Kinetics of Metal Ion and Metal Chelate Catalyzed Oxidation of Ascorbic Acid. III. Vanadyl Ion Catalyzed Oxidation[1]

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Received January 17, 1968

Abstract: The kinetics of the oxidation of ascorbic acid by vanadyl ion in the presence and in the absence of molecular oxygen at 25 and 0.4° is reported. Equilibrium vanadyl ion hydrolysis data are reported for an ionic strength of 0.10 *M* (KNO_3). In the pH range investigated (1.75–2.85), more than 99% of the metal ion was found to be in the unhydrolyzed form. When vanadyl ion is the oxidant (absence of molecular oxygen), the oxidation of ascorbic acid proceeds by a path first order with respect to hydrogen ion concentration, in accordance with the rate law, rate = $k[H_2A][VO^{2+}][H^+]$. A mechanism is proposed whereby the reduction of vanadyl ion to V(II) takes place through an intermediate VOH_3A^{3+} species. In the presence of molecular oxygen, the oxidation of ascorbic acid catalyzed by vanadyl ion proceeds by a path first order with respect to hydrogen ion and oxygen concentrations and is given by the rate law, rate = $k[H_2A][VO^{2+}][H^+][O_2]$. The catalytic activity of vanadyl ion was found to be less than that of ferric and cupric ions. Based on the observed kinetics in the presence and in the absence of oxygen, a possible mechanism for the vanadyl ion catalyzed oxidation of ascorbic acid is presented.

In earlier papers of this series[3,4] the kinetics of the oxidation of ascorbic acid catalyzed by cupric and ferric ions, and by the chelates which they form with aminopolycarboxylic acids, was described. The present paper extends this work to vanadyl ion and vanadyl chelate catalysis. The kinetics and mechanism of metal ion catalysis in the oxidation of ascorbic acid have been the subject matter of several studies,[5–10] most of which involved the copper(II) ion. The present work is the first attempt at a kinetic investigation of the vanadyl ion as a catalyst, and as an oxidant, in the oxidation of ascorbic acid. In addition to the determination of the activity of a new catalyst, this study was extended to include reaction rates in the presence and in the absence of molecular oxygen, and the determination of activation parameters, for comparison with similar data on Cu(II) and Fe(III) chelate catalysis. It was hoped that this type of detailed study would lead to an elucidation of the mechanism of vanadyl ion and vanadyl chelate catalysis.

Experimental Section

The *l*-ascorbic acid used in the present investigation was Kodak White Label grade and was used without further purification. The equivalent weight of the sample was determined, however, by titration with standard base. A solution of vanadyl sulfate was prepared from Fisher analytical grade material in a known strength of sulfuric acid solution. The vanadyl sulfate solution was standardized by an oxidation-reduction titration with potassium permanganate.[11] Estimation of the free acid in vanadyl sulfate solution was carried out by addition of 1 equiv of EDTA to the solution, followed by potentiometric titration with standard base. 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 hydrolysis constant of vanadyl ion at 25 and 0.4° 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[12] were used to convert hydrogen ion activity functions obtained in acetic acid titrations to 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.

Kinetic Measurements. The pH of the experimental solution was set to the desired value by a Beckman Model K automatic titrator fitted with extension glass and calomel electrodes. Once set, the pH was maintained constant throughout a particular kinetic run by the automatic titrator operating as a pH-stat. The pH meter was calibrated with acetic acid buffer and by titration of standard HCl and NaOH solutions. The ionic strength of the experimental solution was maintained at approximately 0.10 *M* with KNO_3. After the pH was adjusted to the desired value, a stream of oxygen was passed through the cell in such a way as to ensure very intimate contact between gas phase and solution. The oxygen used was 99% pure, and any CO_2 present was removed by passing it through a wash bottle maintained at the same temperature and electrolyte concentration as the reacting solution. Oxygen was passed through the solution at the rate of 0.75 l./min (30 mmoles/min). Since the rate of the reaction is slow compared to the rate of replacement of dissolved oxygen, the experimental solution was considered to be saturated with respect to oxygen at all times. 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 established by Roe.[13]

Results

Equilibrium Studies. Dissociation of Ascorbic Acid. The dissociation constants of ascorbic acid were re-

(1) This work was supported by Research Grants WP-00744 and WP-01197 from the Federal Water Pollution Control Administration, U. S. Department of the Interior.
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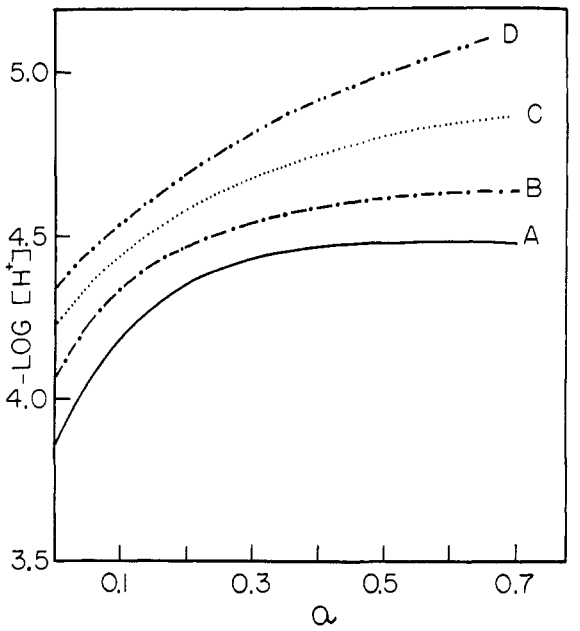


Figure 1. Potentiometric titration of VO^{2+} ion at 25°, with the following concentrations of metal ion: (A) 3.52×10^{-3} *M*, (B) 1.76×10^{-3} *M*, (C) 8.80×10^{-4} *M*, (D) 4.40×10^{-4} *M*; *a* = moles of base per mole of metal ion; $\mu = 0.10$ *M* (KNO_3).

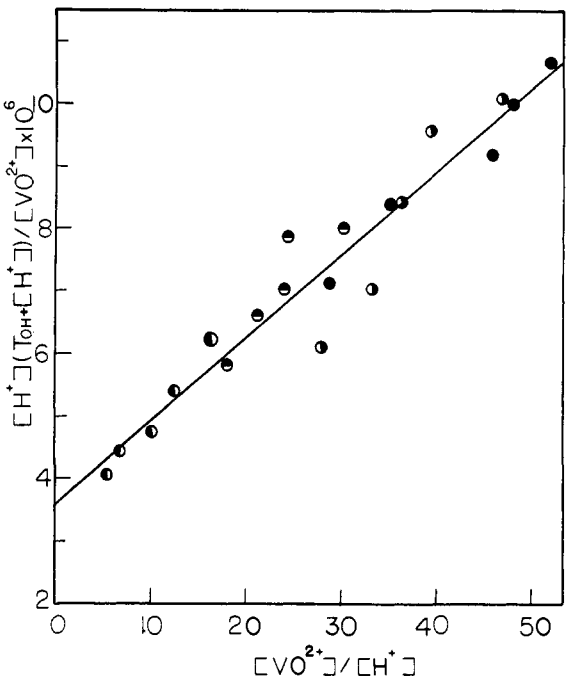


Figure 2. Graphical demonstration of dimer of VO^{2+} ion at 25°: ●, 3.52×10^{-3} *M*; ◑, 1.76×10^{-3} *M*; ◓, 8.80×10^{-4} *M*; ◐, 4.40×10^{-4} *M*; $\mu = 0.10$ *M* (KNO_3).

ported in a previous publication[3] as $K_1 = 9.16 \times 10^{-5}$ and 3.24×10^{-5} at 25 and 0.4°, respectively, and $K_3 = 4.57 \times 10^{-12}$ and 1.91×10^{-13} at 25 and 0.4°, respectively.

Hydrolysis of Vanadyl Ion. Since previous work[14] on the hydrolysis of the VO^{2+} ion was carried out under experimental conditions different from those employed in this work, it was necessary to study hydrolysis equilibria at 0.10 *M* ionic strength and at 0.4 and 25°. In Figure 1 are plotted data obtained from potentiometric titration of vanadyl sulfate with NaOH at 25° and an ionic strength of 0.10 *M* (KNO_3). The titration curve $-\log [H^+]$ *vs.* *a*, moles of NaOH per mole of metal ion, indicates a concentration-dependent buffer region characteristic of the formation of polynuclear species followed by precipitation beyond $a = 0.75$. A similar plot was obtained at 0.4°. Up to $a = 0.50$, consistent values of pH are obtained without drift even after 48 hr. Beyond $a = 0.50$ there was drifting in the pH values, and precipitation occurred beyond $a = 0.75$. In the early stages of the reaction (up to $a = 0.30$), it is reasonable to assume the existence of a simple monohydroxo complex followed by polynuclear species formation. Thus the reactions taking place in the region of the titration curve, where $a < 0.30$, would be

$$VO^{2+} \overset{K_1}{\rightleftharpoons} VO(OH)^{+} + H^{+}$$

$$2VO^{2+} \overset{\beta_{22}}{\rightleftharpoons} (VO(OH))_2^{2+} + 2H^{+}$$

$$2VO(OH)^{+} \overset{K_{22}}{\rightleftharpoons} (VO(OH))_2^{2+}$$

With these equilibrium constants and the stoichiometric relationships for the metal ion and for T_{OH}, total equivalents of base added, one obtained the equation

$$K_1 + 2\beta_{22}[VO^{2+}]/[H^+] = [H^+](T_{OH} + [H^+])/[VO^{2+}] \quad (1)$$

(14) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1177 (1955).

If a binuclear diolate species is formed, a plot of $[H^+] \cdot (T_{OH} + [H^+])/[VO^{2+}]$ as ordinate *vs.* $[VO^{2+}]/[H^+]$ as abscissa should yield a straight line with a slope equal to $2\beta_{22}$ and an intercept equal to K_1. Such a plot is shown in Figure 2 for vanadyl ion hydrolysis at 25°. As may be seen in Figure 2, a straight line is obtained indicating a value of K_1 of 3.61×10^{-6} and β_{22} of 6.63×10^{-8}. A similar plot was obtained at 0.4°. A summary of the values obtained is given in Table I. The

Table I. Hydrolysis and Olation of Vanadyl Ion in Aqueous Solution[a]

Temp, °C	Log K_1	Log β_{22}	Log K_{22}
25	-5.44 ± 0.05	-7.18 ± 0.07	3.70 ± 0.06
0.4	-6.30 ± 0.05	-8.01 ± 0.07	4.59 ± 0.06
$\Delta H^\circ_{K_1} = 13.0 \pm 0.4$[b]		$\Delta S^\circ_{K_1} = 18.7 \pm 1$[c]	
$\Delta H^\circ_{\beta_{22}} = 12.6 \pm 0.8$[b]		$\Delta S^\circ_{\beta_{22}} = 9.4 \pm 1$[c]	
$\Delta H^\circ_{K_{22}} = -13.5 \pm 0.8$[b]		$\Delta S^\circ_{K_{22}} = -28.3 \pm 2$[c]	

[a] $\mu = 0.10$ *M* (KNO_3). [b] Units of kcal mole^{-1}. [c] Units of cal deg^{-1} mole^{-1}.

values of log K_1 and log β_{22} of -5.44 and -7.18, respectively, at 25° compare satisfactorily with the values of -6.0 and -6.88 in a medium of ionic strength 3 *M* ($NaClO_4$) reported by Rossotti and Rossotti.[14]

Kinetic Studies. Vanadyl Ion Catalyzed Oxidation. The experimental results at 25 and 0.4° indicated a first-order rate of oxidation with respect to the total concentration of unreacted ascorbic acid. In the pH range 1.75–2.85, the rate varied linearly with the concentration of vanadyl ion. Since the concentration of the vanadyl ion was unchanged at the end of the reaction, it behaved as a true catalyst under the reaction conditions employed. In the pH range under consideration, calculation of the hydrolyzed species of the

Table II. Apparent Second-Order Rate Constants for Vanadyl Ion Catalyzed Oxidation of Ascorbic Acid[a]

−Log [H+]	Catalyzed reaction, k, M^{-1} sec^{-1} 25°	Catalyzed reaction, k, M^{-1} sec^{-1} 0.4°	Uncatalyzed reaction, 10^6k, sec^{-1} 25°	Uncatalyzed reaction, 10^6k, sec^{-1} 0.4°
1.75	81 ± 6	8.9 ± 0.5	0.58 ± 0.02	0.18 ± 0.01
2.00	42 ± 3	4.7 ± 0.3	5.3 ± 0.2	0.34 ± 0.01
2.25	28 ± 2	3.1 ± 0.2	9.3 ± 0.3	1.15 ± 0.03
2.50	15 ± 1	1.7 ± 0.1	16.5 ± 0.5	1.60 ± 0.05
2.85	5 ± 0.3	0.60 ± 0.04	36 ± 1	2.30 ± 0.07
	$(4.4 \pm 0.3) \times 10^{3}$ [b]	$(5.1 \pm 0.3) \times 10^{2}$ [b]		

[a] $\mu = 0.10\ M$ (KNO_3); $T_A = 1.0 \times 10^{-3}\ M$; $[VO^{2+}] = 1.0 \times 10^{-4}$–$8.0 \times 10^{-4}\ M$. Oxygen pressure, 1 atm. [b] Third-order rate constants for vanadyl ion catalyzed oxidation of ascorbic acid.

metal ion, with the help of the constants in Table II, indicated that nearly 99% of the catalyst was in the unhydrolyzed form, so that hydrolysis and dimerization of the metal ion may be neglected. The rate data obtained on the vanadyl ion catalyzed oxidation at 25 and 0.4° are given in Table II. Figure 3 indicates the variation of rate at 25° with the concentration of vanadyl ion at a particular pH; similar results were obtained at 0.4°. The specific rate constants given in Table II were calculated from the slopes of the straight lines given in Figure 3 for 25° and obtained from a similar plot for 0.4°. The data for a particular straight line were obtained by measuring rates over a wide range of catalyst concentration.

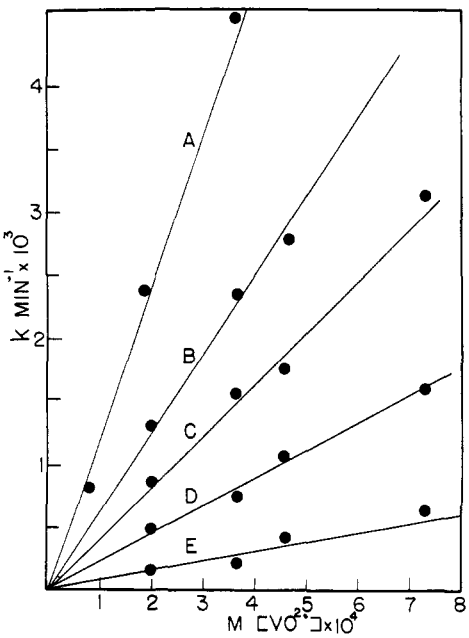


Figure 3. Catalytic effect for the oxidation of ascorbic acid in the presence of vanadyl ion at 25° in 0.10 M KNO_3, at −log [H+] values of (A) 1.75, (B) 2.00, (C), 2.25, (D) 2.50, (E) 2.85. k = difference between the first-order rate constants in the presence and in the absence of the metal ion; $\mu = 0.10\ M$ (KNO_3).

The apparent second-order rate constants given in Table II also include any dependence on hydrogen ion concentration. It may be readily seen from Table II that the rate decreases regularly with increasing pH. Calculation of the concentration of unhydrolyzed metal species by the use of the data in Table I indicates that in the pH range investigated more than 99% of the catalyst is in VO^{2+} form, and the decrease in rate with increase in pH is therefore not due to hydrolysis of the metal ion. The dependence of rate on hydrogen ion concentration was found to be linear. This may be readily verified from Figure 4, where the rate constants of Table II are plotted *vs.* the corresponding values of hydrogen ion concentration. The plots in Figure 4 have nearly zero intercepts. Thus there appears to be a pathway for the vanadyl ion catalyzed oxidation of ascorbic acid which involves first power in hydrogen ion concentration. The rate constants for this reaction at 25 and 0.4° were determined from the slopes of the straight lines in Figure 4 and are tabulated in Table II.

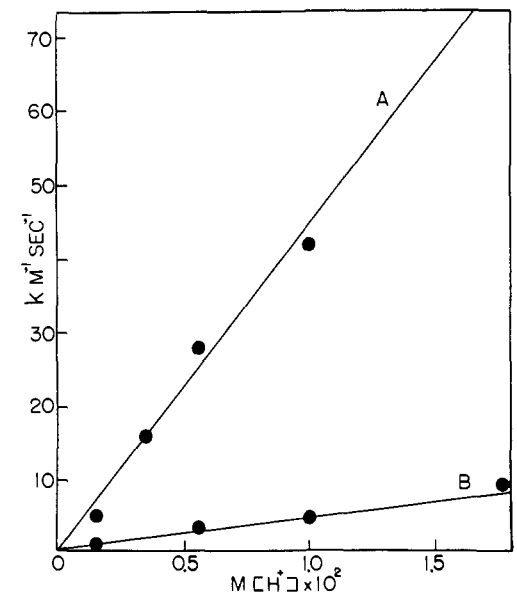


Figure 4. Dependence of the specific rate constant "k" of vanadyl ion catalyzed oxidation of ascorbic acid on the hydrogen ion concentration at (A) 25° and (B) 0.4°; $\mu = 0.10\ M$ (KNO_3).

Dependence of the VO^{2+} Ion Catalyzed Oxidation of Ascorbic Acid on Oxygen Concentration. The oxygen dependence of the rates of vanadyl ion catalyzed oxidation of ascorbic acid was studied at 25° and at −log [H+] values of 2.85 and 2.25. By the use of a sintered-glass tube, mixtures of oxygen and nitrogen of known partial pressure of oxygen were passed through the experimental solution in fine bubbles in such a way that there was intimate contact between the gas phase and the solution at any given instant. The mixture of gases ($O_2 + N_2$) was passed through the solution at the rate of 0.75 l./min, and the concentration of oxygen in solution was calculated on the assumption that Henry's law was obeyed. Since the rate at which oxygen was passed through the solution (3–30 mmoles/

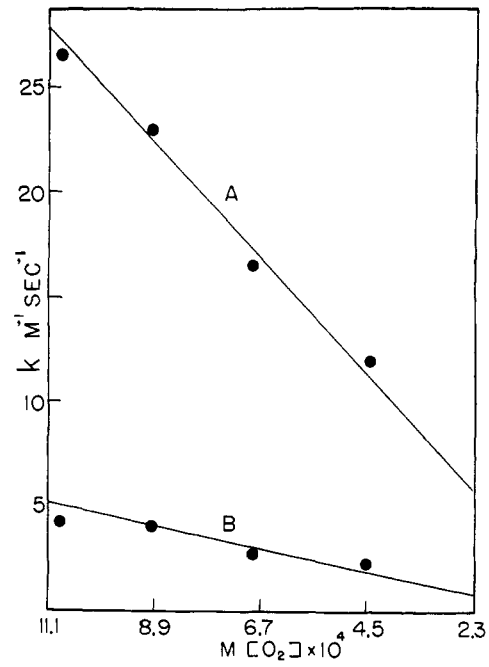


Figure 5. Dependence of the specific rate constant "k" of vanadyl ion catalyzed oxidation of ascorbic acid on oxygen concentration at $-\log [H^+]$ values of (A) 2.25, (B) 2.85; $t = 25°$; $\mu = 0.10\ M$ (KNO_3).

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 observed oxygen dependence is therefore not due to lack of oxygen. The rates were found to vary linearly with the concentration of oxygen. This behavior is similar to that observed[3] for cupric and ferric ion catalyzed oxidation under the same conditions. The variation of rate of vanadyl ion catalyzed oxidation with the concentration of oxygen at $-\log [H^+]$ values of 2.85 and 2.25 is shown in Figure 5, and the data are tabulated in Table III. The rate constants of oxygen dependence, calculated from the slopes of the straight lines in Figure 5, are given in Table III.

Table III. Variation of Rate Constants of Vanadyl Ion Catalyzed Oxidation of Ascorbic Acid with the Partial Pressure of Oxygen at 25°[a]

Partial pressure of oxygen, atm	Second-order rate constants, M^{-1} sec^{-1}	
	$-\log [H^+] = 2.25$	$-\log [H^+] = 2.85$
0.99	28 ± 1	5.0 ± 0.2
0.81	23 ± 1	4.3 ± 0.2
0.62	17.0 ± 0.8	2.8 ± 0.2
0.40	12.0 ± 0.5	2.1 ± 0.1
0.20	6.0 ± 0.3	0.80 ± 0.05
0.10	5.5 ± 0.2 (4.0 ± 0.2)	0.80 ± 0.05 (0.50 ± 0.03)
0.05	5.0 ± 0.2 (3.4 ± 0.2)	0.80 ± 0.05 (0.50 ± 0.03)
	2.5 ± 0.1 × 10⁴[b]	0.50 ± 0.03 × 10⁴[b]

[a] $\mu = 0.10\ M$ (KNO_3); $T_A = 1.0 \times 10^{-3}\ M$; $[VO^{2+}] = 1.5 \times 10^{-3}\ M$. [b] Third-order rate constants for the oxygen dependence of vanadyl ion catalyzed oxidation of ascorbic acid at 25°. Values in parentheses indicate constants corrected for direct oxidation of ascorbic acid by VO^{2+}.

The vanadyl ion catalyzed oxidation below 20% concentration of molecular oxygen seems to be complicated by a possible simultaneous reaction in which vanadyl ion is initially reduced by ascorbic acid. The validity of this assumption is verified by applying a correction for the rates in the absence of O_2 to the rates of vanadyl ion catalyzed oxidation at 10 and 5% concentration of molecular oxygen. The corrected constants are given in parentheses in Table III. It may be noted from Table III that the correction brings the constants at 10% concentration of molecular oxygen in line with the other constants at higher concentrations of molecular oxygen. Nevertheless, the rate at 5% concentration of molecular oxygen still remains nonlinear. The true situation at very low concentration of molecular oxygen (5%) thus seems to be more complicated than the simple assumption of only one side reaction of V(IV) with ascorbic acid. One of the other possible reactions may be the reoxidation of V(III) or V(II) by molecular oxygen, and oxidation of the substrate by free metal ion species.

Oxidation of Ascorbic Acid by VO^{2+} in the Absence of Oxygen. The experimental technique used for the oxidation of ascorbic acid by vanadyl ion in the absence of oxygen was essentially the same as that used for VO^{2+} ion catalyzed oxidation, with the only difference that an atmosphere of pure nitrogen was maintained in the former case. For this purpose, nitrogen was scrubbed successively through wash bottles containing chromous sulfate and alkaline pyrogallol and finally through a wash bottle containing ascorbic acid and cupric ions to ensure complete removal of oxygen. Nitrogen was then passed through the reaction cell in a fine stream at the rate of approximately 0.5 l./min. The method for the analysis of dehydroascorbic acid was the same as described earlier.[3,13]

Stoichiometry. The over-all stoichiometry of the reaction of ascorbic acid with vanadyl ion is represented by

$$H_2A + VO^{2+} \longrightarrow V^{2+} + H_2O + A$$

where H_2A and A represent the neutral and oxidized forms of ascorbic acid, respectively. The stoichiometry of the reaction was determined in an atmosphere of pure nitrogen, by mixing known concentrations of ascorbic acid and vanadyl ion in 4 M H_2SO_4 and allowing the reaction to go to completion, as indicated by the yield of dehydroascorbic acid. The over-all reaction is expressed by

$$H_2A + O_2 \longrightarrow A + H_2O_2$$

The Order of the Reaction. The order of the reaction was determined by varying the concentration of the reactants, ascorbic acid and VO^{2+} ion. If the reaction is first order with respect to the concentration of the reactants, then a plot of $\log [b(a - x)/a(b - x)]$ *vs.* time t should give a straight line with zero intercept, where a and b are the initial concentration of vanadyl ion and ascorbic acid, respectively, and x is the concentration of the product (dehydroascorbic acid) at time t. Rate constants calculated from the slopes of these straight lines for the oxidation of ascorbic acid by vanadyl ion at 25° are given in Table IV. It may be seen from Table IV that the rate constant is independent of the initial concentration of VO^{2+} and ascorbic acid. Thus the rate of the reaction is first order with respect to the concentration of each reactant.

Table IV. Determination of the Order of the Reaction of VO^{2+} Ion and Ascorbic Acid[a]

T_A,[b] $M \times 10^3$	T_M,[c] $M \times 10^3$	k, M^{-1} sec^{-1}
1.00	2.28	1.10 ± 0.06
1.00	0.91	1.00 ± 0.05
1.00	0.46	0.90 ± 0.05
1.00	4.00	1.10 ± 0.05
2.00	3.00	1.00 ± 0.05
		Mean = 1.00 ± 0.05

[a] $t = 25°$; $\mu = 0.10$ M (KNO_3); $-\log [H^+] = 2.25$. [b] T_A = total concentration of ascorbic acid. [c] T_M = total concentration of vanadyl ion.

The apparent second-order rate constants for the oxidation of ascorbic acid by vanadyl ion in the absence of oxygen at 25 and 43° are given in Table V. In calculating the rate constants in Table V, the concentration of the metal ion is corrected for hydrolysis at 25 and 43° with the data in Table I.

Table V. Apparent Second-Order Rate Constants (M^{-1} sec^{-1}) for the Oxidation of Ascorbic Acid by VO^{2+} Ion in the Absence of Oxygen[a]

$-\log [H^+]$	25°	43°
1.75	3.3 ± 0.2	6.2 ± 0.4
2.00	1.8 ± 0.1	4.0 ± 0.2
2.25	1.00 ± 0.06	2.4 ± 0.1
2.50	0.60 ± 0.03	1.00 ± 0.06
2.85	0.20 ± 0.01	0.60 ± 0.03
	$1.8 \pm 0.1 \times 10^{2}$[b]	$3.7 \pm 0.2 \times 10^{2}$[b]

[a] $\mu = 0.10$ M (KNO_3); $T_A = 1.0 \times 10^{-3}$ M; $[VO^{2+}] = 3.0 \times 10^{-3}$ M. [b] Third-order rate constants for the hydrogen ion dependence of the oxidation of ascorbic acid by the vanadyl ion.

pH Dependence. The dependence of rates on hydrogen ion concentration was determined by plotting the rate constants in Table V *vs.* the corresponding value of hydrogen ion concentration. Such a plot is shown in Figure 6. A straight line was obtained both at 25 and 43° with nearly zero intercept. Thus the rate of oxidation of ascorbic acid by VO^{2+} ion in the absence of oxygen involves a path first power in hydrogen ion concentration. The rate constants for this path were obtained from the slopes of the straight lines in Figure 6 and are given in Table V.

Discussion

The rate of vanadyl ion catalyzed oxidation of ascorbic acid in the presence of oxygen was found to depend directly on the concentration of total unreacted ascorbic acid, and on the vanadyl ion, oxygen, and hydrogen ion concentrations. In the absence of oxygen, the rate was found to be first order with respect to each of the species, ascorbic acid, vanadyl ion, and hydrogen ion concentration. The rate laws in the presence and in the absence of oxygen are expressed by eq 2 and 3, respectively, where T_A = total concentration

$$-\frac{dT_A}{dt} = kT_A[VO^{2+}][H^+][O_2] \quad \text{oxygen oxidation} \quad (2)$$

$$-\frac{dT_A}{dt} = kT_A[VO^{2+}][H^+] \quad \text{vanadyl oxidation} \quad (3)$$

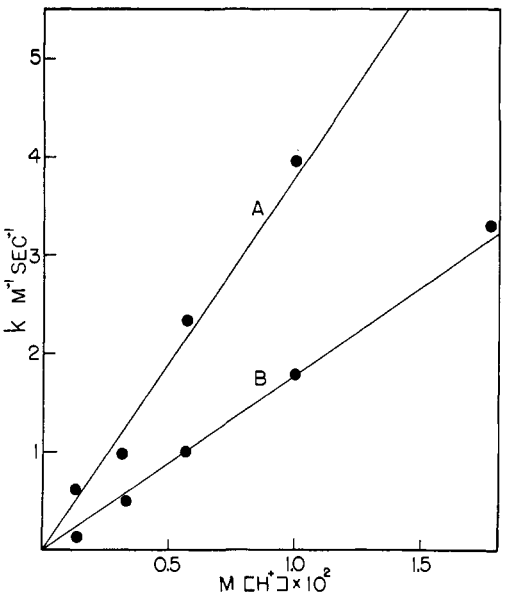


Figure 6. Dependence of the second-order rate constant "k" of the oxidation of ascorbic acid by vanadyl ion (absence of oxygen) on hydrogen ion concentation at (A) 43° and (B) 25°; $\mu = 0.10$ M (KNO_3).

of unreacted ascorbic acid and $[VO^{2+}]$ = concentration of unhydrolyzed vanadyl ion.

In both the oxygen and vanadyl ion oxidations, the hydrogen ion dependent constants listed in Tables II and V, respectively, were obtained from the slope of the rate constant k against the hydrogen ion concentration, in the pH range 1.75–2.85. Such plots have been presented in Figure 4 for the vanadyl ion catalyzed oxidation at 25 and 0.4° and in Figure 6 for the vanadyl ion oxidation at 25 and 43°.

Comparison of the constants k_1 and k_2 in the presence and in the absence of oxygen (Tables II and V) indicates that the rates in the presence of oxygen are at least 30 times faster than the rates in the absence of oxygen. The activation parameters corresponding to these rate constants are given in Table VI. It may be readily seen from Table VI that the activation parameters in the presence and in the absence of oxygen are entirely different.

Table VI. Activation Parameters for the Vanadyl Ion Catalyzed Oxidation of Ascorbic Acid and the Oxidation of Ascorbic Acid by VO^{2+} in the Absence of Oxygen[a]

Conditions	$\Delta H^{\ddagger}$, kcal mole^{-1}	$\Delta S^{\ddagger}$, eu	$\Delta F^{\ddagger}$, kcal mole^{-1}
O_2 present	+13.8 ± 0.7	4.1 ± 0.2	12.6 ± 0.4
O_2 absent	+7.0 ± 0.5	−25 ± 2	14.4 ± 0.7
O_2 present; no metal ion	+10.7 ± 0.4	−37 ± 2	+22 ± 1

[a] $\mu = 0.10$ M (KNO_3).

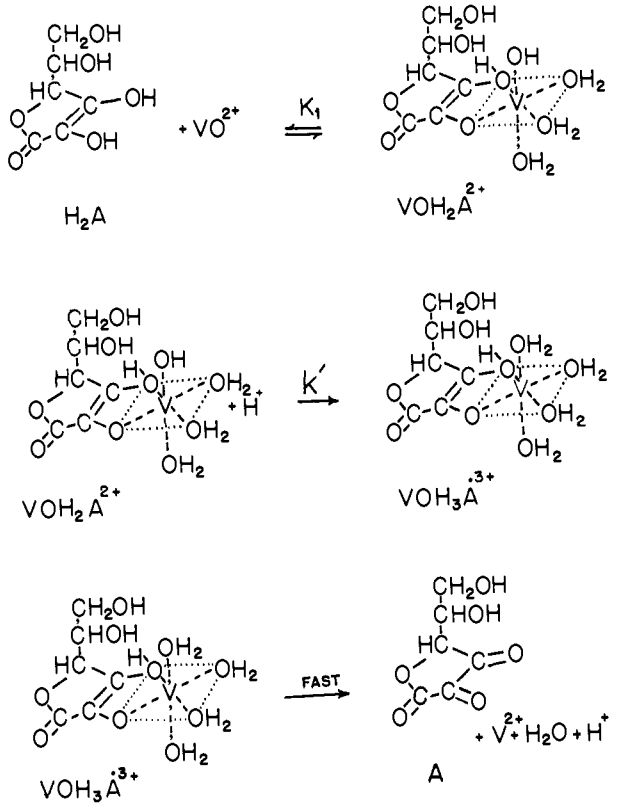
Evidence on the Nature of the Activated Complex. The reaction of ascorbic acid with vanadyl ion in the presence of oxygen was found to be nicely first order with respect to the substrate, metal ion catalysis, and hydrogen ion concentration. It also depends linearly on concentration of molecular oxygen. The rate in the absence of oxygen is first order with respect to each of

the substrate, metal ion oxidant, and hydrogen ion concentrations. In both cases reaction takes place only through a hydrogen ion dependent path. Thus the activated complex in both cases may be postulated as involving a vanadyl–ascorbate complex. The difference in the activation parameters of the oxidation in the presence and in the absence of oxygen, however, indicates a different rate-determining step for the two reactions. This is further supported by the linear dependence of the rate of vanadyl ion catalyzed oxidation on oxygen concentration.

The hydrogen ion plays a very important role in both reactions by forming presumably a highly protonated derivative of the vanadyl–ascorbate complex and thus facilitating electron transfer within the metal–substrate complex. Hydrogen ion may have a similar function in the exchange reaction of NpO_2^+ and NpO_2^{2+}. For this reaction Sullivan, *et al.*,[15] have reported a path which is first power in hydrogen ion concentration.

On the basis of the kinetic observations, a mechanism for the oxidation of ascorbic acid by vanadyl ion in the absence of oxygen may be formulated as indicated in Scheme I. In the proposed mechanism, a vanadyl–

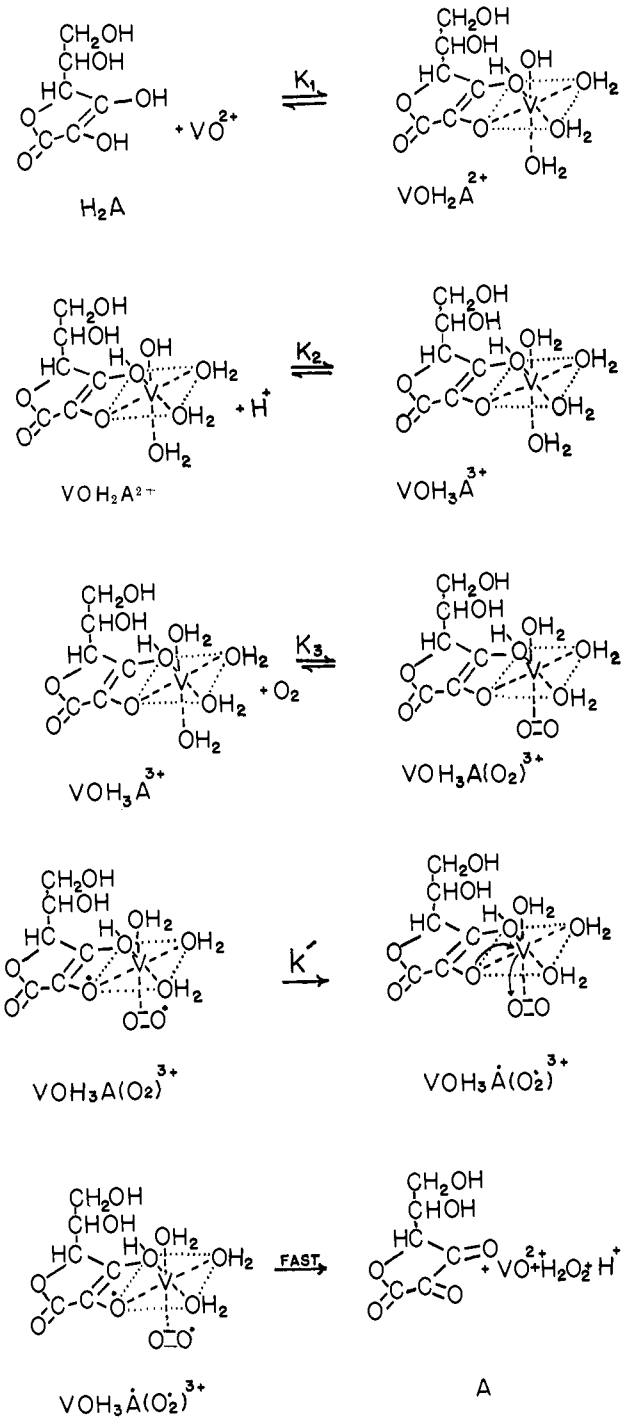
Scheme I



ascorbate chelate is formed in a preequilibrium step. The formation of this chelate is supported by the work of Sobskowska, *et al.*,[16] who have reported the value 150 for the stability constant of the $VOHA^+$ complex. Protonation of this complex would then produce the proposed intermediate VOH_2A^{2+}. In this diprotonated species, one of the protons may be combined with the oxo oxygen of the vanadyl ion. Rate-determining electron transfer then is visualized as taking place within this protonated vanadyl–ascorbate complex. The electron transfer in this step would be facilitated by the contribution of a second proton. As explained above, the presence of this proton would help the formation of a highly charged VOH_3A^{3+} species, thus facilitating electron transfer and reduction of VO^{2+} ion to lower valence species. The complex VOH_3A^{3+} then dissociates in a fast step to V(II), A·, H^+, and H_2O.

In the proposed mechanism the reduction of V(IV) to V(II) is postulated as occurring in one step. It is also possible that the vanadyl ion is reduced to V(II) in two steps through the intermediate formation of V(III). The existence of VOH^{2+} as a stable form of V(III) was

Scheme II



(15) J. C. Sullivan, D. Cohen, and J. C. Hindman, *J. Am. Chem. Soc.*, 79, 3672 (1957).

(16) A. Sobskowska and J. Minczewski, *Roczniki Chem.*, 36, 17 (1962).

postulated by Rabideau[17] and Ramsey, *et al.*,[18] to explain their experimental observations. If one assumes intermediate formation of VOH^{2+}, the complex VOH_3A^{3+} would probably dissociate in a fast step to VOH^{2+}, HA·, and H^+. In a final fast step, the semiquinone HA· would be oxidized to dehydroascorbic acid, A, and VOH^{2+} would be reduced to V(II). The present kinetic data cannot differentiate, however, between the one-step and two-step electron transfer in the reduction of vanadyl ion to V(II).

The following mechanisms may be proposed for the vanadyl ion catalyzed oxidation of ascorbic acid in the presence of oxygen: (1) a rate-determining electron transfer to vanadyl ion, followed by a rapid reoxidation of V(III) species to VO^{2+}; (2) a rapid reduction of vanadyl ion to V^{3+} or VOH^{2+} by ascorbic acid, followed by a rate-determining reoxidation of the reduced species by molecular oxygen; (3) rate-determining electron transfer within the metal–ascorbate–oxygen complex formed in preequilibrium steps, followed by a rapid oxidation of semiquinone HA by molecular oxygen.

The first mechanism may be ruled out on the basis of the dependence of the rate of vanadyl ion catalyzed oxidation on oxygen concentration. Further, since this mechanism indicates the same rate-determining step for the metal-catalyzed reaction and the reaction where vanadyl ion is the oxidant, there would not be any difference in the activation parameters for the two reactions. The observed differences in the activation parameters of the two reactions rule out this mechanism.

The second mechanism is out of the question for two reasons. The rate of oxidation of ascorbic acid by vanadyl ion in the absence of oxygen is not a very rapid reaction; on the contrary, it is much slower than the rate in the presence of oxygen. Ramsey, *et al.*,[18] reported an inverse dependence of rate on hydrogen ion concentration for the oxidation of VOH^{2+} to VO^{2+} by molecular oxygen. In the vanadyl ion catalyzed oxidation of ascorbic acid a direct dependence of rate on hydrogen ion concentration was observed.

(17) S. W. Rabideau, *J. Phys. Chem.*, **62**, 414 (1958).
(18) J. B. Ramsey, R. Sugimoto, and H. Devorkin, *J. Am. Chem. Soc.*, **63**, 3480 (1941).

On the basis of a direct dependence of the rate of vanadyl ion catalyzed oxidation on hydrogen ion and oxygen concentrations, mechanism 3 is favored. It may be formulated as in Scheme II.

The proposed mechanism for the VO(IV)-catalyzed oxidation of ascorbic acid has the first preequilibrium step in common with the proposed mechanism of the oxidation of ascorbic acid by vanadyl ion. In a second preequilibrium step, a vanadyl–ascorbate–oxygen complex containing an additional proton is formed, with either a concerted or subsequent rate-determining transfer of an electron from the substrate through the metal ion to the oxygen molecule. The transfer of the electron from the substrate to the metal ion may take place in the nonbonding b_2 ($3d_{xy}$) orbital of VO^{2+} with the subsequent transfer to the antibonding levels of molecular oxygen through the metal antibonding e_π^* or b_1^* levels.[19] The semiquinone formed is oxidized to dehydroascorbic acid, A, either by a second intramolecular electron transfer in the activated complex or by dissociation to free semiquinone with subsequent oxidation by oxygen or $HO_2\cdot$.

The order of catalytic reactivities of the metal ions Cu(II), Fe(III), and VO(IV) merits consideration. The catalytic acitivity increases in the sequence VO(IV) < Fe(III) < Cu(II). In the case of cupric and ferric ion catalyzed oxidation,[3] the oxidation of neutral and monoionic species of ascorbic acid involves a hydrogen ion independent and an inverse hydrogen ion dependent path, respectively. The latter path predominates over the former. Vanadyl ion catalyzed oxidation of ascorbic acid is thus different from cupric and ferric ion catalyzed oxidation in that it involves a path which is first power in hydrogen ion concentration. It seems that this reversal of hydrogen ion dependence between oxo ions and aquo ions must be due to the requirement of oxo groups for protons during the rate-determining electron-transfer step. Apparently the protons facilitate conversion of the oxo group to a hydroxo (or aquo) group when the metal ion goes to a lower oxidation state.

(19) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).