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The Photochemical Formation of the π-Cation Radical from Chloro(5,10,15,20-tetraphenylporphyrinato)cobalt(III) in Aerated Dichloromethane

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Chloro(5,10,15,20-tetraphenylporphyrinato)cobalt(III), $Co^{III}(tpp)Cl$, in an aerated dichloromethane(DCM) solution undergoes photooxidation to produce the porphyrin π-cation radicals, $Co^{III}(tpp)^{+\cdot}Cl_2$. The formation mechanism of the π-cation radical was investigated by means of optical absorption and ESR spectroscopy: $Co^{III}(tpp)Cl$ in DCM decomposes photochemically to yield $Co^{II}(tpp)$ and chlorine atoms, which then abstract hydrogen atoms from DCM molecules to yield solvent radicals, $\cdot CHCl_2$, and HCl. The solvent radicals react with oxygen molecules, resulting in the generation of peroxyl radicals, which then oxidize $Co^{III}(tpp)Cl$ to produce the π-cation radicals, $Co^{III}(tpp)^{+\cdot}Cl_2$.

In an earlier paper[1] we reported that chloro (5, 10, 15, 20-tetraphenylporphyrinato)cobalt(III), $Co^{III}(tpp)Cl$, in chlorinated hydrocarbon solutions is converted, partially and reversibly, into a π-cation radical of (tetraphenylporphyrinato)cobalt(III), $Co^{III}(tpp)^{+\cdot}Cl_2$, by thermal and light activations. Such behavior of $Co^{III}(tpp)Cl$ is considered to be closely related to the enzymatic reactions of natural metalloporphyrins. In previous papers,[2,3] we reported that crystals of $Co^{III}(tpp)Cl$ always contain a small amount of the π-cation radical and $Co^{II}(tpp)$. This fact suggests that these oxidation and reduction products are easily formed in the process of preparing $Co^{III}(tpp)Cl$. The elucidation of the redox behavior of $Co^{III}(tpp)Cl$ is expected to give useful information for an understanding of the functions of peroxidases in vivo.[4] In the present study, we examined in detail the effects of air and light on the redox behavior of $Co^{III}(tpp)Cl$ by using optical absorption and ESR techniques. It was found from these experiments that $Co^{III}(tpp)Cl$ in aerated DCM solutions is efficiently oxidized by irradiation of $\lambda < 500$ nm to produce π-cation radicals, $Co^{III}(tpp)^{+\cdot}Cl_2$. The photochemical formation mechanism of $Co^{III}(tpp)^{+\cdot}Cl_2$ is discussed on the basis of optical and ESR measurements of the irradiated DCM solutions.

Experimental

Materials. Chloro(5, 10, 15, 20-tetraphenylporphyrinato) cobalt(III), $Co^{III}(tpp)Cl$, was prepared by the method previously reported[5] (Found C, 72.66; H, 3.98; N, 7.71; Co, 8.29; Cl. 4.90%).

High-purity dichloromethane (DCM) supplied from Merck Co., Inc., was used as the solvent. The concentration of $Co^{III}(tpp)Cl$ was ca. 1.5×10^{-3} mol dm^{-3} throughout this study.

Instruments. The optical-absorption spectra were recorded on a HITACHI 330 spectrophotometer. The ESR spectra were measured by means of a JEOL FE-2XG spectrometer.

Measurements. Two portions of $Co^{III}(tpp)Cl$ in aerated DCM solutions were preserved, in a light room or in a dark room, over a period of one month. At about one-week intervals, the optical absorption and ESR spectra of the stored solutions were measured. The spectra of $Co^{III}(tpp)Cl$ in deaerated DCM solutions stored in the light room over the period of one week were also measured. For an examination of the effects of light on the photochemical reaction, $Co^{III}(tpp)Cl$ in aerated DCM solutions was irradiated by using a 500 W mercury lamp as a light source, with and without cut-off filters.

The unstable radicals generated from the solvent molecules by UV irradiation were examined by means of a spin-trapping method. Nitrosodurene(3 mg), a spin-trapping reagent, was added to neat DCM(1 cm^3) in vacuo, and the mixture was irradiated.

Results and Discussion

The Optical Absorption and ESR Spectral Changes of $Co^{III}(tpp)Cl$ in Aerated DCM Solutions Preserved in the Light Room. The optical absorption spectrum of $Co^{III}(tpp)Cl$[6] in DCM has a Soret band at 406 nm (ε=112000), a Q band at 543.5 nm (ε=13200), a small peak at 900 nm (ε=330), and an absorption shoulder at 1080 nm (ε=250). When the aerated DCM solution of $Co^{III}(tpp)Cl$ was preserved in the light room for one month, the optical-absorption spectrum changed, as is shown in Fig. 1. The intensities of the absorption bands of $Co^{III}(tpp)Cl$ gradually decreased with the preservation time, and broad absorption bands around 620 and 680 nm appeared. When methanol was added to the preserved solution, the broad absorption bands disappeared.

Since the solids of $Co^{III}(tpp)Cl$ used for the present study contain a small amount of the π-cation radical, $Co^{III}(tpp)^{+\cdot}Cl_2$, the ESR spectrum observed for the solution of $Co^{III}(tpp)Cl$ immediately after preparation showed a weak signal due to the π-cation radical.[1,2,7] The ESR signal increased in intensity with the preservation time. When methanol was added to the solution, the signal disappeared immediately.

On the other hand, the optical absorption spectra of $Co^{III}(tpp)Cl$ in aerated DCM solutions preserved in the dark room did not show any appreciable changes except for a slight decrease in the absorption intensity around

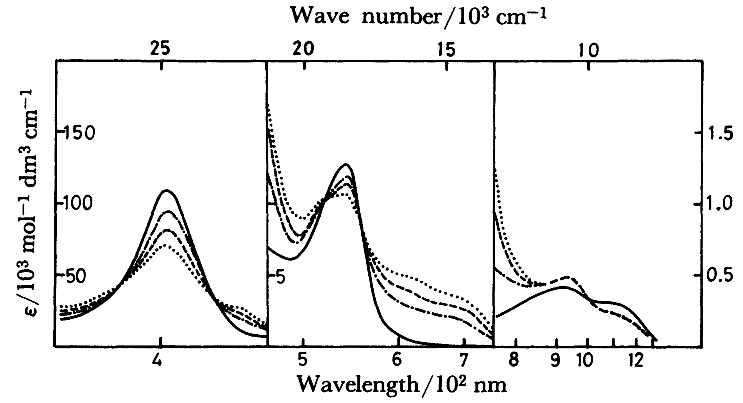

Fig. 1. Absorption spectral changes observed for aerated DCM solutions of Co^{III}(tpp)Cl preserved in the light room. Measured immediately after preparation (——), and measured after preservation for 6 (–·–·–), 13 (----), and 17 (······) days in the light room.

580—720 nm. The ESR spectra of the solutions showed a considerable decrease in the signal intensity of Co^{III}(tpp)$^{+\cdot}$Cl$_2$. This reveals that the π-cation radical decomposes thermally, while Co^{III}(tpp)Cl does not, so long as the solution is preserved in a dark room.

From these results, we may conclude that: (1) The absorption bands around 620 and 680 nm observed for the preserved solution are to be ascribed to the π-cation radicals, Co^{III}(tpp)$^{+\cdot}$Cl$_2$, and (2) the π-cation radical is produced photochemically when the aerated DCM solution of Co^{III}(tpp)Cl is preserved in a light room.

Participation of Solvent Radicals in the Formation of Co^{III}(tpp)$^{+\cdot}$Cl$_2$. The photochemical decomposition of chlorinated hydrocarbons is well-established. In order to examine the participation of the solvent radicals in the photochemical reactions, an aerated DCM solution of Co^{III}(tpp)Cl was irradiated by a mercury lamp without and with a cut-off filter transmitting the light of $\lambda>360$ nm. Since DCM molecules absorb only the light of $\lambda<360$ nm, Co^{III}(tpp)Cl can be selectively irradiated by the use of this filter.

Figure 2 shows the ESR signal intensity of Co^{III}(tpp)$^{+\cdot}$Cl$_2$, represented as a function of the irradiation time. The formation rate of Co^{III}(tpp)$^{+\cdot}$Cl$_2$ observed for the aerated solution irradiated without a filter becomes faster than that irradiated with the filter ($\lambda>360$ nm). This result indicates that the photooxidation of Co^{III}(tpp)Cl in DCM occurs by the photolysis of both Co^{III}(tpp)Cl and DCM, as will be discussed later.

The aerated DCM solution of Co^{III}(tpp)Cl was also irradiated by the use of a mercury lamp with a cut-off filter transmitting the light of $\lambda>500$ nm. No increase in the ESR signal intensity of Co^{III}(tpp)$^{+\cdot}$Cl$_2$ was observed. From this observation, we may conclude that the Q-band excitation gives no oxidation product, Co^{III}(tpp)$^{+\cdot}$Cl$_2$.

Detection of Solvent Radicals Generated from Neat DCM. Radicals generated by the direct photolysis of neat DCM in vacuo were examined by using the spin-trapping method. When the mixture was irradiated by the use of a mercury lamp without a filter, the ESR spectrum shown in Fig. 3 was obtained. The following ESR parameters were obtained for the generated radical: One nitrogen (a_N=1.37 mT) and two hydrogen (a_H=0.86 mT) nuclei. The radical was identified as a spin adduct of nitrosodurene with the ·CH$_2$Cl radical. This result clearly indicates that DCM molecules undergo the C–Cl bond cleavage upon UV irradiation to produce ·CH$_2$Cl radicals and chlorine atoms.

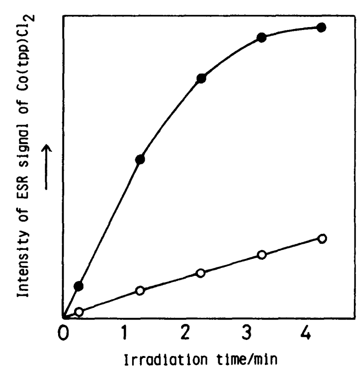

Fig. 2. ESR signal intensity of Co^{III}(tpp)$^{+\cdot}$Cl$_2$ generated from Co^{III}(tpp)Cl in aerated DCM solutions by irradiation with the light of $\lambda>360$ nm (○) and without filter (●).

The Optical Absorption and ESR Spectral Changes of Co^{III}(tpp)Cl in Degassed DCM Solutions Preserved in the Light Room. As is shown in Fig. 4, the optical absorption spectrum observed for the degassed DCM solution of Co^{III}(tpp)Cl preserved for one week in the light room showed a red shift of the Soret band and a blue shift of the Q band. The spectrum of pure Co^{II}(tpp) in DCM shows a Soret band at 409.5 nm (ε=295000), a Q band at 527.5 nm (ε=16200), and a band at 860 nm (ε=140). The spectral changes in Fig. 4 may be interpreted in terms of the photochemical formation of Co^{II}(tpp) by the photodissociation of the

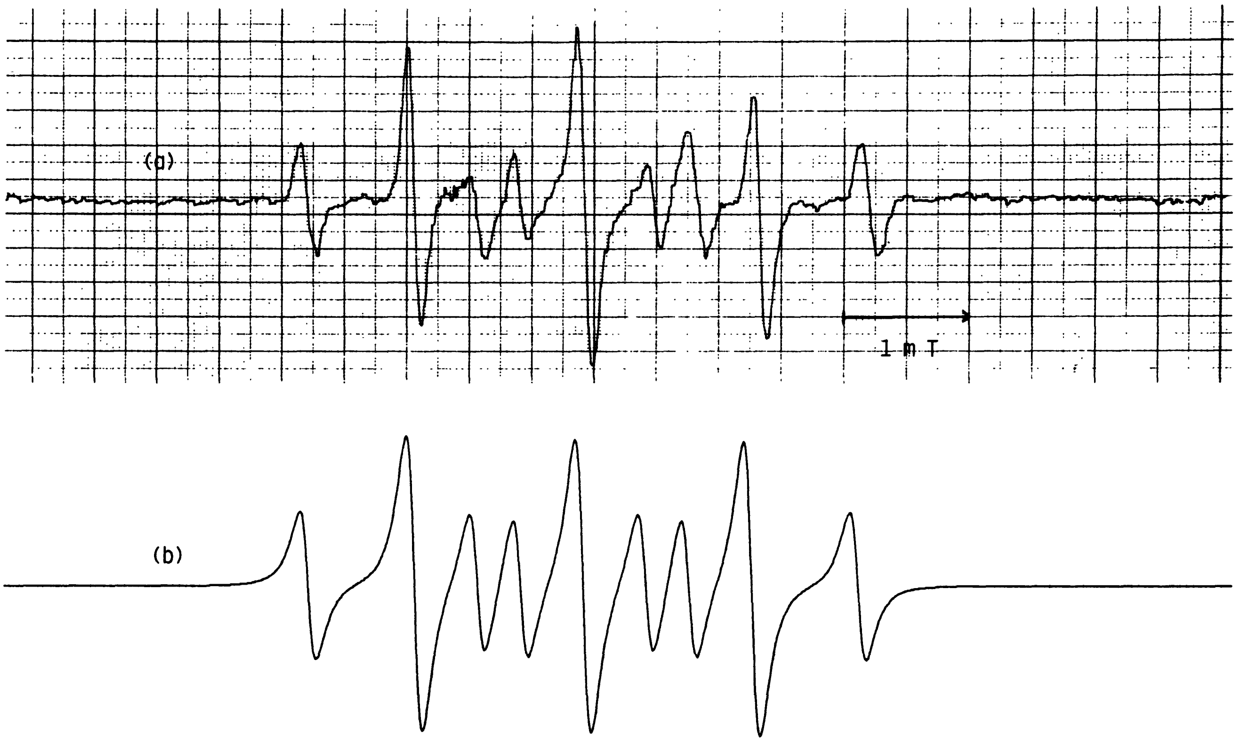

Fig. 3. ESR spectrum of spin adduct of nitrosodurene with $\cdot CH_2Cl$ radical. Observed (a) and simulated (b) spectra.

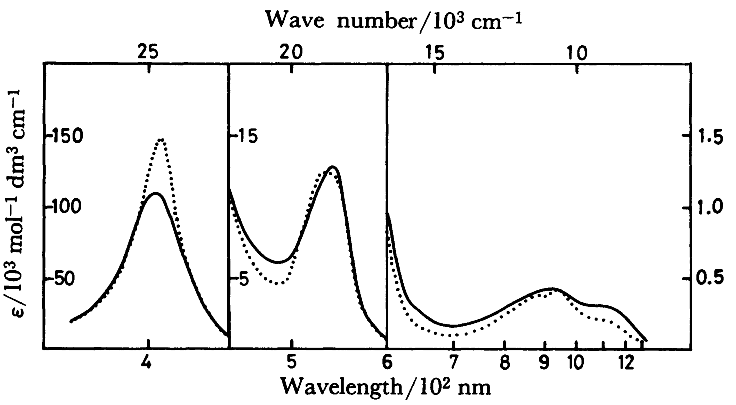

Fig. 4. Absorption spectral changes observed for degassed DCM solutions of $Co^{III}(tpp)Cl$ preserved in the light room. Measured immediately after preparation (——) and after preservation for 7 days (⋯⋯) in the light room.

chlorine atom from $Co^{III}(tpp)Cl$. In fact, the ESR spectrum measured for the degassed solution stored in the light room for one week shows an increase in the signal intensity of $Co^{II}(tpp)$.[8] No formation of the π-cation radical was observed in the degassed conditions.

Oxidation Mechanism of $Co^{III}(tpp)Cl$ in Aerated DCM Solutions. The photoinduced homolytic Co–Cl bond cleavage of $Co^{III}(tpp)Cl$ gives rise to the formation of $Co^{II}(tpp)$ and chlorine atoms:[9]

$$Co^{III}(tpp)Cl \xrightarrow{h\nu} Co^{II}(tpp) + Cl\cdot \qquad (1)$$

The occurrence of this reaction is demonstrated by the result that the concentration of $Co^{II}(tpp)$ in the degassed DCM solutions of $Co^{III}(tpp)Cl$ increases with the preservation time in the light room. The formation of the chlorine atoms in $Co^{III}(tpp)Cl$ solutions was also detected by using another spin-trapping method.[10] Subsequently, the chlorine atoms abstract hydrogen atoms from DCM molecules to yield solvent radicals, $\cdot CHCl_2$, and hydrochloric acid:

$$Cl\cdot + CH_2Cl_2 \longrightarrow \cdot CHCl_2 + HCl \qquad (2)$$

In the aerated solutions, the solvent radicals react with oxygen molecules, forming peroxyl radicals,

$CHCl_2O_2\cdot$. They oxidize $Co^{III}(tpp)Cl$ to produce π-cation radicals, $Co^{III}(tpp)^{+\cdot}Cl(CHCl_2O_2)$, which are then converted into the stable π-cation radicals of $Co^{III}(tpp)^{+\cdot}Cl_2$, presumably as a result of axial-ligand substitution.[1,11]

$$\cdot CHCl_2 + O_2 \longrightarrow [CHCl_2O_2\cdot] \qquad (3)$$

$$[CHCl_2O_2\cdot] + Co^{III}(tpp)Cl \longrightarrow Co^{III}(tpp)^{+\cdot}Cl(CHCl_2O_2) \qquad (4)$$

$$Co^{III}(tpp)^{+\cdot}Cl(CHCl_2O_2) + HCl \longrightarrow Co^{III}(tpp)^{+\cdot}Cl_2 + CHCl_2O_2H \qquad (5)$$

It should be noted here that the formation of the peroxyl radicals is essential to give the π-cation radicals.

As revealed from the spin-trapping study, solvent molecules, CH_2Cl_2, undergoes photodecomposition with the light of $\lambda < 360$ nm:

$$CH_2Cl_2 \xrightarrow{h\nu} Cl\cdot + \cdot CH_2Cl \qquad (6)$$

The solvent radicals produced by the photolysis of DCM molecules may also react with oxygen molecules, forming peroxyl radicals:

$$\cdot CH_2Cl + O_2 \longrightarrow CH_2ClO_2\cdot \qquad (7)$$

The radicals also oxidize $Co^{III}(tpp)Cl$ to form $Co^{III}(tpp)^{+\cdot}Cl_2$.

$$CH_2ClO_2\cdot + Co^{III}(tpp)Cl \longrightarrow Co^{III}(tpp)^{+\cdot}Cl(CH_2ClO_2) \qquad (8)$$

$$Co^{III}(tpp)^{+\cdot}Cl(CH_2ClO_2) + HCl \longrightarrow Co^{III}(tpp)^{+\cdot}Cl_2 + CH_2ClO_2H \qquad (9)$$

Thus, the fast formation rate of the $Co^{III}(tpp)^{+\cdot}Cl_2$ radical observed for the conditions without a filter (Fig. 2) is conducted with the two oxidation mechanisms described above. When we use the filter absorbing the light of $\lambda < 360$ nm, the first five reactions (1—5) dominate the formation of the π-cation radical.

According to Reaction (1), $Co^{III}(tpp)Cl$ decomposes photochemically to produce $Co^{II}(tpp)$. However, we can not detect $Co^{II}(tpp)$ in the aerated DCM solution of $Co^{III}(tpp)Cl$ upon irradiation. This fact suggests that the oxidant radicals, such as $CHCl_2O\cdot$, $CH_2ClO\cdot$, and $HO\cdot$, which are produced from $CHCl_2O_2H$ and CH_2ClO_2H, oxidize $Co^{II}(tpp)$ to reproduce $Co^{III}(tpp)Cl$.

Conclusion

Studies on the mechanism of the formation of the porphyrin π-cation radicals, $Co^{III}(tpp)^{+\cdot}Cl_2$, from $Co^{III}(tpp)Cl$ in aerated DCM solutions in the light room have revealed that: (1) $Co^{III}(tpp)Cl$ undergoes the homolytic cleavage of the Co–Cl bond in $Co^{III}(tpp)Cl$ upon Soret-band excitation to yield $Co^{II}(tpp)$ and chlorine atoms; (2) the hydrogen abstraction of the chlorine atoms from DCM molecules produces solvent radicals, which then react with oxygen molecules to form oxidant radicals; (3) oxidant radicals are also formed by the photolysis of aerated DCM, and (4) these oxidant radicals oxidize $Co^{III}(tpp)Cl$ to produce $Co^{III}(tpp)^{+\cdot}Cl_2$.

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