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Kinetic Studies on the Peroxo Complex Formation of Oxo(5,10,15,20-tetra-4-pyridylporphinato)titanium(IV) with Hydrogen Peroxide. Evidence for an Associative Mechanism

MASAHIKO INAMO, SHIGENOBU FUNAHASHI and MOTOHARU TANAKA

Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa Nagoya 464, Japan

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Dioxygen, superoxo, and peroxo complexes of transition metal ions have been the subject of extensive study. In particular, some of the current work is focused on metalloporphyrins because they are considered as model complexes of oxygen carrying and activating hemoproteins in biological systems [1–3]. Guilard *et al.* [4] have recently reported on the synthesis, stereochemistry and properties of oxotitanium(IV) and peroxotitanium(IV) complexes of 2,3,7,8,12,13,17,18-octaethylporphine and 5,10,15,20-tetraphenylporphine. Oxotitanium(IV) porphyrins react with hydrogen peroxide to form the corresponding peroxotitanium(IV) porphyrins. Geometry of the coordination of peroxo group at the central titanium(IV) ion is of the side-on type.

We are interested in the formation kinetics of peroxo complexes of transition metal ions in aqueous solution [5–10]. To extend our investigation to metalloporphyrins we newly synthesized water-soluble oxo(5,10,15-20-tetra-4-pyridylporphinato)-titanium(IV), TiO(tpyp), and studied the kinetics of the reaction of this metalloporphyrin with hydrogen peroxide in acidic aqueous solution at pressures up to 1250 kg cm^{-2} in order to elucidate the mechanism of the peroxo complex formation.

The composition of the complex in the crystalline state was determined by IR, NMR, and elementary analysis to be $\mathrm{TiO(tpyp)\cdot \frac{1}{2}CHCl_3\cdot \frac{1}{2}(CH_3CH_2)_2O}$. The chloroform and diethylether come from the mixed solvent of chloroform and diethylether used in recrystallization. The reaction studied is expressed as

$$\mathrm{TiO(tpypH_4)^{4+} + H_2O_2 \overset{K}{\rightleftharpoons} Ti(O_2)(tpypH_4)^{4+} + H_2O} \qquad (1)$$

Four pyridyl groups of the porphyrin are protonated in acidic aqueous solution. The composition of the peroxo complex was confirmed by the mol ratio method. The equilibrium constant, K, was determined to be 3.1×10^6 mol^{-1} dm^3 at 25 °C and I = 0.80 mol dm^{-3}.

TABLE I. Pressure Dependence of Rate Constant.[a]

Pressure/kg cm^{-2}	k/mol^{-2} kg^2 s^{-1}
1	48.5 ± 0.3
250	50.5 ± 1.5
500	51.9 ± 0.8
750	53.3 ± 0.7
1000	55.6 ± 0.3
1250	57.3 ± 1.5

[a] $[\mathrm{TiO(tpypH_4)^{4+}}] = 5.8 \times 10^{-7}$ mol kg^{-1}, $[\mathrm{H_2O_2}] = 5.42 \times 10^{-2}$ mol kg^{-1}, $[\mathrm{H^+}] = 5.73 \times 10^{-2}$ mol kg^{-1}, I = 1.05 mol kg^{-1} ((Na, H)$\mathrm{ClO_4}$), 25.0 °C.

In all kinetic experiments $\mathrm{H_2O_2}$ was used in large excess over TiO(tpyp) ($[\mathrm{H_2O_2}] = 2 \times 10^{-3}$–$5 \times 10^{-2}$ mol dm^{-3}, $[\mathrm{TiO(tpypH_4)^{4+}}] \cong 10^{-6}$ mol dm^{-3}). First-order plots were linear for at least 3 half-lives. First-order rate constants were exactly proportional to both hydrogen peroxide concentration and hydrogen ion concentration ($[\mathrm{H^+}] = 7 \times 10^{-3}$–$1 \times 10^{-1}$ mol dm^{-3}). The rate law is thus expressed as

$$d[\mathrm{Ti(O_2)(tpypH_4)^{4+}}]/dt = k[\mathrm{TiO(tpypH_4)^{4+}}][\mathrm{H_2O_2}][\mathrm{H^+}] \qquad (2)$$

From the values of rate constant, k, at 15, 20, 25, 30, and 35 °C and I = 1.00 mol dm^{-3}, the following activation parameters were obtained: k (25 °C) = 55.4 ± 0.5 mol^{-2} dm^6 s^{-1}, $\Delta H^\ddagger = 34.9 \pm 0.2$ kJ mol^{-1}, $\Delta S^\ddagger = -94.7 \pm 0.7$ J mol^{-1} K^{-1}. According to the transition state theory the change in rate constant with pressure, P, is related to the activation volume, $\Delta V^\ddagger$: $(\partial \ln k/\partial P)_T = -\Delta V^\ddagger/RT$. High-pressure stopped-flow technique was used to follow the fast reactions under various pressures [11, 12]. Values of rate constants under various pressures are tabulated in Table I. Since logarithmic rate constants are linearly related with pressure, the activation volume is assumed to be independent of pressure. The rate constant at zero pressure and the activation volume were determined to be 48.6 ± 1.0 mol^{-2} kg^2 s^{-1} and −3.3 ± 0.2 cm^3 mol^{-1}, respectively, at 25 °C and I = 1.05 mol kg^{-1}.

From the above termolecular rate law (2), this reaction is thought to be a bimolecular reaction which is preceded by the pre-equilibrium of protonation at oxygen atom of the oxotitanium group of $\mathrm{TiO(tpypH_4)^{4+}}$. Activation volume is very useful in diagnosing the mechanism. The measured activation volume is the sum of an intrinsic part, $\Delta V^\ddagger_{\mathrm{int}}$, and an electrostrictive part, $\Delta V^\ddagger_{\mathrm{el}}$ [13]. In the present case, since hydrogen ions may attach to the oxygen atom of the oxotitanium group in the pre-equilibrium, the

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release of electrostriction of hydrogen ion causes a small positive volume change [14]. Because of the neutral charge of H_2O_2 there seems to be little or no contribution of solvation changes in the transition state. Therefore, the overall negative value of activation volume of -3.3 cm^3 mol^{-1} strongly indicates the insertion of a hydrogen peroxide molecule into the inner coordination sphere of central titanium(IV) ion in the activation process. The activation mode of the reaction should be associative. This is consistent with the large negative value of activation entropy.

Further investigation on metalloporphyrins of the other early transition metal ions are in progress and will be directed toward a more complete elucidation of the reaction mechanism of these reactions.

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