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# Temperature Dependence of the Rate Constants for Reactions of the Carbonate Radical with Organic and Inorganic Reductants

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## Abstract

Rate constants have been measured by pulse radiolysis for the reactions of the carbonate radical,  $\text{CO}_3^{\cdot-}$ , with a number of organic and inorganic reactants as a function of temperature, generally over the range 5 to 80°C. The reactants include the substitution-inert cyano complexes of  $\text{Fe}^{II}$ ,  $\text{Mo}^{IV}$ , and  $\text{W}^{IV}$ , the simple inorganic anions  $\text{SO}_3^{2-}$ ,  $\text{ClO}_2^-$ ,  $\text{NO}_2^-$ ,  $\text{I}^-$ , and  $\text{SCN}^-$ , several phenolates, ascorbate, tryptophan, cysteine, cystine, methionine, triethylamine, and allyl alcohol. The measured rate constants ranged from less than  $10^5$  to  $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , the activation energies ranged from  $-11.4$  to  $18.8 \text{ kJ mol}^{-1}$ , and the pre-exponential factors ranged from  $\log A = 6.4$  to  $10.7$ . The activation energies for the metal complexes and inorganic anions generally decrease with increasing driving force for the reaction, as expected for an outer sphere electron transfer. For highly exothermic reactions, however, the activation energy appears to increase, probably reflecting the temperature dependence of diffusion. For many of the organic reactants, the activation energies were low and independent of driving force, suggesting that the oxidation is via an inner sphere mechanism.

## Introduction

In previous work, we have reported on the temperature dependence of the rate constants for reaction of the sulfate radical with a number of organic and inorganic anions [1], of several other inorganic radicals with organic reductants [2], and of the dihalide and azide radicals with inorganic reductants [3]. For most of these reactions, there seemed to be little correlation between the driving force, or exothermicity, of the electron transfer reaction and the observed activation energy. Indeed, the variations in the rate constants appeared to be more strongly dependent on changes in the pre-exponential factor in the Arrhenius equation than on changes in the activation energy. The exception to this was found in the reactions of the dihalide radicals,  $\text{Cl}_2^{\cdot-}$ ,  $\text{Br}_2^{\cdot-}$ ,  $\text{I}_2^{\cdot-}$ , and the  $(\text{SCN})_2^{\cdot-}$  radical with the substitution-inert metal complexes  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{Mo}(\text{CN})_8^{4-}$ , and  $\text{W}(\text{CN})_8^{4-}$ . These results were interpreted to imply that whereas the radicals react with these metal complexes by an outer-sphere electron transfer, they react with the other reductants by an inner-sphere mechanism which involves the reversible formation of a transient intermediate.

In this work, we extend our study of the temperature dependence of free radical reactions in aqueous solutions to include a number of reactions of the

carbonate radical,  $\text{CO}_3^{\cdot-}$ , a strong one-electron oxidant (1.59 V vs. NHE [4]). Room temperature rate constants for the reactions of  $\text{CO}_3^{\cdot-}$  have been compiled recently [5]. This radical appears to react primarily as an oxidant, although the electron transfer may take place via an addition mechanism [6]. Studies of the reactions of  $\text{CO}_3^{\cdot-}$  with substituted phenols [7] and anilines [8] found that the rate constants correlated with the Hammett substituent constant  $\sigma$ , with negative slopes of  $\rho = -1.0$  and  $-1.1$ , respectively, suggesting that the radical is strongly electrophilic. Hydrogen abstraction reactions appear generally to be slow. In this study, we have included the reactions of  $\text{CO}_3^{\cdot-}$  with the three metal complexes, with several inorganic anions, and with several organic compounds. The inorganic anions chosen ( $\text{SO}_3^{2-}$ ,  $\text{ClO}_2^-$ ,  $\text{NO}_2^-$ ,  $\text{I}^-$ ,  $\text{SCN}^-$ ) have reported room temperature rate constants ranging from  $4 \times 10^5$  to  $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Mo}(\text{CN})_8^{4-}$  were reported to react with rate constants of  $5 \times 10^8$  and  $6.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , respectively [9]. The organic compounds chosen include ascorbate, tryptophan, and several phenolates, which generally have reported room temperature rate constants near  $10^9 \text{ M}^{-1} \text{ s}^{-1}$  and are expected to react by electron transfer; cysteine, cystine, and methionine, which react with rate constants of about  $5 \times 10^7$  to  $4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , each of which may have a different reaction mechanism; a tertiary amine, which was suggested to react by electron transfer with a rate constant of  $6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ; and allyl alcohol, which is expected to react by either addition to the double bond or hydrogen abstraction.

The carbonate radical has a reported  $\text{pK}_a$  value of 9.6 [10] or 7.9 [11] for the process  $\text{CO}_3\text{H}^\cdot \rightleftharpoons \text{CO}_3^{\cdot-} + \text{H}^+$ . At low ionic strength, there appeared to be little dependence of the rate constant on pH, suggesting that the two forms of the radical have similar intrinsic reactivities [6], [8], and [12]. The present experiments have been carried out at  $\text{pH} > 11$  and relate to reactions of the anionic form of the radical.

## Experimental

The rate constants were determined by kinetic spectrophotometric pulse radiolysis. The pulse radiolysis of aqueous solutions produces mostly  $\text{OH}^\cdot$  and  $e_{\text{aq}}^-$ , along with a small amount of  $\text{H}^\cdot$ . The solutions were saturated with  $\text{N}_2\text{O}$  to convert the  $e_{\text{aq}}^-$  to  $\text{OH}^\cdot$  and the  $\text{CO}_3^{\cdot-}$  radical was produced by the reaction of  $\text{OH}^\cdot$  radicals with  $\text{CO}_3^{2-}$ . The ionic strength of the solution was established mainly by the precursor salt,  $\text{Na}_2\text{CO}_3$ . The reactions were carried out at  $\text{pH } 11.2\text{--}11.6$ , except for the triethylamine reaction which was carried out with the addition of 0.1 M KOH to ensure that the reactant would be totally unprotonated. Under all of our experimental conditions, the precursor will be in the  $\text{CO}_3^{2-}$  form and the carbonate radical also will be deprotonated [10,11]. The reactions were monitored by following the decay of the  $\text{CO}_3^{\cdot-}$  at 600 nm ( $\epsilon = 1860 \text{ M}^{-1} \text{ cm}^{-1}$ ) [13] and first-order rate constants derived from weighted linear least-squares fits of  $\log(A_{600})$  vs. time. The second order rate constants were determined from the slopes of the plots of  $k_{\text{obs}}$  vs. concentration employing three substrate concentrations that differed by a factor of four. The whole experiment was repeated at five temperatures, generally between 5 and 80°C. The temperature was attained in a flow system by passing the solution through a thin coiled quartz tubing im-

mersed in a thermostated fluid before entering the irradiation cell and the temperature was read by a thermocouple immersed in the solution at the point of its exit from the cell. Other details of the experimental procedures and the materials used were as described before [2,3]. Materials not mentioned before were of the purest grade commercially available and were used as received.

### Results

The second-order rate constants determined for the various reactions at the different temperatures are summarized in Table I. The ionic strength is specified but no correction to zero ionic strength has been made. The second-order rate constants were fit to the Arrhenius expression,  $k = Ae^{-E_a/RT}$ , by a least squares routine [14], weighted by the reciprocal of the squares of the standard errors derived from the second-order fits. The Arrhenius plots for the reactions of the complexed metal ions are shown in Figure 1, for the other inorganic anions in Figure 2, and for the organic compounds in Figures 3 and 4. The Arrhenius parameters are presented in Table II, along with the calculated value of the rate constant at 298 K. The error limits reported for the activation energy are the standard errors from the least-squares fit. Due to the long extrapolation involved, we have chosen not to report the calculated statistical error limits for the pre-exponential factors. We estimate that over the temperature range of these studies, the errors in the rate constants calculated from the Arrhenius expressions are  $\pm 20\%$ . Table II also includes the driving force for each reaction, calculated as the difference between the one-electron reduction potential of the carbonate radical (1.59 V vs. NHE [4]) and that of the other reactant (taken from recent reviews [15], [16], except for the phenolates which were taken from more recent work [17]).

The values of  $k_{298}$  calculated from the Arrhenius parameters (Table II) are found to be, in most cases, slightly higher than the rate constants reported for room temperature measurements in the absence of temperature control, possibly due to the room temperature being lower than 298 K. Our rate constant for the SCN<sup>-</sup> reaction is substantially lower than that reported previously (an unpublished result quoted in ref. [5]) which, being a very low rate constant, could have been influenced by traces of reactive impurities. Also, there is an inconsistency between our results and the flash photolysis results for the reactions of CO<sub>3</sub><sup>2-</sup> with cysteine and methionine [12], although we are in agreement with the pulse radiolysis results for these two amino acids [18]. The flash photolysis experiments were carried out at low ionic strength ( $\mu = 0.01$  M). The methionine rate constant was about two times lower than measured here, which is consistent with the lower ionic strength. The cysteine rate constant, however, is somewhat higher than measured here, although, from the lower ionic strength, a lower rate constant would be expected.

The activation energies (Table II) range from a negative value of -11.4 to a positive value of 18.8 kJ mol<sup>-1</sup>; the logarithm of the pre-exponential factor varies from 6.4 to 10.7. The reactions of CO<sub>3</sub><sup>2-</sup> with ascorbate, hydroquinone, and *p*-methoxyphenol are sufficiently fast that they are likely to be at least partly limited by the rate at which the reactants can diffuse

TABLE I. Rate constants for reactions of  $\text{CO}_3^{\cdot-}$  at different temperatures.

Reactant	pH	$\mu(\text{M})$	T°C	$k(\text{M}^{-1} \text{s}^{-1})$								
$\text{Fe(CN)}_6^{4-}$	11.4	0.3	4	$3.1 \times 10^8$	15	$3.4 \times 10^8$	35	$3.9 \times 10^8$	53	$4.9 \times 10^8$	79	$5.0 \times 10^8$
$\text{W(CN)}_8^{4-}$	11.2	0.4	11	$2.3 \times 10^8$	27	$2.1 \times 10^8$	46	$2.3 \times 10^8$	68	$2.5 \times 10^8$	89	$2.8 \times 10^8$
$\text{Mo(CN)}_8^{4-}$	11.2	0.4	12	$1.9 \times 10^7$	28	$2.3 \times 10^7$	48	$3.1 \times 10^7$	68	$6.4 \times 10^7$	91	$3.9 \times 10^7$
$\text{SO}_3^{2-}$	11.4	0.3	9	$2.7 \times 10^7$	18	$2.9 \times 10^7$	32	$2.7 \times 10^7$	51	$2.5 \times 10^7$	74	$3.9 \times 10^7$
$\text{SO}_4^{2-}$	11.4	0.3	8	$2.9 \times 10^7$	18	$3.1 \times 10^7$	33	$3.8 \times 10^7$	50	$4.2 \times 10^7$	72	$4.8 \times 10^7$
$\text{ClO}_2^-$	11.4	0.3	8	$5.6 \times 10^5$	18	$4.8 \times 10^5$	34	$5.9 \times 10^5$	51	$9.3 \times 10^5$	73	$1.0 \times 10^6$
$\text{NO}_2^-$	11.4	1.5	9	$3.5 \times 10^6$	16	$2.9 \times 10^6$	35	$2.1 \times 10^6$	59	$1.3 \times 10^6$	79	$1.3 \times 10^6$
$\text{I}^-$	11.4	0.3	4	$5.3 \times 10^4$	17	$4.8 \times 10^4$	34	$1.8 \times 10^5$	55	$3.1 \times 10^5$	79	$3.5 \times 10^5$
$\text{SCN}^-$	11.6	3.0	6	$1.0 \times 10^9$	17	$1.2 \times 10^9$	35	$1.6 \times 10^9$	55	$1.9 \times 10^9$	79	$1.9 \times 10^9$
ascorbate	11.4	0.3	6	$1.5 \times 10^9$	17	$1.9 \times 10^9$	35	$2.2 \times 10^9$	55	$2.9 \times 10^9$	79	$3.1 \times 10^9$
hydroquinone	11.4	0.3	6	$1.1 \times 10^9$	17	$1.3 \times 10^9$	36	$1.6 \times 10^9$	56	$1.7 \times 10^9$	78	$1.6 \times 10^9$
<i>p</i> -methoxyphenolate	11.4	0.3	6	$2.4 \times 10^8$	17	$2.6 \times 10^8$	34	$2.9 \times 10^8$	56	$3.8 \times 10^8$	79	$3.3 \times 10^8$
phenolate	11.4	0.3	6	$6.6 \times 10^7$	16	$6.9 \times 10^7$	34	$6.6 \times 10^7$	55	$7.1 \times 10^7$	79	$7.7 \times 10^7$
<i>p</i> -cyanophenolate	11.4	0.3	6	$5.0 \times 10^8$	16	$5.0 \times 10^8$	34	$4.8 \times 10^8$	55	$4.6 \times 10^8$	79	$4.8 \times 10^8$
tryptophane	11.4	0.3	6	$1.5 \times 10^8$	16	$1.7 \times 10^8$	33	$2.0 \times 10^8$	53	$2.3 \times 10^8$	78	$2.6 \times 10^8$
cysteine	11.4	0.3	6	$9.5 \times 10^6$	17	$1.0 \times 10^7$	35	$1.5 \times 10^7$	55	$1.8 \times 10^7$	79	$2.2 \times 10^7$
cystine	11.4	0.3	6	$1.4 \times 10^8$	17	$1.6 \times 10^8$	35	$1.2 \times 10^8$	55	$8.1 \times 10^7$	79	$6.3 \times 10^7$
methionine	13.0	3.1	6	$6.9 \times 10^6$	19	$9.6 \times 10^6$	36	$1.1 \times 10^7$	56	$1.7 \times 10^7$	81	$2.0 \times 10^7$
triethylamine	11.6	3.0	7	$2.0 \times 10^5$	19	$2.4 \times 10^5$	36	$3.8 \times 10^5$	56	$5.8 \times 10^5$	80	$8.2 \times 10^5$

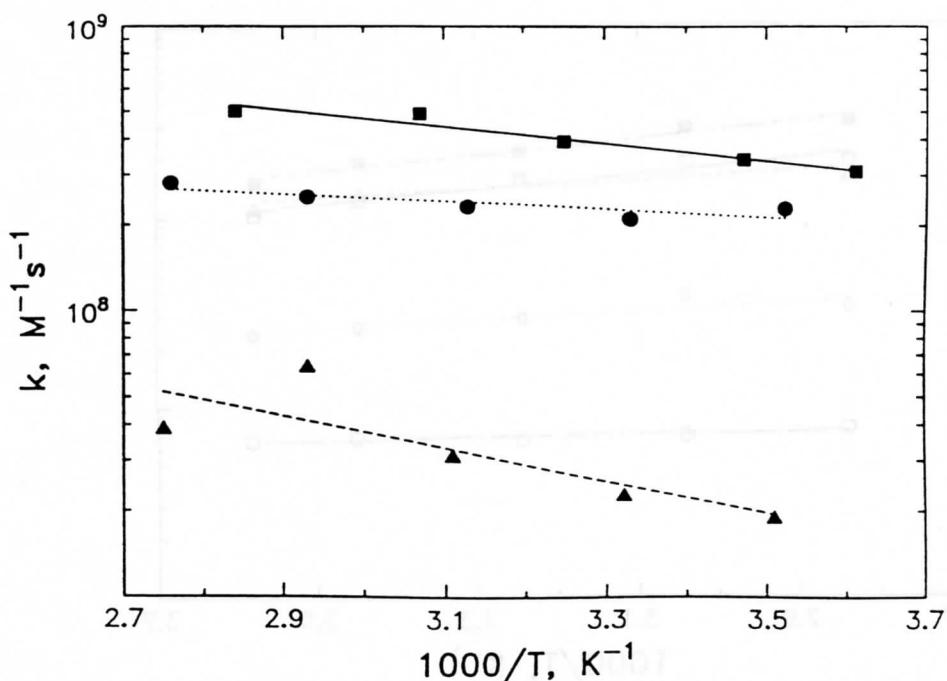


Figure 1. Arrhenius plots for the reactions of  $\text{CO}_3\cdot^-$  radicals with the metal complexes,  $\text{Fe}(\text{CN})_6^{4-}$  (■),  $\text{Mo}(\text{CN})_8^{4-}$  (▲), and  $\text{W}(\text{CN})_8^{4-}$  (●).

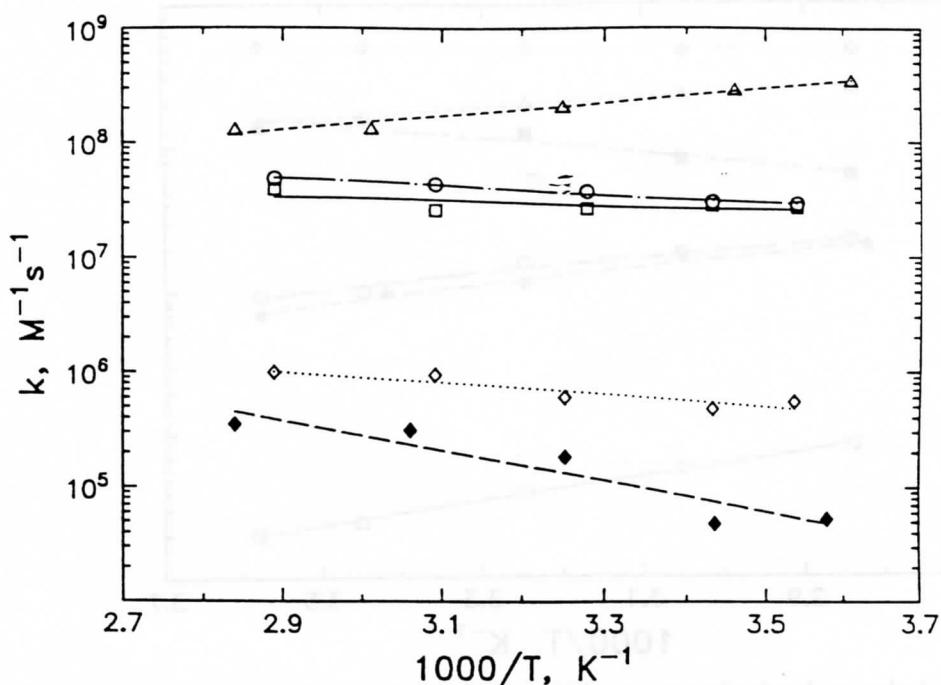


Figure 2. Arrhenius plots for the reactions of  $\text{CO}_3\cdot^-$  radicals with inorganic anions,  $\text{SO}_3^{2-}$  (□),  $\text{I}^-$  (△),  $\text{SCN}^-$  (◆),  $\text{NO}_2^-$  (◇), and  $\text{ClO}_2^-$  (○).

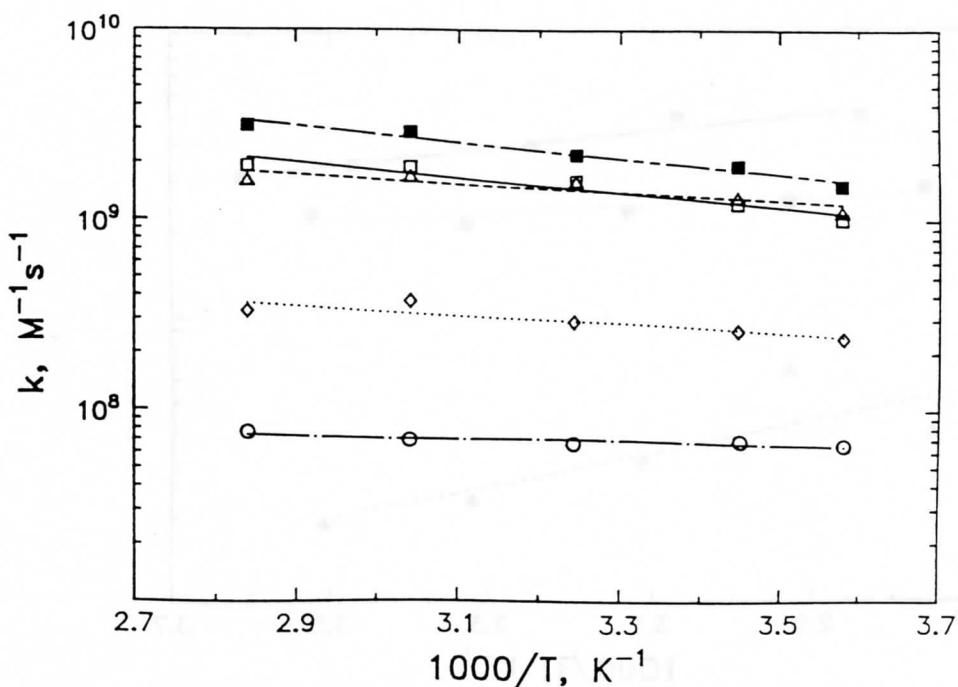


Figure 3. Arrhenius plots for the reactions of  $\text{CO}_3\cdot^-$  radicals with phenolate and ascorbate ions; phenolate ( $\diamond$ ), *p*-methoxyphenolate ( $\triangle$ ), *p*-cyanophenolate ( $\circ$ ), hydroquinone ( $\blacksquare$ ), and ascorbate ( $\square$ ).

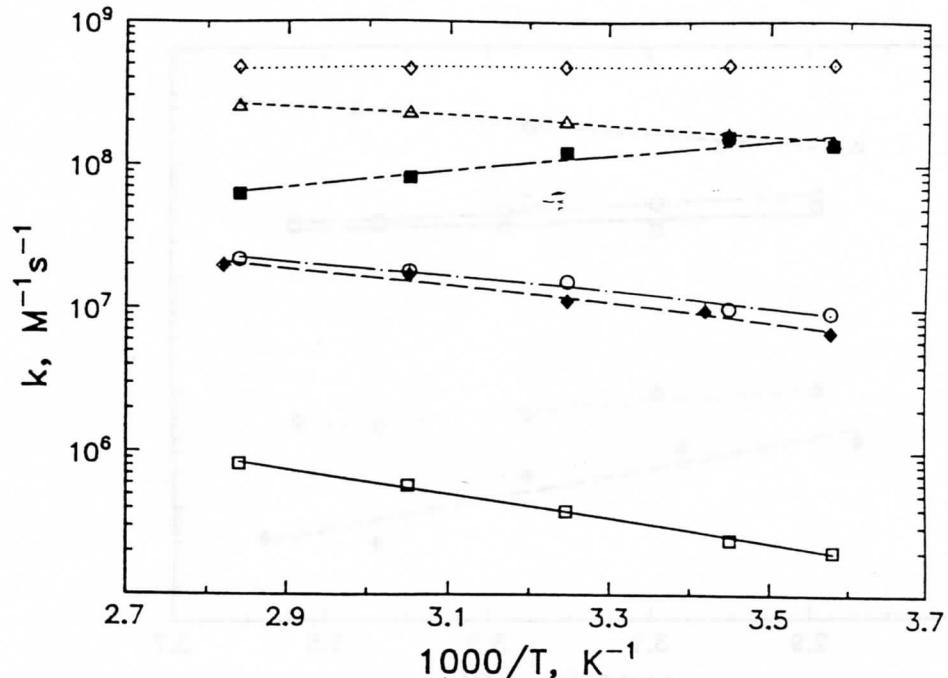


Figure 4. Arrhenius plots for the reactions of  $\text{CO}_3\cdot^-$  radicals with organic compounds: tryptophane ( $\diamond$ ), cysteine ( $\triangle$ ), cystine ( $\circ$ ), methionine ( $\blacksquare$ ), triethylamine ( $\blacklozenge$ ), and allyl alcohol ( $\square$ ).

TABLE II. Arrhenius parameters and room temperature rate constants for the reactions of  $\text{CO}_3^{2-}$ .

Reactant ( <i>R</i> )	pH	$E^\circ(\text{CO}_3^{2-}) - E^\circ(R)$ (V)	$E_a$ (kJ mol <sup>-1</sup> )	log <i>A</i>	$k_{298} (\text{M}^{-1} \text{s}^{-1})$
$\text{Fe(CN)}_6^{4-}$	11.4	1.13	6.5 ± 1.4	9.7	$3.6 \times 10^6$
$\text{W(CN)}_8^{4-}$	11.2	1.02	3.3 ± 0.8	8.9	$2.4 \times 10^6$
$\text{Mo(CN)}_8^{4-}$	11.2	0.75	8.4 ± 1.1	8.4	$3.5 \times 10^7$
$\text{SO}_4^{2-}$	11.4	0.83	3.9 ± 1.3	8.2	$2.9 \times 10^7$
$\text{ClO}_2^-$	11.4	0.65	6.8 ± 0.3	8.7	$3.4 \times 10^7$
$\text{NO}_2^-$	11.4	0.56	7.1 ± 1.1	7.1	$6.6 \times 10^3$
$\text{I}^-$	11.4	0.56	-11.4 ± 0.6	6.4	$2.5 \times 10^6$
$\text{SCN}^-$	11.6	0.26	18.8 ± 4.6	8.5	$1.6 \times 10^5$
ascorbate	11.4	1.51	8.3 ± 1.2	10.6	$1.4 \times 10^9$
hydroquinone	11.4	1.54	8.0 ± 0.8	10.7	$2.1 \times 10^9$
<i>p</i> -methoxyphenolate	11.4	1.05	4.3 ± 1.0	9.9	$1.3 \times 10^9$
phenolate	11.4	0.80	4.8 ± 1.3	9.3	$2.7 \times 10^8$
<i>p</i> -cyanophenolate	11.4	0.47	1.9 ± 1.1	8.2	$6.5 \times 10^7$
tryptophane	11.4	ca. 0.94	-0.9 ± 0.2	8.5	$4.9 \times 10^8$
cysteine	11.4		6.4 ± 0.3	9.4	$1.8 \times 10^8$
cystine	11.4		10.5 ± 0.9	8.9	$1.2 \times 10^7$
methionine	11.4		-9.2 ± 1.5	6.5	$1.2 \times 10^8$
triethylamine	13		11.4 ± 0.9	9.0	$9.8 \times 10^6$
allyl alcohol	11.6		18.3 ± 0.6	8.7	$2.9 \times 10^5$

close enough to undergo reaction. The magnitude of the possible effect of diffusion on the measured rate constants can be investigated by calculating the diffusion-controlled rate constant, assuming that the reactants are simple spherical balls [19] and then correcting the measured rate constants. If we assume that the radius of  $\text{CO}_3^{\cdot-}$  is the same as the effective ionic radius of  $\text{CO}_3^{2-}$  (0.45 nm) and that of the organic anions 0.6 nm [20], we calculate the expected diffusion-limited rate constant to be:

$$k_{\text{dif}} = 3.1 \times 10^{12} \exp(-16.9 \text{ kJ mol}^{-1}/RT) M^{-1} s^{-1}$$

We can correct for diffusion control by use of the eq. [21]

$$1/k_{\text{act}} = 1/k_{\text{obs}} - 1/k_{\text{dif}}$$

where  $k_{\text{act}}$  is the activation-controlled rate constant and  $k_{\text{obs}}$  is the observed rate constant. We then find that  $k_{\text{act}}$  for these three reactions are almost independent of temperature, with average rate constants of  $2.3 \times 10^9$  for ascorbate,  $5.0 \times 10^9$  for hydroquinone, and  $2.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for *p*-methoxyphenol.

The rate constants for the reactions of  $\text{CO}_3^{\cdot-}$  with  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{W}(\text{CN})_8^{4-}$  are also likely to be limited by diffusion, even though their rate constants are less than  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ . This is because of the high negative charges on these complexes. If we assume that the radii are 0.45 and 0.5 nm (the effective ionic radius of  $\text{Fe}(\text{CN})_6^{4-}$  [20]) this large negative charge results in a diffusion rate less than the experimental reaction rate. This suggests that ion pairing has reduced the effective negative charge on the metal complexes [22]. If we assume that the charge has become -3, diffusion rate constants higher than the measured reaction rate constants are calculated, but the reaction is still strongly influenced by the diffusion rate.

## Discussion

In this work, we have determined the temperature dependence of the rate constants for the reactions of the carbonate radical with several different types of reactants. The metal-cyano complexes are expected to react by outer-sphere electron transfer.



We found that the reactivity of the complexes increased with decreasing reduction potential of the complex, or increasing driving force for the reaction, as expected for an electron transfer reaction. The apparent activation energy varied between 3.3 and 8.4 kJ mol<sup>-1</sup> but did not simply decrease with decreasing reduction potential as expected. Probably this is due to the effect of diffusion on the reaction rate, which becomes more pronounced as the rate constant increases. Since the measured activation energies are much below the activation energy for diffusion (ca. 17 kJ mol<sup>-1</sup>), when the rate of reaction approaches that of diffusion the apparent activation energy increases. In our study [3] of the reactions of the dihalide radicals with these metal complexes, we found a different order of reactivity, with  $\text{Fe}(\text{CN})_6^{4-}$  intermediate in reactivity between  $\text{W}(\text{CN})_8^{4-}$  and  $\text{Mo}(\text{CN})_8^{4-}$ . Those rate constants, however, were considerably lower than the values for  $\text{CO}_3^{\cdot-}$  and thus

were less affected by diffusion and more reflective of the driving force and the self-exchange rates [3].

The reactivity patterns for the inorganic anions are also different in the present results than those found for the reactions of the dihalide radicals and  $(\text{SCN})_2^-$  [3]. For the latter radicals, reaction with  $\text{SO}_3^{2-}$  was more rapid than with any of the other inorganic anions; in the present work,  $\text{SO}_3^{2-}$  is intermediate in reactivity.  $\text{NO}_2^-$  and  $\text{ClO}_2^-$  react with similar rate constants with  $\text{Br}_2^-$ , but with different activation energies.  $\text{NO}_2^-$  reacts fifty times slower with  $\text{CO}_3^-$  than does  $\text{ClO}_2^-$ , but the reactions have similar activation energies. These differences in behavior may suggest a difference in mechanism, i.e., the dihalide radicals react by an inner sphere mechanism, or via an intermediate adduct, as suggested before [3], whereas the carbonate radical may react with the inorganic anions examined here by an outer sphere electron transfer. Indeed, the activation energies for the reactions of  $\text{CO}_3^-$  with  $\text{SO}_3^{2-}$ ,  $\text{ClO}_2^-$ ,  $\text{NO}_2^-$ , and  $\text{SCN}^-$  increase with decreasing driving force.

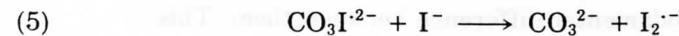
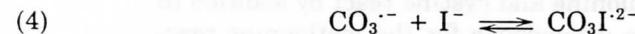
The reaction of  $\text{CO}_3^-$  with  $\text{I}^-$ , however, has a pronounced negative temperature dependence. A negative  $E_a$  was previously found [1] for the reaction of  $\text{SO}_4^{2-}$  with  $\text{CN}^-$ , where the electron transfer path  $\text{SO}_4^{2-} + \text{CN}^- \rightarrow \text{SO}_4^{2-} + \text{CN}$  is probably somewhat endothermic and the reaction probably takes place by addition of the radical to the  $\text{C}\equiv\text{N}$  triple bond, with subsequent hydrolysis of the product. For the reaction of  $\text{CO}_3^-$  with  $\text{I}^-$ , the path



is 0.26 V exothermic. If the secondary reaction

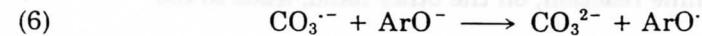


is included, the overall reaction is 0.56 V exothermic. Therefore, the reaction would be expected to involve a simple electron transfer and to have a positive activation energy. The negative  $E_a$  for this reaction, however, along with the fact that its rate constant is greater than that of the more exothermic reactions of  $\text{CO}_3^-$  with  $\text{SO}_3^{2-}$  or  $\text{ClO}_2^-$ , suggests that this reaction also involves the formation of an intermediate addition product. A possible mechanism for this reaction is:



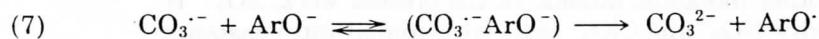
If  $k_{-4}$  is larger than  $k_5$  and has a higher activation energy than  $k_4$ , then the observed activation energy for the overall process will be negative.

The  $\text{CO}_3^-$  radical reacts rapidly with the hydroquinone anion, ascorbate, and *p*-methoxyphenolate, similar to the behavior of other inorganic radicals [3].



Phenolate is less reactive, as expected from its higher reduction potential [17]. Cyanophenolate, with an even higher reduction potential [17], reacts more slowly. The lower rate of this latter reaction does not arise from an increase in the activation energy, which is very low, but from a decrease in the pre-exponential factor, suggesting that the effect of a CN group on the reac-

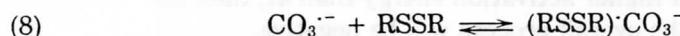
tivity of phenolate is to reduce the rate at which an intermediate adduct is formed. The finding that the activation energies for the reactions of the various phenolates do not correlate with the driving force for the reaction also indicates that the oxidation is not via outer-sphere electron transfer but probably via adduct formation.



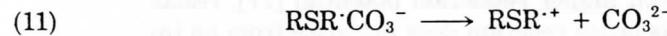
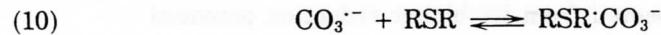
We have measured the temperature dependence of the rate constants for the reactions of  $\text{CO}_3^{\cdot-}$  with a number of biologically important molecules. The reactivity of ascorbate is partly diffusion-controlled and probably has little intrinsic activation energy. The reaction with tryptophan is fast and has almost no temperature dependence. This reaction has been proposed to take place by addition of the radical to the  $\pi$  system of the indole rings, rather than by direct electron transfer [6].

Cysteine reacts rapidly with  $\text{CO}_3^{\cdot-}$  with a moderately low activation energy. Cystine reacts about ten times slower with a higher activation energy. Methionine reacts with about the same rate constant as cysteine at room temperature, but has a negative activation energy. These disparate results probably arise from different reaction mechanisms for these three sulfur-containing amino acids with oxidants in general. Whereas cysteine can react by electron transfer from the  $-\text{S}^-$  group, the reactions with cystine and methionine probably involve addition to the sulfur. As a result, the electron transfer agent  $\text{N}_3^\cdot$  reacts rapidly with the cysteine anion, less rapidly with neutral cysteine, but reacts slowly with methionine [23]. On the other hand,  $\text{Br}_2^{\cdot-}$ , which reacts by electron transfer or by addition on the sulfur, reacts with both methionine [24] and cysteine [18] very rapidly, and with cystine [25] at a somewhat slower rate. Also,  $\text{O}_3$  reacts with methionine and the cysteine anion with similar rate constants, but slower with cystine or neutral cysteine [26], [27]. The fact that  $\text{O}_3$  reacts with methionine more rapidly than  $\text{N}_3^\cdot$  strongly supports addition to the sulfur as the mechanism of reaction of methionine with the various oxidizing radicals.

At room temperature, the relative reactivities of  $\text{CO}_3^{\cdot-}$  with methionine, cysteine, and cystine are similar to what was observed for  $\text{Br}_2^{\cdot-}$  and  $\text{O}_3$ . Although the results suggest that methionine and cystine react by addition to the sulfur, the negative temperature dependence for the methionine reaction suggests that there is a fundamental difference between them. This may be because the cystine reaction leads to a perthiyl radical



so that there is a facile path from the intermediate complex, not involving a charge separation. The methionine reaction, on the other hand, leads to the radical cation



Since the decomposition of the intermediate complex involves a charge separation, it is less facile and, as the temperature is increased, decomposition to

reactants is able to compete with the path to products. This then results in a negative temperature dependence for the overall reaction.

The reactions of  $\text{CO}_3^{2-}$  with a number of aliphatic amines have been investigated previously [28]. Whereas the reactions of the primary amines appeared to proceed primarily by hydrogen abstraction, the reactions with the tertiary amines, such as triethylamine, were suggested to take place by electron transfer. The one-electron oxidation potential for triethylamine has not been reported, but it is oxidized by both  $\text{ClO}_2$  [29] and  $\text{O}_3$  [27], suggesting that its potential is less than 1 V. Therefore, the driving force for oxidation of triethylamine by  $\text{CO}_3^{2-}$  is  $\geq 0.6$  V and the present results on the rate constant and activation energy are in line with the electron transfer mechanism.

The reaction of  $\text{CO}_3^{2-}$  with allyl alcohol could proceed by either hydrogen abstraction from the  $\alpha\text{CH}_2$  group or addition to the  $\text{C}=\text{C}$  double bond. The relatively high activation energy ( $18.3 \text{ kJ mol}^{-1}$ ) supports the hydrogen abstraction mechanism.

In conclusion, the activation energies for reaction of  $\text{CO}_3^{2-}$  with various organic and inorganic compounds are lower than the activation energy for diffusion. When the rate constant for the reaction approaches the rate constant for diffusion, the apparent activation energy of the reaction increases due to the influence of diffusion-control on the reaction. For outer-sphere electron transfer reactions, the activation energy is expected to decrease with increase in driving force [3]. The metal complexes and the inorganic anions, except for  $\text{I}^-$ , show a general decrease in activation energy with increase in driving force, suggesting that they may involve outer-sphere electron transfer. The fact that the reactions of  $\text{CO}_3^{2-}$  with  $\text{I}^-$  and with methionine have strongly negative temperature dependencies, however, indicate that these reactions, at least, proceed by a more complex mechanism. For the phenolates and ascorbate, if we accept a near-zero activation energy for the reactions of ascorbate, hydroquinone, and *p*-methoxyphenolate as calculated above (by correcting for diffusion), we find that the reactions for the substituted phenolates and ascorbate do not correlate with the reduction potentials, suggesting that these reactions also take place via addition, as mentioned before [6]. On the time scales of these experiments, the addition of  $\text{CO}_3^{2-}$  to these reactants does not appear to lead to observable intermediates, suggesting that their steady-state concentrations are very low.

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