Direct Evidence for the Peroxo Substitution of the Oxo Group in the Oxotitanium(IV) Porphyrin Complex in the Aqueous Solution

Masahiko Inamo, Shigenobu Funahashi,† and Motoharu Tanaka†,*
Department of Chemistry, Faculty of Education, Aichi University of Education, Kariya 448
†Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

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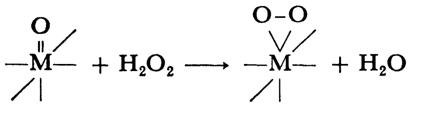
Synopsis. Labeling experiments for IR and NMR spectra of oxo- and peroxotitanium(IV) complexes show that the oxo group of oxotitanium(IV) porphyrin is fully substituted by a peroxo group in the course of the reaction with hydrogen peroxide in the aqueous solution, i.e. the O-O bond of H_2O_2 remains intact in the peroxo complex.

In recent years interests have been focused on dioxygen complexes of transition metals for their interesting features as catalysts, reagents, or key intermediates of selective oxidation involving molecular oxygen, hydrogen peroxide, or alkyl hydroperoxide.[1] Of the high valent d^0 transition metal complexes, those of molybdenum(VI), vanadium(V), and titanium(IV) complexes are especially known to play an important role in the oxidation by peroxide species.[2] The exchange of oxygen atoms bound to the central metal ion has been investigated in order to elucidate the mechanisms of the catalytic action of these metal complexes. Modena et al. have reported that the oxygen exchange between the oxo and peroxo groups occurs in complexes containing both oxo and peroxo moiety,[3] while controversy still surrounds the mechanisms of these reactions.[4]

We have been interested in the formation of peroxo complexes in the aqueous solution and studied the kinetics of these reactions.[5] Oxo complexes of early transition metal ions react with hydrogen peroxide to give rise to the corresponding peroxo compounds with release of a water molecule:



$$\overset{\mathrm{O}}{\underset{/|}{\overset{\|/}{-\mathrm{M}-}}} + H_2O_2 \longrightarrow \overset{\mathrm{O-O}}{\underset{/|}{\overset{\backslash/\,/}{-\mathrm{M}-}}} + H_2O \qquad (1)$$

In these oxo-peroxo substitution reactions there are two possibilities: (1) The oxo group in the reactant is fully substituted by the peroxo group in hydrogen peroxide, i.e. the O-O bond of H_2O_2 remains intact in the peroxo compound, and (2) the peroxo group in the product results from both the oxo complex and hydrogen peroxide. There is, however, no direct evidence to distinguish whether the oxo group in the reactant or the oxygen atom in hydrogen peroxide is released as a water molecule. In general, oxygen exchange between the oxo complex and water in aqueous solution, i.e. oxo-oxo substitution, is very slow in comparison with the oxo-peroxo substitution[6] and mostly their rates are dependent on hydrogen ion concentration.[7,8] The latter substitution reaction has been studied on the titanium(IV) porphyrins in the organic solvent.[9] Little is known, however, about the mechanisms of this type of reaction in the aqueous solution. In this paper we will discuss the mechanism of the oxo-peroxo substitution reaction of titanium(IV) porphyrin in the aqueous solution.

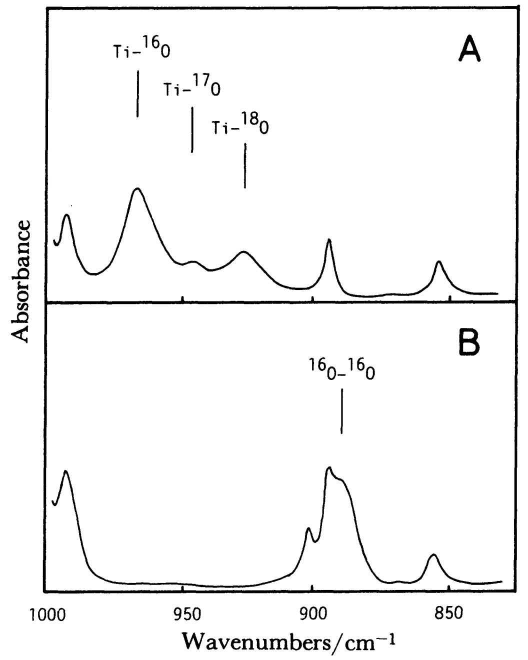


Fig. 1. Infrared spectra of ^{17}O- and ^{18}O-enriched TiO(tpyp) (A) and its peroxo derivative, $Ti(O_2)(tpyp)$ (B), both recorded in absorbance mode. Scales of the ordinate are in arbitrary unit. The IR spectra were obtained by subtracting the spectrum of chloroform from that of the chloroform solution of each complex.

Oxotitanium(IV) porphyrin, TiO(tpyp) (tpyp:5,10,15,20-tetra-4-pyridylporphine) was prepared according to the method described previously.[5c] Isotopically enriched water was purchased from C.E.A.-C.E.N.-Saclay: 35.8 wt% $^{16}OH_2$, 20.2 wt% $^{17}OH_2$, 44.0 wt% $^{18}OH_2$. The mixture involving 10 g of 0.012 mol kg^{-1} chloroform solution of TiO(tpyp) and 0.2 g of isotopically enriched water stood for ten days at 100°C in a sealed glass tube. The infrared spectrum of ^{17}O and ^{18}O labeled complex TiO*(tpyp) in chloroform, measured on a Nicolet MX-1 FT-IR spectrometer, shows three peaks due to titanium-oxygen stretching vibration (Fig. 1A); 966.5 cm^{-1} (Ti-^{16}O), 945.5 cm^{-1} (Ti-^{17}O), and 927.1 cm^{-1} (Ti-^{18}O). The measured IR spectrum was simulated to estimate the isotopic composition of the oxygen atom in TiO(tpyp) on the assumption that the absorption bands are Lorentzian and that the band widths are the same for these three peaks. The oxo group consists of 67.2% of ^{16}O, 9.2% of ^{17}O, and 23.4% of ^{18}O. Therefore 50% of oxygen

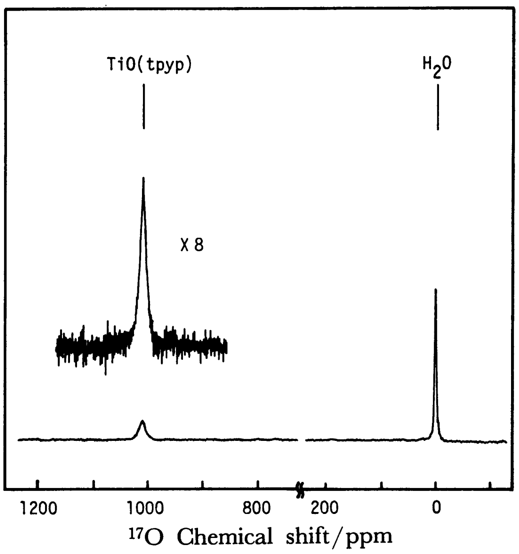


Fig. 2. 13.51-MHz ^{17}O NMR spectrum of TiO(tpyp). Chemical shifts were measured relative to the internal water. In the area of water is seen only one peak because of the proton noise decoupling.

atom of TiO(tpyp) exchanged with that of labeled water present in large excess over the complex under the present experimental conditions. Figure 2 shows the ^{17}O NMR spectrum of Ti^{17}O(tpyp) in a 2.7×10^{-2} mol kg^{-1} chloroform solution at room temperature, recorded on a JEOL FX-100 spectrometer (δ=1010 ppm, $\nu_{1/2}$=186 Hz). The extent of the oxygen exchange estimated by the integration of the ^{17}O NMR spectrum is consistent with that evaluated from the IR spectrum.

The oxo-peroxo substitution reaction in aqueous solution was accomplished by the following procedure. The titanium(IV) porphyrin complex, TiO(tpyp), is soluble in acidic aqueous solution as $[TiO(H_4tpyp)]^{4+}$, where H$_4$tpyp represents porphyrin ligand of which four pyridyl groups are protonated. The isotopically labeled complex was extracted from the chloroform solution to the aqueous phase at pH 1.7, and then hydrogen peroxide was added to the aqueous phase to perform the oxo-peroxo substitution. As soon as the reaction proceeded completely (<1 min),[10] the produced peroxo complex, Ti(O$_2$)(tpyp), was again extracted into the chloroform phase by neutralizing the acidic aqueous solution with sodium carbonate. This procedure can be carried out within 15 min. Addition of diethyl ether to the chloroform solution yielded the Ti(O$_2$)(tpyp) crystals. The infrared spectrum of the peroxo complex thus obtained is the same as that synthesized from nonlabeled TiO(tpyp) (See Fig. 1B). This fact indicates that this procedure afforded the nonlabeled peroxo complex. On the other hand, the control experiment showed that both oxygen exchange reactions between $[TiO^*(H_4tpyp)]^{4+}$ and bulk water and between $[Ti(O_2)(H_4tpyp)]^{4+}$ and bulk H$_2$O* in acidic aqueous solution do not occur to a significant extent (<10%) for a period of 15 min under the present experimental conditions. Consequently it is concluded that the oxo group of $[TiO(H_4tpyp)]^{4+}$ is fully substituted by hydrogen peroxide to give the peroxo complex in which the oxygen atoms come entirely from H$_2$O$_2$ as shown by Eq. 2.

$$[TiO^*(H_4tpyp)]^{4+} + H_2O_2 \longrightarrow [Ti(O_2)(H_4tpyp)]^{4+} + H_2O^* \qquad (2)$$

This substitution process includes both the entering of hydrogen peroxide into the inner sphere of the central titanium(IV) ion and the leaving of the oxo group which should be expelled as water or hydroxide ion. Since the titanium(IV) atom lies about 0.6 Å above the mean plane of the porphyrin skeleton toward the oxo group in the case of oxotitanium(IV) octaethylporphine in the crystalline state,[11] the similar situation will prevail in solution. In our previous paper,[5a] the associative mode of activation has been proposed for the reaction of titanium(IV) porphyrin with hydrogen peroxide on the basis of the kinetic feature, and we have put forward the acid-base catalyzed mechanism for the oxo-peroxo substitution which would include some assistance of hydrogen bonding between the oxo group of the complex and the hydrogen atom of hydrogen peroxide in the transition state. Such a mechanism is now strongly supported by the present work.

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