Formation Kinetics of Peroxovanadium(V) Complexes in Strongly Acidic Media as Studied by a High-pressure Stopped-flow Technique*

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Abstract

A high-pressure stopped-flow vessel was made of acid-proof tantalum block which enabled us to follow reactions of vanadium(V) ion with hydrogen peroxide in strongly acidic media. The rate for the formation of the monoperoxo complex $(VO(O_2)^+)$ is expressed as $d[VO(O_2)^+]/dt = (k_1[H^+]^{-1} + k_2 + k_3[H^+])[VO_2^+]$-$[H_2O_2]$ where k_1 (s^{-1}) $(25\ °C) = 60.2$ $[\Delta H^{\neq}$ (kJ $mol^{-1} = 21.1 \pm 2.6$, $\Delta S^{\neq}$ (J mol^{-1} $K^{-1}) = -140 \pm 9$, $\Delta V^{\neq}$ $(cm^3\ mol^{-1}) = 9.9 \pm 1.7]$, k_2 $(mol^{-1}\ dm^3\ s^{-1})$ $(25\ °C) = 3.47 \times 10^3$ $[\Delta H^{\neq} = 46.5 \pm 1.3$, $\Delta S^{\neq} = -21 \pm 4$, $\Delta V^{\neq} = 2.8 \pm 1.0]$ and k_3 $(mol^{-2}\ dm^6\ s^{-1})$ $(25\ °C) = 1.63 \times 10^3$ $[\Delta H^{\neq} = 20.1 \pm 4.7$, $\Delta S^{\neq} = -116 \pm 16$, $\Delta V^{\neq} = 14.2 \pm 3.2]$. The rates of formation and dissociation of the diperoxo complex are described as $d[VO(O_2)_2^-]/dt = k_f[VO(O_2)^+][H_2O_2]$ and $-d[VO(O_2)_2^-]/dt = k_d[VO(O_2)_2^-][H^+]^2$, respectively, where k_f $(mol^{-1}\ dm^3\ s^{-1})$ $(25\ °C) = 3.49 \times 10^3$ $[\Delta H^{\neq}$ (kJ $mol^{-1}) = 40.2 \pm 0.8$, $\Delta S^{\neq}$ (J $mol^{-1}\ K^{-1}) = -42 \pm 3$, $\Delta V^{\neq}$ $(cm^3\ mol^{-1}) = 0.0 \pm 0.2]$ and k_d $(mol^{-2}\ dm^6\ s^{-1})$ $(25\ °C) = 3.79 \times 10^3$ $[\Delta H^{\neq} = 45.7 \pm 1.7$, $\Delta S^{\neq} = -23 \pm 6]$. Positive volumes of activation for the monoperoxo complex formation have been attributed to an expanded transition state with the distorted pentagonal-bipyramidal structure.

Introduction

Reactions of hydrogen peroxide with various chemical species have been the subject matter of many investigations especially because of the biological significance [2]. In analytical chemistry, hydrogen peroxide has been used as an analytical

reagent for early transition metal ions and in the analysis of trace metal ions using their catalytic effect on the H_2O_2 decomposition [3]. However, little attention has been drawn to the mechanism of these reactions. We have been interested in the formation kinetics of peroxo complexes of early transition metal ions in aqueous solution [1]. Previously we have reported the kinetics of the reaction between hydrogen peroxide and vanadium(V) complexes with aminopolycarboxylic acids such as *N*-methyliminodiacetic acid (MIDA) [4], 2,6-pyridinedicarboxylic acid (PDA) [5], nitrilotriacetic acid (NTA, H_3nta) [5], ethylenediamine-*N,N'*-diacetic acid (EDDA, H_2edda) [6], *N,N'*-dimethylethylene-*N,N'*-diacetic acid [6], and ethylenediamine-*N,N,N',N'*-tetraacetic acid [6]. At that time, since we had exploited a high-pressure stopped-flow apparatus (Type FIT-1, named later) of which the dead time was *ca.* 0.1 s [7], we had measured, at high pressure up to 120 MPa, the reaction of (nitrilotriacetato)dioxovanadate(V) ·with hydrogen peroxide in order to obtain some information on the reaction mechanism. Soon after, we constructed a new high-pressure stopped-flow apparatus (Type FIT-3) with much more sophisticated mechanics of which the dead time was *ca.* 3 ms at high pressure up to 200 MPa [8]. Since the mixer of the high-pressure stopped-flow vessel was made of stainless steel, we could not use it for reactions in strongly acidic media. In order to overcome the matter, first we selected Daiflon (polychlorotrifluoroethylene, trademark of Daikinkogyo Co., Osaka, Japan) as an acid-proof material. However pressure higher than 90 MPa was not sealed due to the deformation of Daiflon although it was mounted inside a stainless-steel block. As presented in this paper, we were successful in constructing a high-pressure stopped-flow vessel made of tantalum mounted within a stainless-steel block. Now we can follow the fast reaction of vanadium ion with hydrogen peroxide in strongly acidic aqueous solution under high pressures up to 200 MPa.

Reaction of vanadium(V) with hydrogen peroxide in strongly acidic media gives two species of peroxo complex, *i.e.* $VO(O_2)^+$ and $VO(O_2)_2^-$ [9], in which

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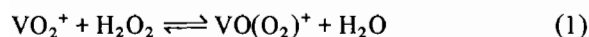coordinated water molecules are omitted for simplicity. Under the present experimental conditions, vanadium(V) exists as VO_2^+ [9]. Thus the peroxo complexes are produced by the following reactions

$$VO_2^+ + H_2O_2 \rightleftharpoons VO(O_2)^+ + H_2O \qquad (1)$$

$$VO(O_2)^+ + H_2O_2 \rightleftharpoons VO(O_2)_2^- + 2H^+ \qquad (2)$$

Equilibrium constants and rate laws of these reactions have already been reported by Orhanović and Wilkins [9]. However temperature dependence of the rate constants has not been fully examined, so we here measured the reaction rates not only under various temperatures, but also various pressures to obtain activation parameters.

Experimental

Reagents

Solutions of sodium perchlorate, hydrogen peroxide and vanadium(V) perchlorate were prepared as described previously [6]. Perchloric acid of special purity (Wako Pure Chemical Industries, Ltd., Osaka, Japan) was used without further purification.

Measurements and Apparatus

The temperature of the solutions was controlled to within ±0.1 °C. The ionic strength was maintained at 3.00 mol dm^{-3} with sodium perchlorate and perchloric acid. In all kinetic measurements reactions were followed spectrophotometrically under pseudo-first-order conditions. A stopped-flow spectrophotometer (Type RA401, Union Giken, Osaka) was used to obtain the kinetic data. The progress of reactions under various pressures up to 200 MPa was measured by an acid-proof high-pressure stopped-flow apparatus (Type FIT-4) which has just been constructed for this study. The constitution of this apparatus is the same as that of the FIT-3 apparatus [8] reported previously except for the high-pressure vessel depicted in Fig. 1.

As shown in Fig. 1, the vessel made of tantalum was mounted within a stainless-steel (AISI 630) block. Reactant solutions are in contact only with acid-proof materials such as tantalum, Daiflon, and Teflon. Pressure sealing was performed, not at the stainless steel used as a reinforcing material, but within the tantalum block as shown in Fig. 1. A pair of rings, Teflon-coated O-ring (a) and Teflon back-up ring (b), was used for sealing pressure, since tantalum is neither hard nor strong enough to be used as a cone-type seal. Daiflon tubes (g) were inserted into the twin cylinders to prevent the tantalum piston (e) from being damaged due to the same materials rubbing together. The pistons were connected to the knob with a special device (j); a self-aligning device

was adopted lest the pistons should be bent by an eccentric force because of insufficient hardness of tantalum. High-pressure caps (i) were elaborated so that an anaerobic reaction system could be measured. The temperature was maintained by circulating thermostated water through channel (c).

Results

In all kinetic experiments, hydrogen peroxide was used in large excess (>20-fold excess) over vanadium(V) to secure pseudo-first-order conditions. The reaction proceeded by two phases. The first faster step is the formation of the monoperoxo complex $VO(O_2)^+$ (reaction (1)), and the second slower reaction is that of the diperoxo complex $VO(O_2)_2^-$ (reaction (2)). The first-order plot for the first step is excellently linear. Thus the rate is first order with respect to the concentration of VO_2^+. The first-order rate constants are proportional to the concentration of hydrogen peroxide at a constant acidity. In Fig. 2 is shown an example of the hydrogen ion concentration dependence of conditional second-order rate constant $k_{0(H)}$ at different temperatures and pressures. The values of $k_{0(H)}$ are tabulated in Tables 1 and 2. The rate law is thus expressed as

$$d[VO(O_2)^+]/dt = k_{0(H)}[VO_2^+][H_2O_2]$$
$$= (k_1[H^+]^{-1} + k_2 + k_3[H^+])[VO_2^+][H_2O_2] \qquad (3)$$

Activation enthalpies and activation entropies for the k_1, k_2 and k_3 paths were determined by using a total of 107 points at 15, 25 and 35 °C and are summarized in Table 3. According to the transition state theory, the change in rate constant, k, with pressure, P, is related to the activation volume, $\Delta V^{\neq}$: $(\partial \ln k/\partial P)_T = -\Delta V^{\neq}/RT$. After confirming that logarithmic values of the rate constants are linearly related to the pressure, activation volumes for the rate constants k_1, k_2 and k_3 were estimated simultaneously by applying the non-linear least-squares fitting to the total data of 353 points, and are listed in Table 3.

The rate of formation of the diperoxo complex $VO(O_2)_2^-$ from $VO(O_2)^+$ (forward reaction of eqn. (2)) was measured under conditions where the reverse reaction could be neglected. Since the rate is first order in H_2O_2 and independent of hydrogen ion concentration, the rate law for formation is expressed as follows

$$d[VO(O_2)_2^-]/dt = k_f[VO(O_2)^+][H_2O_2] \qquad (4)$$

The dissociation reaction of the diperoxo complex to $VO(O_2)^+$ occurs when the hydrogen ion concentration of the solution is raised. Rates of this reaction were confirmed to be second order in hydrogen ion concentration. Thus we have
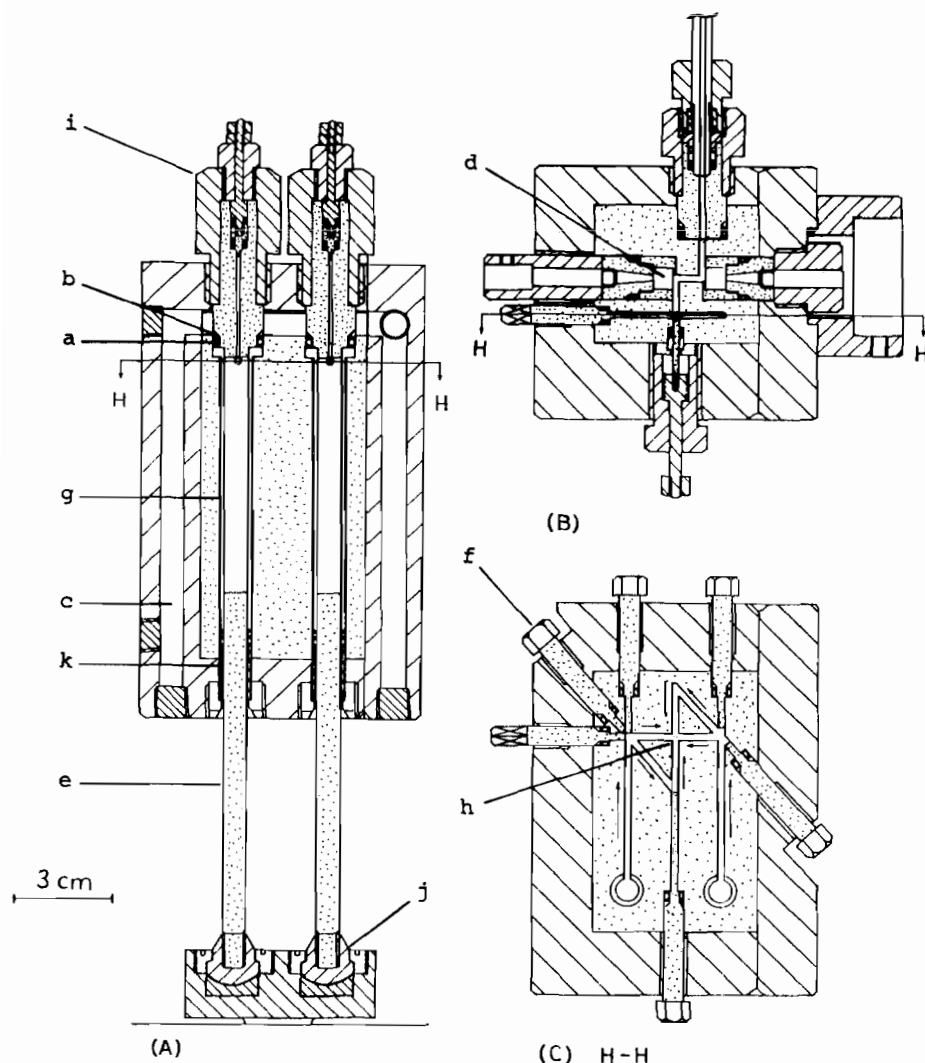
Fig. 1. High-pressure stopped-flow vessel made of tantalum reinforced with stainless steel. (A) high-pressure vessel, (B) optical cell, (C) four-jet type of mixer: H–H cross section in (A) and (B). Tantalum parts are represented by dots. a, O-ring; b, Teflon ring; c, channel for thermostated water; d, sapphire window; e, piston made of tantalum; f, tantalum bolt with whom the drilled hole is filled; g, reservoir made of Daiflon; h, mixer; i, high-pressure cap; j, self-aligning device; k, duralmin.

$$-\mathrm{d}[\mathrm{VO}(\mathrm{O}_2)_2{}^-]/\mathrm{d}t = k_\mathrm{d}[\mathrm{VO}(\mathrm{O}_2)_2{}^-][\mathrm{H}^+]^2 \qquad (5)$$

Values of k_f and k_d at various temperatures, values of k_f under various pressures and obtained activation parameters are summarized in Table 4.

Discussion

The crystal structure of ammonium oxodiperoxo-amminevanadate(V) has been determined to be a pentagonal pyramid, the four oxygens of the two peroxo groups and the ammonia nitrogen atom forming the distorted base of the pyramid, while the oxo oxygen occupies the apical position [10]. The vanadium atom environment of the crystal structure

of ammonium oxoperoxo(pyridine-2,6-dicarboxy-lato)vanadate(V) is a seven-coordinate distorted pentagonal bipyramid [11]. Recently, the same coordination has been confirmed by [51]V and ^{17}O NMR studies of peroxovanadates in aqueous solution [12]. On the other hand, in aqueous solution, we have studied the hydrolysis reaction of the per-vanadyl cation [13] and the complexation equilibria with some aminopolycarboxylates [14]. Pervanadyl ion in acidic solution is a dioxovanadium(V) cation where two oxo groups are in the *cis* position to one another, and the $\mathrm{VO}_2{}^+$ complexes with amino-polycarboxylates keep the *cis* configuration of the VO_2 unit [15–17].

It has been pointed out that for the reaction of $\mathrm{VO}_2{}^+$ with EDDA to form the $\mathrm{VO}_2(\mathrm{edda})^-$ complex,
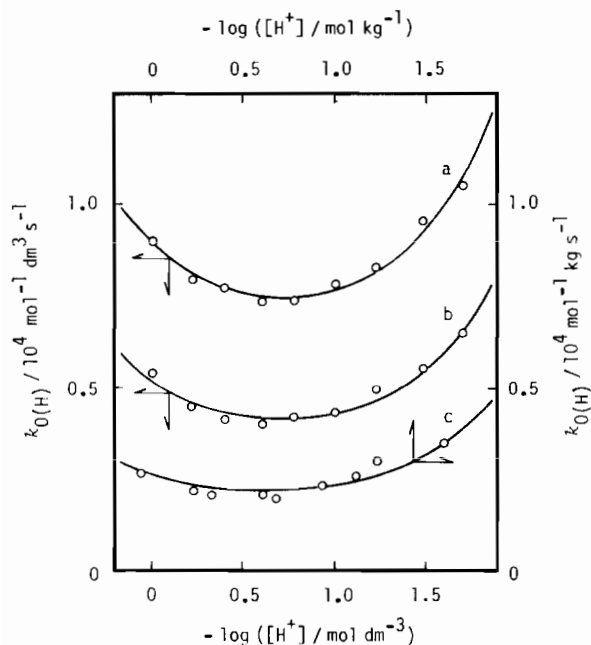
Fig. 2. Dependence of $k_{0(H)}$ on hydrogen ion concentration: a, at 35.0 °C and 0.1 MPa; b, at 25.0 °C and 0.1 MPa; c, at 20.1 °C and 98.1 MPa. The solid lines were calculated by using the activation parameters obtained.

TABLE 1. Second-order Rate Constants of the Formation Reaction of $VO(O_2)^+$ under Atmospheric Pressure[a]

T (°C)	$-\log\left(\dfrac{[H^+]}{\text{mol dm}^{-3}}\right)$	$10^{-3} \times k_{0(H)}$ [b] $(\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1})$
15.0	0.014	3.02 ± 0.03
	0.232	2.46 ± 0.05
	0.405	2.18 ± 0.01
	0.617	2.17 ± 0.02
	0.785	2.09 ± 0.02
	1.009	2.30 ± 0.03
	1.237	2.60 ± 0.03
	1.485	3.37 ± 0.05
	1.706	3.64 ± 0.07
25.0	0.014	5.42 ± 0.04
	0.232	4.44 ± 0.10
	0.405	4.09 ± 0.11
	0.617	3.97 ± 0.05
	0.785	4.17 ± 0.10
	1.009	4.33 ± 0.09
	1.237	4.97 ± 0.05
	1.485	5.55 ± 0.07
	1.706	6.44 ± 0.16
35.0	0.014	8.98 ± 0.11
	0.232	7.90 ± 0.11
	0.405	7.70 ± 0.11
	0.617	7.29 ± 0.10
	0.785	7.39 ± 0.15
	1.009	7.84 ± 0.32

(continued)

TABLE 1. *(continued)*

T (°C)	$-\log\left(\dfrac{[H^+]}{\text{mol dm}^{-3}}\right)$	$10^{-3} \times k_{0(H)}$ [b] $(\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1})$
	1.237	8.30 ± 0.06
	1.485	9.58 ± 0.18
	1.706	10.47 ± 0.27

[a]$C_V = 3.71 \times 10^{-4}$ mol dm^{-3} and $C_{H_2O_2} = (0.453 \sim 1.04) \times 10^{-2}$ mol dm^{-3}, where C_V and $C_{H_2O_2}$ are the total concentration of vanadium(V) and hydrogen peroxide, respectively.
[b]Each rate constant is the average of several determinations. Errors are given by the standard deviation.

TABLE 2. Second-order Rate Constants of the Formation Reaction of $VO(O_2)^+$ under Various Pressures at $T = 20.1$ °C[a]

$-\log\left(\dfrac{[H^+]}{\text{mol kg}^{-1}}\right)$	$10^{-3} \times k_{0(H)}$ [b] $(\text{mol}^{-1}\ \text{kg s}^{-1})$
$P = 0.1$ MPa	
−0.052	3.81 ± 0.19
−0.051	3.93 ± 0.22
0.243	2.61 ± 0.10
0.337	2.59 ± 0.24
0.624	2.52 ± 0.10
0.692	2.45 ± 0.14
0.943	3.02 ± 0.13
1.125	3.03 ± 0.12
1.235	3.73 ± 0.21
1.607	4.64 ± 0.45
$P = 24.5$ MPa	
−0.052	3.15 ± 0.04
−0.051	3.31 ± 0.14
0.243	2.54 ± 0.11
0.337	2.33 ± 0.21
0.624	2.43 ± 0.10
0.692	2.05 ± 0.13
0.943	2.79 ± 0.16
1.125	3.02 ± 0.24
1.235	3.48 ± 0.12
1.607	3.80 ± 0.28
$P = 49.0$ MPa	
−0.052	3.06 ± 0.19
−0.051	3.09 ± 0.09
0.243	2.40 ± 0.14
0.337	2.38 ± 0.19
0.624	2.37 ± 0.18
0.692	2.15 ± 0.12
0.943	2.51 ± 0.13
1.125	3.06 ± 0.36
1.235	3.39 ± 0.16
1.607	3.60 ± 0.32

(continued)

TABLE 2. *(continued)*

$-\log\left(\dfrac{[H^+]}{\text{mol kg}^{-1}}\right)$	$10^{-3} \times k_{0(H)}$ [b] $(\text{mol}^{-1}\,\text{kg s}^{-1})$
P = 73.5 MPa	
−0.052	2.75 ± 0.25
−0.051	2.74 ± 0.16
0.243	2.36 ± 0.12
0.337	2.09 ± 0.10
0.624	2.14 ± 0.02
0.692	2.12 ± 0.18
0.943	2.44 ± 0.06
1.125	2.51 ± 0.12
1.235	3.05 ± 0.13
1.607	3.66 ± 0.20
P = 98.0 MPa	
−0.052	2.92 ± 0.24
−0.051	2.77 ± 0.18
0.243	2.20 ± 0.06
0.337	2.11 ± 0.07
0.624	2.11 ± 0.08
0.692	1.95 ± 0.15
0.943	2.36 ± 0.12
1.125	2.63 ± 0.38
1.235	2.99 ± 0.08
1.607	3.48 ± 0.19
P = 122.5 MPa	
−0.052	2.66 ± 0.24
−0.051	2.77 ± 0.09
0.243	2.09 ± 0.09
0.337	1.78 ± 0.06
0.692	1.92 ± 0.14
0.943	2.25 ± 0.07
1.125	2.21 ± 0.16
1.235	2.80 ± 0.03
1.607	3.13 ± 0.20
P = 147.0 MPa	
−0.051	2.62 ± 0.08
0.243	2.07 ± 0.04
0.943	2.02 ± 0.08
1.607	3.15 ± 0.06

$C_V = 4.32 \times 10^{-4}$ mol kg^{-1} and $C_{H_2O_2} = 1.12 \times 10^{-2}$ mol kg^{-1}. [b]Each rate constant is the average of several determinations. Errors are given by the standard deviation.

TABLE 4. Rate Constants of the Formation and Dissociation Reactions of $VO(O_2)_2^-$ and Their Activation Parameters[a]

T (°C)	$10^{-3} \times k_f$ $(\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1})$	$10^{-3} \times k_d$ $(\text{mol}^{-2}\,\text{dm}^6\,\text{s}^{-1})$
15.0	1.99 ± 0.01	1.95 ± 0.01
25.0	3.49 ± 0.06	3.79 ± 0.25
35.0	6.33 ± 0.24	7.21 ± 0.31
$\Delta H^{\neq}$ (kJ mol^{-1})	40.2 ± 0.8	45.7 ± 1.7
$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	−42 ± 3	−23 ± 6

P (MPa)	$10^{-3} \times k_f$ [b] $(\text{mol}^{-1}\,\text{kg s}^{-1})$
0.1	2.16 ± 0.12
24.9	2.12 ± 0.11
49.0	2.22 ± 0.11
73.5	2.17 ± 0.13
98.1	2.15 ± 0.10
122.5	2.19 ± 0.09
147.0	2.16 ± 0.16
196.0	2.07 ± 0.06
$\Delta V^{\neq}$ (cm^3 mol^{-1})	0.0 ± 0.2

[a]$C_V = 3.71 \times 10^{-4}$ mol dm^{-3}, $C_{H_2O_2} = (0.2 \sim 2.2) \times 10^{-2}$ mol dm^{-3}, $[H^+] = (0.16 \sim 3.2) \times 10^{-1}$ mol dm^{-3}. [b]Measured at 20.1 °C.

the rate-determining step is water loss from the metal ion ($k = 1.0 \times 10^8$ mol^{-1} dm^3 s^{-1}, $\Delta H^{\neq} = 29$ kJ mol^{-1} and $\Delta S^{\neq} = 8$ J mol^{-1} K^{-1}) [18]. The rate for the EDDA complex formation is much faster than that for the peroxo complex formation.

It should be remembered that MIDA−, NTA−, and PDA−vanadium(V) complexes react with H_2O_2 through an associatively activated transition state [5]. In fact, the activation volume for the reaction of $VO_2(nta)^{2-}$ with H_2O_2 is negative ($\Delta V^{\neq} = -3.4 \pm 0.5$ cm^3 mol^{-1}) [7]. Interestingly, however, the activation volume for reaction of VO_2^+ with H_2O_2 (k_2 path) in the present system is positive. There seems to be two successive processes in the peroxo complex formation, i.e. the associative attack by an H_2O_2 molecule as an entering ligand into the face of the octahedral VO_2 complex followed by the rearrangement of the VO_2 octahedron to a distorted

TABLE 3. Kinetic Parameters of the Formation Reaction of $VO(O_2)^+$ [a]

|	k_1 (25 °C) (s^{-1})	k_2 (25 °C) $(\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1})$	k_3 (25 °C) $(\text{mol}^{-2}\,\text{dm}^6\,\text{s}^{-1})$
	60.2	3.47 × 10^3	1.63 × 10^3
$\Delta H^{\neq}$ (kJ mol^{-1})	21.1 ± 2.6	46.5 ± 1.3	20.1 ± 4.7
$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	−140 ± 9	−21 ± 4	−116 ± 16
$\Delta V^{\neq}$ (cm^3 mol^{-1})[b]	9.9 ± 1.7	2.8 ± 1.0	14.2 ± 3.2

[a]Errors are given by the standard deviation. [b]Measured at 20.1 °C.

pentagonal bipyramid of the peroxo complex. In the case of the $VO_2(nta)^{2-}$ complex, the nucleophilic attack of H_2O_2 is unfavorable due to the electron donation from the ligand nta^{3-} to the central metal ion, while the rearrangement is favored because of the strain imposed by the coordination of nta^{3-} on the VO_2^+ octahedron. Thus, the rate-determining step may be the associative attack of H_2O_2 as reflected by a negative volume of activation. On the other hand, in the case of VO_2^+, due to the absence of an electron donating ligand such as nta^{3-}, the nucleophilic attack of H_2O_2 is easier and faster than the next step of the rearrangement. This will result in the shift of the rate-determining step to the rearrangement. The octahedral precursor complex should be rearranged to a distorted pentagonal bipyramid leading to a somewhat expanded transition state. This is reflected in the positive value of the activation volume.

The peroxo complex formation reaction (reaction (1)) also contains two proton-dependent paths: k_1 and k_3 paths (see eqn. (3)). The rates of the k_1 and k_3 paths are inversely and directly proportional to the hydrogen ion concentration, respectively. Judging from the dissociation constants: $[H^+] \cdot [H_2O_2][H_3O_2^+]^{-1} \cong 10^3$ and $[H^+][HO_2^-][H_2O_2]^- = 10^{-11.27}$ [19], a reacting species of hydrogen peroxide should be H_2O_2 in the present experimental conditions. A first-order hydrogen ion dependence has been established for the reactions involving oxo anions [20] or VO_2^+ [21]. It is thought that the acid catalysis arises from a reactive species presumably protonated at the oxo group of the VO_2^+ ion. We expect less than $+4$ cm^3 mol^{-1} as the reaction volume for the step of protonation in the k_1 path, because the partial molal volume of a proton is -4.5 cm^3 mol^{-1} [22]. Thus the activation volume for the activation process in the peroxo complex formation seems to be more than 10 cm^3 mol^{-1}. This positive value reflects the volume expansion at the transition state. On the other hand, the inverse hydrogen ion dependence may be attributed to the formation of a hydrolyzed species [13] prior to the reaction with H_2O_2

$$VO_2^+ \rightleftharpoons VO(OH)_3 + H^+ \qquad (6)$$
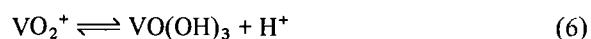
Thermodynamic parameters of reaction (6) are as follows: $K = [VO(OH)_3][H^+][VO_2^+]^{-1} = 10^{-3.70}$ M (25 °C, $I = 1.0$ mol dm^{-3}), $\Delta H° = 0$ kJ mol^{-1}, $\Delta S° = -71$ J mol^{-1} K^{-1} [13]. Reaction volumes for the hydrolysis of several metal complexes have been measured and discussed in terms of the electrostriction effects by Kitamura and van Eldik [23]. The value of the reaction volume for the hydrolysis reaction in which the neutral complex and hydrogen ion are produced from the unipositive complex (like reaction (6)) is suggested to be -5.1 ± 0.8 cm^3 mol^{-1}. If we assume -5 cm^3 mol^{-1} as the reaction volume for reaction (6), activation parameters for the

reaction of hydrolyzed vanadium(V) species with H_2O_2 are $\Delta H^{\neq} = 21$ kJ mol^{-1}, $\Delta S^{\neq} = -69$ J mol^{-1} K^{-1} and $\Delta V^{\neq} = 15$ cm^3 mol^{-1}. This positive value of $\Delta V^{\neq}$ may also indicate a considerably expanded transition state.

The second reaction (reaction (2)) is the diperoxo complex formation through the reaction of the monoperoxo complex $VO(O_2)^+$ with hydrogen peroxide. The rate of the forward reaction is independent of the hydrogen ion concentration, while rate of the reverse reaction depends on the second power of the hydrogen ion concentration. These findings indicate that the transition state should involve both $VO(O_2)^+$ and H_2O_2 and that the hydrogen peroxide may attack the central metal as a neutral form of H_2O_2. One of the coordinated water molecules is thought to be substituted in this process. The activation volume $(\Delta V_f^{\neq})$ for the forward reaction is 0 cm^3 mol^{-1}. Therefore, the activation process of the diperoxo complex formation is concluded to be an interchange mechanism, where the decrease in volume due to the penetration of the oxygen atom of the H_2O_2 molecule into the inner coordination sphere of the vanadium(V) complex is almost compensated by the increase in volume due to the elongation of the $V-OH_2$ bond.

Acknowledgements

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