81.95, χ_M for $(CH_3)_2Si(OC_2H_5)_2$ = 104.20, and χ_{CH_2} = 11.17 gives $C = -0.02$.

Using these parameters, χ_M values for dimethyl di-*n*-alkoxysilanes have been calculated and summarized in Table III.

For χ_M values of acetoxy- and propionoxysilanes of the general formula $(CH_3)_aSi(OC{=}OC_nH_{2n+1})_d$, Hameka's equation has been used as

$$\chi_M = aA + dD + adE$$

where

$$D = 0.25\chi(Si) + \chi(OCOC_nH_{2n+1}) + \chi(Si{-}OCOC_nH_{2n+1}) + 1.5\chi\left(Si\begin{matrix}\diagup OCOC_nH_{2n+1}\\ \diagdown OCOC_nH_{2n+1}\end{matrix}\right)$$

and

$$E = \chi\left(Si\begin{matrix}\diagup CH_3\\ \diagdown OCOC_nH_{2n+1}\end{matrix}\right) - 0.5\chi\left(Si\begin{matrix}\diagup OCOC_nH_{2n+1}\\ \diagdown OCOC_nH_{2n+1}\end{matrix}\right) - 0.5\chi\left(Si\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}\right)$$

Substitution of χ_M for $Si(OCOCH_3)_4$ = 129.26, χ_M for $Si(OCOC_2H_5)_4$, and χ_{CH_2} = 11.35 gives D = 32.17. χ_M for $(CH_3)_2Si(OCOCH_3)_2$ = 101.18 and χ_M for $(CH_3)_2Si(OCOC_2H_5)_2$ = 123.97 give $E = -0.08$. χ_M values calculated for acetoxy- and propionoxysilanes with these parameters have been recorded in Table III.

The agreement between the calculated and experimentally determined χ_M values is excellent and is very encouraging as the divergence is practically of the negligible order. This good agreement is due to the fact that in Hameka's equation the contribution of bond interactions has been fully accounted for which could not be taken in earlier wave-mechanical calculations.[1] No doubt since silicon is the larger atom, it would be expected that these interactions would be less, but they do occur. The environmental bond interactions do play an important role in the compounds containing Si–O bonds and this role affects diamagnetism considerably like other properties. The studies of these bond interactions open an entirely new field which is yet to be explored for the exact behavior of the organic derivatives of metals.

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Kinetics of Metal Ion and Metal Chelate Catalyzed Oxidation of Ascorbic Acid. IV. Uranyl Ion Catalyzed Oxidation[1]

M. M. Taqui Khan and A. E. Martell[2]

Contribution from the Departments of Chemistry, Illinois Institute of Technology, Chicago, Illinois, and Texas A&M University, College Station, Texas.
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Abstract: The kinetics of the uranyl ion catalyzed oxidation of ascorbic acid at 25 and 40° is reported. The dissociation constants of ascorbic acid at 40°, and at an ionic strength of 0.10 *M* (KNO_3), have been obtained from potentiometric titration data and are 2.69×10^{-4} and 1.05×10^{-12}. The dissociation constants of ascorbic acid in D_2O at 25° and at an ionic strength of 0.10 *M* (KNO_3) are 2.7×10^{-5} and 6.00×10^{-13}. The uranyl ion catalyzed oxidation of ascorbic acid catalyzed by uranyl ion proceeds by a path first order with respect to substrate, catalyst, molecular oxygen, and hydrogen or deuterium ion concentrations, in accordance with the rate law, $k[H_2A][UO_2^{2+}]\cdot[H^+][O_2]$. The uranyl ion is less active as a catalyst than is the vanadyl ion. The deuterium isotope effect, k_H/k_D, for the uranyl ion catalyzed reaction was found to have the low value of 1.24. Activation parameters for the uranyl ion catalyzed oxidation are reported and compared with those of vanadyl ion catalyzed and uncatalyzed oxidations of ascorbic acid. A probable mechanism is proposed for the uranyl ion catalyzed reaction.

In an earlier paper[3] the kinetics of the catalysis of oxidation of ascorbic acid by the vanadyl ion, and by its aminopolycarboxylic acid chelates, was described. The present paper extends this work to uranyl ion catalysis. The kinetics and mechanism of metal ion catalysis in the oxidation of ascorbic acid have been the subject matter of several studies,[4-9] most of which were concerned with catalysis by copper(II) ion. The present work was undertaken as part of a general study of the effect of oxo metal ions as catalysts in the oxidation of ascorbic acid, and for comparison with earlier work on catalysis by the oxovanadium(IV) ion.

(1) This work was supported by Research Grants WP00744 and WP01197, Federal Water Pollution Control Administration, U. S. Department of the Interior.
(2) Department of Chemistry, Texas A&M University, College Station, Texas 77843.
(3) M. M. T. Khan and A. E. Martell, *J. Am. Chem. Soc.*, **90**, 6011 (1968).
(4) E. S. G. Barron, R. De Meio, and F. W. Klemperer, *J. Biol. Chem.*, 112, 625 (1936).
(5) A. O. Dekker and R. G. Dickinson, *J. Am. Chem. Soc.*, **62**, 2165 (1940).
(6) R. Grinstead, *ibid.*, **82**, 3464 (1960).
(7) H. Nord, *Acta Chem. Scand.*, **9**, 442 (1955).
(8) A. Weissberger, J. E. Luvalle, and D. S. Thomas, *J. Am. Chem. Soc.*, **65**, 1934 (1943).
(9) A. Weissberger and J. E. Luvalle, *ibid.*, **66**, 700 (1944).

Experimental Section

Reagents. The *l*-ascorbic acid was Kodak White Label grade and was used without further purification. The equivalent weight of the sample was found to be 88 by titration with standard base. Aqueous uranyl nitrate solution was prepared from Fisher certified reagent grade uranyl nitrate and was standardized gravimetrically by ignition of suitable aliquots to U_3O_8. Standard carbonate-free sodium hydroxide was prepared by the usual procedure employing saturated sodium hydroxide solution.

Potentiometric Measurements. The dissociation constants of *l*-ascorbic acid and the stability constant of a 1:1 uranyl–ascorbate complex were determined by potentiometric titration in a medium adjusted to ionic strength 0.10 *M* with potassium nitrate. A Beckman Model G pH meter fitted with extension glass and calomel electrodes was used. The pH meter was calibrated in terms of hydrogen ion concentration with acetic acid buffer as well as with standard HCl and NaOH. The data given by Harned and Owen[10] were used in the acetate buffer range to determine hydrogen ion concentrations. The solution of ascorbic acid was prepared with air-free distilled water, and an atmosphere of purified nitrogen was maintained in the titration cell to avoid any disturbing effects resulting from oxidation.

The dissociation constants of ascorbic acid in D_2O were determined by potentiometric measurement at 25° in a medium of ionic strength 0.10 *M* (KNO_3). The pH meter was calibrated in terms of deuterium ion concentration with acetic acid buffer as well as with standard DCl and NaOD. The data given by Gary, *et al.*,[11] for the dissociation of acetic acid in D_2O were used in the acetate buffer range to correct for the deuterium ion concentration. In the alkaline range deuterium ion concentrations were calculated from the value[12] of $K_W(D_2O)$ at 25° of 1.54×10^{-15}. The activity coefficient function, $\gamma_D\gamma_{OD}/a_{D_2O}$, for D_2O in 0.10 *M* (KNO_3) has been taken as 0.61 (nearly the same as that of H_2O). Since there is only 0.4% difference in the dielectric constants of H_2O and D_2O at 25°, the activity coefficient function for D_2O in 0.10 *M* KNO_3 is expected to be about the same as that of H_2O. Gary, *et al.*,[13] have reported that the activity coefficient of DCl in D_2O is slightly smaller than that of HCl in H_2O at the same molality. The ionic concentration product $[m_D{}^+m_{OD}{}^-]$ calculated from the above values of K_W and activity coefficient function is 2.49×10^{-15} at 25°.

Kinetic Measurements. In the pH range investigated (0.99–2.00) the pH or pD of the experimental solution was set by adding the required quantity of 0.4 *M* HCl or DCl. Once set, the pH or pD remained constant throughout a particular kinetic run and was checked periodically by a Beckman Model G pH meter fitted with extension glass and calomel electrodes. The pH meter was calibrated with acetic acid buffer and by titration of standard HCl and NaOH solutions. At very low pH or pD (0.99–1.5), hydrogen ion concentration was calculated from the amount of HCl or DCl added. The ionic strength of the experimental solution was maintained at approximately 0.10 *M* with KNO_3. After the pH or pD was adjusted to the desired value, a stream of oxygen was passed through the cell in such a way as to ensure intimate contact between the solution and a large excess of gas. The oxygen used was 99.9% pure and any CO_2 present was removed by passing it through an Ascarite tube. It was presaturated with water vapor by streaming through a wash bottle maintained at the same temperature and electrolyte concentration as the reacting solution. The rate of oxidation was measured by the amount of dehydroascorbic acid produced during the course of oxidation. The analytical procedure employed for the estimation of dehydroascorbic acid was that described by Roe.[14] Uncertainties in rate constants were estimated from the scatter of the experimental points.

Results

Equilibrium Studies. Dissociation of Ascorbic Acid. The p*K* values (*i.e.*, logs of successive proton association constants) of ascorbic acid determined from potentiometric data are $pK_1 = 11.34$ (25°), 11.98 (40°) and $pK_2 = 4.04$ (25°), 3.57 (40°). The p*K* values of ascorbic acid at 25° ($\mu = 0.10$ *M* (KNO_3)) in D_2O are $pK_1 = 12.22$ and $pK_2 = 4.56$.

Stability of the Uranyl–Ascorbate Complex. Addition of uranyl ion to ascorbic acid results in the formation of a brown solution, the intensity of which increases with pH. Since uranyl ion oxidizes ascorbic acid extremely slowly at pH values above 2.00, a rapid 1:1 titration of ascorbic acid and uranyl ion was conducted at 25° at an ionic strength of 0.10 *M* (KNO_3). The titration could not be carried to completion since a precipitate appeared at 0.75 mole of base per mole of ascorbic acid ($a = 0.75$). The stability constant of the uranyl–ascorbate complex, K_{MHA}, corresponding to the equilibrium

$$UO_2^{2+} + HA^- \rightleftharpoons UO_2HA^+ \qquad K_{MHA} = \frac{[UO_2HA^+]}{[UO_2^{2+}][HA^-]}$$

was calculated from hydrogen ion concentrations determined over the early stages of the reaction (up to a values of 0.50). The value of log K_{MHA} at 25° ($\mu = 0.10$ *M* (KNO_3)) is 3.5 ± 0.1).

Kinetic Studies. The over-all reaction under study, in the presence and in the absence of the uranyl ion, may be represented by

$$H_2A + O_2 \xrightarrow{(UO_2^{2+})} A + H_2O_2$$

where H_2A represents ascorbic acid.

a. Spontaneous Oxidation of Ascorbic Acid in D_2O. The spontaneous oxidation of ascorbic acid in D_2O solution saturated with 100% oxygen gas at 25° ($\mu = 0.10$ *M* (KNO_3)) indicated a first-order reaction with respect to the total concentration of unreacted ascorbic acid. In the pD range 0.99–1.6, the rate of oxidation varied inversely with the deuterium ion concentration. Table I gives the rate data obtained for the spontaneous oxidation of ascorbic acid in D_2O at 25°. The specific rate constant for the oxidation of ascorbic acid in D_2O has been obtained in a manner similar to that reported[3] for the spontaneous oxidation of ascorbic acid in H_2O.

Table I. Spontaneous Oxidation of Ascorbic Acid by Molecular Oxygen in D_2O[a]

[H⁺] or [D⁺]	k (sec⁻¹) × 10⁷	
	H_2O	D_2O
1.02×10^{-1}	5.9 ± 0.2	3.5 ± 0.2
8.51×10^{-2}	6.3 ± 0.2	3.8 ± 0.2
6.76×10^{-2}	7.9 ± 0.3	4.8 ± 0.2
3.98×10^{-2}	14.0 ± 0.4	8.5 ± 0.5
2.51×10^{-2}	21.0 ± 0.7	13.0 ± 0.6
	(5.9 ± 0.2 × 10⁻⁴)[b]	(3.7 ± 0.2 × 10⁻⁴)[b]
	$k_H/k_D = 1.6$	

[a] 25°; $\mu = 0.10$ *M* (KNO_3); $T_A = 1.0 \times 10^{-3}$ *M*. [b] Specific rate constant for the spontaneous oxidation of the monoionic species of ascorbic acid.

b. Uranyl Ion Catalyzed Oxidation. The experimental results indicated a first-order reaction with respect to the total concentration of unreacted ascorbic acid. In the pH or pD range 0.99–2.00, the rate varied linearly with the concentration of uranyl ion, which remained unchanged during the oxidation reaction. Thus uranyl ion behaves as a true catalyst under the reaction

(10) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, pp 638 and 752.
(11) R. Gary, R. G. Bates, and R. A. Robinson, *J. Phys. Chem.*, 69, 2750 (1965).
(12) R. W. Kingerly and V. K. La Mer, *J. Am. Chem. Soc.*, 63, 3256 (1941).
(13) R. Gary, R. G. Bates, and R. A. Robinson, *J. Phys. Chem.*, 68, 1186 (1964).
(14) J. H. Roe, "Methods of Biochemical Analysis," Vol. I, Interscience Publishers, New York, N. Y., 1954, pp 115–139.

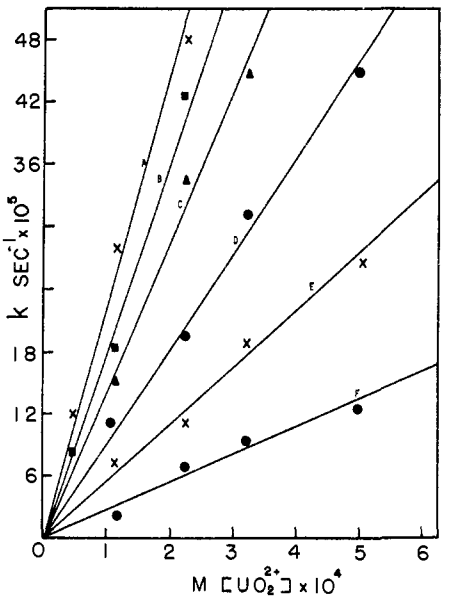

Figure 1. Catalytic effect for the oxidation of ascorbic acid in the presence of uranyl ion at 25° in 0.10 M KNO_3, at $-\log [H^+]$ values of: A, 0.99; B, 1.07; C, 1.17; D, 1.40; E, 1.60; and F, 2.00. k = difference between the first-order rate constants in the presence and in the absence of the metal ion; μ = 0.10 M (KNO_3).

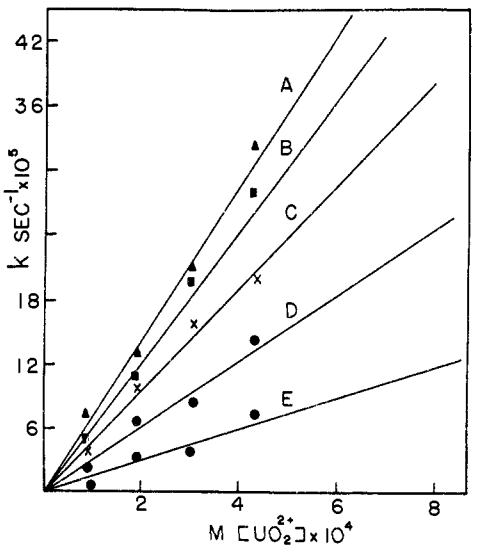

Figure 2. Catalytic effect for the oxidation of ascorbic acid in the presence of uranyl ion in D_2O at 25° in 0.10 M (KNO_3), at $-\log [D^+]$ values of: A, 0.99; B, 1.07; C, 1.17; D, 1.40; E, 1.60. k = difference between the first-order rate constants in the presence and in the absence of the metal ion in D_2O; μ = 0.10 M (KNO_3).

conditions employed. From the data reported[15] for the hydrolysis and dimerization of uranyl ion at 25° ($\log K_1 = -6.10$, $\log \beta_{22} = -5.84$), a calculation of the degree of hydrolysis of the metal ion in the pH range under consideration indicated that more than 99% of the catalyst was in the unhydrolyzed form. Thus the hydrolysis and dimerization of the metal ion may be neglected. The data obtained on the uranyl ion catalyzed oxidation of ascorbic acid in H_2O at 25 and 40°, and in D_2O at 25°, are given in Table II. Figure 1 indicates the variation

Table II. Apparent Second-Order Rate Constants (M^{-1} sec^{-1}) for Uranyl Ion Catalyzed Oxidation of Ascorbic Acid[a]

$-\log$ [H^+] or [D^+]	25°, H_2O	25°, D_2O	40°, H_2O
0.99	0.86 ± 0.06	0.72 ± 0.05	2.2 ± 0.1
1.07	0.74 ± 0.05	0.62 ± 0.04	1.80 ± 0.08
1.17	0.60 ± 0.04	0.49 ± 0.03	1.50 ± 0.07
1.40	0.36 ± 0.02	0.30 ± 0.02	0.90 ± 0.04
1.60	0.18 ± 0.01	0.15 ± 0.01	0.50 ± 0.02
2.00	0.10 ± 0.01	...	0.30 ± 0.02
	8.7 ± 0.6[b]	7.0 ± 0.5[b]	22 ± 1[b]
		k_H/k_D = 1.24	

[a] μ = 0.10 M (KNO_3), oxygen pressure = 1.0 atm, $T_A = 1.0 \times 10^{-3}$ M, $[UO_2^{2+}] = 1.0 \times 10^{-4}$–$8.0 \times 10^{-4}$ M. [b] Third-order rate constants for the hydrogen or deuterium ion dependent path of uranyl ion catalyzed oxidation of ascorbic acid.

of rate at 25°, with the concentration of uranyl ion at a particular pH. The apparent second-order rate constants given in Table II were calculated from the slopes of the straight lines given in Figure 1 for 25° and were obtained from a similar plot for 40°. The data for a particular straight line were obtained by measuring the rate over a wide range of catalyst concentration. The rate data on the uranyl ion catalyzed oxidation of ascorbic acid in D_2O are plotted in Figure 2.

The specific rates given in Table II also include any dependence on hydrogen or deuterium ion concentration. The dependence of the rate on hydrogen or deuterium ion concentration was found to be always linear. This generalization may be readily verified in Figure 3, where the specific rates of Table II are plotted *vs.* the corresponding value of hydrogen or deuterium ion concentration. Since the plots in Figure 3 have nearly zero intercepts, the main reaction pathway for the uranyl ion catalyzed oxidation of ascorbic acid involves first power dependence on hydrogen or deuterium ion concentration. In this respect uranyl ion is similar to vanadyl ion,[3] which catalyzes the oxidation of ascorbic acid by a pathway having first power dependence on hydrogen ion concentration. The rate constants for the hydrogen ion dependent path of uranyl ion catalyzed oxidation in H_2O at 25 and 40°, and in D_2O at 25°, were determined from the slopes of the straight lines in Figure 3, and are presented in Table II.

c. Dependence of the Uranyl Ion Catalyzed Oxidation of Ascorbic Acid on Oxygen Concentration. The oxygen dependence of the rates of uranyl ion catalyzed oxidation of ascorbic acid was studied at 40° and at $-\log [H^+]$ values of 1.07 and 1.17. With the use of a sintered glass delivery tube, mixtures of oxygen and nitrogen of known partial pressure were passed through the experimental solution in such a way that there was intimate contact between the gas phase and the solution at all times. The mixture of gases was passed through the experimental solution at the rate of 0.75 l./min, and the concentration of oxygen in solution was calculated[16] on the assumption that Henry's law is obeyed. Since the rate at which oxygen is passed through the solution (3–30 mmoles/min for mixtures from 10 to 100% oxygen) is orders of magnitude higher than the rate of the reaction, the solution was considered to be saturated with respect to oxygen at all times, and the oxygen con-

(15) R. L. Gustafson, C. Richard, and A. E. Martell, *J. Am. Chem. Soc.*, 82, 1526 (1960).

(16) "International Critical Tables," Vol. III, 1928, p 271.

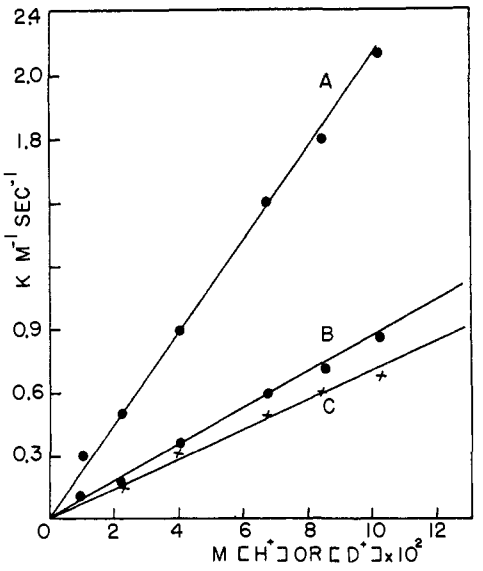

Figure 3. Dependence of the specific second-order rate constants "k" of uranyl ion catalyzed oxidation of ascorbic acid on the hydrogen ion concentration at (A) 40°, (B) 25°; and on the deuterium ion concentration at (C) 25°; μ = 0.10 M (KNO_3) in all cases.

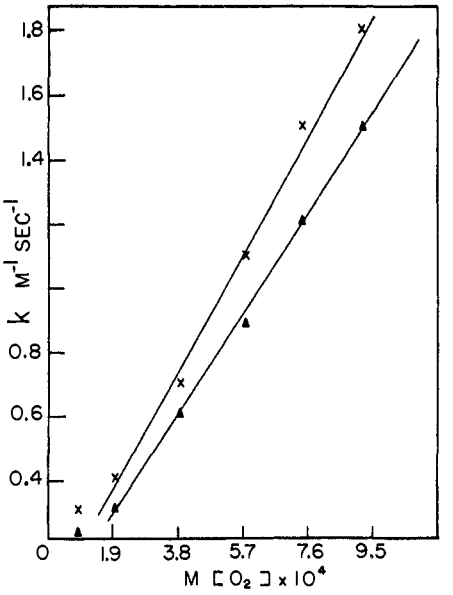

Figure 4. Dependence of the specific second-order rate constant "k" of uranyl ion catalyzed oxidation of ascorbic acid on oxygen concentration at −log [H⁺] values of: A, 1.07; B, 1.17; t = 40°; μ = 0.10 M (KNO_3).

centration remained constant during all experimental runs. The rates were found to vary linearly with the concentration of oxygen for mole fractions of oxygen of from 0.20 to 1.0. This behavior is similar to that observed for cupric, ferric, and vanadyl ion catalyzed oxidation with the concentration of oxygen at −log [H⁺] values of 1.07 and 1.17, shown in Figure 4; the data are tabulated in Table III. The rate constants for oxygen dependence, calculated from the slope of the straight lines in Figure 4, are tabulated in Table III.

Table III. Variation of the Rate Constant of Uranyl Ion Catalyzed Oxidation of Ascorbic Acid with the Partial Pressure of Oxygen at 40°[a]

Partial pressure of O_2, atm	Second-order constants, M^{-1} sec^{-1} −Log [H⁺] = 1.07	−Log [H⁺] = 1.17
0.99	1.80 ± 0.08	1.50 ± 0.07
0.81	1.50 ± 0.08	1.20 ± 0.07
0.62	1.10 ± 0.06	0.90 ± 0.06
0.40	0.70 ± 0.04	0.60 ± 0.04
0.20	0.40 ± 0.02	0.30 ± 0.02
0.10	0.30 ± 0.02	0.20 ± 0.01
	(4.4 ± 0.2 × 10³)[b]	(3.6 ± 0.2 × 10³)[b]

[a] μ = 0.10 M (KNO_3); T_A = 1.0 × 10⁻³ M; [UO_2^{2+}] = 1.5 × 10⁻³ M. [b] Third-order rate constants for the oxygen dependence of uranyl ion catalyzed oxidation of ascorbic acid at 40°.

Discussion

In the presence of excess oxygen, the rate of oxidation of ascorbic acid was found to depend directly on the total concentration of unreacted ascorbic acid, the uranyl ion concentration, and the hydrogen ion concentration. The rate law in the presence of oxygen is expressed by

$$-\frac{dT_A}{dt} = kT_A[UO_2^{2+}][H^+][O_2] \quad (1)$$

where T_A = total concentration of unreacted ascorbic acid and [UO_2^{2+}] = concentration of unhydrolyzed uranyl ion. The hydrogen ion dependent constants at 25 and 4° and the deuterium ion dependent constant at 40° listed in Table II were obtained from the slope of the rate constant k against the hydrogen or deuterium ion concentration, in the pH or pD range 0.99–2.00.

The activation parameters of the uranyl ion catalyzed oxidation of ascorbic acid are given in Table IV and compared with the corresponding constants obtained[3] for vanadyl ion catalysis.

Table IV. Apparent Activation Parameters for the Uranyl Ion Catalyzed Oxidation of Ascorbic Acid[a]

Conditions	$\Delta H^{\ddagger}$, kcal mole^{-1}	$\Delta S^{\ddagger}$, eu	$\Delta F^{\ddagger}$, kcal mole^{-1}
UO_2^{2+} ion	+10.8 ± 0.6	−18 ± 1	+16.2 ± 0.6
VO^{2+} ion	+13.8 ± 0.7	+4.1 ± 0.2	+12.6 ± 0.4
No metal ion catalysis	+10.7 ± 0.4	−37 ± 2	+22 ± 1

[a] Corresponding to the third-order [H⁺]-dependent constants listed in Table II. μ = 0.10 M (KNO_3).

Mechanism of the Reaction. Uranyl ion catalyzed oxidation of ascorbic acid is first order with respect to the substrate, uranyl ion, oxygen, and hydrogen ion concentrations. The hydrogen ion probably plays an important role in the reaction by forming a protonated derivative of the uranyl–ascorbate complex in a manner analogous to that reported[3] for the vanadyl–ascorbate complex. The increased positive charge on the complex facilitates electron transfer within the metal–substrate system.

On the basis of the kinetic observations, a mechanism for the uranyl ion catalyzed oxidation of ascorbic acid may be formulated in the following way.

$$H_2A \overset{K_1}{\rightleftharpoons} HA^- + H^+$$

$$HA^- + UO_2^{2+} \overset{K_2}{\rightleftharpoons} UO_2HA^+$$

$$UO_2HA^+ + H^+ \overset{K_3}{\rightleftharpoons} UO_2H_2A^{2+}$$

$$UO_2H_2A^{2+} + H^+ \overset{K_4}{\rightleftharpoons} UO_2H_3A^{3+}$$

$$UO_2H_3A^{3+} + O_2 \overset{K_5}{\rightleftharpoons} UO_2H_3A(O_2)^{3+}$$

$$UO_2H_3A(O_2)^{3+} \xrightarrow{k} UO_2H_3A\cdot(O_2\cdot)^{3+}$$

$$UO_2H_3A\cdot(O_2\cdot)^{3+} \xrightarrow{\text{fast}} UO_2^{2+} + H_2O_2 + H^+ + A$$

The proposed mechanism involves five preequilibrium steps. The equilibrium constants for the first two steps were obtained from potentiometric measurements. The third, fourth, and fifth equilibria are inferred from kinetic data, which show the dependence of the rate of oxidation of ascorbic acid on the first power of hydrogen ion and oxygen concentrations. The triprotonated species, $UO_2H_3A(O_2)^{3+}$, would probably have two protons associated with oxo oxygens of the uranyl ion, and the third on one of the ascorbate oxygen donor atoms. The formation of the protonated complex in preequilibrium steps is supported by the small deuterium isotope effect ($k_H/k_D = 1.24$) observed in the reaction. A uranyl–ascorbate–oxygen complex is proposed in the fifth preequilibrium step. The formation of similar oxygen complexes was proposed[3] to explain the oxygen dependence of cupric, ferric, and vanadyl ion catalyzed oxidation of ascorbic acid. The rate-determining step, which is the decomposition of the activated complex formed in the fifth preequilibrium (K_5), is pictured above as involving a single electron transfer within the activated complex, followed by a second rapid electron transfer leading to reaction products. This second step may involve the formation of an intermediate $UO_2H_3A(O_2^{2-})^{3+}$, or even $UO_2H_2A(O_2H^-)^{3+}$. The peroxo complex would then dissociate to the final products shown above. There is nothing in these results, however, that precludes dissociation of the complex immediately after the first electron transfer, followed by completion of the reaction through rapid reactions of the ascorbate and HO_2 radicals in solution.

It is of interest to compare the catalytic activity of the two oxo metal ions, VO^{2+} and UO_2^{2+}, in the oxidation of ascorbic acid. In both the cases, the oxidation of ascorbic acid is first power with respect to hydrogen ion, oxygen, and metal ion concentrations. The rate of oxidation of ascorbic acid catalyzed by uranyl ion is much slower than that of the vanadyl ion (by a factor of 1000 or more), though the uranyl–ascorbate complex has a higher stability than that of the vanadyl–ascorbate complex (log K_{MHA} for VO^{2+} and UO_2^{2+} are respectively 2.2 and 3.5). The difference in the catalytic activity of the two oxo metal ions seems to depend on the step involving combination with molecular oxygen. The two oxo oxygens of the uranyl ion may interfere with the formation of the proposed oxygen complex by hindering the attack of oxygen on the back side of the metal ion, a mode of reaction which is possible for the VO^{2+} catalysis[3].

The difference in the catalytic activities of the uranyl and vanadyl ions is reflected in their apparent activation parameters. A comparison between the two reactions on this basis would seem to be valid in view of the close similarity between them. Thus both may be expressed by the same unique rate law

$$-\frac{dT_A}{dt} = kT_A[M^{2+}][H^+][O_2]$$

where M^{2+} is UO_2^{2+} or VO^{2+}. The entropy of activation for the catalysis by uranyl ion is -18 eu compared to that of $+4$ eu for vanadyl ion catalysis, indicating a less probable activated complex in the case of the former ion. The enthalpies of activation for uranyl ion and vanadyl ion catalysis are similar, within about 3 kcal/mole. It may be further noticed from Table III that the enthalpies of activation are the same for the uranyl ion catalyzed and the uncatalzyed oxidation of ascorbic acid, and not much different from the enthalpies of activation for vanadyl catalysis. Thus the main difference in the catalyzed and uncatalyzed reactions lies in the entropy of activation which is 19 eu more positive for uranyl ion catalyzed reaction. On this basis it seems that in these reactions the principal function of the metal ion is to bring the oxygen and substrate together. The much higher value of $\Delta S^{\ddagger}$ for the vanadyl ion indicates that it is able to accomplish this more effectively than does the uranyl ion, as has been inferred above.