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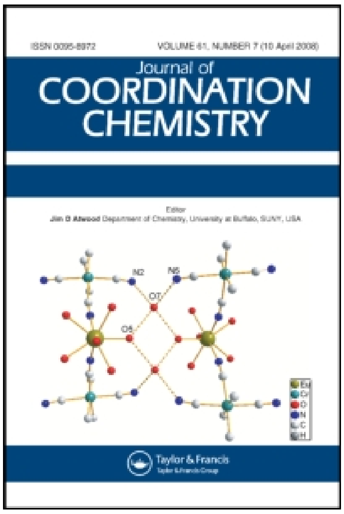

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REACTION OF HYDROGEN PEROXIDE WITH METAL COMPLEX.

I. The Kinetics of the Reaction of Hydrogen Peroxide with N-Methyliminodiacetatodioxovanadate

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The kinetics of the reaction of N-methyliminodiacetatodioxovanadate with hydrogen peroxide has been studied spectrophotometrically by a stopped-flow technique. Over the pH range 3 to 4, the rate of the mixed-ligand complex formation is of the first-order with respect to N-methyliminodiacetatodioxovanadate and hydrogen peroxide:

$$\frac{d[VO(O_2)(mida)^-]}{dt} = k[VO_2(mida)^-][H_2O_2]$$

where k is $9.2 \times 10^3\ M^{-1}\ sec^{-1}$ at 25°C and $\mu = 1.0$ ($NaClO_4$), $\Delta H^{\neq}$ 6.3 Kcal/mole and $\Delta S^{\neq}$ −19 e.u. Some discussions are made on the reactivity of vanadium (V) complexes.

INTRODUCTION

Reactions of hydrogen peroxide with various chemical species have been extensively studied.[1,2] From the analytical point of view, the reaction of hydrogen peroxide with metallic species has been used for the determination of various metals. The reaction often utilized in the kinetic method of analysis is the oxidation by hydrogen peroxide, of which the rate depends on the concentration of catalyst in solution.[3,4] For some color reactions, on the other hand, the molar absorbance is enhanced considerably in the presence of hydrogen peroxide owing to the formation of mixed-ligand complexes with hydrogen peroxide.[5–10] Mechanisms of these reactions have hardly been elucidated. Wilkins *et al* have reported the kinetics of formation of peroxy species of chromium (VI), vanadium (V) and titanium (VI) in acid media.[11,12] These reactions involve replacement of oxo group by the entering hydrogen peroxide.

On the other hand, there has been a good deal of interest in the study of mechanism of formation, decomposition and substrate reactions of peroxy compounds of biologically important metal chelates such as catalase and peroxidase.[13–18] Present trends in this area are towards identifying the role of complexes in the catalysed decomposition of hydrogen peroxide. Sigel *et al* have shown a mechanism that decomposition of hydrogen peroxide proceeds through the intermediate involving hydrogen peroxide in the inner-sphere.[15,16] However, little attention has been drawn to the processes of coordination of hydrogen peroxide to metal complexes preceding the decomposition of hydrogen peroxide.

The kinetic behavior of the formation of the pentavalent vanadium complex has been little investigated.[19] Recently, we have studied the kinetics of the formation of the vanadium (V)-N-methyliminodiacetate complex.[20] Now, since some data are available on the kinetics of vanadium (V), we attempt to relate the water exchange and hydrogen peroxide entry rates for vanadium (V). Then in this paper we describe the results on the following reaction:

$$\text{V(V)-MIDA} + H_2O_2 \rightleftharpoons \text{V(V)-MIDA-}H_2O_2 \qquad (1)$$

where MIDA refers to N-methyliminodiacetic acid (H_2mida).

EXPERIMENTAL

Reagents

Hydrogen peroxide Nonstabilized 60% hydrogen peroxide obtained from Mitsubishi Edogawa Kagaku Co. was purified by the distillation under reduced

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pressure. A solution of hydrogen peroxide was titrated with a standard potassium permanganate immediately before use.

Vanadium (V) perchlorate Ammonium metavanadate was recrystallized once from purified ammonia water. Pure ammonium metavanadate was dissolved in sodium hydroxide solution obtained by electrolysis of pure sodium perchlorate, and ammonia was expelled by evaporation. Vanadium (V) perchlorate solution was prepared by addition of perchloric acid. Vanadium (V) was reduced by sulfur dioxide and resulted vanadium (IV) was titrated with a standard potassium permanganate.

N-Methyliminodiacetic acid N-Methyliminodiacetic acid was synthesized from methylamine and monochloroacetic acid.[21] The product was recrystallized three times from aqueous methanol solution.

Stability of Reagents

Vanadium (V) can be reduced in an acid medium only on heating in the presence of excess aminopolycarboxylic acids, for example ethylenediaminetetraacetic acid.[22] Under the present experimental conditions (see Table I and Table II), vanadium (V) was not reduced at least for one day in the presence of excess methyliminodiacetic acid. After seven days, the absorbance of the vanadium (V)-MIDA complex decreased by about one percent.

Concentrated hydrogen peroxide (30%) can oxidize aminopolycarboxylic acids, especially completely on boiling.[23] We detected carbon dioxide and ammonia liberated on heating EDTA and MIDA with concentrated hydrogen peroxide. Under the present experimental conditions, MIDA was stable at least for five hours. After one day, several percents of MIDA was decomposed in an acid medium.

Measurements

The ionic strength was maintained at 1.0 M with sodium perchlorate. Hydrogen ion concentration was determined by a Radiometer PHM-22 and a Radiometer PHM-4d (Copenhagen) with a glass electrode, Type G202 B, and a calomel electrode, Type K401, filled with a saturated sodium chloride solution instead of a saturated potassium chloride solution as an internal solution to avoid precipitation of potassium perchlorate. A 1.00×10^{-2} M perchloric acid at an ionic strength of 1.00 M was used as a standard solution. The liquid junction potential was taken into consideration.

A Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer, a Hitachi double-beam spectrophotometer Type 124, and a Jasco Model ORD/UV-5 optical rotatory dispersion recorder were used to characterize the species spectrally.

The kinetics of formation was studied spectrophotometrically by means of a stopped-flow technique using a Rapid Scan Spectrophotometer Type RSP-2 (Hitachi, Ltd., Tokyo). The method employed for the kinetic measurements was essentially the same as described previously.[24]

RESULTS AND DISCUSSION

Equilibria

Recently we have studied the equilibria between vanadium (V) ion and N-methyliminodiacetic acid at 25°C and $\mu = 1.0$ M ($NaClO_4$):[25]

$$VO_2{}^+ + H_2mida \rightleftharpoons VO_2(mida)^- + 2H^+$$

$$:K^{H_2mida}_{VO_2(mida)} = 10^{-6.68 \pm 0.03}$$

$$VO_2(mida)^- \rightleftharpoons VO_2(OH)(mida)^{2-} + H^+$$

$$:K^{-H}_{VO_2(OH)(mida)} = 10^{-6.13 \pm 0.05}$$

$$VO_2(OH)(mida)^{2-} \rightleftharpoons HVO_4{}^{2-} + Hmida^- + H^+$$

$$:K^{-H}_{HVO_4} = 10^{3.5 \pm 0.2}$$

On the basis of these observations, all experiments in the present study were carried out under conditions where the 1:1 vanadium (V)-MIDA complex, $VO_2(mida)^-$, forms quantitatively.

Curves 1–6 in Figure 1 show the change of absorption spectra during the formation of the mixed-ligand complex. In Figure 2 the absorbance is plotted as a function of the total concentration of hydrogen peroxide. The plot consists of two intersecting linear portions and the intersection points to the composition of the mixed-ligand complex: vanadium (V):MIDA:H_2O_2 = 1:1:1.

It is possible that coordination of hydrogen peroxide to the vanadium (V)-MIDA complex gives rise to a proton from hydrogen peroxide. If one proton were liberated by coordination of hydrogen peroxide to the vanadium (V)-MIDA complex, the pH of the solution under the present experimental conditions (see Table I) would change from pH 4.09 ± 0.01 to pH 3.78 ± 0.02. (In the calculation we used the following values of protonation constants of

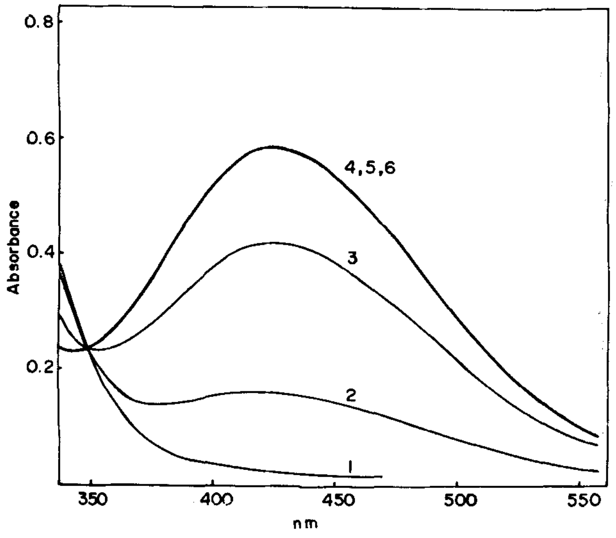

FIGURE 1 Spectral change in the course of the formation of the mixed-ligand complex.
$C_V = 1.63 \times 10^{-3}$ M, $C_{MIDA} = 0.200$ M, $-\log\ [H^+] = 3.87 \pm 0.01$, $C_{H_2O_2}$: Curve 1, 0 M; Curve 2, 3.74×10^{-4} M; Curve 3, 1.12×10^{-3} M; Curve 4, 1.87×10^{-3} M; Curve 5, 2.99×10^{-3} M; Curve 6, 4.49×10^{-3} M.

MIDA: $K^H_{H_2mida} = 10^{1.57\pm0.02}$, $K^H_{H_2mida} = 10^{2.36\pm0.02}$ and $K^H_{Hmida} = 10^{9.34\pm0.02}$ at 25°C and $\mu = 1.0$ M $(NaClO_4)^{25}$.) As apparent from the result shown in Table I, the pH of the solution did not change by the addition of hydrogen peroxide. Therefore, there are the following three possible formulations for the mixed-ligand complex:

$$VO_2(mida)(H_2O)^- + H_2O_2 \rightleftharpoons VO_2(H_2O_2)(mida)^- + H_2O \quad (2)$$

$$VO_2(mida)(H_2O)^- + H_2O_2 \rightleftharpoons VO(OH)(OOH)(mida)^- + H_2O \quad (3)$$

$$VO_2(mida)(H_2O)^- + H_2O_2 \rightleftharpoons VO(O_2)(mida)^- + 2H_2O \quad (4)$$

The coordination of peroxide O_2^{2-} to vanadium (V) has been described in some compounds.[26,27] The strong absorption band at 425 nm is expected for electron transfer from peroxide to the central ion.[28] From these results, the formulation given in equation (4) seems to be reasonable.

Kinetics of Formation of the Mixed-ligand Complex

The equilibrium (4) is much favored to the right under the present experimental conditions, so that the reverse reaction can be neglected in the kinetic study. The formation was studied at several wave lengths, mainly at 425 nm.

The rate of formation of the mixed-ligand complex from the N-methyliminodiacetatodioxovanadate

TABLE I
Effect of hydrogen peroxide addition on the pH of the solution involving vanadium (V)-MIDA complex

$C_{VO_2} = 8.17 \times 10^{-4}$ M. $C_{MIDA} = 4.09 \times 10^{-2}$ M, 25°C, $\mu = 1.0$ M $(NaClO_4)$

$C_{H_2O_2}$, M	$C_{H_2O_2}/C_{VO_2(mida)}$	$-\log\ [H^+] \pm 0.01$
0	0	4.09
2.54×10^{-4}	0.311	4.09
5.07×10^{-4}	0.621	4.08
7.61×10^{-3}	0.931	4.08
1.01×10^{-3}	1.24	4.07

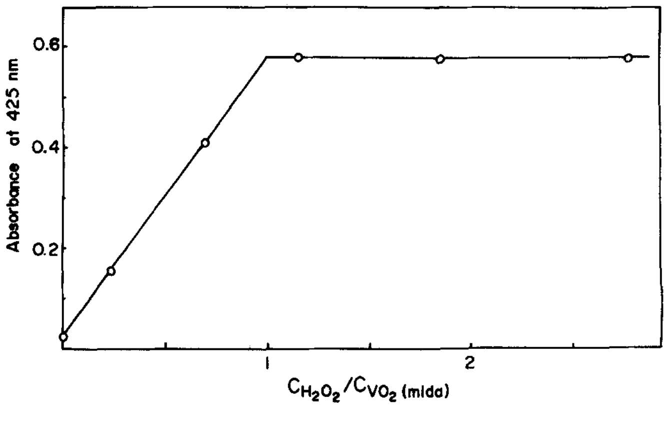

FIGURE 2 Absorbance at 425 nm as a function of hydrogen peroxide concentrations at a constant vanadium (V)-MIDA complex concentration. The conditions are the same in Figure 1.

(V) complex and hydrogen peroxide is of the first-order with respect to the vanadium (V)-MIDA complex and hydrogen peroxide:

$$\frac{d[VO(O_2)(mida)^-]}{dt} = k[VO_2(mida)^-]\,[H_2O_2] \qquad (5)$$

Values of rate constants for this reaction under various conditions are given in Table II. As apparent from Figure 3, the rate constant is independent of concentrations of reagents which confirms the rate equation (5). The value of the rate constant is 25°C and the ionic strength of 1.0 M ($NaClO_4$) is $9.2 \pm 1.5 \times 10^3\ M^{-1}\ sec^{-1}$.

The rate constants at various temperatures are given in Table III. A plot of log k against the reciprocal temperature was linear, and the values of activation parameters were estimated. The low enthalpy of activation (6.3 Kcal/mole) and the highly negative entropy of activation (−19 e.u.) are characteristic of the reaction of pervanadyl (VO_2^+) so far studied (see Table IV).

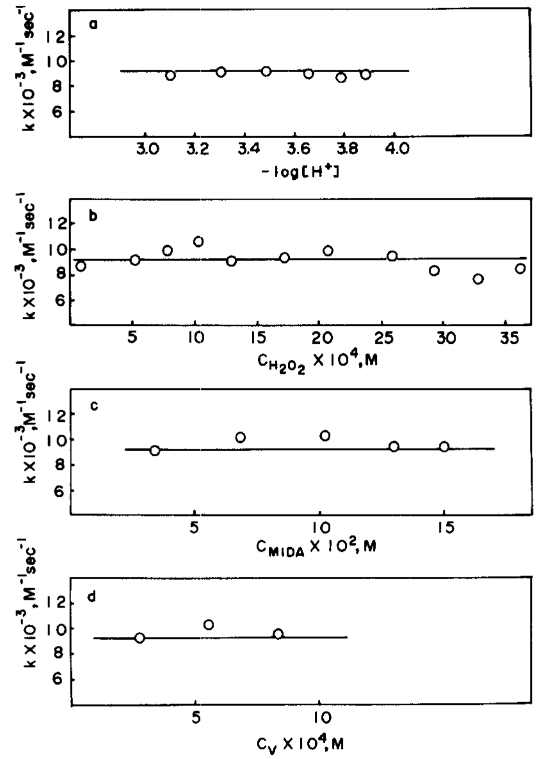

FIGURE 3 Dependence of rate constants on concentrations of reagents. At 25°C and μ = 1.0 M ($NaClO_4$).
a: Plot of k *vs.* −log [H^+]
b: Plot of k *vs.* $C_{H_2O_2}$
c: Plot of k *vs.* C_{MIDA}
d: Plot of k *vs.* C_V

TABLE II
Rate constants[a] of the reaction of the N-methyliminodiacetatodioxovanadate (V) complex with hydrogen peroxide at 25°C and μ = 1.0 M ($NaClO_4$)

Run No.	C_V, M	C_{MIDA}, M	$C_{H_2O_2}$, M	−log [H^+]	k x 10^{-3}, M^{-1} sec^{-1}
1	2.80×10^{-4}	3.41×10^{-2}	3.17×10^{-4}	3.11	8.8
2				3.31	9.1
3				3.49	9.2
4				3.66	9.0
5				3.79	8.7
6				3.89	9.0
7			8.62×10^{-5}	3.35	8.8
8			7.76×10^{-4}		9.9
9			1.04×10^{-3}	2.91	10.5
10			1.29×10^{-3}	3.35	9.1
11			1.72×10^{-3}		9.3
12			2.07×10^{-3}	2.91	9.9
13			2.59×10^{-3}	3.35	9.4
14			2.93×10^{-3}	2.91	8.2
15			3.28×10^{-3}		7.6
16			3.62×10^{-3}		8.4
17			5.17×10^{-4}	3.35	9.2
18		6.82×10^{-2}		3.34	10.2
19		1.02×10^{-1}		3.24	10.3
20		1.30×10^{-1}		3.27	9.4
21		1.50×10^{-1}		3.26	9.4
22	5.56×10^{-4}	1.02×10^{-1}	6.04×10^{-4}	3.05	10.3
23	8.34×10^{-4}			2.86	9.5

[a] Each value is the average of two or more determinations.

Now a brief account is made on the formation of some vanadium (V) complexes (Table IV). As seen from Table IV, the values of the rate constants given by the second order (Nos. 2, 4, 6, 7) are comparable, the difference in experimental conditions being taken into consideration. This seems to imply that the rate is controlled by dissociation of a water molecule coordinated to vanadium (V). The value of the enthalpy of activation for the reaction of $VO_2(mida)^-$ and H_2O_2 is lower than those for the other reactions. This fact is attributable to the ease of dissociation of a water molecule from the central metal by electron donation of MIDA coordinated to vanadium (V). It has been quantitatively accounted for that when a ligand coordinated to central metal donates to a greater extent, the bond of the central metal with the leaving ligand will be weakened and more easily broken.[29,30]

TABLE III

Rate constants[a] at various temperatures and activation parameters $C_V = 5.56 \times 10^{-4}$ M, $C_{MIDA} = 6.81 \times 10^{-2}$ M, $C_{H_2O_2} = 6.90 \times 10^{-4}$ M, $\mu = 1.0$ M ($NaClO_4$)

Temperature, °C	k, M^{-1} sec^{-1}	
15.8	6.3×10^3	$\Delta F^{\neq} = 12.0$ Kcal/mole
17.0	6.9×10^3	$\Delta H^{\neq} = 6.3$ Kcal/mole
20.2	8.7×10^3	$\Delta S^{\neq} = -19$ e.u.
25.0[b]	9.2×10^3	
30.0	1.2×10^4	
35.6	1.4×10^4	

[a] Each value is the average of three or more determinations.

[b] The value at 25°C is the average of rate constants indicated in Table II.

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TABLE IV

Kinetic data for formation of vanadium (V) complexes so far studied

No.	Rate law	Product	K, (M, sec)	Activation parameters	Conditions	Ref
1	$k[VO_2{}^+][H_2O_2][H^+]^{-1}$	$VO(O_2)^+$	70	6°C, $\mu = 3$	6°C, $\mu = 3$	12
2	$k[VO_2{}^+][H_2O_2]$	$VO(O_2)^+$	4.0×10^2	6°C, $\mu = 3$	6°C, $\mu = 3$	12
3	$k[VO_2{}^+][H_2O_2][H^+]$	$VO(O_2)^+$	3.3×10^3	1.9×10^{11} exp (−9900/RT)	6°C, $\mu = 3$	12
			1.1×10^4	$\Delta H^{\neq} = 9.4$ Kcal/mole $\Delta S^{\neq} = -7$ e.u.	25°C[a]	
4	$k[VO(O_2)^+][H_2O_2]$	$VO(O_2)^{-1}$	1.3×10^3	1.8×10^{10} exp (−9100/RT)	6°C, $\mu = 3$	12
			3.9×10^3	$\Delta H^{\neq} = 8.5$ Kcal/mole $\Delta S^{\neq} = -11$ e.u.	25°C[a]	
5	$k[VO_2{}^+][mida'][H^+]^{-1}$[b]	$VO_2(mida)^-$	5.2	$\Delta H^{\neq} = 10$ Kcal/mole $\Delta S^{\neq} = -22$ e.u.	25°C, $\mu = 1.0$	20
6	$k[VO_2(OH)][mida']$	$VO_2(mida)^-$	1.3×10^4		25°C, $\mu = 1.0$	20
7	$k[VO_2(mida)^-][H_2O_2]$	$VO(O_2)(mida)^-$	9.2×10^3	$\Delta H^{\neq} = 6.3$ Kcal/mole $\Delta S^{\neq} = -19$ e.u.	25°C, $\mu = 1.0$	This work

[a] Calculated from the kinetic data at 6°C.

[b] [mida'] indicates the total concentration of MIDA not combined with vanadium (V).

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