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# Electrochemical and Spectroscopic Studies of α,β,γ,δ-Tetrakis-[1-(2-hydroxyethyl)pyridinium-4-yl]porphine and Its Metal Complexes

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The preparation and properties of a water soluble porphyrin having functional groups, α,β,γ,δ-tetrakis[1-(2-hydroxyethyl)pyridinium-4-yl]porphine, are described. This porphyrin is water soluble from below pH 0 to above pH 14. Acid-base titration revealed the diprotonated diacid-monocation equilibrium ($pK_4=1.0$) and the monocation-free base equilibrium ($pK_3=1.9$) in the acidic range and the free base-monoanion equilibrium ($pK_2=13.0\pm0.2$) in the basic region. The zinc, iron, and cobalt derivatives of the porphyrin were also synthesized and purified. Catalytic properties of the iron and cobalt complexes for reduction of molecular oxygen in water are reported in terms of cyclic voltammetry. The electrochemical reduction utilizing these complexes was interpreted to proceed *via* electrochemical catalytic regeneration mechanism as had been observed for tetrakis(1-methylpyridinium-4-yl)porphinatoiron(III). The apparent rate constants for electron transfer from the iron and cobalt porphyrins to oxygen were estimated to be $3—4\times10^7$ and $1\times10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$, respectively.

Since its magnificent achievement[1)] by Hans Fischer as long as a half century ago, porphyrin synthesis has been constantly of primary importance among many investigators. Hitherto various porphyrin skeltons occurring naturally have been synthesized, and the use of modified or newly prepared porphyrins with simpler structure has accumulated ample information for various purposes.[2)] Especially recent advent of water soluble porphyrins accelerated a new field to open in their chemistry. Their demand is expanding not only as model compounds related to living body but also from industrial point of view. Recently, in relation to the study to find effective energy conversion/storage systems such as fuel cells, an eminent catalytic capability of α,β,γ,δ-tetrakis(1-methylpyridinium-4-yl)porphinatoiron(III) (Abbr; Fe$^{\text{III}}$TmP) has attracted attention[3,4)] for the reduction of molecular oxygen to hydrogen peroxide.

In this paper, preparation and spectroscopic properties of a new water soluble porphyrin having hydroxyl groups, α,β,γ,δ-tetrakis[1-(2-hydroxyethyl)pyridinium-4-yl]porphine (Abbr; ThoepyP), and its zinc, iron and cobalt derivatives (Abbr; Zn$^{\text{II}}$ThoepyP, Fe$^{\text{III}}$ThoepyP, and Co$^{\text{III}}$ThoepyP, respectively) are reported. Catalytic aspects of Fe$^{\text{III}}$ThoepyP and Co$^{\text{III}}$ThoepyP for the reduction of molecular oxygen to hydrogen peroxide are also presented in terms of cyclic voltammetry, in comparison mainly with the results reported for Fe$^{\text{III}}$TmP[3)] and iron and cobalt tetrakis(*o*-aminophenyl)porphines (Abbr; Fe$^{\text{III}}$TapP and Co$^{\text{III}}$TapP, respectively).[5)]

## Experimental

*Materials.* Most of the chemicals were commercially available guaranteed reagents and used without further purification. 2-iodoethanol was prepared from 2-chloroethanol and excess sodium iodate in dry acetone under reflux. 0.05 M Sulfuric acid (abbr; $H_2SO_4$) for cyclic voltammetric experiments was obtained from $H_2SO_4$ and doubly distilled water. Glassy carbon electrodes (area 0.785 cm$^2$) were purchased from Tokai Carbon Co. Ltd. and polished to a bright surface with alumina powder (final polish using 0.05 μm particle size), washed with 0.05 M $H_2SO_4$ and distilled water.

*α,β,γ,δ-Tetrakis[1-(2-hydroxyethyl)pyridinium-4-yl]-porphinatozinc*(II) *Tetraiodide, Zn$^{\text{II}}$ThoepyP.* α,β,γ,δ-Tetra-4-pyridylporphinatozinc (II), Zn$^{\text{II}}$TpyP, was prepared by the method of Fleischer.[6)] *N*-Hydroxyethylation was accomplished accoriding to the same method of *N*-methylation[7)] using *ca.* 300 molar excess of 2-iodoethanol, although reaction time was 2 d rather than 10 h.[8)] Yield 54%. Found: C, 41.91; H, 3.39; N, 7.91%. Calcd for $Zn_1C_{48}H_{44}N_8O_4I_4$: C, 42.09; H, 3.24; N, 8.18%.

*α,β,γ,δ-Tetrakis[1-(2-hydroxyethyl)pyridinium-4-yl]porphine Hexachloride, ThoepyP.* The *N*-hydroxyethylated diacid was prepared by stirring 2.36 g of Zn$^{\text{II}}$ThoepyP in 600 cm$^3$ of 1.5 M $H_2SO_4$. When the dark blue solid dissolved to form a green solution, 190 g of sodium perchlorate was added, immediately producing a green precipitate of perchlorate salt. The mixture was refrigerated for 12 h and the precipitate was isolated by filtration, half dried in air, and acetone was added to the still moist product to wash away extra sodium perchlorate. The residue was dissolved in distilled water and imposed on an anion-exchange resin (Dowex 2X-8, Cl form) to get chloride salt solution, which was evaporated to dryness. The crude solid was recrystallized from water-methanol-ether. Drying at 110 °C for 14 h left 1.12 g (69%) of a solid. Found: C, 56.21; H, 4.61; N, 10.37%. Calcd for $C_{48}H_{48}N_8O_4Cl_6$: C, 56.99; H, 4.59; N, 11.08%.

*α,β,γ,δ-Tetrakis[1-(2-hydroxyethyl)pyridinium-4-*yl]*-porphinatodiaquairon(III) Pentachloride, Fe$^{\text{III}}$ThoepyP.* ThoepyP 400 mg (0.425 mmol) and *ca.* 600 mg of $FeCl_2\cdot nH_2O$ were heated at reflux in water (50 cm$^3$) for 0.5 h, when metal incorporation was ascertained from absorption spectra in 450—700 nm region. The addition of 30 g of $NaClO_4$ caused dark brownish solution of the perchlorate salt of the aiming compound. The solution was chilled in a refregirator for 12 h and the product was collected on a funnel and washed with acetone containing 10 (v/v) percent ether to remove $FeCl_2\cdot nH_2O$ and $NaClO_4$. To further separate those concomitant inorganic salts more perferctly from the porphyrin, the crude solid was dissolved in a distilled water and imposed on a Sephadex LH-20 column. The elute was then passed through ion-exchange resin (Dowex 2X-8, Cl form) to get chloride salt. After evaporation of water, drying at 110 °C for 12 h left 211 mg (48.3%) of the dark bluish solid. Found: C, 53.63; H, 4.65; N, 10.27%. Calcd for $Fe_1C_{48}H_{44}N_8O_4Cl_5(H_2O)_2$: C, 54.08; H, 4.54; N, 10.51%.

*α,β,γ,δ-Tetrakis[1-(2-hydroxyethyl)pyridinium-4-yl]porphinatodiaquacobalt(III) Pentachloride, Co$^{III}$ThoepyP.* Cobalt was incorporated into the porphyrin ring by refluxing water solution containing *ca.* 500 mg of $CoCl_2 \cdot 6H_2O$ and 300 mg (0.319 mmol) of ThoepyP for 2 h. Then the solution was treated in a manner described for Fe$^{III}$ThoepyP. Drying at 110 °C for 15 h in a reduced pressure left 119 mg (35%) of a bluish purple solid. Found: C, 52.44; H, 4.71; N, 10.10%. Calcd for $Co_1C_{48}H_{44}N_8O_4Cl_5(H_2O)_2$: C, 53.92; H, 4.53; N, 10.48%.

*Measurement.* Absorption spectra were measured with a JASCO UVIDEC-1 spectrophotometer. Cyclic potential sweeps were generated by an NF Circuit Design Block FG-100AD function generator in conjunction with a potentiostat which was home-made according to the literature.[9] Nitrogen 99.9% pure was used for dearation of all solutions, and 5 min of air bubbling was conducted in order to saturate a solution with oxygen. Potentials were referred to a saturated calomel electrode (SCE). pH values were measured with a Hitachi-Horiba M-7 pH meter.

## Results and Discussion

*Spectroscopy.* Because of the presence of four hydroxyl groups and four quaternary ammonium groups, ThoepyP is highly water soluble from pH 0 to above 14 and slightly soluble even in methanol or ethanol. Spectrophotometric titrations were used to determine the acid-base equilibria present.

TABLE 1. ABSORPTION MAXIMA AND EXTINCTION COEFFICIENTS OF ThoepyPs AND SOME OF ITS COMPLEXES IN WATER

| Compound | pH of medium | Absorption maxima/nm | Extinction coefficient ($10^{-3}$) |
|---|---|---|---|
| Free base | 5.64 | 422 | 202 |
| | | 519 | 12.9 |
| | | 557 | 7.0 |
| | | 583 | 6.9 |
| | | 641 | 2.7 |
| Diacid | 0.0 | 447 | 101 |
| | | 593 | 8.2 |
| | | 642 | 9.9 |
| Monoanion | 14.0 | 448 | 53.5 |
| | | 578 | 8.3 |
| | | 622 | 6.3 |
| Zn$^{II}$ThoepyP | 5.64 | 439 | 159 |
| | | 563 | 15.2 |
| | | 606 | 5.3 |
| Fe$^{III}$ThoepyP | 5.64 | 422 | 84.4 |
| | | 519 | 9.3 |
| | | 580(shoulder) | 4.4 |
| | | 638 | 3.5 |
| Co$^{III}$ThoepyP | 5.64 | 435 | 184 |
| | | 548 | 16.9 |

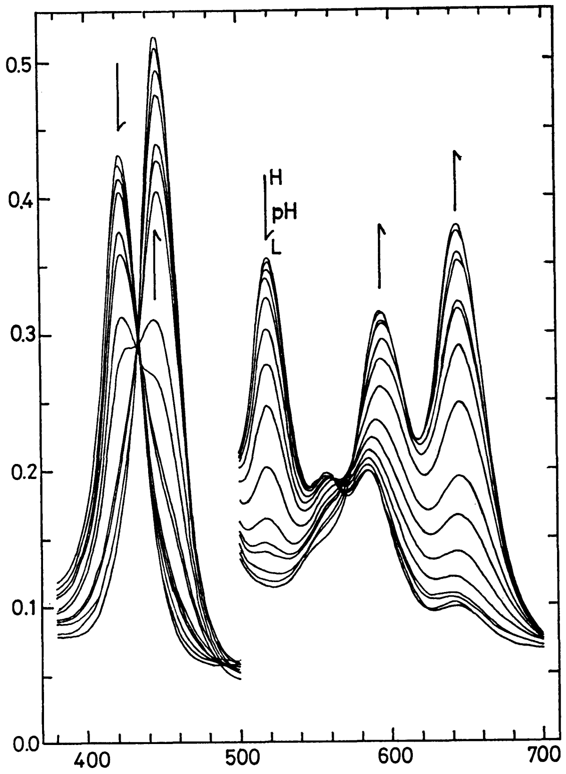

Fig. 1. Absorption spectra of ThoepyP when titrated with $HNO_3$ at $\mu=2.0$ ($NaNO_3$). The spectra are from pH 4.3 to 0.3. The Soret was run in 1 mm cells and visible in 10 mm cells, at the same concentration of ThoepyP ($2.13\times10^{-5}$ M). Temperature=21 °C

*Equilibria at* pH *0—7*: Table 1 lists the main absorption maxima and extinction coefficients of ThoepyP at various pH values, as well as those of some metallated derivatives at neutral pH value. The four bands in the visible region from pH 4 to 7 were independent of pH value. Beer's law experiments ($2\times10^{-4}$—$3.7\times10^{-6}$ M (1 M=1 mol dm$^{-3}$)) conducted using the 447 and 422 nm bands at pH 0 and 7, respectively, gave linear plots at both wavelength maxima, indicating that the diacid and free base forms of the *N*-hydroxyethylated porphine are probably monomeric. Figure 1 shows spectrophotometric titrations from 380 to 700 nm of ThoepyP with nitric acid at ionic strength 2.0 ($NaNO_3$) at 21 °C. Seemingly one isosbestic point (435 nm) appeared in the Soret region, however, two isosbestic points were observed in the visible region at 562 and 575 nm corresponding to pH 4.3 to 1.6 and 1.5 to 0.3, respectively. Accordingly more than two protonated porphyrin species must be present between pH 0.3 and 4. Assuming that these species are to be diprotonated diacid ($H_4P^{2+}$), monocation ($H_3P^+$) and free base ($H_2P$), and that diacid-monocation, and monocation-free base equilibria

$$H_4P^{2+} = H_3P^+ + H^+ \qquad K_4 \qquad (1)$$

$$H_3P^+ = H_2P + H^+ \qquad K_3 \qquad (2)$$

are present and neglecting deviation of activity coefficients from unity, $K_3$ and $K_4$ were calculated from the visible region spectra, owing to the method by Baker *et al.*[10] That is, using the absorbance changes at high pH at 519 nm, $K_3$ could be obtained from the following

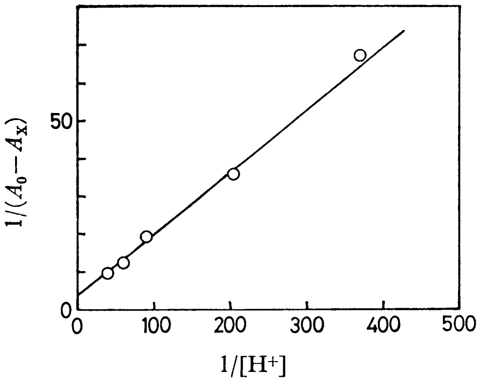

Fig. 2. Plot of $1/(A_0-A_x)$ vs. $1/[H^+]$ from the data in Fig. 1 to determine $K_3$ from Eq. 3. The wavelength is 517 nm for $\mu=2.0$. Temperature=21 °C

equation.[11]

$$\frac{1}{A_0-A_x}=\frac{K_3}{A_0-A_\infty}\frac{1}{[H^+]}+\frac{1}{A_0-A_\infty}, \qquad (3)$$

where $A_0$ and $A_\infty$ are the absorbances of the free base and monocation forms of the porphyrin, and $A_x$ is that of a mixture of $H_3P^+$ and $H_2P$ at a constant wavelength. $K_3$ was calculated from the linear relationship between $1/(A_0-A_x)$ and $1/[H^+]$ to be *ca.* $1.3\times10^{-2}$ (Fig. 2). $K_4$ was obtained from the low pH absorbances appeared at 562 nm to be *ca.* $10^{-1}$. Therefore p$K_4$ and p$K_3$ of the equilibrium (1) and (2) are about 1.0 and 1.9, respectively. In agreement with the case for $\alpha,\beta,\gamma,\delta$-tetrakis(1-methylpyridinium-4-yl)porphine, TmpyP, p$K_3$ and p$K_4$ values were found to increase with ionic strength (p$K_4$=1.2, p$K_3$=2.2 at $\mu$=5.0).[10]

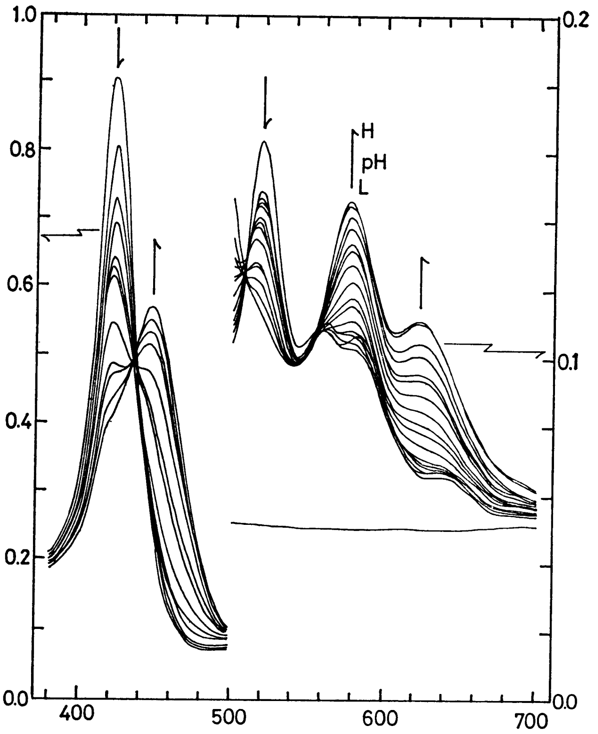

Fig. 3. Spectrophotometric titration of $H_2P$ with NaOH forming $HP^-$.

*Equilibria at* pH *7—14*: To investigate the acidity of the free base, a spectrophotometric titration from pH 7 to 14 was performed with sodium hydroxide. Figure 3 shows the resulting titration of $H_2P$ with sodium hydroxide and the isosbestic points at 556, 504, and 418 nm. Assuming that $H_2P$ and monoanion, $HP^-$, are absorbing species, and that free base-monoanion equilibrium

$$OH^- + H_2P = HP^- + H_2O \qquad K_b \qquad (4)$$

is present, Eq. 5 is obtained.

$$\log[HP^-]/[H_2P] = \log K_b - p(OH) \qquad (5)$$

Thus the plots of the left-hand side of Eq. 5 *vs.* p(OH) should be linear with a slope of −1. The log ($[HP^-]/[H_2P]$) *vs.* p(OH) plots at 422, 578, and 622 nm (Fig. 4) showed a linear relation with an average slope of 1.0±0.2 and a log $K_b$ of 1.0±0.2. Hence the dissociation constant, $K_2$, of the free base to monoanion and proton at 21 °C is 13.0±0.2 in close accordance with the result for TmpyP (12.9±0.2).[7]

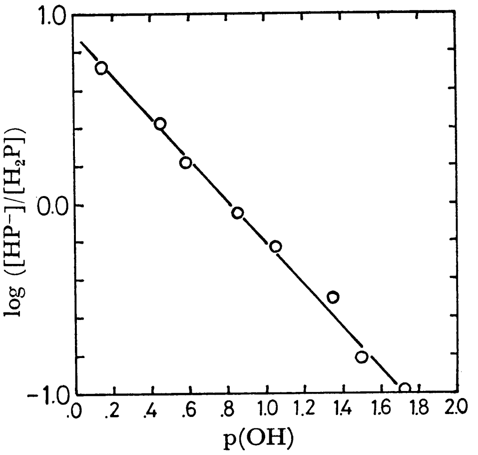

Fig. 4. Plots of log ($[HP^-]/[H_2P]$) *vs.* p(OH) at 578 nm to determine $K_2$ in Eq. 4.

As so far mentioned, ThoepyP as well as TmpyP[7] was found to exist from pH 0 to 7 as monomers of diacid, monocation, and free base forms in contrast to the trend that most porphyrins are apt to exist as dimers or polymers in solution, with formation constants large enough such that in the usual spectrophotometric concentration range ($10^{-4}$ to $10^{-6}$ M), appreciable association occures.[12] Acid-base titmetric data were analyzed at a fixed ionic strength and temperature using Q bands because of their multiplicity. Results indicated that ThoepyP behaves apparently in the same fashion as TmpyP. The relatively low basicity and high acidity compared with other porphyrins[13] seem common aspects of porphyrins having quaternary ammonium ion and are not much influenced by the alkyl groups attached to nitrogen. A slight difference owing to side group was, however, reflected on the position of redox potential of its iron complex, a 0.020 V negative shift of ThoepyP (−0.048 V) from that of TmpyP (−0.028 V).

*Cyclic Voltammetry.* The cyclic voltammogram illustrated in Fig. 5 for $Fe^{III}$ThoepyP indicated an

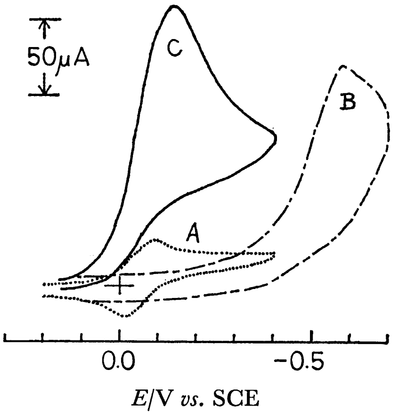

Fig. 5. Cyclic voltammetric current-potential curves at glassy carbon electrode in 0.05 M $H_2SO_4$. (A) $2.4\times10^{-4}$ M $Fe^{III}$ThoepyP, saturated with $N_2$, scan rate$=$ 64 mV $s^{-1}$: (B) only $O_2$ (air-saturated), scan rate$=$110 mV $s^{-1}$, replotted from Ref. 3; (C) $2.4\times10^{-4}$ M $Fe^{III}$ ThoepyP and $O_2$ (air-saturated), scan rate$=$64 mV $s^{-1}$.

electrochemical (*ec*) catalytic regeneration as for $Fe^{III}$TmP.[3)]

$$Fe^{III}ThoepyP + e^- = Fe^{II}ThoepyP, \quad E_1 \qquad (6)$$

$$Fe^{II}ThoepyP + 1/2O_2 + H^+ \xrightarrow{k} Fe^{III}ThoepyP + 1/2H_2O_2, \qquad (7)$$

where $Fe^{III}$ThoepyP was reduced on the glassy carbon electrode and the generated $Fe^{II}$ThoepyP transferred its electron to oxygen, $O_2$, to return to the iron(III) porphyrin. The catalytic aspects of the $O_2$ electroreduction was recognized by comparing the cyclic voltammetric current-potential (*i-E*) curves, curve A to C in Fig. 5, (A) for a 0.05 M sulfuric acid solution containing $2.4\times10^{-4}$ M $Fe^{III}$ThoepyP, (B) saturated with $O_2$ from the air, and (C) containing the iron porphyrin and saturated with $O_2$ from air, respectively. Although the $O_2$ reduction occurred at the peak potential, $E_p$, of *ca.* $-0.057$ V *vs.* SCE in the absence of $Fe^{III}$ThoepyP, the addition of the iron porphyrin shifted the reduction potential to $-0.08$ V which is close to redox potential of $Fe^{III/II}$ThoepyP ($-0.06$ V). The redox potential of $Fe^{III/II}$ThoepyP couple, trace A, was independent of scan rate, $v$, from 0.016 to 0.256 V $s^{-1}$ and the separation between the cathodic and anodic potentials, $\Delta E_p$, was 60—70 mV, which indicated that Reaction 6 was a diffusion controlled one-electron transfer reaction.

If the two-electron reduction of $O_2$ to form $H_2O_2$ in proton donating media is taken place rapidly, the theoretically calculated value[14,15)] of the peak current versus square root of scan rate ($i_p$ *vs.* $v^{1/2}$) would be 880 $\mu A(V/s)^{-1/2}$, assuming an $O_2$ concentration of $2.9\times10^{-4}$ M[16)] and a diffusion coefficient, $D_{O_2}$, value of $2.6\times10^{-5}$ $cm^2\,s^{-1}$.[17)] At low concentration of the porphyrin ($10^{-6}$—$10^{-5}$ M), the catalytic $O_2$ wave appeared as a prewave to the main $O_2$ wave and at potentials approximately corresponding to Reaction 6. With the increase of concentration of the iron porphyrin, the wave height dramatically increased, and at or above *ca.* $2\times10^{-4}$ M, the $i_p$ for the catalyzed wave became diffusion controlled in $O_2$. When this latter condition was satisfied, the slope of the $i_p$ *vs.* $v^{1/2}$ approached to *ca.* 800 $\mu A(V/s)^{-1/2}$ which is close to that expected for a two-electron, diffusion controlled reduction of $O_2$ to hydrogen peroxide, $H_2O_2$, under reversible conditions. In alkaline pH solution (above *ca.* pH 11) the slope of the $i_p$ *vs.* $v^{1/2}$ plot attained to the ideal value (880 $\mu A(V/s)^{-1/2}$). When the iron porphyrin concentration was much lower (*ca.* $10^{-6}$ M) than that of oxygen, the apparent rate constant for Reaction 7 was calculated using Eq. 8[18)] from the height of the catalytic $O_2$ wave under the approximation of the pseudo first order *ec* catalytic mechanism with Reaction 7 being irreversible.

$$i_k = nFAC_{por}D_{por}^{1/2}k^{1/2}C_{O_2}^{1/2}, \qquad (8)$$

where $i_k$ is the catalytic current observed in A, $F$; Faraday constant in C $mol^{-1}$, $A$; area of electrode in $cm^2$, $C_{por}$; concentration of porphyrin in mol $cm^{-3}$, $D_{por}$; diffusion coefficient of porphyrin in $cm^2\,s^{-1}$, $k$; apparent rate constant in $mol^{-1}\,cm^3\,s^{-1}$ and $C_{O_2}$; concentration of oxygen in mol $cm^{-3}$. Taking the average of three independent experiments, the rate constant was calculated to be *ca.* 3—$4\times10^{-7}$ $dm^3\,mol^{-1}\,s^{-1}$ for the $10^{-6}$ M iron porphyrin in air-saturated $O_2$ solutions (0.05 M $H_2SO_4$). This rate constant answers for why the catalytic wave becomes diffusion controlled in $O_2$ when the iron porphyrin concentration exceeds that of $O_2$.

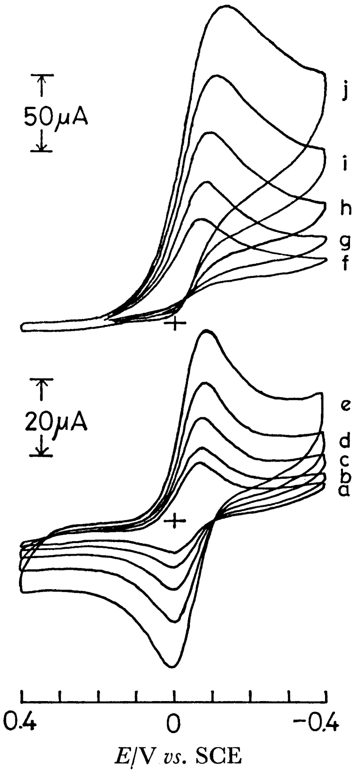

Fig. 6. Cyclic *i-E* curves of $2.4\times10^{-4}$ M $Co^{III}$ThoepyP in 0.05 M $H_2SO_4$ at 16, 32, 64, 128, and 256 mV $s^{-1}$, $N_2$ saturated solution (a to e) and $O_2$ (air-saturated) solution (f to j).

Typical cyclic *i-E* curves are shown in Fig. 6 for $2.4\times10^{-4}$ M Co(III)ThoepyP in 0.05 M $H_2SO_4$. In the potential range of +0.40 to −0.40 V under nitrogen, a well-defined voltammetric wave of a diffusion controlled electrode reaction was observed (line a to e). The $Co^{III/II}$ThoepyP redox potential was −0.035 V and their peak potentials ($E_P$=−0.07—−0.08 V) were almost independent of scan rate in the range from 0.016 to 0.256 V $s^{-1}$. When oxygen was introduced into the above solution (line f to j), a cathodic current increased at the peak potential of this cobalt complex and its peak height was linearly proportional to $O_2$ concentration at a constant scan rate. When this solution was fully saturated with air, the peak current increased at its potential with the increase of scan rate as seen for $Fe^{III}$ThoepyP. But the most distinct difference was the rate of increase. If we plot this peak current against $v^{1/2}$, its slope attains 490 $\mu A(V/s)^{-1/2}$ which is 56% of that theoretically expected for a two-electron, diffusion controlled reduction of $O_2$ under reversible conditions (880 $\mu A(V/s)^{-1/2}$). At low concentrations of the cobalt complex ($10^{-6}$—$10^{-5}$ M), the catalytic $O_2$ wave appeared as a prewave to the main $O_2$ wave. As the concentration of the cobalt porphyrin increased, the wave height increased dramatically, and at or above $2.4\times10^{-4}$ M, the $i_p$ for the catalytic wave became saturated. Thus the above mentioned electrochemical behavior was similar in many points to that of $Fe^{III}$ThoepyP. So by applying *ec* catalytic regeneration mechanism, we evaluated the apparent rate constant for this system (which corresponds to $k$ in Eq. 7) from the catalytic current when $Co^{III}$ThoepyP concentration is quite low. If we again assume the pseudo first order *ec* catalytic mechanism, the calculated rate constant was *ca.* $1\times10^{7}$ $dm^3\ mol^{-1}\ s^{-1}$ for the $10^{-6}$ M cobalt porphyrin in air-saturated solution (0.05 M $H_2SO_4$).

In the course of studies on various water soluble iron porpyrins such as $Fe^{III}$TpyP,[19] $Fe^{III}$TmP,[3] $Fe^{III}$-ThoepyP, and $Fe^{III}$TapP,[5] we could extract some electrochemically interesting features for those iron complexes as follows. (1) The redox potentials ranged between 0 and −0.06 V in 0.05 M $H_2SO_4$ solution and when cyclic voltammetric experiments were carried out in deaerated solution, they revealed *i-E* curves characteristic of a reversible diffusion controlled electrode reaction. (2) They could be good catalysts for the reduction of molecular oxygen and the potentials for the *ec* catalysis were governed by the $Fe^{III/II}$porphyrin redox couples which also depended on pH values; shifted to negative direction with the rise of pH value. (3) Electron transfer from electrode to oxygen by these complexes was so swift that if the porphyrin concentrations were enriched to some extent, then catalytic current became diffusion controlled in $O_2$, and the slope of the $i_p$ *vs.* $v^{1/2}$ plot increased to that expected for a two-electron, diffusion controlled reduction of $O_2$ to $H_2O_2$ under "reversible conditions." (4) The apparent rate constants of the iron porphyrins to transfer electron(s) to oxygen were dissimilar among species used. For example that of $Fe^{III}$ThoepyP was estimated to be around 1/3—1/4 of that of $Fe^{III}$TmP ($1.2\times10^{8}$ $dm^3\ mol^{-1}\ s^{-1}$).[3]

In contrast to the case of iron porphyrins, only a few electrochemical studies[5,20] have been reported on the reduction of molecular oxygen with the cobalt incorporated water soluble porphyrins. Although we are still, in the present stage, in want of basic data if we dared to pick up what differed electrochemically from those of the corresponding iron porphyrins, they would be as follows. (1) The redox potentials were always more positive than those of corresponding iron porphyrins. (2) In common with the case of $Co^{III}$TapP[5] the slope of $i_p$ vs. $v^{1/2}$ plots of $O_2$ reduction with $Co^{III}$-ThoepyP was approximately 60% of that of the corresponding iron porphyrin. Phenomenon (1) is easily understandable from the trend that potentials of metal(III/II) redox couple in the first transition metal period in the periodic table parallel to the 3rd ionic potentials, *i.e.*, metals which have less tendency to produce trivalent ions indicate more positive redox potentials.[21]

In order to estimate the apparent rate constant in Eq. 7, the assumptions have been made that these reactions proceeded *via ec* catalytic regeneration mechanism and that reactions were pseudo first order. However, we confronted the fact that these values depended on scan rates, though their degree was not so striking. For such a fact following three reasons may be casted. (1) Though reactions proceed *via ec* catalytic regeneration mechanism, $O_2$ concentration might be still too low compared with that of the porphyrins ($10^{-6}$—$10^{-5}$ M) to postulate pseudo first order reaction. (2) Reaction in Eq. 7 *per se* may not simply be a pseudo first order. (3) Adosorption of porphyrins might be occurred. Within these possibilities, however, (3) is eliminated by the finding of the linearity of the $i_p$ *vs.* $v^{1/2}$ plot from Fig. 6, curve a to e (not shown), because if adsorption occurred the slope would be increased with increment of scan rate.

## Conclusion

It was indicated that ThoepyP behaves mostly in the same fashion as for TmpyP in water. Catalytic properties of its iron and cobalt complexes for reduction of molecular oxygen in water were recognized and interpreted to proceed *via ec* catalytic regeneration mechanism. The apparent rate constants for electron transfer from porphyrin to oxygen were calculated, assuming pseudo first order reaction, to be 3—$4\times10^{7}$, and $1\times10^{7}$ $dm^3\ mol^{-1}\ s^{-1}$ for its iron and cobalt complexes, respectively. Simultaneously, the doubt was casted whether the above reactions were actually pseudo first order or not.

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11) Since $[H_2P]=[A_0-A_\infty]-[A_0-A_x]$, it is readily shown from Eq. 2 that

$$\frac{[H_2P]}{[H_3P^+]}=\frac{[A_x-A_\infty]}{[A_0-A_x]}=\frac{K_3}{[H^+]}$$

$$\therefore\ \frac{1}{[A_0-A_x]}=\frac{K_3}{[H^+][A_x-A_\infty]}$$

Removal of brackets by expansion and rearrangements of this equation afford Eq. 3.

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