

Kinetics of the Reaction of Hydrogen Peroxide with Some Oxotitanium(IV) Complexes As Studied by a High-Pressure Stopped-Flow Technique¹

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The reaction of H₂O₂ with oxotitanium(IV) (TiO²⁺(aq)), aqua(nitritotriacetato)oxotitanate(IV) (TiO(nta)(H₂O)⁻), and oxo(5,10,15,20-tetra-4-pyridylporphinato)titanium(IV) (TiO(tpypH₄)⁴⁺) leading to the corresponding 1:1 monoperoxo complexes has been investigated in acidic aqueous solution at *I* = 1.0 or 3.0 M at various temperatures and pressures. The formation of the peroxo complexes is first order in the concentration of hydrogen peroxide and titanium(IV) complexes and proceeds through both the proton-independent and proton-dependent paths. The values of enthalpy, entropy, and volume of activation for all reaction paths were determined. The negative activation volumes strongly point to an associative mode of activation operative in these reactions.

Introduction

Reactions of hydrogen peroxide with various chemical species have been the subject of extensive study because of their intrinsic interest and biological significance.^{2,3} In analytical chemistry, hydrogen peroxide has been used as an analytical reagent for early transition metals and in the analysis of trace metal ions using their catalytic effect on the H₂O₂ decomposition.⁴ However little attention has been drawn to the mechanism of these reactions.

We are interested in the formation kinetics of peroxo complexes of early transition-metal ions in aqueous solution¹ and have extended our investigation to the titanium(IV) complexes. There have been several reports on the formation of peroxo-titanium(IV) complexes.⁵⁻⁹ The kinetics of formation of the 1:1 peroxotitanium(IV) complex from the titanium(IV) ion and H₂O₂ in acidic aqueous solution was once studied by Orhanović and Wilkins.⁵ However because of rather complex rate laws and uncertainty of the species of titanium(IV) ion, they did not give the reaction mechanism. According to Wiegardt et al.,⁷ H₂O₂ reacts with titanium(IV)-NTA¹⁰ tetramer, [TiO(nta)]₄⁴⁺, at higher pH, while at lower pH it reacts with a monomeric species. They have noticed the similarity of activation parameters for reactions of H₂O₂ with titanium(IV) complexes of DIPIC,¹⁰ IDA,¹⁰ and NTA and proposed a dissociative-interchange mechanism. Their results do not agree with ours. Shepherd et al.⁸ have proposed an associative-interchange mechanism for the formation of the peroxo complex of titanium(IV)-EDTA,¹⁰ as for the formation of vanadium(V) complexes.¹¹ On the other hand, some current researches are focused on macrocyclic complexes of titanium(IV).¹²⁻¹⁴ Guilard et al.^{12a} have reported the synthesis,

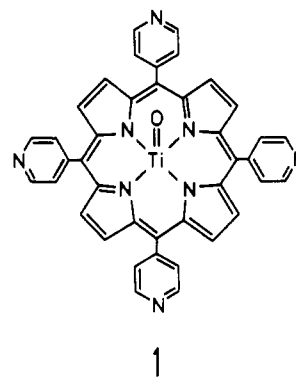
stereochemistry, and properties of peroxo complexes of titanium(IV) porphyrins (OEP¹⁰ and TPP¹⁰).

We report the kinetics of the reaction of H₂O₂ with three types of titanium(IV) complexes, i.e. the oxotitanium(IV) ion, the titanium(IV)-NTA complex, and the titanium(IV)-TPyP¹⁰ complex. Activation volumes should provide some information on the mechanisms of these reactions.

Experimental Section

Reagents. Solutions of sodium perchlorate and sodium hydroxide were prepared as described previously.^{11b} Perchloric acid of special purity (Wakojunyaku Co., Osaka, Japan) was used without further purification. The titanium(IV) hydroxide prepared by a homogeneous precipitation method from titanil sulfate solution (Wakojunyaku) containing urea was dissolved in a 2 M perchloric acid solution.¹⁵ The concentration of the titanium(IV) perchlorate solution was determined by gravimetric analysis. The 60% hydrogen peroxide solution containing no stabilizing agent (Mitsubishi Gasukagaku Co., Kanagawa, Japan) was purified by distillation under reduced pressure. A solution of hydrogen peroxide was titrated with a standard solution of potassium permanganate. Nitritotriacetic acid and *N*-methyliminodiacetic acid were recrystallized twice from distilled water and aqueous methanol, respectively.

Oxo(5,10,15,20-tetra-4-pyridylporphinato)titanium(IV), TiO(tpyp) (1), was prepared as follows: A 0.5-g portion of 5,10,15,20-tetra-



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4-pyridylporphine (H₂tpyp) (Strem Chemicals) was dissolved in 300 cm³ of *N,N*-dimethylformamide containing 3 cm³ of pyridine and then 5 cm³ of titanium(IV) chloride was added dropwise under an argon atmosphere. The solution was refluxed for 30 h, then cooled, and mixed with 300 cm³ of cold water. Chloroform was added to the mixture, and the aqueous phase was neutralized with sodium carbonate. The uncomplexed TPyP and metalloporphyrin were extracted into

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- Mühlebach, J.; Müller, K.; Schwarzenbach, G. *Inorg. Chem.* **1970**, *9*, 2381.
- Ligand abbreviation: NTA, nitritotriacetic acid (H₃nta); DIPIC, dipicolinic acid; IDA, iminodiacetic acid; EDTA, ethylenediamine-*N,N,N',N'*-tetraacetic acid (H₄edta); MIDA, *N*-methyliminodiacetic acid; OEP, 2,3,7,8,12,13,17,18-octaethylporphine; TPP, 5,10,15,20-tetra-phenylporphine; TPyP, 5,10,15,20-tetra-4-pyridylporphine (H₂tpyp).
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- M = mol dm⁻³. The pressure-independent molal scale is used at high pressure (*m* = mol kg⁻¹).

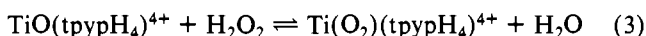
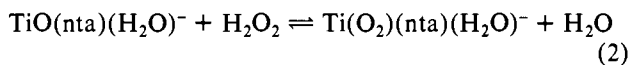
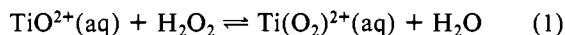
the organic phase. After being washed with water, the organic phase was evaporated to dryness. The metalloporphyrin in the residue was soluble in methanol, while the TPyP was insoluble in it. The methanol solution was evaporated to dryness, and the residue was dissolved in chloroform. Anhydrous sodium carbonate was then added to the solution in order to remove protons. After the excess Na₂CO₃ was filtered, the filtrate was applied to a plate of preparative-layer chromatography (PLC plates, silica gel 60, Merck) and eluted with a methanol-chloroform (8:92) mixture. Recrystallization from a mixture of chloroform and diethyl ether gave flaky purple crystals. The composition of the complex in the crystalline state was determined by elemental analysis, ¹H NMR, and IR spectroscopy: TiO(tpyp)·¹/₂CHCl₃·¹/₂(CH₃CH₂)₂O. The chloroform and diethyl ether came from the mixed solvent used in the recrystallization. Anal. Calcd: C, 65.66; H, 3.82; N, 14.41. Found: C, 65.54, H, 3.46; N, 14.65. ¹H NMR (CDCl₃): δ 9.22 (8 H, s, pyrrole β-H), 9.13 (8 H, m, py *m*-H), 8.40 (4 H, m, py *o*-H), 8.23 (4 H, m, py *o*-H), 7.25 (1 H, s, chloroform), 3.49 (4 H, qrt, *J* = 7 Hz, diethyl ether), 1.20 (6 H, t, *J* = 7 Hz, diethyl ether). IR (KBr disk): 1595 (s), 1408 (m), 1340 (w), 1200 (w), 1065 (w), 1020 (s), 1005 (s) 980 (s), 800 (s), 724 (w), 660 (m) cm⁻¹.

Measurements. In all kinetic measurements temperature was controlled to within ± 0.1 °C and the ionic strength was maintained at 3.00 M for the oxotitanium(IV) system and at 1.00 M for the titanium(IV)-NTA and titanium(IV)-TPyP systems with sodium perchlorate and perchloric acid. The hydrogen ion concentration was determined by an Orion Research pH meter (Model 701A) when pH was higher than 2.0. A 1.000 × 10⁻² M perchloric acid solution at *I* = 1.00 M was used as a pH standard solution. Visible absorption spectra were recorded on a highly sensitive spectrophotometer (Type SM401, Union Giken Co., Osaka, Japan). The titanium(IV)-NTA complex solution was prepared by mixing a titanium(IV) ion solution and an excess NTA solution, while the titanium(IV)-TPyP complex solution was made by dissolving the titanium(IV)-TPyP complex in a perchloric acid solution. The four pyridyl groups of the porphyrin are protonated in acidic aqueous solutions, and the metalloporphyrin exists as TiO(tpypH₄)⁴⁺.

The reaction was followed spectrophotometrically at 415 nm for the oxotitanium(IV) system, at 380 nm for the titanium(IV)-NTA system, and at 432 nm for the titanium(IV)-TPyP system. Fast reactions were followed by a stopped-flow spectrophotometer (Type RA401, Union Giken). Slower reactions were started by a sample-mixing device (Type MX7, Union Giken). Reactions at high pressure up to 1250 kg cm⁻² were followed with a high-pressure stopped-flow apparatus.¹⁶

Results

Equilibria of Peroxo Complexes. Under the present experimental conditions, titanium(IV) exists as TiO²⁺(aq) that has been substantiated by Sykes et al.^{17,18} It has been found that in the oxotitanium(IV) system reaction with hydrogen peroxide gives a monoperoxo species, Ti(O₂)²⁺(aq).^{5,6} In the titanium(IV)-NTA and titanium(IV)-TPyP systems, the mole ratio method was employed to determine the composition of the peroxo complexes produced (see the mole ratio diagram in Figure 1 as an example). The three reaction systems are then expressed as



The wavelengths of maximum absorption (ϵ , molar absorption coefficient, M⁻¹ cm⁻¹) of the peroxotitanium(IV) complexes are 415 nm ($\epsilon = 6.40 \times 10^2$) for Ti(O₂)²⁺(aq), 376 nm ($\epsilon = 1.42 \times 10^3$) for Ti(O₂)(nta)(H₂O)⁻, and 444 nm ($\epsilon = 2.2 \times$

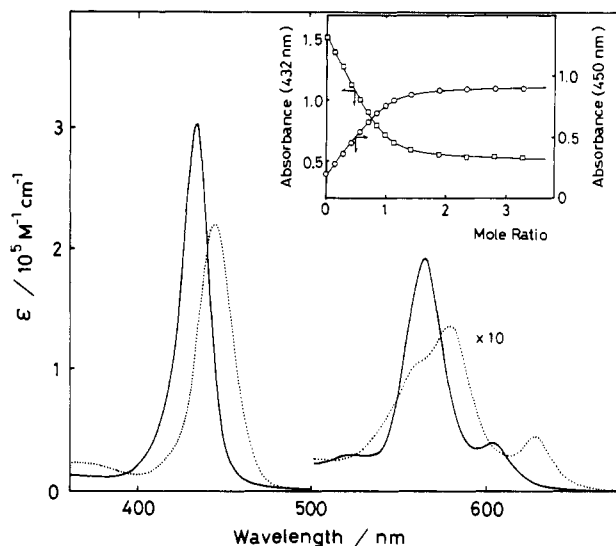


Figure 1. Visible absorption spectra of TiO(tpypH₄)⁴⁺ (—) and Ti(O₂)(tpypH₄)⁴⁺ (···) in acidic aqueous solution (pH 0.1). In the inset, mole ratio is defined as C_{H₂O₂}/C_{Ti(IV)-TPyP} and the total concentration of Ti(IV)-TPyP, C_{Ti(IV)-TPyP}, was kept constant at 4.95 × 10⁻⁶ M ([H⁺] = 0.798 M, 25 °C). The curves in the inset were calculated by using the obtained values of equilibrium constant and molar absorption coefficients.

10⁵), 578 nm ($\epsilon = 1.4 \times 10^4$), and 628 nm ($\epsilon = 4.8 \times 10^3$) for Ti(O₂)(tpypH₄)⁴⁺. The equilibrium constant for reaction 3 was determined to be $(4.0 \pm 0.4) \times 10^6$ M⁻¹ at 25 °C by spectrophotometric titration (Figure 1).

Kinetics. In all kinetic experiments, hydrogen peroxide was used in large excess (>10-fold excess) over titanium(IV) complexes to guarantee the pseudo-first-order conditions. The first-order plots were linear at least for 3 half-lives. The first-order rate constants were proportional to the hydrogen peroxide concentration at constant acidity in every case (see Table SI, supplementary material). The rate law is thus expressed as

$$d[\text{Ti}(\text{O}_2)\text{L}^{n+}]/dt = k_{0(\text{H})}[\text{TiOL}^{n+}][\text{H}_2\text{O}_2] \quad (4)$$

where L represents the coordinated ligand and $k_{0(\text{H})}$ is the conditional second-order rate constant that depends on the hydrogen ion concentration. Coordinated water molecules are omitted for simplicity.

For the oxotitanium(IV) system $k_{0(\text{H})}$ is constant over the range of titanium(IV) concentration of 1.82×10^{-5} – 9.12×10^{-4} M at constant acidity (see Table SI). For the titanium(IV)-NTA system, values of $k_{0(\text{H})}$ do not change with excess NTA concentration (C_{NTA} = 1.00 × 10⁻⁴–1.00 × 10⁻³ M) at constant acidity (see Table SI). $k_{0(\text{H})}$ is linearly related to the hydrogen ion concentration for the oxotitanium(IV) and titanium(IV)-NTA systems (see Figure 2):

$$k_{0(\text{H})} = k_1 + k_2[\text{H}^+] \quad (5)$$

For the titanium(IV)-TPyP system, the k_1 term is missing at the hydrogen ion concentration, 7.25×10^{-3} – 1.02×10^{-1} M: $k_{0(\text{H})} = k_2[\text{H}^+]$ (see Table SI). Values of activation enthalpy and entropy were obtained from the temperature dependence of rate constants, and they are summarized in Table I.

According to the transition-state theory, the change in rate constant, k , with pressure, P , is related to the activation volume ΔV^\ddagger : $(\partial \ln k / \partial P)_T = -\Delta V^\ddagger / RT$. The pressure dependence of the rate constant k_2 for the titanium(IV)-TPyP system is shown in Figure 3. Since the logarithmic values of the rate constants are linearly related to pressure, the activation volume is independent of pressure. For the oxotitanium(IV) and titanium(IV)-NTA systems, rate constants under various

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(17) Ellis, J. D.; Thompson, G. A. K.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 3172.

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Table I. Rate Constants and Activation Parameters for the Peroxo Complex Formation of Titanium(IV)

reaction system	rate constant ^a (25 °C)	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J mol}^{-1} \text{K}^{-1}$	$\Delta V^\ddagger/\text{cm}^3 \text{mol}^{-1}$	ref
$\text{TiO}^{2+}(\text{aq}) + \text{H}_2\text{O}_2$	$k_1 = (1.13 \pm 0.02) \times 10^2$ $k_2 = (6.0 \pm 0.2) \times 10$	50.4 ± 0.7 37 ± 3	-37 ± 3 -86 ± 10	-6.0 ± 0.4^b -0.1 ± 0.3	<i>c</i> <i>c</i>
$\text{TiO}(\text{nta})(\text{H}_2\text{O})^- + \text{H}_2\text{O}_2$	$k_1 = (4.52 \pm 0.08) \times 10^2$ $k_2 = (5.4 \pm 0.2) \times 10^4$	28 ± 4 9 ± 1	-100 ± 10 -126 ± 4	-19 ± 2 13 ± 1	<i>c</i> <i>c</i>
$\text{TiO}(\text{tpypH}_4)^{4+} + \text{H}_2\text{O}_2$	$k_2 = (5.57 \pm 0.08) \times 10$	34.9 ± 0.5	-95 ± 1	-3.3 ± 0.2	<i>c</i>
$\text{TiO}(\text{edta})^{2-} + \text{H}_2\text{O}_2$	$k_1 = 4.9 \times 10$	24	-140		<i>d</i>
$\text{TiO}(\text{edtaH})(\text{H}_2\text{O})^- + \text{H}_2\text{O}_2$	$k_2 = 5.25 \times 10^6$	20	-92		<i>d</i>

^a k_1 is a second-order rate constant in $\text{M}^{-1} \text{s}^{-1}$. k_2 is a third-order rate constant in $\text{M}^{-2} \text{s}^{-1}$, which is first order with respect to hydrogen ion concentration. ^b Errors indicate the standard deviation. ^c This work. ^d Reference 8.

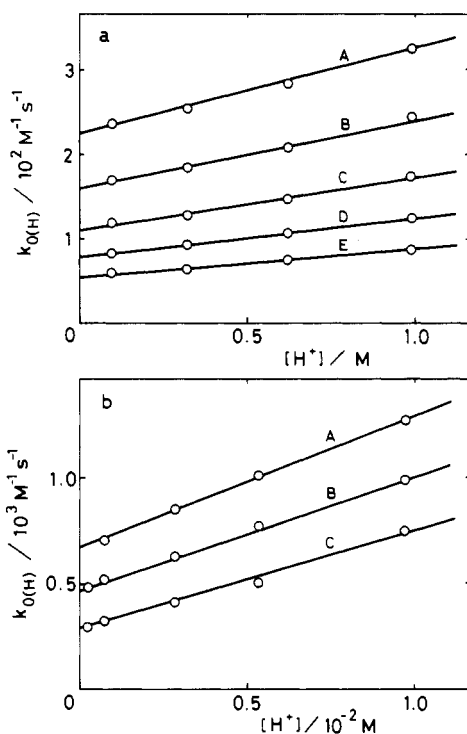


Figure 2. Hydrogen ion dependence of $k_{0(\text{H})}$ for the oxotitanium(IV) system (a) and for the titanium(IV)-NTA system (b). a: A, 35 °C; B, 30 °C; C, 25 °C; D, 20 °C; E, 15 °C. b: A, 35 °C; B, 25 °C; C, 15 °C. Each point is the average of several runs. The solid lines were calculated by using the activation parameters obtained.

pressures at different hydrogen ion concentrations were obtained (Table SI). In the case of the pressure independence of activation volumes, we have

$$k_{0(\text{H})} = k_1^0 \exp(-\Delta V_1^* P / RT) + k_2^0 \exp(-\Delta V_2^* P / RT) [\text{H}^+] \quad (6)$$

where k_1^0 and k_2^0 are rate constants at zero pressure. The values of k_1^0 , k_2^0 , ΔV_1^* , and ΔV_2^* were refined by applying the nonlinear least-squares fitting¹⁹ to eq 6, after confirming the pressure independence of ΔV_1^* and ΔV_2^* . The values of k_1^0 and k_2^0 were revealed to be essentially the same as the corresponding values obtained at atmospheric pressure. The obtained parameters are tabulated in Table I.

Discussion

The kinetic results reported by Orhanović and Wilkins⁵ for the oxotitanium(IV) system are as follows: $k_{0(\text{H})} = k_1 + k_2[\text{H}^+] + k_3[\text{H}^+]^2$, where $k_1 = 1.2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, $k_2 = 5 \times 10 \text{ M}^{-2} \text{ s}^{-1}$, and $k_3 = 9 \text{ M}^{-3} \text{ s}^{-1}$ at 25 °C, $I = 3.0 \text{ M}$, and $[\text{H}^+] = 0.1\text{--}3.0 \text{ M}$. We also determined the rate constant $k_{0(\text{H})}$ at hydrogen ion concentrations up to 3 M (see Table SI). Their

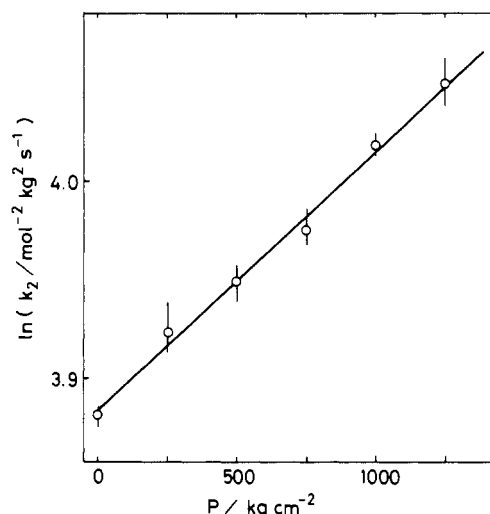


Figure 3. Pressure dependence of the third-order rate constant k_2 for the titanium(IV)-TPyP system ($C_{\text{Ti(IV)-TPyP}} = 5.8 \times 10^{-7} \text{ mol kg}^{-1}$, $C_{\text{H}_2\text{O}_2} = 5.42 \times 10^{-2} \text{ mol kg}^{-1}$, $[\text{H}^+] = 5.73 \times 10^{-2} \text{ mol kg}^{-1}$, $I = 1.05 \text{ mol kg}^{-1}$, 25 °C).

data agree with ours. However the ionic atmosphere of the 3 M perchloric acid solution should differ considerably from that of the perchlorate solution containing small amount of perchloric acid ($I = 3.0 \text{ M}$). Therefore, we disregarded data at $[\text{H}^+]$ higher than 1 M in Table SI, and kinetic data up to 1 M hydrogen ion concentration ($I = 3.0 \text{ M}$) were taken to analyze the reaction. Then the following rate equation was obtained missing the quadratic term in the hydrogen ion concentration: $k_{0(\text{H})} = k_1 + k_2[\text{H}^+]$.

The measured activation volume is the sum of an intrinsic part, $\Delta V_{\text{intr}}^\ddagger$, and an electrostrictive part, $\Delta V_{\text{el}}^\ddagger$.²⁰ $\Delta V_{\text{intr}}^\ddagger$ is the change in partial molar volume caused by bond making or bond breaking in the transition state and $\Delta V_{\text{el}}^\ddagger$ is the change in volume with variation of solvation. Because of the neutral charge of hydrogen peroxide, there seems to be little or no contribution of solvation change in the activation process. Therefore the negative value of activation volume in the k_1 path for both the oxotitanium(IV) and titanium(IV)-NTA systems strongly points to the associative mode of activation. This is in harmony with the negative value of activation entropy (Table I).

In the oxotitanium(IV) and titanium(IV)-TPyP systems the proton may assist the reaction by addition to the oxo group.²¹ The protonation at the oxo group is reflected in the decrease of both the activation enthalpy and entropy. The effect of the protonation must involve a small positive contribution to ΔV^\ddagger judging from the small partial molar volume of proton²² and

(20) Swaddle, T. W. *Coord. Chem. Rev.* **1974**, *14*, 217.

(21) (a) According to the equilibrium data^{21b} for H_2O_2 , $[\text{H}^+][\text{H}_2\text{O}_2] / [\text{H}_3\text{O}_2^+] = 10^3$, $[\text{H}^+][\text{HO}_2^-] / [\text{H}_2\text{O}_2] = 10^{-11.27}$, the reacting species under our experimental conditions is H_2O_2 . (b) Evans, M. G.; Uri, N. *Trans. Faraday Soc.* **1949**, *45*, 224.

(22) $\bar{V}^\circ(\text{H}^+) = -4.2 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$ (Millero, F. J. *J. Chem. Phys.* **1971**, *71*, 147).

(19) Nakagawa, T.; Oyanagi, Y. Program Library SALS (Statistical Analysis with Least-Squared Fitting), Nagoya University Computation Center, 1979.

the small electrostriction on the oxo group, as expected from its very weak basicity. Therefore the activation volume for the rate-determining step of the k_2 path is expected to be more negative than the measured value. Thus, for the oxotitanium(IV) and titanium(IV)-TPyP systems, the k_2 path should also be associatively activated with the transition state involving H₂O₂ bonded as a monodentate. The titanium(IV) ion in the metalloporphyrin is thought to lie at about 0.6 Å from the mean plane of the porphyrin skeleton, as shown for the titanium(IV)-OEP complex by an X-ray diffraction method.^{12a} Therefore the hydrogen peroxide molecule would approach the titanium(IV) ion from the side in which the oxo group lies. The geometry of the coordination of the peroxy group in the product should be the side-on type as found for the other titanium(IV) porphyrin complexes.¹²

According to the kinetic studies on the peroxy complex formation of the titanium(IV)-NTA, -DIPIC, and -IDA complexes,⁷ the kinetic parameters obtained in the pH range of 0–1.3 were very similar to those of the oxotitanium(IV) system. According to our kinetic study on the reaction of oxotitanium(IV) with hydrogen peroxide in the presence of excess MIDA¹⁰ ($C_{\text{MIDA}} = 1.00 \times 10^{-2}$ M, $C_{\text{Ti(IV)}} = 4.56 \times 10^{-5}$ M) in the pH range of 1–3, reaction rates were the same as in the absence of MIDA. This result indicates that the oxotitanium(IV) ion does not form the MIDA complex in this pH range. Therefore the results in the pH range of 0–1.3 given by Wieghardt et al.⁷ for the titanium(IV)-NTA, -DIPIC, and -IDA systems with no excess ligand should all correspond to those for the reaction of the oxotitanium(IV) ion with H₂O₂.

In the presence of a large excess of NTA and at pH 2.0–3.6, titanium(IV) combines with the NTA ligand and the titanium(IV)-NTA complex reacts with hydrogen peroxide to form the peroxy complex as shown in eq 2. In the k_1 path the negative activation volume of -19.0 cm³ mol⁻¹ is consistent with an associative mechanism as stated earlier. Meanwhile in the k_2 path, a proton may attach to the oxo group or to the carboxylate group of NTA in the complex. These two possibilities can be distinguished by the volume effect.

The reaction volume of about 13 cm³ mol⁻¹ is expected for the protonation of a carboxylate group.²³ Since the volume change due to the release of electrostriction of the hydrogen ion is accepted to be about 4 cm³ mol⁻¹,²² the volume effect by the release of electrostriction of the carboxylate anion is thought to be about 9 cm³ mol⁻¹. If the carboxylate partially dissociates from the titanium(IV) ion of the titanium(IV)-NTA complex, a large volume increase (ca. 30 cm³ mol⁻¹) should result by the carboxylate going out of the inner coordination sphere and a volume decrease (ca. -9 cm³ mol⁻¹) caused by the electrostriction on the carboxylate may be offset

to give a considerably large positive volume effect (ca. 21 cm³ mol⁻¹).

The above estimation is confirmed by the recent dynamic studies on EDTA complexes of Zn²⁺, Cd²⁺, Co²⁺, and alkaline-earth cations by an ultrasonic absorption method.²⁴ The reaction volume of the partial dissociation reaction of the hexacoordinate complex to form the pentacoordinate complex involving a coordinated water has been estimated to be ca. -5 cm³ mol⁻¹ for all these EDTA complexes. The molar volume of water is 18 cm³ mol⁻¹. Thus, the partial molar volume of the pentacoordinate complex is ca. 13 cm³ mol⁻¹ larger than that of the hexacoordinate complex.

If the dissociated carboxylate is protonated, the volume increase caused both by the protonated carboxylate going out of the inner coordination sphere and by the release of electrostriction of the hydrogen ion should lead to a large positive volume change (26–34 cm³ mol⁻¹). With the coordination of water molecule (18 cm³ mol⁻¹) to the vacant coordination site taken into account, the overall volume change will reduce to a smaller value (8–16 cm³ mol⁻¹).

On the other hand, the volume effect of protonation at the oxo group of the titanium(IV)-NTA complex must be small and positive as stated earlier. Assuming a large negative volume effect (ca. -19 cm³ mol⁻¹) caused by the entering of a hydrogen peroxide molecule into the inner sphere of the titanium(IV) ion in the activation process as in the k_1 path, the overall activation volume is expected to be negative. This is not consistent with the experimental value of 13.0 cm³ mol⁻¹.

The measured activation volume for the k_2 path in the titanium(IV)-NTA system can be regarded as the sum of the large positive volume effect due to the protonated carboxylate going out of the inner sphere of the central titanium(IV) ion and the negative volume effect caused by the penetration of the entering hydrogen peroxide into the inner sphere. Hence, the reaction mechanism for the k_2 path is also of the associative type. Entering of a hydrogen peroxide molecule will be facilitated by the dissociation of a carboxylate by protonation. To conclude, the reaction of these titanium(IV) complexes with H₂O₂ are all associatively activated.

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Registry No. 1·4H⁺, 85183-87-5; TiO(nta)(H₂O)⁻, 87495-19-0; Ti, 7440-32-6; H₂O₂, 7722-84-1.

Supplementary Material Available: Table SI giving rate constants under various conditions (4 pages). Ordering information is given on any current masthead page.

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