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THERMALLY REVERSIBLE FORMATION OF COBALT(III) TETRAPHENYLPORPHIN π-CATION RADICAL GENERATED FROM CHLOROTETRAPHENYLPORPHINATOCOBALT(III) IN CHLORINATED HYDROCARBONS

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In the solution of chlorotetraphenylporphinatocobalt(III) (CoTPPCl), a π-cation radical of six-coordinate Co(III)TPP is reversibly formed by thermal or light activation with a small enthalpy change.

The redox properties of metalloporphyrins and their related compounds play a key role in their biological functions, and many studies on their cation or anion radicals produced by chemical, electrochemical, or photochemical oxidation or reduction have extensively been performed.1) One of the authors has described that Co(III)TPPCl (Fig. 1) is a five-coordinate Co(III) complex of TPP having a square-pyramidal structure with the chlorine atom at the apex.2) Subsequent ^{1}H FT-NMR study3) has shown that this complex in chlorinated hydrocarbons changes partially into paramagnetic species by thermal activation. We now report that the species is a π-cation radical of six-coordinate Co(III)TPP and that the radical in the solution is generated under ambient temperature, air, and light, without using any oxidizing reagent. The formation of the radical in the solution occurs reversibly with a small enthalpy change. Such behavior of Co(III)TPPCl can closely be related to the enzymatic reactions of the biometallopigments.

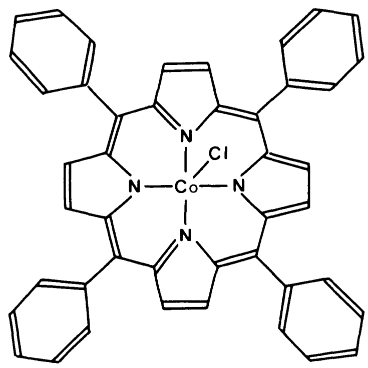

Fig. 1.

A solution of Co(III)TPPCl[4)] in chloroform, dichloromethane (DCM), or 1,1,-2,2-tetrachloroethane (TCE) showed an ESR spectrum at room temperature both in the absence and in the presence of air. The spectrum showed reversible temperature dependence (Fig. 2). The signal intensities decreased with lowering temperature. The spectrum at low temperatures as low as -40°C consists of eight hyperfine lines with the hyperfine coupling constant of about 10 gauss (g=2.0029 in DCM; 2.0047 in TCE). The number of the lines indicates clearly the coupling of an unpaired electron with the nuclear spin of ^{59}Co (I=7/2). The solution quenched at -196°C showed also the spectrum similar to that at -40°C, which means that the g value of the signal is quite isotropic. These facts imply that the signal is due to a free radical to which a TPP π-orbital participates mainly.

It has been confirmed by an electrochemical-ESR technique[5)] that the signal is attributed to a π-cation radical of six-coordinate Co(III)TPP with axial ligands. Namely Co(II)TPP in DCM was electrochemically oxidized in the presence of supporting electrolyte, tetrabutylammonium chloride. The ESR spectrum of the product obtained by two one-electron oxidation steps is shown in Fig. 3 together with the simulated one. The spectrum measured at temperature above -50°C agreed entirely with that of the species derived from Co(III)TPPCl in DCM. The spectrum simulated with one cobalt, four nitrogens, and two chlorines (a_{Co}=10.3G, a_N=2.80G, and $a_{^{35}Cl}$=2.20G ($a_{^{37}Cl}$=1.80G) (Fig. 3b) excellently coincided with the observed one. On the other hand, the π-cation radical generated in TCE is in the following equilibrium.[6)]

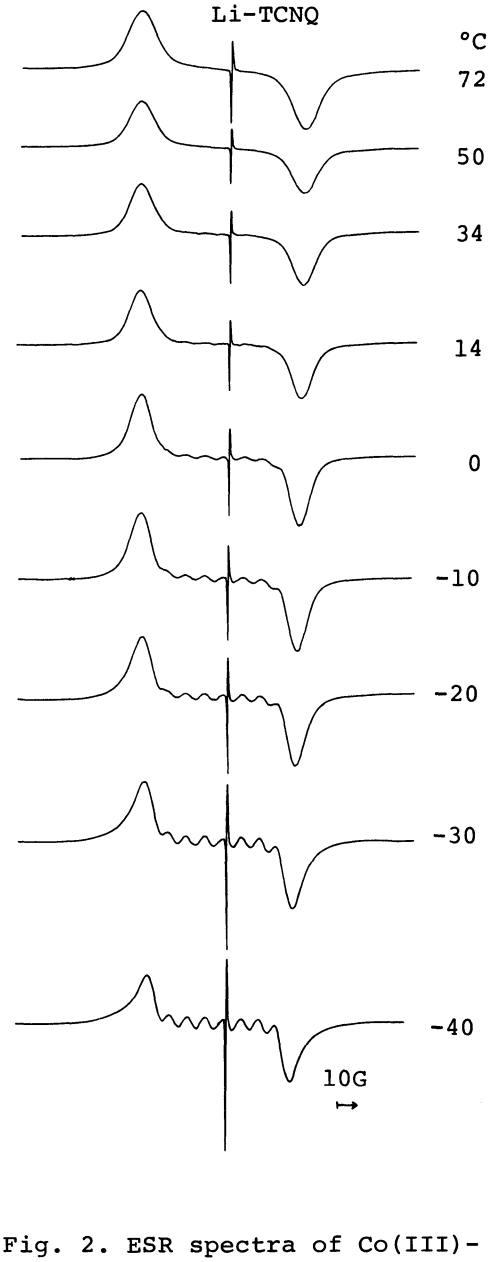

Fig. 2. ESR spectra of Co(III)-TPPCl in TCE as a function of temperature.

$$[Co^{III}TPP]^{\cdot 2+}2Cl^{-} + TCE \rightleftharpoons [Co^{III}TPP]^{\cdot 2+}(TCE)Cl^{-} + Cl^{-}$$

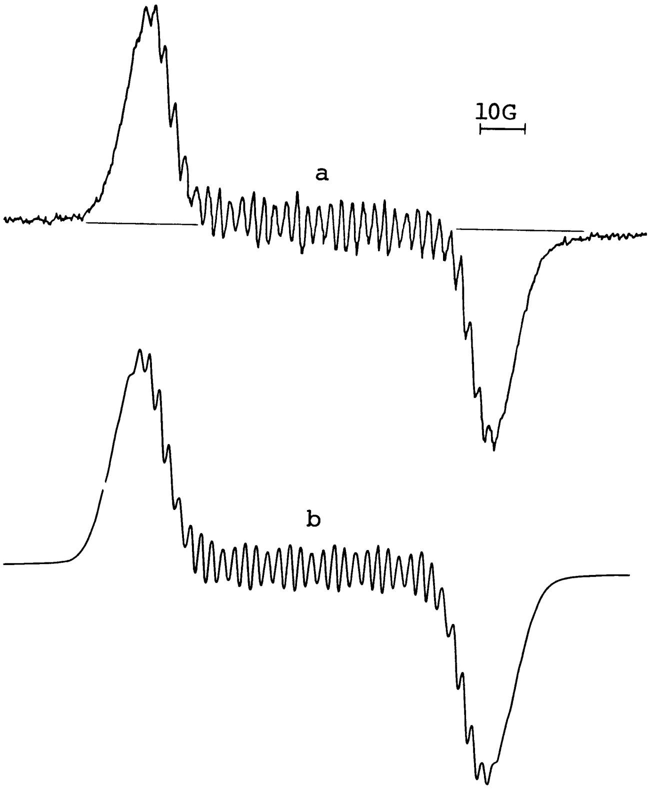

Fig. 3. a: The ESR spectrum of the paramagnetic species generated by electrochemical oxidation of Co(II)-TPP in DCM at -70°C. Supporting electrolyte: n-Bu_4NCl.
b: Simulated spectrum. See text about the hfcc used for the simulation.

Temperature dependence of the signal intensities relative to that of Li-TCNQ used as an external standard indicated that the concentration of the radical increased exponentially with raising the temperature up to room temperature, above which the intensity approached to a constant value as shown in Fig. 4. From the exponential portion the enthalpy change was estimated to be 4 and 10 kJ mol^{-1} in TCE and in DCM, respectively.

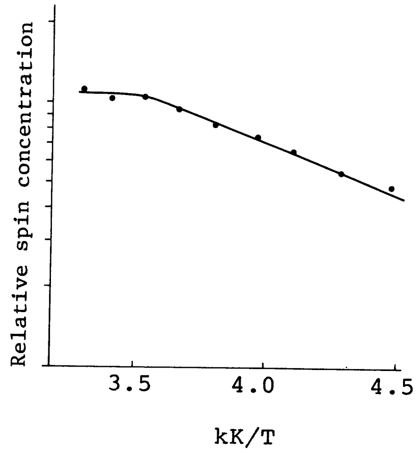

Fig. 4. Relative concentration of π-cation radical generated from Co(III)TPPCl in TCE as a function of temperature.

The formation of the radical was also accelerated by 500W Hg-lamp irradiation. Except for a transient increase at the beginning of the irradiation the intensity of the signal was enhanced constantly, the increasing rate at -60°C being eight times as large as that at -30°C. After the irradiation the concentration of the radical in TCE was retained for a period more than one hour at around -60°C.

A study on the mechanism of the formation of the radical by thermal and light activation is now in progress.

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References and Notes

1) J. FAJER and M.S. DAVIS, "Electron Spin Resonance of Porphyrin π Cations and Anions", in "The Porphyrins", ed by D. DOLPHIN, Academic Press, New York (1979), Vol. IV, pp. 197–256, and other references cited therein.

2) T. SAKURAI, K. YAMAMOTO, H. NAITO, and N. NAKAMOTO, Bull. Chem. Soc. Jpn., 49, 3042 (1976).

3) K. YAMAMOTO, J. UZAWA, and T. CHIJIMATSU, Chem. Lett., 1979, 89.

4) The complex was prepared by the method previously reported$^{2)}$ and identified by visible spectrum and analysis.

5) H. OHYA-NISHIGUCHI, Bull. Chem. Soc. Jpn., 52, 2064 (1979).

6) This result was obtained by comparison of ESR parameters of Co and N of the radicals generated by the oxidation of Co(II)TPP in various solvents and supporting electrolytes (H. OHYA-NISHIGUCHI, M. KOHNO, and K. YAMAMOTO, submitted to Bull. Chem. Soc. Jpn.).

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