 6000 Å, based on the ϵ of $\text{Fe}(\text{CN})_6^{3-}$ at 4200 Å, were obtained using a spectrograph with photomultipliers at 6000 and 4200 Å, as previously described.⁵

Reagent grade chemicals were used for all of the experiments without further purification. J. T. Baker Chemical Co. sodium carbonate monohydrate and Mallinckrodt Chemical Works sodium hydroxide were used. Less than 0.5% carbonate was detected in the 1 M NaOH stock solutions. The kinetic results indicate that the carbonate impurity in the NaOH solutions was much lower and could be ignored. Where applicable, corrections were made for all concentrations of CO_3^{2-} and pH values for the equilibrium: $\text{H}_2\text{O} + \text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$. Unless otherwise stated, 0.1 atm of N_2O was present in all of the solutions in order to convert e_{aq}^- to OH. The N_2O was passed through three alkaline pyrogallol solutions in order to eliminate small amounts of O_2 . With this procedure, N_2O containing 0.03% O_2 by volume was obtained and used without further purification. All experiments were carried out at room temperature (ca. 23°).

Results and Discussion

In the alkaline carbonate system, the effect of the following species produced during the electron pulse must be considered: H_2 , H_2O_2 , $(\text{H}_3\text{O})_{\text{aq}}^+$, $(\text{OH})_{\text{aq}}^-$, e_{aq}^- , H, OH.

H_2 does not react with carbonate ions. H_2O_2 decomposes slowly in alkaline carbonate solutions but has no effect on the carbonate ions. The properties of carbonate in solutions containing $(\text{H}_3\text{O})_{\text{aq}}^+$ and $(\text{OH})_{\text{aq}}^-$ are well known and need not be discussed here. Of the short-lived species, e_{aq}^- does not react with carbonate ions,⁸ although it may react with bicarbonate ions⁹ and is known to react very fast with CO_2 .¹⁰ H atoms may react with bicarbonate ions,⁹ but the reaction is very slow compared to other reactions of H atoms. The optical absorption with the peak at 6000 Å has also been obtained⁴ in the presence of O_2 , which is a known H atom scavenger. Thus, it seems evident that OH radicals are the main precursor and probably the only one for forming this absorption. This conclusion is confirmed by the effects of OH scavengers on the absorption^{2,3,11} at 6000 Å.

In order to investigate the carbonate radical ion, it is desirable to eliminate e_{aq}^- , since it still has a high absorption at 6000 Å (about 5 times more absorption^{2,5,8,12} than CO_3^{2-}). Adams, Boag, and Michael¹¹

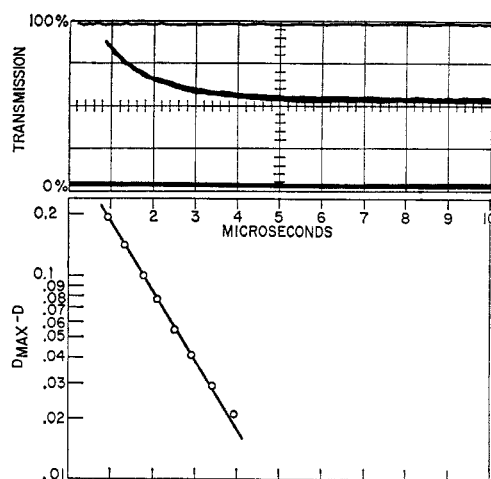
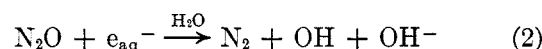


Figure 1. Formation of CO_3^{2-} : upper, typical oscilloscope trace; lower, pseudo-first-order kinetics. Conditions: 1.97 mM CO_3^{2-} , 0.1 atm of N_2O , pH 10.76.

have used O_2 and N_2O in order to eliminate e_{aq}^- . However, since O_2 can react with O^- to form O_3^- at alkaline pH,¹³⁻¹⁵ the presence of oxygen was usually avoided in the present system. Most of these experiments have been carried out in the presence of N_2O , which, it is assumed, reacts rapidly with e_{aq}^- and forms¹⁶ OH or O^- , as in



This reaction has been discussed in earlier papers, and it has been concluded^{14,17} that, if N_2O^- is formed as an intermediate, it should live either less than 1 μsec , or else have the same properties as OH has in the ferrocyanide¹⁴ and bromide¹⁷ systems. As will be seen later, the present results with carbonate ions are consistent with the same conclusion.

- (8) E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.*, **84**, 4090 (1962).
- (9) S. Nehari and J. Rabani, *J. Phys. Chem.*, **67**, 1609 (1963).
- (10) (a) L. M. Dorfman and M. S. Matheson, *Progr. Reaction Kinetics*, **3**, 237 (1965); (b) J. T. Allan, N. Getoff, H. P. Lehmann, K. E. Nixon, G. Scholes, and M. Simic, *J. Inorg. Nucl. Chem.*, **19**, 204 (1961).
- (11) G. E. Adams, J. W. Boag, and B. D. Michael, *Trans. Faraday Soc.*, **61**, 1417 (1965).
- (12) (a) L. M. Dorfman and I. A. Taub, *J. Am. Chem. Soc.*, **85**, 2370 (1963); (b) J. P. Keene, *Discussions Faraday Soc.*, **36**, 304 (1963).
- (13) G. Czapski and L. M. Dorfman, *J. Phys. Chem.*, **68**, 1169 (1964).
- (14) J. Rabani and M. S. Matheson, *ibid.*, **70**, 761 (1966).
- (15) G. E. Adams, J. W. Boag, and B. D. Michael, *Nature*, **205**, 898 (1965).
- (16) F. S. Dainton and D. B. Peterson, *Proc. Roy. Soc. (London)*, **A267**, 443 (1962).
- (17) M. S. Matheson, W. A. Mulac, J. L. Weeks, and J. Rabani, *J. Phys. Chem.*, **70**, 2092 (1966).

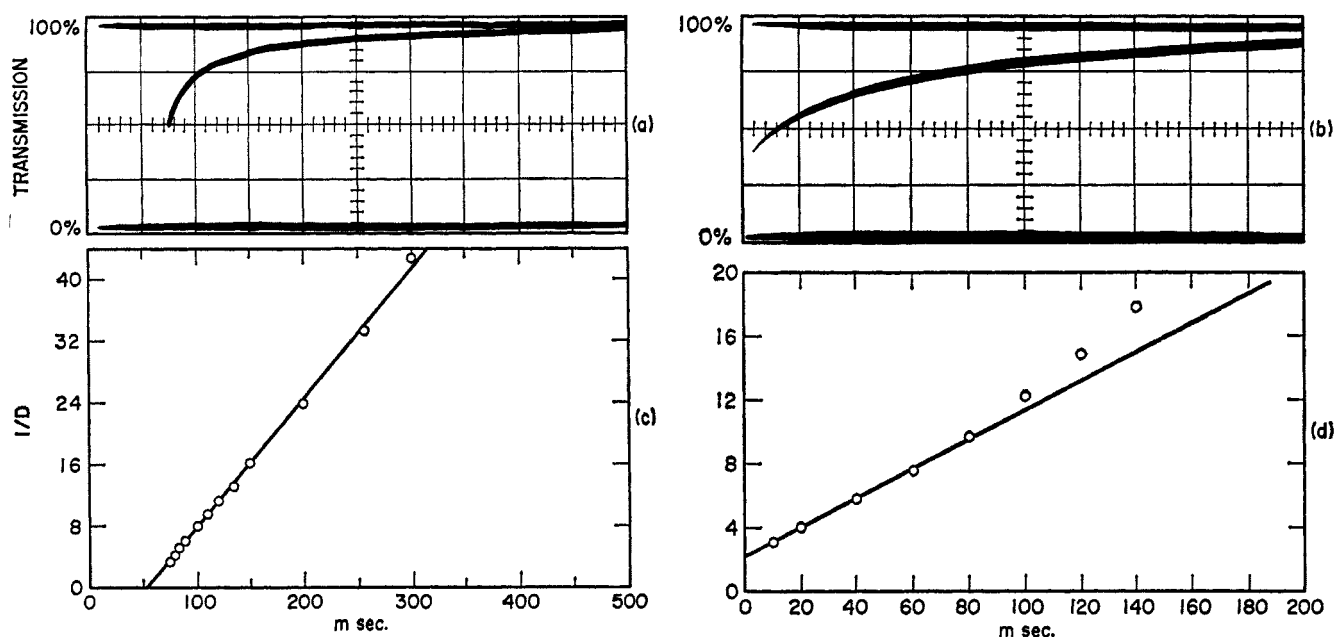


Figure 2. Carbonate radical decay curves and second-order plots. (a) 6.24 mM CO_3^{2-} , 0.1 atm of N_2O , pH 12.61. (b) 1.97 mM CO_3^{2-} , 0.1 atm of N_2O , pH 10.76. (c) Second-order plot for (a). (d) Second-order plot for (b).

The formation of the CO_3^- absorption in solutions containing N_2O is first order in both $[\text{OH}]$ and $[\text{CO}_3^{2-}]$. From the appropriate plots, a second-order rate constant " k_1 " has been calculated, defined as

$$"k_1" = (1/[\text{CO}_3^{2-}]) \frac{d}{dt} \{ \ln (D_{\max} - D_t) \}$$

where D_{\max} is the maximum value of the optical density after all of the OH radicals have reacted and D_t is the optical density at time t . As will be seen later, " k_1 " is pH dependent, and only under certain specific conditions does " k_1 " = k_1 , where k_1 is the rate constant of reaction 1.

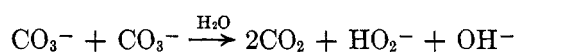
The buildup of optical density is followed by a slower decay, which is well separated in time from the formation. In Figure 1 a typical oscilloscope trace (upper part) for the formation of carbonate radical ions is presented. The straight line obtained (lower part of Figure 1), when $D_{\max} - D_t$ is plotted *vs.* time on a semilog scale, shows that the reaction is pseudo first order. The same result was obtained when either N_2O or CCl_4 was used to scavenge e_{aq}^- .

Figures 2a and 2b present typical oscilloscope traces for the decay of the transient absorption with time for solutions containing N_2O . A straight line is obtained when $1/D$ from Figure 2a is plotted *vs.* time in Figure 2c. In some experiments, deviations from linearity occurred (Figure 2d), indicating additional processes. It appears that there is a positive curvature (*e.g.*, Figure

2d) at pH < 11.5, very little or no curvature (*e.g.*, Figure 2c) at pH 12–13, and again positive curvature at pH 13.5. In most cases, however, the plots were linear within experimental errors until after 80% of the CO_3^- decayed away. The main reaction responsible for the decay is believed to be



or



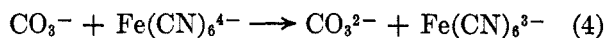
No explanation for the deviations from second order seems apparent. All of the rate constants reported in this paper for solutions containing N_2O are calculated from the initial slopes of the kinetic plots.

The Spectrum of CO_3^- . The spectrum of CO_3^- is given in Figure 3. In the ultraviolet region, optical absorption appears in the absence as well as in the presence of carbonate ions and/or bicarbonate ions. CO_3^- is probably responsible for the absorption in the presence of carbonate ions and bicarbonate ions. In the absence of these last ions, it may be due to OH in neutral and O_{aq}^- in alkaline solutions.¹⁸

The Extinction Coefficient of CO_3^- . The Reaction of CO_3^- with Ferrocyanide. The extinction coefficient of CO_3^- at 6000 Å, $\epsilon_{\text{CO}_3^-}^{6000}$, has been determined by a

(18) J. Rabani and M. S. Matheson, *J. Am. Chem. Soc.*, **86**, 3175 (1964).

method similar to that used before⁵ for $\epsilon_{\text{aq}}^{-5780}$. It was found that CO_3^{2-} oxidizes ferrocyanide by



Simultaneous traces at both 6000 and 4200 Å were obtained. In the presence of ferrocyanide, the decay of CO_3^{2-} is enhanced owing to reaction 4. From pseudo-first-order plots, k_4 was calculated. Since $2k_3 \approx 10^7 \text{ M}^{-1} \text{ sec}^{-1}$, it is easy to choose high enough ferrocyanide concentrations so that no corrections for second-order decay⁵ are necessary. Reaction 4 is between two negatively charged species and is expected to be enhanced at higher ionic strengths. The values reported in Table I are for the actual ionic strengths and were not

Table I: Simultaneous Rates of Formation of $\text{Fe}(\text{CN})_6^{3-}$ at 4200 Å and Disappearance of CO_3^{2-} at 6000 Å

pH	$[\text{Na}_2\text{CO}_3]^a$	$[\text{K}_4\text{Fe}(\text{CN})_6]^a$	D_{max}^b at 4200 Å	k_4^c at 4200 Å	k_4^c at 6000 Å
11.6	71	0.12	0.19	2.7	2.8
13.0	100	0.10	0.25	3.5	3.5
13.0	100	0.41	0.25	4.0	3.6

^a In units of mM. ^b D_{max} was constant by 100 μsec after pulse and was followed to at least 200 μsec . ^c In units of $10^8 \text{ M}^{-1} \text{ sec}^{-1}$. Each result is an average of at least two experiments.

calculated for zero ionic strength. The same rate constant is obtained at both 6000 and 4200 Å. A typical oscilloscope trace used for these calculations is shown in Figure 4. The initial absorption at 4200 Å is due to CO_3^{2-} .

From traces such as shown in Figure 4, ΔD_{6000} values were plotted *vs.* ΔD_{4200} (see ref 5 for the definition of ΔD). The results are given in Figure 5 for pH 11.6. From the slope of Figure 5 and other similar plots, the ratio $\epsilon_r = \epsilon_{\text{CO}_3^{2-}}^{6000} / \epsilon_{\text{Fe}(\text{CN})_6^{3-}}^{4200}$ can be calculated using⁵ $\epsilon_r = \text{slope} / (1 + A \times \text{slope})$, where $A = \epsilon_{\text{CO}_3^{2-}}^{4200} / \epsilon_{\text{CO}_3^{2-}}^{6000}$. The ratio A was calculated from simultaneous traces at 6000 and 4200 Å, using the spectrograph, in solutions containing carbonate in 0.1 atm of N_2O (no ferrocyanide). $A = 0.184 \pm 0.005$ (standard deviation) was obtained for 0.1 M NaOH, 0.1 atm of N_2O , and $3 \times 10^{-3} \text{ M Na}_2\text{CO}_3$, and $A = 0.182$ for $5 \times 10^{-3} \text{ M NaHCO}_3$ (near neutral pH) and 0.1 atm of N_2O . These results indicate that A is independent of whether CO_3^{2-} is produced from carbonate ions or from bicarbonate ions. From Figure 5, and other such figures, $\epsilon_r = 1.78$ has been calculated for both pH 11.6 and 13.0. Other conditions for such calculations were the same as described in Table I.

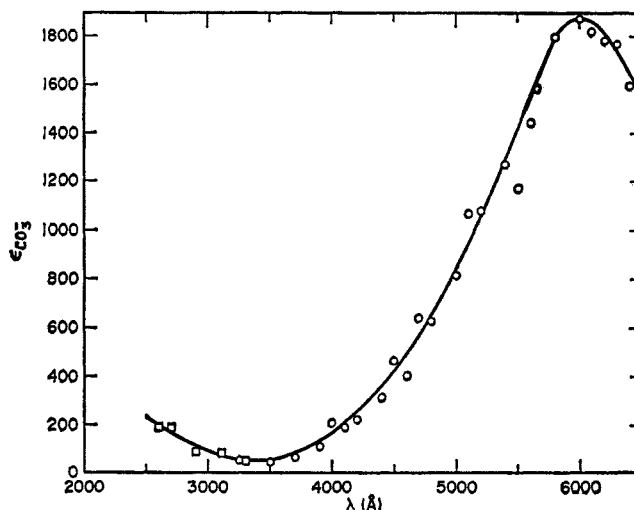


Figure 3. Spectrum of CO_3^{2-} . Circles are values at pH 13 determined "point by point" using two monochromators (one used as pulse monitor); squares are values at pH 11 where no monitor monochromator was used.

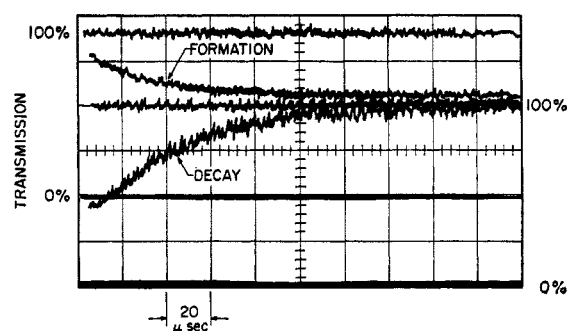


Figure 4. Simultaneous formation of $\text{Fe}(\text{CN})_6^{3-}$ at 4200 Å (upper set of curves) and decay of CO_3^{2-} at 6000 Å (lower set of curves). Conditions: 72 mM CO_3^{2-} , 0.122 mM $\text{Fe}(\text{CN})_6^{4-}$, 0.1 atm of N_2O , pH 11.6.

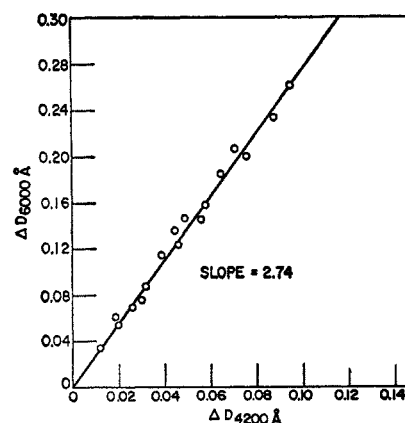


Figure 5. A typical comparison of ΔD at 6000 Å with that at 4200 Å for use in the calculation of $\epsilon_{\text{CO}_3^{2-}}^{6000} / \epsilon_{\text{Fe}(\text{CN})_6^{3-}}^{4200}$. Conditions: 72 mM CO_3^{2-} , 0.122 mM $\text{Fe}(\text{CN})_6^{4-}$, 0.1 atm of N_2O , pH 11.6.

From Figure 3, $A = 0.135 \pm 0.015$, which yields $\epsilon_r = 1.95$. The difference between the results with the monochromator and spectrograph may be due in part to a difference in the effective wavelengths. Based on the average value of ϵ_r and $\epsilon_{Fe(CN)_6^{4-}}^{200} = 1000$, a value of $\epsilon_{CO_3^{2-}}^{600} = 1860 \pm 160 M^{-1} cm^{-1}$ is obtained.

The Rate of Decay of CO_3^{2-} . As can be seen from Figures 2c and 2d, the initial decay of optical density in carbonate- N_2O solutions is closely second order. At the higher pH values, the rate of decay was some-

Table II: Rate of Formation and Decay of CO_3^{2-} in Solutions Containing 0.1 Atm of N_2O

(A) With No Added Salts

pH	$[CO_3^{2-}]^a$	$D_{initial}$	D_{max}	% CO_3^{2-} decayed before non-linear ^b	" k_1 " ^c	$2k_2^d$
8.4	1.0 ^d	0.19	0.34	80	1.49	1.94
10.6	0.8	0.06	0.33	70	40.7	1.33
10.8	2.2	0.09	0.35	70	38.6	1.57
11.1	2.4	0.20	0.31	70	...	1.49
11.4	3.1	0.10	0.34	70	32.0	1.64
11.4	8.8	0.12	0.29	70	28.9	1.83
11.6	72	...	0.32	80	...	2.90
12.0	3.0	0.11	0.54	80	15.8	1.75
12.0	5.8	0.11	0.24	80	15.0	2.15
12.3	6.4	0.20	0.44	80	8.22	2.20
12.6	6.2	0.11	0.34	90	5.42	2.71
13.0	1.0	~ 0.01	0.40	80	3.20	3.93
13.0	3.2	~ 0.01	0.44	90	2.65	2.93
13.0	8.4	~ 0.01	0.46	90	2.68	2.25
13.0	15.0	0.14	0.62	90	3.18	2.23
13.0	15.0	0.12	0.35	90	2.31	3.33
13.0	100	0.29	0.49	80	...	3.69
13.0	109 ^e	...	~ 0.25	90	...	5.12
13.5	9.1	0.03	0.40	70	0.94	...
13.5	36	0.15	0.62	80	0.91	4.5

(B) With Added Na_2SO_4 or $NaClO_4$

pH	$[CO_3^{2-}]^a$	Ionic strength, μ^a	$D_{initial}$	D_{max}	% CO_3^{2-} decayed before non-linear ^b	$2k_2^c$
10.6	0.8	18.2	0.05	0.34	70	1.54
10.6	0.8	31.9	0.04	0.27	70	1.76
10.5	0.8	91.2	0.04	0.23	80	2.30
10.6	0.8	123	0.06	0.33	80	1.98
10.5	0.7	327	0.06	0.33	80	2.79

^a In units of mM. ^b Measure of linearity on second-order plot of $1/D$ vs. t . ^c In units of $10^7 M^{-1} sec^{-1}$. ^d $[HCO_3^-]$. ^e Also contained 0.1 atm of air. Each result is an average of two to six experiments.

what faster and the scatter was larger. In Table II, the rate constants for the formation and decay of CO_3^{2-} are presented. Apart from the effect of the ionic strength (see Figure 6), $2k_2$ seems to be unaffected by the various pH values, carbonate ion concentrations, and intensities of the electron beam. The presence of 0.1 atm of air has little effect, if any, on the rate of CO_3^{2-} decay. Adams, Boag, and Michael⁵ reported an enhanced decay of CO_3^{2-} in the presence of O_2 , but in the absence of N_2O . This was interpreted⁴ as a reaction of CO_3^{2-} with O_2^- . In several of the experiments in the present work when both N_2O and air were present, most of the e_{aq}^- reacted with N_2O , and practically no O_2^- was formed.

In Figure 6, $\log 2k_{2,\mu}$, where $2k_{2,\mu}$ is $2k_2$ at ionic strength μ , has been plotted vs. $\mu^{1/2}/(1 + \alpha\mu^{1/2})$, using the values in Table II. The combination $\alpha = 0.4$ and a slope of 1.02 gave a good fit with the results. If $\alpha = 1.0$ were chosen, a slope of 1.3 would also give a good fit; however, the theory requires^{19,20} a slope of

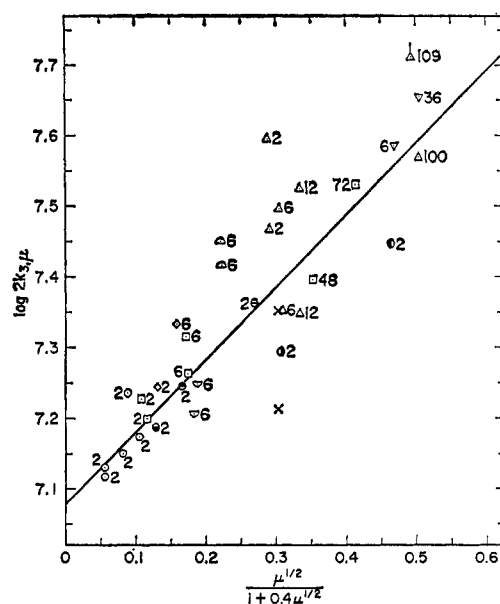


Figure 6. Ionic strength effect on k_2 . Conditions: all solutions contained 0.1 atm of N_2O . Numbers following symbols in the figure indicate approximate $[CO_3^{2-}]$ in mM: pH 8.4, \times , ~ 100 mM HCO_3^- ; pH 10.5–10.8, \circ , no added salt; pH 10.5–10.8, \ominus , 5 mM Na_2SO_4 ; pH 10.5–10.8, \bullet , 40 mM Na_2SO_4 ; pH 10.5–10.8, \odot , 108 mM Na_2SO_4 ; pH 10.5–10.8, \oplus , 29 mM $NaClO_4$; pH 10.5–10.8, \ominus , 89 mM $NaClO_4$; pH 11.1, \square ; pH 11.3–11.6, \square ; pH 12.0, \diamond ; pH 12.3, \circ ; pH 12.6, \circ ; pH 13.0, Δ ; pH 13.0, Δ , also contained 0.1 atm of air; pH 13.5, ∇ .

(19) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 525.

(20) P. J. Durrant and B. Durrant, "Introduction to Advanced Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1962, p 319.

1.02 and $\alpha \approx 0.7$ to 0.8, assuming the C-O bond length in CO_3^- is the same²⁰ as in CO_3^{2-} .

Figure 6 demonstrates that the dependence of k_3 on pH is in fact a dependence on μ . Additionally, it shows that the decay of the transient absorption is mainly by a reaction of two species of the same charge. Reaction 3 appears to be the only one which can account for this observation. From Figure 6, $2k_3$ is $1.25 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ at zero ionic strength.

The Decay of CO_3^- in the Presence of CCl_4 . In some experiments CCl_4 was used to scavenge e_{aq}^- , as in reaction 5, instead of N_2O . This presence of CCl_4 did



not affect the rate of CO_3^- formation; however, the decay was different. Table III summarizes the results.

Table III: Rate of Formation and Decay of CO_3^- in Solutions Containing $\sim 0.5 \text{ mM}$ CCl_4 (No N_2O)^a

pH	$[\text{CO}_3^{2-}]^a$	D_{initial}	D_{max}	" k_1 " ^b	$\frac{d}{dt} \left(\frac{1}{D} \right)_{\text{initial}} \times \epsilon \times l^c$
12.0	3.0	0.13	0.33	19.4	2.2
12.0	6.1	0.08	0.14	14.5	1.8
12.0	12.3	0.05	0.15	...	2.0
12.6	5.9	0.06	0.15	5.90	1.7
13.0	6.0	0.09	0.33	3.41	...
13.0	15.0	0.18	0.37	2.95	...
13.5	6.2	0.02	0.12	0.80	1.1
13.5	36.0	0.15	0.38	1.00	1.1

^a In units of mM. ^b In units of $10^7 \text{ M}^{-1} \text{ sec}^{-1}$. ^c In units of $10^9 \text{ M}^{-1} \text{ sec}^{-1}$. ^d l = light path, ϵ = extinction coefficient of CO_3^- at 6000 Å ($1.78 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). ^e Each result is an average of two to five experiments.

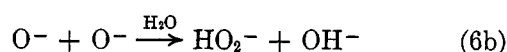
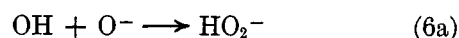
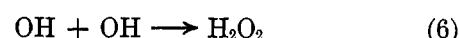
The decay of CO_3^- in CCl_4 solutions is much faster than in the N_2O solutions. Apparently, CO_3^- must react with CCl_4 or its products, but, at present, efforts to advance a full mechanism have not succeeded. D_{max} in CCl_4 is about one-half of D_{max} in N_2O , when the other conditions are the same.

The Effect of pH on the Formation of CO_3^- . Tables II and III present the effect of pH on " k_1 ". D_{max} can be used for the calculation of the electron beam intensity, since $G(\text{CO}_3^-)$, the yield of CO_3^- radicals per 100 ev, under these conditions, is known. The "linearity" is defined here as the percentage CO_3^- which has disappeared when the deviation from linearity just equals the error in $1/D$. D_{initial} is the optical density measured at the smallest t value. Some reaction takes place during the pulse and the electronic "noise"; the duration of both together is $\sim 1 \mu\text{sec}$.

From Table II it is seen that $k_{1a} \ll k_1$, where reaction 1a is

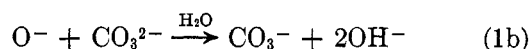


The reaction of OH with bicarbonate ions also produces CO_3^- , as indicated by the similar optical density in both bicarbonate and carbonate solutions, when irradiated with the same pulse intensity. Also, the rate of decay of the optical density is the same in both carbonate and bicarbonate solutions (see Figure 6). Small corrections have been made for the effect of reactions 6, 6a, and 6b



An effective " $2k_6$ " was taken from previous measurements or obtained by interpolation.¹⁴ The possible reactions of CCl_3 with OH or O^- were neglected because of lack of data.

A striking phenomenon is the pH dependency of " k_1 ". The carbonate ion reactivity toward OH and O^- parallels the reactivity of ferrocyanide.^{14,18} Reaction 1b can be neglected even at the highest pH used by us, since



$k_{1b} < 10^7 \text{ M}^{-1} \text{ sec}^{-1}$. Figure 7 shows a plot of $\log [(k_1/k_1') - 1]$ vs. pH. $k_1 = 4.2 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ has

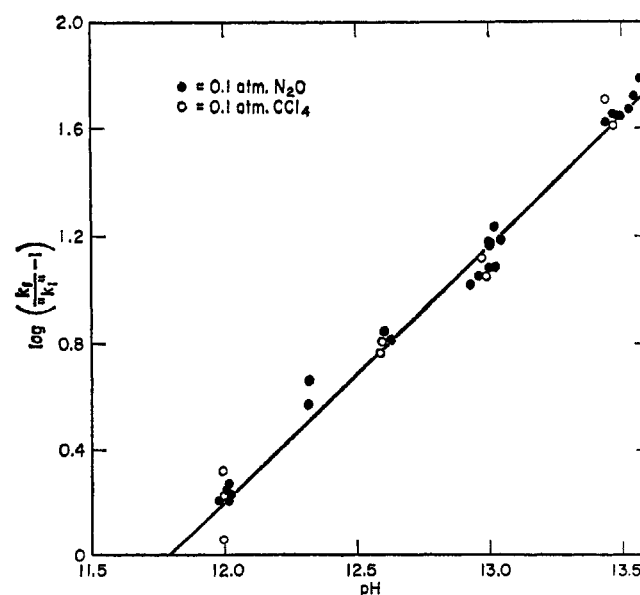


Figure 7. Determination of the ionic dissociation constant of OH radicals. The points are independent of $[\text{CO}_3^{2-}]$ in the range 1 to 50 mM.

been calculated from the results at $\text{pH} < 11.6$ by means of successive approximations, assuming that the $\text{p}K$ for OH radicals is higher than 11.5. Thus, our present determination of $\text{p}K_{\text{OH}}$ does not depend on the exact numerical value obtained previously.^{14,18} The results in both N_2O and CCl_4 solutions gave $\text{p}K_{\text{OH}} = 11.8 \pm 0.2$ (an error of ± 0.1 in the intercept of Figure 7 and an additional error of ± 0.1 due to k_1). This result is in excellent agreement with the value of 11.9 ± 0.2 which has been reported previously.^{14,18}

Conclusions

A mechanism which accounts for most of the observations in the pulse-irradiated carbonate solutions is given. The results are in very good agreement with previous work^{3,4,14,18} except for the value of k_1 . Adams, Boag, and Michael⁴ report $k_1 = 2 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ but mention certain difficulties in the measurements. A correction for the unreacted bicarbonate ions would raise their value a little. Since carbonate ions show a strong pH-dependent reactivity toward OH, it is not suitable as a reference system for competition reactions.

The constancy of k_3 (see Figure 6) and the similarity of the spectrum or optical density, in the whole pH

region investigated, indicates that only one form of carbonate radical was present in our systems. The ionic strength effect indicates that this form was CO_3^- and not HCO_3^- . Thus, HCO_3^- appears to be a stronger acid than HCO_3^- —a reasonable result.

The ionic dissociation constant for OH radicals was obtained again, in very good agreement with the previous value.^{14,18} The results show again that OH radicals produced from N_2O by reaction 2 reacted in our system in the same way as the primary OH radicals did. One must conclude that in this system $(\text{N}_2\text{O})_{\text{aq}}^-$ or N_2OH radicals, possible intermediates of reaction 2, are short-lived (less than 1 μsec) or else react in the same way and with the same rates as does OH, and have the same $\text{p}K$. The same conclusion was reached in two other systems.^{14,17,18}

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