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On the Interaction of Oxygen with Cobalt Phthalocyanine in Solution as investigated by ESR

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The interaction of oxygen with cobalt phthalocyanine in solution has been investigated by an ESR method. When the solution was exposed to oxygen, $g \sim 2.3$ singal due to the complex decreased while new resonance line developed at g-value very close to that of a free spin. The change of the two ESR signals was reversible with respect to ambient oxygen pressure. Moreover, when ascorbic acid was present initially in the solution, the uptake of oxygen took place in a catalytic way.

Prolonged contact of the cobalt complex with oxygen in the absence of ascorbic acid gave rise to another narrower signal irreversibly again very close to that of a free spin, resulting in very poor catalytic ability.

The behavior of the ESR signals was discussed in association with weak or destructive oxidation of the complex.

Introduction

The mode of coordination of ligands to a transition metal atom may profoundly alter the electronic property of the central atom and thereby determine the chemical reactivity of the resulting complex. Thus, Co^{2+} ion, coordinated with pentacyano ligands, was able to donate an electron to a variety of inorganic and organic ligands which possess OH or SH groups. As a result, stable hexacoordinated Co^{3+} complexes were formed accompanied by the evolution of hydrogen.[2)] The uptake of H_2,[3)] O_2,[4)] CO_2[5)] and CS_2[6)] by this complex in aqueous solution has already been demonstrated in this laboratory.

Electronic properties of metal phthalocyanine or porphin has also been investigated in connection with its biological significance. In this paper, we shall report an electron spin resonance (ESR) study concerning the interaction of oxygen with cobalt phthalocyanine in solution with special reference to electron transfer between the complex and oxygen.

Experimental

Samples of cobalt phthalocyanine and metal-free phthalocyanine were prepared according to Linstead[7)] and purified by repeated sublimations in vacuum. The elementary analysis and ultraviolet (UV) spectrum of the sample well agreed with that expected or reported earlier.[8)] Cobalt phthalocyanine has limited solubility in most solvents. We employed conc. sulfuric acid, pyridine and acetic acid saturated with trichloroacetic acid as the solvent. Experiments were carried out mostly with the saturated complex solution of CCl_3COOH–CH_3COOH; the supersaturated complex was carefully passed through a glass filter before use to remove traces of suspensions.

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2) T. Suzuki, T. Mizuta and T. Kwan, *Shokubai*, **9**, 36 (1967).

3) T. Mizuta and T. Kwan, *Nippon Kagaku Zasshi*, **86**, 1010 (1965).

4) T. Kwan, *Farumashia*, **2**, 327 (1966).

5) T. Suzuki and T. Kwan, *Nippon Kagaku Zasshi*, **87**, 342 (1966).

6) T. Mizuta, T. Suzuki and T. Kwan, *Nippon Kagaku Zasshi*, **88**, 573 (1967).

7) R.P. Linstead, *J. Chem. Soc.*, **1934**, 1719.

8) M. Whalley, *J. Chem. Soc.*, **1961**, 866.

The uptake of oxygen was studied at 50° by use of a Barcroft respirometer. The oxidation of ascorbic acid was studied also by the same apparatus.

Changes of the ESR spectrum due to oxygen contact were followed by JEOL–P–10 type spectrometer (100 KC, X-band) with samples kept at liquid nitrogen temperature. g-Values were determined on the basis of the resonance line exhibited by Mn^{2+} in MgO. The interaction of the complex with oxygen was investigated also by the Hitachi Type EPS–2 optical absorption spectrometer.

Results and Discussion

The ESR spectrum of cobalt phthalocyanine in solution consisted of a resonance signal with eight components and, in the case of pyridine solution, it was characterized by superhyperfine lines suggesting that the unpaired electron of Co^{2+} interacts with two nitrogen nuclei of the pyridine molecule. A typical ESR spectrum of the complex in CCl_3COOH–CH_3COOH is shown in Fig. 1. The spectrum agrees well with that of the earlier report[9] and can be interpreted by a set of $g_\perp=2.3$ and $g_\parallel=2.0$ resonance lines.

When the solution was exposed to oxygen at room temperature, the color changed from green to violet initially. Then, ESR measurement indicated that the spin density of the $g\sim2.3$ due to Co^{2+} is decreased. On the other hand, a new symmetrical signal appeared at $g=2.002$ with line width of about 14 G. When oxygen was pumped off, the $g\sim2.3$ signal was increased to an extent accompanied by simultaneous decay of the $g=2.002$ signal; the change was partly reversible. Addition of ascorbic acid, triphenyl phosphine or pyridine also resulted in a partial recovery of the original intensity of the $g\sim2.3$ signal. The reversible change may readily be explained in terms of the oxidation–reduction of the central cobalt ion. We shall discuss the origin of the new signal at $g=2.002$ later.

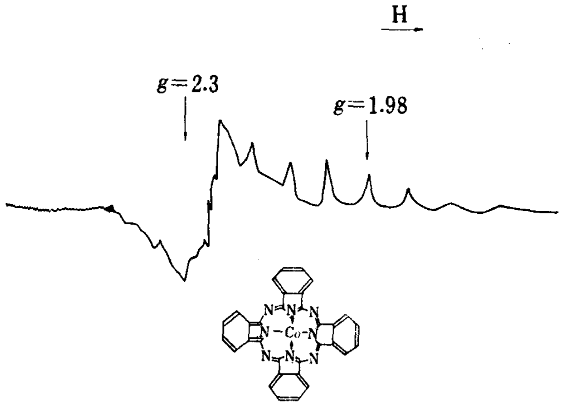

Fig. 1. ESR Spectrum of Cobalt Phthalocyanine in CCl_3COOH-CH_3COOH

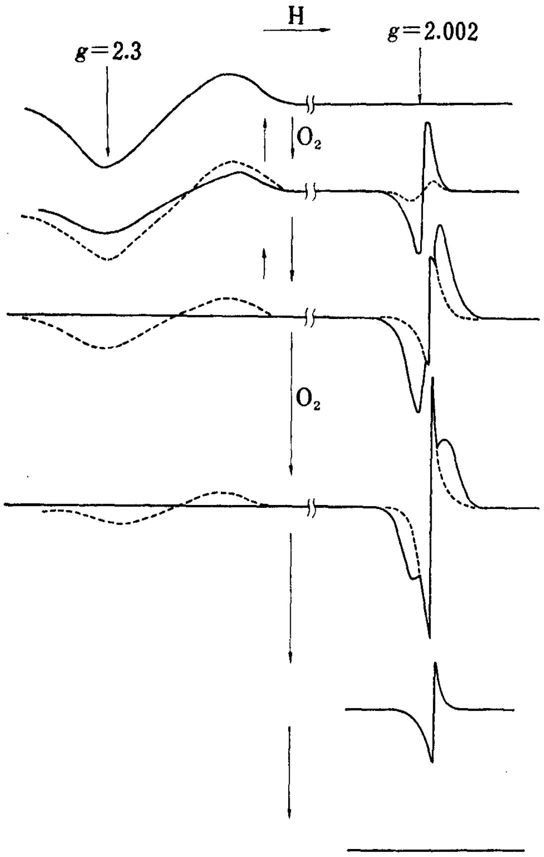

Fig. 2. Changes of the ESR Spectrum of Cobalt Phthalocyanine upon Exposure to Oxygen

The reaction temperature was raised from about 25° to 100°.

It is noted that such a reversible redox behavior is not perceptible when conc. sulfuric acid or pyridine is used as the solvent. The solvent seems to occupy z-axis of the complex

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[9] J.M. Assour, *J. Am. Chem. Soc.*, **87**, 207, 470 (1965).

protecting Co^{2+} from oxygen attack, or the unpaired electron of d_{z^2} orbital of Co^{2+} seems to ineract with solvent or oxygen molecule.

Prolonged contact of cobalt phthalocyanine in CCl_3COOH–CH_3COOH gave rise to another narrower signal at $g=2.004$ (4 G) overlapping with the foregoing $g=2.002$ signal. This change was no longer reversible at all with respect to ambient oxygen pressure. Also, addition of ascorbic acid did not affect the signal intensity. When the solution was heated up to 100° in the presence of oxygen, the color of the solution gradually changed to pale yellow. During the period of such change, both $g\sim2.3$ and $g=2.002$ singals disappeared and the spectrum consisted of only $g=2.004$ sharp line, which also appeared to decay gradually. Thus, at the final stage no ESR spectrum could be detected. Such changes of the ESR spectra during the contact with oxygen are illustrated in Fig. 2. It is noted that the line width of the $g=2.002$ signal is not constant at all; it changed from 14 to 28 G during the interaction with oxygen. Since no such change of the ESR spectra was observed in high vacuum, the change of the ESR spectra, as shown by Fig. 2, should be associated with the oxidation of cobalt phthalocyanine by oxygen.

Inspection of the change of the optical absorption spectra during the initial stage of the interaction of the complex with oxygen in CCl_3COOH–CH_3COOH indicated that the absorption band at 730 mμ decreased while new absorption band appeared near 530 mμ. Addition of ascorbic acid restored the original absorption band at 730 mμ, showing that the change was reversible. When the color of the cobalt complex solution changed to pale yellow due to prolonged contact with oxygen at 100°, no optical absorption peak could be found in the regions. Thus, the change of the optical absorption spectra are quite parallel with that of the ESR spectra. The spectral change of the cobalt complex is illustrated in Fig. 3.

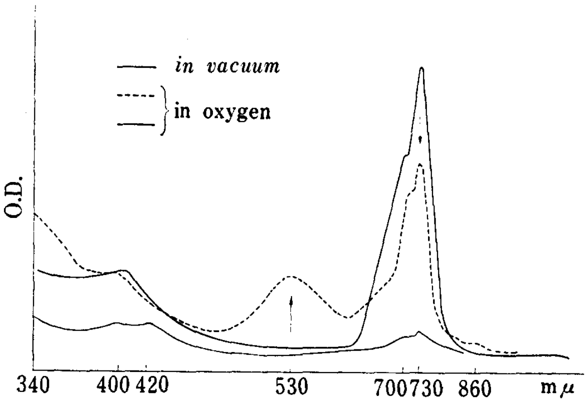

Fig. 3. Optical Absorption Spectrum of Cobalt Phthalocyanine in CCl_3COOH–CH_3COOH with or without Oxygen

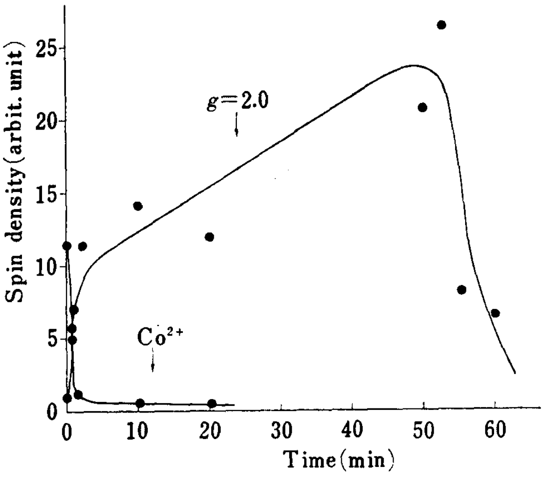

Fig. 4. Relationship between the Rise of $g=2.0$ Signal and the Decay of $g=2.3$ during the Interaction of Cobalt Phthalocyanine with Oxygen (1 atm) at 50°

Let us turn to the change of ESR signals. In Fig. 4 is compared the reversible change of the signal at $g\sim2.3$ and $g\sim2.0$ during the course of the interaction with oxygen. The relation should be regarded as only approximate due to the error in the estimation of the spin density in particular of the $g\sim2.3$ signal. Nevertheless, it is interesting to note that the decrease of the $g\sim2.3$ signal is roughly balanced with the increase of the $g\sim2.0$ spin density during the initial contact with oxygen.

The uptake of oxygen by a saturated CCl_3COOH–CH_3COOH solution of cobalt phthalocyanine was immeasurably small and slow at 30°. Therefore, some excess amount of the complex was employed to investigate the uptake of oxygen accurately. The rate was still not fast at 50° as shown by the curve C of Fig. 5; the uptake of oxygen reached only about

20 mole % of the cobalt complex present during five hours' contact. The color of the solution then became pale yellow. When ascorbic acid was present initially the uptake of oxygen took place until the ascorbic acid was entirely consumed. Cobalt phthalocyanine sulfonate, which dissolves completely in the solvent, showed a similar catalytic activity for the oxidation of ascorbic acid. Typical rate data are illustrated also in Fig. 5. Metal-free phthalocyanine showed no catalytic activity, suggesting that central metal is essential at least to produce the activity.

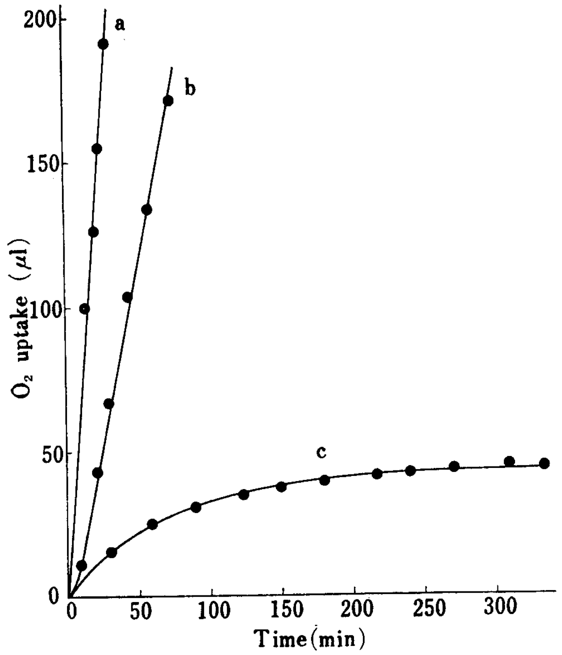

Fig. 5. The Rate of Uptake of Oxygen with or without Ascorbic Acid

a : cobalt phthalocyanine 4×10^{-6} mole
ascorbic acid 8×10^{-5} mole
$T=30°$
b : cobalt phthalocyanine sulfonate 5×10^{-6} mole
ascorbic acid 5×10^{-5} mole
$T=30°$
c : cobalt phthalocyanine 3×10^{-6} mole
no ascorbic acid present
$T=50°$

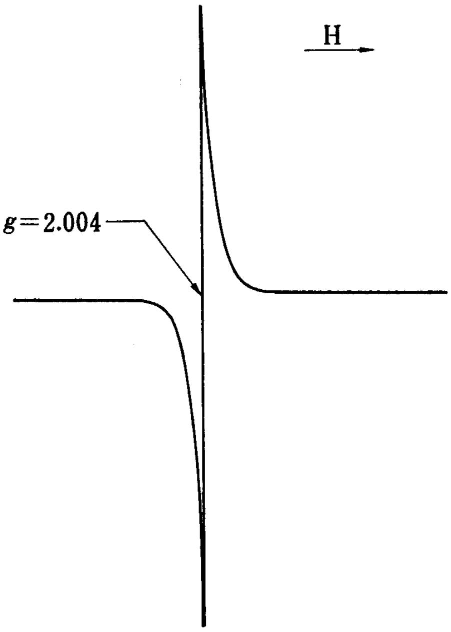

Fig. 6. ESR Spectrum of Cobalt Phthalocyanine in $CCl_3COOH-CH_3COOH$ after Addition of Ce^{4+} in the Absence of Oxygen

The solution contains 7×10^{-6} mole cobalt phthalocyanine and 3×10^{-8} mole Ce^{4+} in 0.3 ml volume.

The catalytic oxidation of ascorbic acid by the cobalt phthalocyanine may probably follow the scheme:

$$O_2 + CoPc \rightleftarrows O_2\cdots\cdots CoPc$$

$$O_2\cdots\cdots CoPc + ASH_2 \longrightarrow CoPc + AS + H_2O_2$$

where CoPc, ASH_2 and AS denote cobalt phthalocyanine, ascorbic acid and dehydroascorbic acid respectively. If cobalt phthalocyanine was irreversibly oxidized, as judged from the appearance of the $g=2.004$ (4 G) signal and its subsequent decay, the complex showed little catalytic activity for the oxidation of ascorbic acid. The result suggests that weak or reversible interaction of the complex with oxygen is necessary for the oxidation catalysis.

The $g\sim2.3$ signal may undoubtedly be regarded as the unpaired electron that occupies the d_z2 orbital of Co^{2+}. Its decay or rise is associated with the redox of the cobalt ion. On the other hand, the origin of the two symmetrical signals very close to that of a free spin having line width of 14—28 G and 4 G respectively can not be identified with certainty. These signals were produced, as mentioned already, in a successive way, and the study of microwave power saturation indicated that two signals were originated from different species.

It should be reminded, in this connection, that the $g\sim2.0$ signal initially formed was reversibly reduced, if not all, by ascorbic acid while the other one formed later was not affected. In other words, the $g=2.002$ (14—28 G) signal must be associated with weakly oxidized state of the O_2...CoPc system. We have already shown that the change of the spin density, with respect to the decay of $g\sim2.3$ and with the rise of the $g\sim2.0$, is approximately balanced at the initial stage. This relation should be anticipated if the unpaired electron of Co^{2+} is transferred to coordinated oxygen molecule to form O_2^- and if the $g=2.002$ signal is due to O_2^-. Recently, ESR evidence was put forward in this laboratory[10] for molecular oxygen ion adsorbed on inorganic semiconductors such as ZnO, TiO_2 and ZrO_2. However, the ESR signal was characterized with three g-values near $g\sim2.0$ and its shape was rather asymmetrical unlike the present one.

Another interpretation would be that phthalocyanine ring is oxidized to leave a positive hole in the ring. So far, the oxidation of metal phthalocyanine has been the object of many investigations. For instance, the oxidation of copper phthalocyanine sulfonate by Ce^{4+} has been investigated in 85% H_3PO_4 by Taube.[11] Accordingly, new absorption band appeared at 530 mμ on addition of Ce^{4+} accompanied by the decay of 725 mμ band originally present, and furthermore the spectral change was reversed on addition of reducing agent such as Fe^{2+} or Sn^{2+}. Thus, the redox behavior of this complex is quite analogous with that described above. The appearance of 530 mμ band has been attributed by Taube to "one-electron oxidation" of the phthalocyanine ring.

Attempts were made, therefore, to investigate the oxidation of cobalt phthalocyanine by Ce^{4+} by optical and ESR spectroscopy, respectively. The optical absorption spectrum of cobalt phthalocyanine showed λ_{max} at 730 mμ in CCl_3COOH–CH_3COOH as shown in Fig. 3. Addition of Ce^{4+} to the system gave 530—540 mμ band. Furthermore, subsequent addition of ascorbic acid restored the original spectrum. Thus, the spectral change was quite similar to that obtained with oxygen as well as with that of copper phthalocyanine sulfonate due to Taube. It is particularly note-worthy that analogous spectral change occurred even when cobalt-free phthalocyanine was subjected to Ce^{4+} treatment.

Let us investigate ESR behaviors of cobalt phthalocyanine or cobalt-free phthalocyanine mixed with Ce^{4+}. Various amounts of Ce^{4+} were used to oxidize cobalt phthalocyanine; one was excess over CoPc and the other far less. Both samples gave rise to essentially the same spectrum, *i. e.* a symmetrical resonance line was produced at g-value very close to a free spin, as shown in Fig. 6.

The color of the solution changed into pale yellow soon after excess amounts of Ce^{4+} was added, and no ESR spectrum was then recognized. The result suggests that the oxidation by Ce^{4+} takes place to an extensive manner. On the other hand, the $g\sim2.0$ signal, produced on addition of a small amount of Ce^{4+}, showed a tendency to be reduced by ascorbic acid. The result suggests that Ce^{4+} oxidation is characterized also by weak or reversible one just as in the case of the interaction of cobalt phthalocyanine with oxygen at the intial stage. It is interesting to note that cobalt-free phthalocyanine shows a similar ESR trend to Ce^{4+} oxidation.

It is known that organic semiconductor or biological material in its solid state often gives ESR signal at g-value close to a free spin.[12,13] Indeed, cobalt-free phthalocyanine gave rise to an ESR signal near $g\sim2.0$ (4 G) in vacuum in both powder and supersaturated solution. No ESR spectrum was observed, however, for a sample in a dissolved state. The ESR spectrum, as shown in Fig. 6, has actually been obtained by adding Ce^{4+} to such a homogeneous

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[10] M. Setaka, S. Fukuzawa, Y. Kirino and T. Kwan, *Chem. Pharm. Bull.* (Tokyo), **16**, 1240 (1968).
[11] A.E. Cahhill and H. Taube, *J. Am. Chem. Soc.*, **73**, 2847 (1951).
[12] Y. Matsunaga, *Can. J. Chem.*, **38**, 323 (1960).
[13] D.J.E. Ingram, *J. Am. Chem. Soc.*, **79**, 1870 (1957).

and hence non-resonant solution. The line width of the $g\sim2.0$ line became broader when Ce^{4+} was added in the presence of air in accordance with the spectrum as shown in Fig. 2.

While the line width of the $g\sim2.0$ signal is not identical for Ce^{4+} and O_2 oxidation, one may infer the fact that the redox behavior of the complex, as indicated by both ESR and optical absorption spectra, is quite parallel with each other; it has been demonstrated that Ce^{4+} produces $g\sim2.0$ signal as well as 530—540 mμ band in a reversible manner just as oxygen does during its initial contact with cobalt phthalocyanine.

Finally, it is tentatively suggested that the $g\sim2.0$ line, produced at the initial stage of oxygen contact with cobalt phthalocyanine, is concerned with weak oxidation of the ring which might be called, after Taube, as "one-electron oxidation". It is considered that this sort of oxidation may be shared also by the cobalt ion. Further investigations are required to elucidate the mechanism of electron transfer along with the scheme. On the other hand, the irreversible growth of another $g\sim2.0$ line would be associated with "more than one-electron oxidation" which ultimately leads to destructive oxidation of the ring.