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Spectrophotometric Study on the Complex Formation of Hydroperoxide with Tetraphenylporphyrin Cobalt(II)

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The rate constants, activation energies, activation entropies and equilibrium constants for the coordination of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide (THP), 1-methyl-1-phenylethyl hydroperoxide (CHP) and *t*-butyl hydroperoxide (BHP) to para-substituted tetraphenylporphyrin Co(II), Co(*p*-X)TPP (X=OCH_3, H, Cl) were obtained by the visible spectral method at 235—245 K. The rate constants of coordination were $k=0.097—2.03\times10^2$ $M^{-1}\,s^{-1}$, the equilibrium constants being $K=0.692—2.5\times10^{-6}$ M^{-1}. As a *para*-substituent effect on k and K, the constants were found to increase with increase in the electron donating property of the substituent group. They also depend on the kind of hydroperoxide, the rate constants decreasing in the order $k_{THP}>k_{CHP}>k_{BHP}$, and the equilibrium constants in the order $K_{CHP}>K_{BHP}>K_{THP}$. Activation energies were 7.0—7.8 kcal mol^{-1} and activation entropies −21— −25 cal K^{-1}. No spectral change by the addition of hydroperoxide to CuTPP and NiTPP was observed.

The decomposition reaction of hydroperoxide catalyzed by transition-metal ion proceeds by the redox reaction[1] of transition-metal ion which has two valences. The reaction seems to consist of three steps, (a) coordination of hydroperoxide molecule to a metal ion, (b) migration of electron from metal ion to hydroperoxide followed by the cleavage of O–O bond of hydroperoxide, and (c) release of the fragmentation products from a metal ion.

Formation of the hydroperoxide–metal ion complex has been anticipated in many kinetic studies[2–8] since George[9] *et al.* proposed its formation. Richardson[10] reported evidence of the formation for the first time using NMR and visible spectral methods. Some qualitative studies using spectral method had been reported until 1971 when Bulgakova *et al.*[11] Svitych *et al.*[12,13] worked out quantitative studies.[11–13] They reported equilibrium constants and enthalpy of formation of hydroperoxide–metal ion complex using NMR method at low temperature.

In this report, tetraphenylporphyrin metal(II) complex was chosen because of its intense absorbance at the Soret band 410—420 nm, being sensitive to the change of coordination number. The coordination reaction was followed by the decrease of the Soret band using the visible spectra method at 235—245 K. The kinetic and thermodynamic data were calculated from experimental data and the results discussed in terms of the effects of *para*-substituent group, hydroperoxide, and central metal ion.

Experimental

Materials. The *para*-substituted tetraphenylporphyrin free bases $H_2(p\text{-}X)TPP$ (X=OCH_3, H, Cl),[14] Co(*p*-X)TPP and CuTPP,[15] and NiTPP[16] were prepared according to reported methods. The products were chromatographed on silica gel four or five times using chloroform in each step. The visible spectra of Co(*p*-X)TPP, CuTPP, and NiTPP were very similar to those reported. 1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide (THP) was prepared by the autoxidation of tetralin and crystallized from heptane.[17] Reagent grade 1-methyl-1-phenylethyl hydroperoxide (CHP) and *t*-butyl hydroperoxide (BHP) (Nippon Oils and Fats Co.) were purified and spectral grade dichloromethane was dried before use.

Measurements. Spectrophotometric measurements were carried out on a JASCO-UVIDEC-1 spectrophotometer equipped with a cryostat (type DN-704, Oxford Instrument Co.) in which a quartz cell was set at prescribed temperature within ±0.05 °C with a controller. Both the solution of M(II)TPP (2 ml) in cell and that of hydroperoxide (0.5 ml) in an injector set above the solution of M(II)TPP were cooled to the reaction temperature. Reaction was started when the solution of hydroperoxide was poured into the cell, and followed by measuring the decrease in the Soret band of M(II)TPP. The solution in the cell was stirred throughout the reaction with a magnetic stirrer set under the cryostat.

Results and Discussion

Spectral Chenges. A typical spectral change of Co(*p*-H)TPP with the addition of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide is shown in Fig. 1. There are three patterns in spectral changes according to the

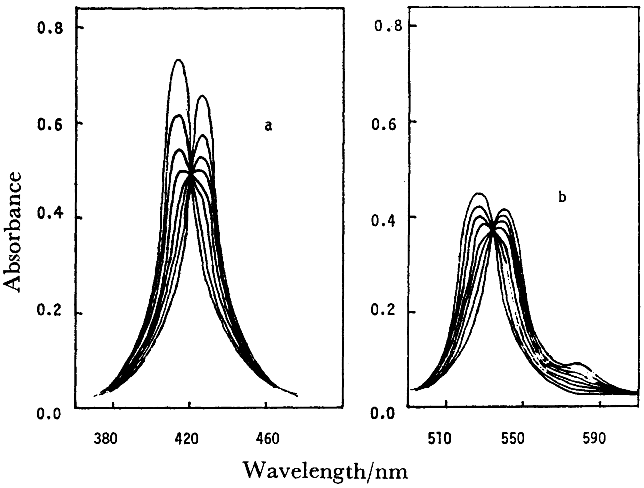

Fig. 1. Visible spectral change observed upon addition of THP to a solution of Co(*p*-H)TPP.
a) [Co(*p*-H)TPP]$=2.1\times10^{-6}$ M, [THP]$=2.1\times10^{-6}$ M, b) [Co(*p*-H)TPP]$=5.0\times10^{-5}$ M, [THP]$=5.0\times10^{-5}$ M in CH_2Cl_2 at 235 K.

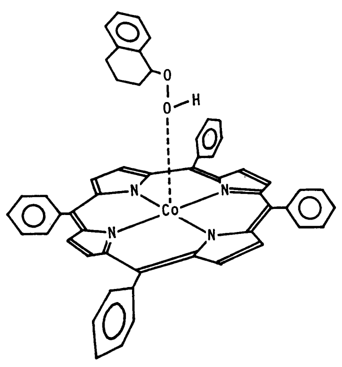

Fig. 2. Supposed structure of hydroperoxide–Co(p-H)-TPP complex.[24)]

reaction temperatures. At 235 K, the Soret band (414 nm) of Co(p-H)TPP decreased with the addition of hydroperoxide, a new absorption band (427 nm) appearing. The isosbestic point at 417 nm is sharp, the decomposition reaction of hydroperoxide being negligible at this temperature. It can be assumed that the new absorption band (427 nm) results from the hydroperoxide–Co(p-H)TPP complex (Fig. 2). Similar spectral changes take place when pyridine or t-butyl alcohol is added to Co(p-H)TPP in line with the published data.[16,18)] Absorption of the Q band (527 nm) also decreased, a new band (540 nm) appearing (Fig. 1). This spectrum is similar to that of Co(III)TPP.[21)]

Rise in temperature from 250 K to 265 K gave rise to a new spectral change. A new absorption band (427 nm) decreased, accompanied by the temporary appearance of 414 nm band, giving a new absorption band (432 nm). Further rise in temperature from 265 K to 295 K made the absorption decrease and disappear.

Kinetic and Thermodynamic Data. Figure 3 shows the decay curve of the Soret band (414 nm) of Co(p-H)TPP caused by the addition of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide. The rate of decrease became slow, reaching an equilibrium state within 30 min after the reaction started. In the case of 1-methyl-1-phenylethyl hydroperoxide or t-butyl hydroperoxide, the initial rate was lower than that of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide, taking a long time to reach an equilibrium state. The results are plotted as a second-order reaction, the initial rate constant being calculated (Fig. 4). Activation energies were evaluated (Fig. 5) from the temperature dependance of the initial rate constant in the temperature range 235—245 K.

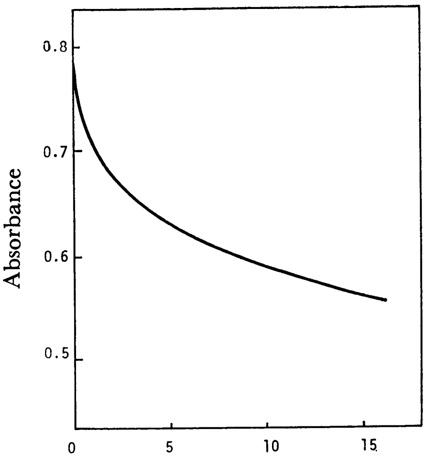

Fig. 3. Absorption decay curve of Co(p-H)TPP at 414 nm.
[Co(p-H)TPP]=2.1×10^{-6} M, [THP]=2.1×10^{-6} M, in CH_2Cl_2 at 235 K.

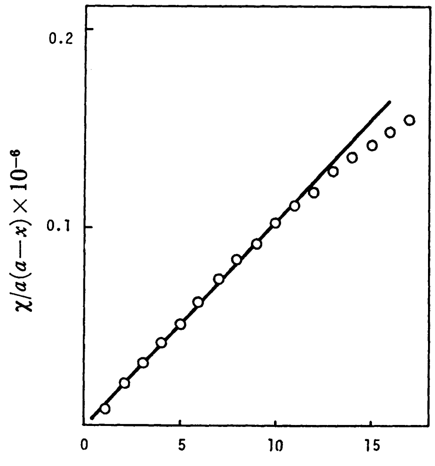

Fig. 4. Second-order plot for formation of Co(p-H)TPP–THP complex.
a=[Co(p-H)TPP]=2.1×10^{-6} M, [THP]=2.1×10^{-6} M in CH_2Cl_2 at 235 K.

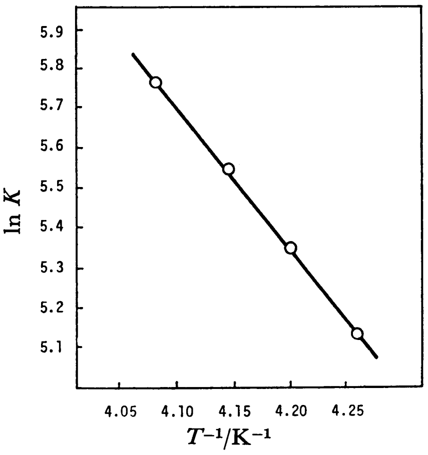

Fig. 5. Temperature dependence of rate constant for formation of Co(p-H)TPP–THP complex.
[Co(p-H)TPP]=2.1×10^{-6} M, [THP]=2.1×10^{-6} M.

The kinetic and thermodynamic data of the coordination of hydroperoxide to M(II)TPP are given in Table 1. The rate constants and equilibrium constants increased with the increase in electron donating property of substituent group of Co(p-X)TPP in all hydroperoxides.

Table 1. Rate constants, activation energies, activation entropies, and equilibrium constants for coordination of hydroperoxide to M(II)TPP

M(II)TPP	ROOH	k/M^{-1} s^{-1}	ΔE/kcal mol^{-1}	ΔS/cal K^{-1}	K/M^{-1}
Co(p-Cl)TPP	THP	1.32×10^2	7.2	-22	6.92×10^5
Co(p-H)TPP	THP	1.67×10^2	7.1	-22	8.31×10^5
Co(p-OCH$_3$)TPP	THP	2.03×10^2	7.3	-21	1.12×10^6
CuTPP	THP	0.00			
NiTPP	THP	0.00			
Co(p-Cl)TPP	CHP	2.53×10	7.5	-24	1.62×10^6
Co(p-H)TPP	CHP	3.20×10	7.3	-24	2.09×10^6
Co(p-OCH$_3$)TPP	CHP	4.05×10	7.0	-25	2.51×10^6
CuTPP	CHP	0.00			
NiTPP	CHP	0.00			
Co(p-Cl)TPP	BHP	0.97×10	7.8	-24	1.12×10^6
Co(p-H)TPP	BHP	1.27×10	7.5	-25	1.38×10^6
Co(p-OCH$_3$)TPP	BHP	1.56×10	7.6	-24	1.74×10^6
CuTPP	BHP	0.00			
NiTPP	BHP	0.00			

[M(II)TPP]=2.1×10^{-6} M, [ROOH]=2.1×10^{-6} M, 235 K, in CH$_2$Cl$_2$. THP=1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide, CHP=1-methyl-1-phenylethyl hydroperoxide, BHP=t-butyl hydroperoxide.

Table 2. Comparison of oxidation potentials with rate constants and equilibrium constants for M(II)TPP

M(II)TPP	M(II)→ M(III)/V	$k^{c)}$/M^{-1} s^{-1}	$K^{c)}$/M^{-1}
Co(p-Cl)TPP	0.75[a)]	1.32×10^2	6.92×10^5
Co(p-H)TPP	0.58[a)]	1.67×10^2	8.31×10^5
Co(p-OCH$_3$)TPP	0.62[a)]	2.03×10^2	1.12×10^6
CuTPP	—[b)]	0.00	
NiTPP	1.00[b)]	0.00	

a) Ref. 19. b) Ref. 21. c) [M(II)TPP]: [THP]=1: 1, 235 K.

Fairly good correlations are observed between the oxidation potentials[19)] and the rate constants or the equilibrium constants of Co(p-H)TPP (Table 2). The oxidation potential of metal ion seems to be an important factor affecting the two constants. This substituent effect is similar to that found in Co(p-H)TPP·py+O$_2\rightleftarrows$Co(p-H)TPP·py(O$_2$) system studied in detail by Walker *et al.*[20)] In the case of NiTPP, its too large oxidation potential[21)] would prevent the coordination of hydroperoxide molecules. CuTPP showed no spectral change because of difficulty for it to take the five-coordination structure as judged from its stability constant. No activity in the decomposition of hydroperoxide on NiTPP and CuTPP can be attributed to the difficulty in coordination.

The rate constants and equilibrium constants change with the kind of hydroperoxide (Table 1). The order of rate constant k is $k_{\mathrm{THP}}>k_{\mathrm{CHP}}>k_{\mathrm{BHP}}$, and the order of equilibrium constant K is $K_{\mathrm{CHP}}>K_{\mathrm{BHP}}>K_{\mathrm{THP}}$ in hydroperoxide–Co(p-X)TPP (X=OCH$_3$, H, Cl) systems. A comparison of the half-wave potential[22)] of hydroperoxide with the rate constant or equilibrium constant is given in Table 3. Except for the case of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide having a larger k and a smaller K than those expected from its half-wave potential, the orders $k_{\mathrm{CHP}}>k_{\mathrm{BHP}}$ and $K_{\mathrm{CHP}}>K_{\mathrm{BHP}}$ can be explained by the order of half-wave potential of hydroperoxide, $E_{1/2}$(CHP)$>E_{1/2}$(BHP). The higher half-wave potential which indicates the energy level of LUMO (Lowest Unoccupied Molecular Orbital) of O–O bond in hydroperoxide[23)] would give a larger rate constant or larger equilibrium constant. The steric factor is attributable to the deviation in the case of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide. A configuration of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide more favorable to Co(II) ion than that of other two hydroperoxides might bring forth a larger constant k. This is in line with the smallest activation entropy of this system. The activation energies for coordination reaction of hydroperoxide to Co(p-X)TPP are 7.0—7.8 kcal mol^{-1}, which is reasonable in view of the activation energy 15—25 kcal mol^{-1} of the decomposition reaction of hydroperoxide. The activation entropies are -21—-25 cal K^{-1}, in line with the formation reaction hydroperoxide–Co(p-X)TPP complex.

It is difficult to obtain the rate constant and the activation energy in the decomposition reaction of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide by Co(p-X)TPP at a temperature above 10 °C since the reaction proceeds too fast and the catalytic activity decreases within 30 s, the colored solution of Co(p-X)-TPP preventing accurate iodometry.

Table 3. Comparison of half-wave potentials with rate constants and equilibrium constants for ROOH

ROOH	$E^{a)}{}_{1/2}$/V	$k^{b)}$/M^{-1} s^{-1}	$K^{b)}$/M^{-1}
BHP	-0.96	1.27×10	1.38×10^6
THP	-0.73	1.67×10^2	8.31×10^5
CHP	-0.68	3.20×10	2.09×10^6

a) Ref. 22. b) [Co(p-H)TPP]: [ROOH]=1: 1, 235 K.

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