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Redox Reaction of the Central Metal Ions Coordinated to Tetra(*p*-sulfophenyl)porphine(TPPS). I. Photoreduction of Co(III)TPPS by Methanol and 2-Propanol

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Trivalent cobalt ion coordinated to 5,10,15,20-tetra(*p*-sulfophenyl)porphine (TPPS) in deaerated solution was reduced to the divalent ion on illumination of light with simultaneous oxidation of alcohols. The resulting divalent ion in the porphyrin was reoxidized by admission of dioxygen or air into the solution. It was found that the metalloporphyrin played a photocatalytic role in the autoxidation of alcohols. The kinetic study on the photoreduction revealed that the reduction rate of Co(III) followed the pseudo-first-order rate expression at 20 °C and pH 6.5 to 11.5 in the presence of excess methanol or 2-propanol. The observed rate constants were dependent on [alcohol] and/or pH. Possible mechanism for the photoreduction of Co(III)TPPS in the aqueous solution was discussed in terms of preequilibrium reactions of the axial ligation of substrates to the metalloporphyrin.

Very few papers have been published on the photoreduction reactions involving changes only in oxidation state of the central metal of metalloporphyrins,[1] although a number of papers have dealt with photohydrogenation of the peripheral porphyrin ring.[2] This paper describes a light-induced redox reaction of cobalt ion coordinated to 5,10,15,20-tetra(*p*-sulfophenyl)porphine (abbreviated as TPPS[3]) with the concomitant catalytic oxidation of alcohols, *i.e.*, photoreduction of Co(III)TPPS by alcohols and the subsequent oxidation of Co(II)TPPS by O_2 without the degradation of the porphyrin ring. A closely related "respiratory" reaction of manganese phthalocyanine and etioporphyrin was reported by Engelsma *et al.*[4] in relation to the photosynthesis reactions. Moreover, clarifying the oxidation state of metal ions, axial ligands, and reducing reagents involved in the photochemical reactions of metalloporphyrins in view of recent advances in the spectral and structural characterization of metalloporphyrins[5] seemed appropriate.

The present work was initiated with the aim of understanding the function-structure relationship of metalloporphyrin enzymes. When we observed the spectral changes induced by light in stock solutions of metalloporphyrins, we were intersted in the photocatalytic activity of them and the possibility of interconversion of photonic energy into chemical energy. Since metalloporphyrins, beside being the analogy of chlorophylls, have intense absorption bands in the visible and near ultraviolet region, they are expected to be good photosensitizers. Furthermore, the redox reaction of metalloporphyrins is of interest with respect to understanding the function of the biologically important hemeproteins such as electron transfer reactions in the photosynthesis. Metal-TPPS, which are easily soluble in water, appear to offer more information with respect to quantitative kinetic studies of the photochemical reactions.

In this paper we show that the cobalt ion in CoTPPS is a photo-catalytic active center in the autoxidation of alcohols. The kinetic results suggest that the manner of the axial coordination of alcohols is crucial to the photoreaction leading to the exclusive metal ion reduction.

Experimental

Materials. Sodium salt of TPPS ($TPPSNa_4$) was prepared as described by Fleischer *et al.*[6] Since Co(II)TPPS is oxidized slowly in aerobic aqueous solution, all the synthetic processes were carried out in nitrogen stream. TPPS was metallized in water using reagent grade $Co(CH_3COO)_2 \cdot 4H_2O$, and the water was removed by rotary evaporation from the reaction mixtures. The resulting solid was extracted with methanol. Co(II)TPPS was purified as a sodium salt by treatment of crude product in methanol with sodium methoxide several times.

Found: C, 43.28; H, 3.61; N, 4.25; S, 11.07%. Calcd for $CoTPPSNa_4 \cdot 8H_2O$, $C_{44}H_{40}N_4S_4O_{20}CoNa_4$: C, 43.18; H, 3.29; N, 4.58; S, 10.48%. UV-Visible spectra in pH 5.0 phosphate buffer; λ_{max}, nm(ε, $M^{-1}\ cm^{-1}$):[7a] 526 (1.2×10^4), 413 (2.1×10^5).

Co(III)TPPS formed in aqueous solution by autoxidation was found to be diamagnetic by electron paramagnetic resonance (EPR) at 77 K, but was not isolated. Spectral data of Co(III)TPPS; λ_{max} (ε), 538 (1.3×10^4), 424 nm ($2.7 \times 10^5\ M^{-1}\ cm^{-1}$) were observed in pH 5.0 phosphate buffer. The molar extinction coefficient at 424 nm diminished to $2.4 \times 10^5\ M^{-1}\ cm^{-1}$ in the pH 8.0 to 10.0.

Water was deionized through ion exchange resins and doubly distilled. 2-Propanol (spectroscopic grade, Katayama Chem. Co.) was used. Methanol of reagent grade was doubly distilled. Phosphate–borate (pH 6.0 to 9.2), borate–carbonate (pH 9.2 to 11.0), and borate–Hydroxide ($\geq$pH 11.0) buffers were prepared according to the reported methods[7b] with the ionic strength maintained at $\mu = 0.1$. pH was adjusted with a pH meter (TOA, HM-7B model).

Instrumentation. Light irradiation was carried out with light source of (a) tungsten projection lamp (either unfiltered or filtered by Toshiba glass filters), or (b) four 700 W medium-pressure mercury lamps equipped with a plant growing apparatus 'phytotron'.

UV-visible absorption spectra and EPR spectra were recorded on a Shimadzu Model 200S spectrophotometer and a JEOL-PE1X X-band spectrometer with 100 kHz field modulation, respectively.

Procedures. A solution of Co(III)TPPS in an appropriate buffer was degassed by three cycles of freeze-pump-thaw in a pyrex tube (i.d. 19 mm) with two side arms: a quartz cell (10 mm light pass) for spectral measurements and a container with a deaerated buffer solution of alcohols. The alcohol solution was poured into the pyrex tube in the dark *in vacuo*, then irradiated by light. The irradiation was carried out at 20 °C in a water bath or an air bath of the phytotron. The intensity of the incident light in the phytotron measured by means of the trioxalatoferrate (III) actinometer[8] using the quantum yield 1.10 in the region 430—300 nm corresponding to the major absorption of the metalloporphyrin, was of the order of 7×10^{16} quanta/ml min. The quantum yield for the present reactions was obtained by one of two methods; (a) spectrometric method using the ratio of absorbed quanta to the incident light intensity (derived by comparison of the actinometer irradiated by the light passed through a dilute Co(III)TPPS solution with that through water using a coaxial photolysis cell[9]), (b) measurement of the quantity of formaldehyde produced in the methanolic solution of about 10^{-2} M CoTPPS which was considered to absorb the full incident light.

Formaldehyde was detected by the chromotropic acid method[10] on a sample condensed from the photolyzed solution by vacuodistillation. Acetone was tested qualitatively by the nitroprusside method.

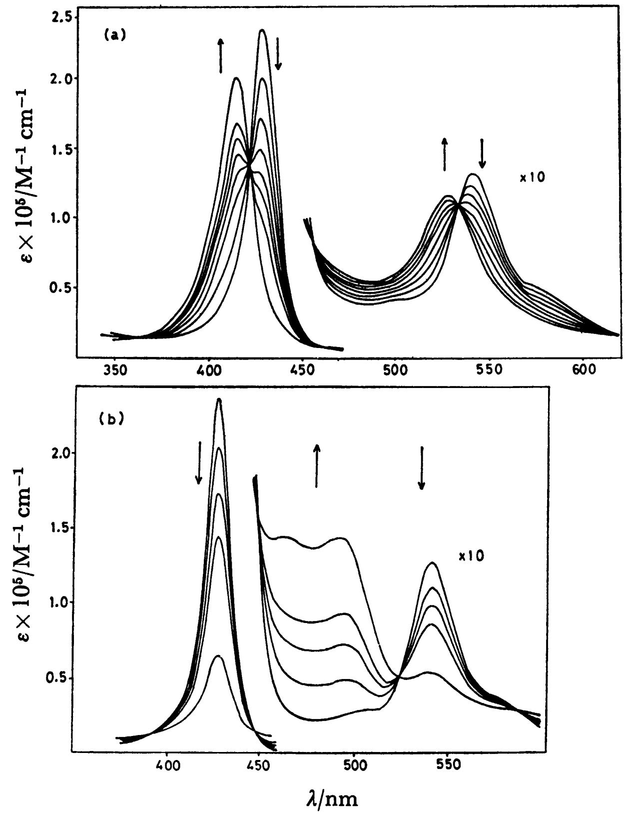
The kinetic studies on the photoreduction and oxidation reactions were carried out by monitoring the changes in the absorption spectra during the light illumination and after O_2 introduction.

Results and Discussion

Photoreduction of Co(III) TPPS. In aqueous solution, the electronic absorption spectra of Co(III)TPPS change slightly with the pH variation and addition of alcohols. However, the fact that the Lambert-Beer law holds for the solution over wide range of concentration (10^{-6} to 10^{-3} M) eliminates the possibility of the participation of oligomeric species in a dilute Co(III)-TPPS solution.[11] Although it is probable that there are several equilibrating reactions involving five- and six-coordination of various solvents and solutes to Co(III)TPPS, the magnitude of the spectral changes is too small and complicated to determine these species definitely.

The typical spectral changes during photolysis of the deaerated Co(III)TPPS solution in the presence of 0.67 M methanol (Fig. 1(a)) have distinct isosbestic points at 360, 419, 454, 534, and 615 nm. The new spectrum appearing on prolonged irradiation is identical with that of Co(II)TPPS prepared and measured in the absence of air.

In order to obtain more information on the nature of species in this photo-reaction, the process was followed by EPR. No signals were detected in the original solution of CoTPPS at 77 K (Fig. 2(a)). As the photolysis proceeds, a new spectrum, having approximate parameters of $g_\perp=2.4$, $g_{/\!/}=2.02$, $A_\perp=55\times10^{-4}$ cm^{-1}, and $A_{/\!/}=105\times10^{-4}$ cm^{-1}, increases its intensity (Fig. 2(b)). By the addition of imidazole to the solution, the spectrum altered into a prototype spectrum of the five-coordinate Co(II)porphyrins with a nitrogen base at the fifth position[12] (Fig. 2(c)). The results show that the photoreduction of CoTPPS occurs at the metal ion of the metalloporphyrin and that the original solution contains the diamagnetic Co(III)species[13] and no paramagnetic species such as Co–O_2. The product can be assigned to a five-coordinate Co(II)TPPS in



Fif. 1. Spectral changes of Co(III)TPPS during photolysis as a function of reaction times in the order shown by arrows; (a) 0, 20, 40, 60, 80, 100, 120, and 180 min in the 0.67 M methanol solution; (b) 0, 20, 40, 60, and 120 min in the 0.54 M 2-propanol solution. Both runs were carried out at pH 8.7 and 20 °C.

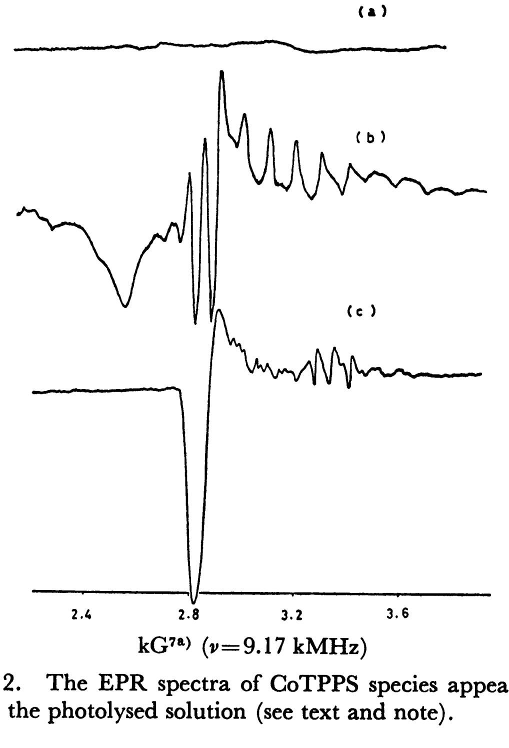


Fig. 2. The EPR spectra of CoTPPS species appearing in the photolysed solution (see text and note).

which the fifth position is occupied weakly by water (or methanol) consistent with the spectra reported by Walker.[14] Our EPR parameters of the product most resemble those of CoTTP(or CoTAP)–acridine system in her paper. The steric constraint of acridine (hindered base) is considered to prevent the metal ion from strong bonding to the base. Thus the EPR parameters should be similar to weakly bonded complexes.

The dependence of the photoreduction on the wavelength of the incident light was examined by setting glass filters in the light path from the projection lamp. The reaction rate resulting from light of 430 nm$>\lambda>$330 nm was compared with that of $\lambda>$450 nm and it was suggested that the light absorbed in the Soret region was more effective in driving the reaction than light in the visible region. However, an accurate determination of the quantum yields in the two regions has not been achieved.

The apparent quantum yield of the formaldehyde formation in degassed solution of *ca.* 10^{-2} M CoTPPS and 0.67 M methanol at pH 8.7 by 30 h irradiation was 0.9×10^{-3}. No gaseous products were detected manometrically in that run. The quantum yield of Co(II)TPPS determined by the spectrometric procedure was 2.2×10^{-3} in solutions of 10^{-6}—5×10^{-5} M CoTPPS and 0.67 M methanol at pH 8.7. The results are consistent with the following stoichiometric reaction within experimental errors. The lack of the evolution

$$2\,\text{Co(III)TPPS} + \text{CH}_3\text{OH} \xrightarrow{h\nu} 2\,\text{Co(II)TPPS} + \text{H}_2\text{CO} + 2\text{H}^+ \qquad (1)$$

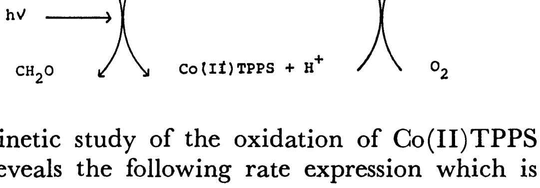
of molecular hydrogen also supports one electron photoreduction of Co(III) in this equation.

The primary and secondary alcohols, *e.g.*, methanol, ethanol, and 2-propanol, were found to be effective reducing reagents. However, t-butyl alcohol did not bring about the photoreduction. This suggests that the photooxidation of alcohols occurs with a proton elimination at α-carbon position.

Autoxidation of Co(II) TPPS. With O_2 or air introduction into the solution photolyzed, the spectrum of Co(II)TPPS returns to the initial Co(III)TPPS spectrum *via* the exact reverse course of the spectral changes in the photoreduction. The ultimate spectrum of Co(III) TPPS is restored with more than 95% of its initial intensity. The reaction must be the following autoxidation of Co(II)TPPS:[15]

$$2\,\text{Co(II)TPPS} + 1/2\text{O}_2 + 2\text{H}^+ \longrightarrow 2\,\text{Co(III)TPPS} + \text{H}_2\text{O}. \qquad (2)$$

Therefore, the overall photochemical reaction is found to be the autoxidation of alcohols catalyzed by CoTPPS:



The kinetic study of the oxidation of Co(II)TPPS by O_2 reveals the following rate expression which is substantially identical to the analogous study reported by Stynes *et al.*[16]

$$-\mathrm{d}[\text{Co(II)TPPS}]/\mathrm{d}t = k'[\text{Co(II)TPPS}][\text{O}_2],$$

where k' is the observed rate constant. A value of 1.8×10^{-4} min^{-1} Torr^{-1} for k' was obtained in the aqueous 2-propanol (1.0×10^{-2} M) solution at 25 °C without buffer. This is comparable with 4.2×10^{-4} min^{-1} Torr^{-1} which is extrapolated from the reported result of the oxidation of CoTTP in toluene with 0.002 M imidazole at 23 °C.[16] It is surprising to obtain such apparently consistent data despite the vastly different properties of the solution and substances.

Other Photochemical Reactions of CoTPPS. In the absence of alcohols and/or organic amines such as piperidine, Co(III)TPPS in aqueous solution is considerably stable against light irradiation. In the case of methanol or ethanol as reducing agent, the photoreduction of Co(III) ion of the metalloporphyrin is predominant over wide range of pH and alcohol concentration [A]. The recovery of Co(III)TPPS, even after several cycles of the photoreduction-autoxidation, usually exceeds 70% of the initial amount. A drastic change in spectral aspects for the photoreaction is observed in solution containing relatively high concentrations of 2-propanol (10^{-1} M). The spectral changes shown in Fig. 1(b) also have some isosbestic points. However, the spectrum of the product shows no recovery to the spectrum of Co(III)TPPS by the admission of air into the cell. The monotonic decrease of the Soret band may be related to the degradation of peripheral porphyrin ring of CoTPPS; although the chemical characterization of the product has not yet been done. Meanwhile the Co(II)TPPS generated by photoreduction in the presence of 2-propanol was found to be stable against long irradiation of light. This rules out the stepwise photodegradation reaction *via* the formation of Co(II)TPPS. The degradation reaction seems to occur *via* a direct process from a Co(III) species formed in the high [2-propanol] solution. The formation of such a species in methanolic or ethanolic solution may be restricted by its stability constant.

Formaldehyde, acetaldehyde, and acetone in water did not function as the reducing reagents for the reaction.

Kinetic Experiments of the Photoreduction of Co(III) TPPS. The reaction rates of the photoreduction at 20 °C were determined by monitoring changes in the optical density at 424 nm (decrease) and 413 nm (increase) with complementary measurements in the visible region for high [Co(III)TPPS]. The different original intensity at 424 nm depending on the nature of solution did not affect the present kinetic treatment, since, during most kinetic runs, satisfactory isosbestic points were obtained. This is expected for a fixed distribution of various coordination states of Co(III)TPPS being reduced to one five coordinate Co(II) species. Two different kinds of photoreaction took place in certain ranges of [2-propanol]. The determination of the photoreduction rate in such cases has been done at the initial stage of the reaction where the conversion of Co(III)TPPS was less than 40% and the recovery by the autoxidation exceeded 85% of the initial intensity.

Plots of $\ln([\text{Co(III)TPPS}]_t/[\text{Co(III)TPPS}]_0)$ *vs.* time,

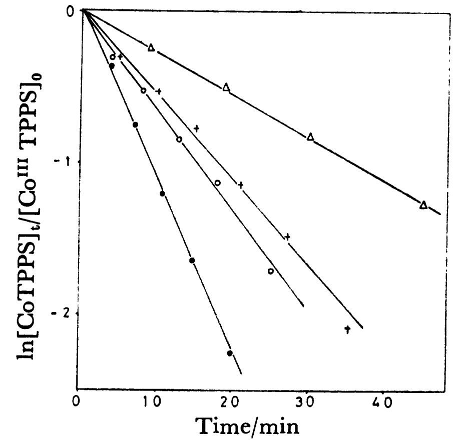


Fig. 3. The first-order rate dependence on Co(III)-TPPS for various methanol concentrations; (△) 1.67 M, (+) 3.21 M, (○) 4.29 M, (●) 6.25 M; in the solution of $[\mathrm{Co(III)TPPS}]_0=6.6\times10^{-6}$ M and pH 9.7.

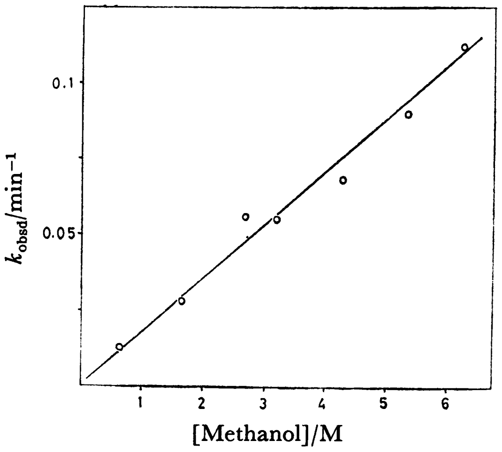


Fig. 4. The k_{obsd} *vs.* [methanol] plots. Conditions are the same as Fig. 3.

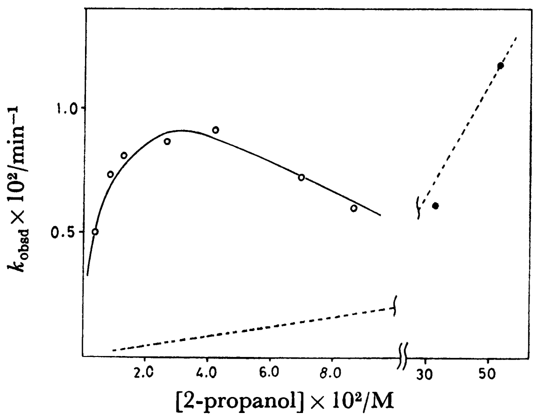


Fig. 5. The k_{obsd} *vs.* [2-propanol] plots, $[\mathrm{Co(III)TPPS}]_0=3.3\times10^{-6}$ M, pH 8.7. The (●) and dashed line denote experimental and estimated rate constants, respectively, for the degradation reaction.

where the subscripts denote time t and zero, are shown in Fig. 3. The linear relationship indicates a first-order rate dependence on Co(III)TPPS. Pseudo-first-order rate constants, k_{obsd}, were obtained from the slope of the plots, and found to be dependent on the concentration of alcohols and/or pH. The profile of k_{obsd} to [methanol] (Fig. 4) shows a first-order relationship to the methanol concentration. However, the dependence of k_{obsd} on [2-propanol] is unusual (Fig. 5). At low [2-propanol] (2×10^{-2} M), the dependence seems to be of first-order, decreasing toward zero to minus with increasing concentration. There is an obvious maximum in the k_{obsd} *vs.* [2-propanol] curve *ca.* 3—4×10^{-2} M 2-propanol at pH 8.7. The photo-degradation reaction is appreciable at higher [2-propanol] than that corresponding to the maximum. However, the increase of the degradation rate (estimated from the data at high [2-propanol] by assuming the first-order dependence on the alcohol concentration) is not responsible for the decrease of photoreduction rate. The anomaly in the curve demonstrates that there are at least two coordination states formed by stepwise attachment of 2-propanol to Co(III)TPPS.

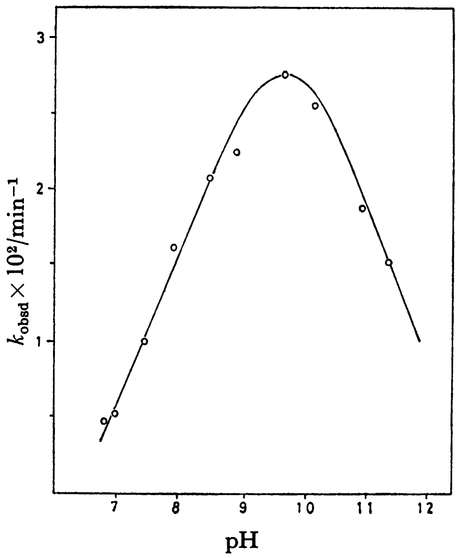


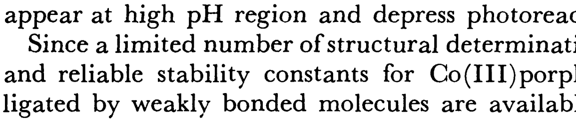
Fig. 6. The pH profile of k_{obsd}, $[\mathrm{Co(III)TPPS}]_0=6.6\times10^{-6}$ M, [methanol] = 1.67 M, ionic strength = 0.1.

The k_{obsd} are also dependent on pH (Fig. 6). The profile of k_{obsd} is volcano-shaped in the solution of constant [methanol], having a peak around pH 9.5 to 10.0. Studies of the rate dependence on pH in 2-propanol solution were not carried out since the rates are very slow at low [2-propanol] where the first-order rate on the alcohol can be expected.

The kinetic studies imply that various coordination states of Co(III)TPPS presented in the aqueous solution behave differently toward light irradiation.

Preequilibrium Reactions in the Aqueous Solution. Both water and alcohol molecules are known to associate with some metalloporphyrins by the definitive X-ray structure determination.[17] However, the stability constants are seldom clear for such weakly bonded molecules owing to the difficulty of spectroscopic characterization of the complexes in solution. Let us assume that Co(III)TPPS has two axial sites to bind ligands, solvents and solutes. Participation of dimeric metalloporphyrin species such as CoTPPS–O_2–CoTPPS[13)] can be ruled out in dilute solution, since the first-order rate laws in cobalt metal are confirmed in both photoreduction and autoxidation processes in conjunction with the EPR evidence of Co(II)TPPS monomer. The observed rate dependence of the photoreduction on pH and [A] can be interpreted by a mechanism in which competitive ligation of alcohols, water, and hydroxide ion to the two axial sites occurs prior to the photoreaction. Accounting for these, we can classify coordination states of Co(III)TPPS in aqueous solution into at least four groups: (i) light-insensitive species formed predominantly in acidic solution and/or in the absence of alcohol, (ii) species to be photoreduced at the central metal ion, (iii) species to be degradated by light, which is appreciable at high [A], especially, [2-propanol], (iv) species which appear at high pH region and depress photoreactions.

Since a limited number of structural determinations[18)] and reliable stability constants for Co(III)porphyrins ligated by weakly bonded molecules are available, we can only speculate about the coordination states of each species and the mechanism involving them. The key species for the photoreduction belongs to group (ii) and can be assigned to Co(III)TPPS(A) (OH) where A denotes a general alcohol. The substance is formed by coordination (or substitution) of alcohol and/or hydroxide ion to species (i) which are represented by Co(III)TPPS$(H_2O)_2$ and Co(III)TPPS(H_2O)(OH). Co(III)TPPS$(A)_2$ and Co(III)TPPS$(OH)_2$ may represent species (iii) and (iv), respectively. Beside the four representative species, there may be many other states and reactions in the actual solution, so that it seems neither feasible nor significant to analyse the kinetic data quantitatively. The following scheme may help elucidate the parts of kinetic data, *i.e.*, the presence of maxima (Figs. 5 and 6). The photoreduction is considered to occur *via* formation of Co(III)TPPS(A)(OH) located in the middle of the scheme. The rate constants, k_{obsd}, are dependent solely on the concentration of this particular species as a function of [A] and pH inasmuch as a constant quantum efficiency is imposed on the photoreduction of the species. Thus, the efficient photoreduction requires optimal control of pH and [A]. In methanolic solution, the equilibrium constant for the second step of methanol coordination is very small as compared with that of 2-propanol. This is rationalized by the photo-degradation reaction which occur *via* formation of bis-alcohol species. The degradation of CoTPPS in methanolic solution was almost negligible under the usual experimental conditions.



It is intriguing to note that the proposed mechanism involving two binding sites for substrates in the catalyst provides similar kinetic aspects to those of certain enzymatic reactions, *e.g.*, fumarase reaction although its active site is not metal ion[19a)] and nitric oxide reductase reaction with NO.[19b)]

The relative broad curve observed in the k_{obsd} *vs.* pH plot (Fig. 6) suggests that the mono-hydroxy attachment to Co(III)porphyrins is favorable in the pH region 8—11 which corresponds to hydroxide concentration 10^{-6}—10^{-3} M. Isolation of such a species may be possible in analogous system. The occupation of two OH ions on the axial sites is possible, since two CN anion ligands have been confirmed in the X-ray structure of FeTPP$(CN)_2$ anion.[20)]

Mechanistic Consideration of the Photoreduction. The observed maximum value of the quantum yield of Co(II) is *ca.* 0.025 under the conditions [methanol]= 6.25 M at pH 9.7. The quantum efficiency[21)] could be enhanced by increasing methanol concentration and we could predict the best efficiency to reach the order of 10^{-1} if the solubility of CoTPPS and other solutes allowed the conditions. The relatively high quantum yield observed or predicted suggests that the photoreduction conjugates with the most efficient deactivation of the metalloporphyrin *via* an allowed electronic transition state induced by light absorption in the Soret region. However, very low yield and short life, if any, of the luminescent excited state of Co(III)-porphyrins are known even in rigid media at low temperatures.[22)] Consequently, the primary photochemical process of Co(III)TPPS can be attributed to the radiationless and direct chemical reaction from the excited Franck-Condon state of the coordinated complexes. An immediate assignment to this process is attained by the photodissociation of a proton at the α-carbon position of the coordinated alcohol molecule. However, such a dissociation reaction is considered to proceed fast with a fast reverse reaction. Thus the primary process can be treated as an additional preequilibrium reaction induced by light irradiation. In order to adjust the additional reaction and keeping consistency with kinetic data, especially, pH dependence, we could rewrite the process as an innersphere proton transfer of Co(III)TPPS(A)(OH).

The determining step of the quantum yield, which we assign to an intramolecular electron transfer from ligand to metal ion of the metalloporphyrin, can be placed after the primary processes. The speculations are summarized by formulation in the case of methanol as follows:

$$\mathrm{Co(III)TPPS(CH_3OH)(OH)} \overset{h\nu}{\rightleftharpoons} \mathrm{Co(III)TPPS(CH_2OH^-)(H_2O)}$$

$$\mathrm{Co(III)TPPS(CH_2OH^-)(H_2O)} \longrightarrow \mathrm{Co(II)TPPS(\dot{C}H_2OH)} + \mathrm{H_2O}.$$

A following fast reaction is required to complete the stoichiometry of the photoreduction.

$$\begin{aligned}&\mathrm{Co(II)TPPS(\dot{C}H_2OH)} + \mathrm{Co(III)TPPS(H_2O)(OH)}\\ &\qquad\qquad (\text{or any Co(III)TPPS})\\ &\longrightarrow 2\,\mathrm{Co(II)TPPS(H_2O)} + \mathrm{CH_2O}\end{aligned}$$

To estimate the difference of free energies in the photoreduction processes is of interest in relation to the possibility of photonic energy utilization. The free energy difference of overall reaction, *i.e.*, autoxidation of methanol to formaldehyde, is exothermic. The value is obtained from the thermodynamic standard data by ignoring solvation energy and estimating coordination energy of methanol as 10 kJ/mol. Based

$$CH_3OH + 1/2\,O_2 \rightleftharpoons CH_2O + H_2O$$
$$\Delta G = -150\ \text{kJ/mol}$$

on the standardization, $\Delta G=0$ for $H_2=2H^+ + 2e^-$on a platinum electrode (SHE), the energy level of a hypothetical system, $CH_2O+2H^+ + 2e^-$ or CH_2O+H_2, can be put at 237 kJ/mol above the product level or 87 kJ/mol above the reactants level (Fig. 7). Since the electrochemical redox properties of CoTPPS have not yet been determined, the free energy difference in the Eq. 1 is estimated by the voltametric data of analogous complexes. The reported value of 0.32 V *vs.* the saturated calomel electrode (SCE) (0.59 V *vs.* SHE was presumed) for the anodic half-wave potential of CoTPP in butyronitrile was used.[23] Therefore, the energy level of the right-hand term of Eq. 1 is calculated as the difference between the hypothetical level by assuming 0.59 V for $Co(III)TPPS+e^- = Co(II)TPPS$ and using the relationship, $\Delta G = -nFU = (-2)(96500)(0.59) = -114$ kJ/mol. Thus we have the free energy diagram shown in Fig. 7. The free energy difference of Eq. 1 is *ca.* −27 kJ/mol.

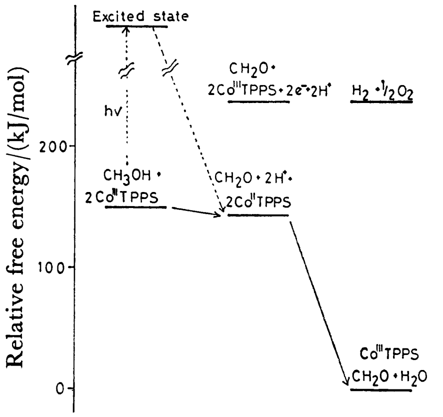


Fig. 7. Energy level diagram for photoreduction of Co(III)TPPS by methanol.

The semi-quantitative treatment leads to the conclusion that the present photoreduction of Co(III)TPPS may not acquire photonic energy in chemical forms, but merely the activation energy by light absorption. However, if there are other metal-TPPSes whose redox potentials are comparable to SHE, it may be possible to interconvert photonic energy into chemical one. We have observed that iron and manganese TPPS undergo similar photoreduction-oxidation reactions in alcoholic solution.

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3) TPPS can also be ionized at sulfonyl positions in aqueous solution. We use this abbreviation similarly to TPP for the dianion of 5,10, 15, 20-tetraphenylporphine, *i.e.*, the possible ionization of sulfonyl is ignored for clarity of expression. Other abbreviations: TTP, the dianion of 5,10,15,20-tetra(*p*-methylphenyl)porphine. TAP, the dianion of 5,10,15,20-tetra(*p*-methoxyphenyl)porphine.

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