Reversible Oxygen Uptake and Catalytic Oxidation by Electrochemically Reduced Sulphonated Cobalt Phthalocyanine

By Shunsuke Meshitsuka*, Masaru Ichikawa, and Kenji Tamaru
(Sagami Chemical Research Centre, Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa 229, Japan)

Summary Reversible oxygen uptake was observed in the electrochemically reduced di-negative anion of cobalt tetrasulphonate phthalocyanine (CoPcTs^{2-}) by visible and e.s.r. spectra; oxygen activated by the reduced CoPcTs in the reversible oxygen uptake system was used for catalytic oxidation of polyhydric phenols.

The reaction of oxygen with metal complexes is of great interest in studies of the oxygen carriers, oxidase and oxygenase;[1] such reactions are also the homogeneous analogues of heterogeneous metal-catalysed oxidations.[2] Oxygen adducts of neutral metal complexes have been well studied,[3] but there have been few studies of adducts with metal complexes in other oxidation states. We report a new catalytic system, the interaction of oxygen with electrochemically reduced tetrasulphonated cobalt phthalocyanines (CoPcTs), oxygen being activated by the reduced CoPcTs.

Cobalt phthalocyanine (CoPc) was synthesized from phthalonitrile and the metal chloride in quinoline. Tetrasulphonated phthalocyanine was prepared by refluxing CoPc in 60% fuming H_2SO_4 for 3 h at 60 °C.[4] An electrolyte consisting of 10^{-3}M CoPcTs in 10^{-1}M-Et_4NClO_4–DMF (dimethylformamide) was used in the reductions; DMF was purified by repeated distillation and dried on a molecular sieve. Pt gauze was used for the working electrode, and a Pt plate for the counter electrode. The catholyte and anolyte were separated by a glass frit.

It was confirmed that the CoPcTs exhibits successive one-electron reductions, as found previously. One- and two-electron reduction products of CoPcTs were obtained by electrolysis at $-1{\cdot}0$ and $-1{\cdot}8$ V (*vs.* SCE) respectively; CoPcTs^{-} was green and CoPcTs^{2-} was purple. The absorption spectra of CoPcTs^{-} (λ_{max} 475 and 704 nm) and CoPcTs^{2-} (λ_{max} 495 nm) were the same as those of the anions obtained by reduction by sodium.[6] No e.s.r. signal was observed for CoPcTs^{-} which was diamagnetic, but the e.s.r. spectrum of CoPcTs^{2-} was in good agreement with the literature.[5]

After electrochemical reduction oxygen gas was admitted to the DMF solution of $CoPcTs^{2-}$, and the visible spectrum was recorded during the reaction. Soon after admission of oxygen the $CoPcTs^{2-}$ absorption bands disappeared and $CoPcTs^-$ and CoPcTs bands appeared instead. The $CoPcTs^-$ bands then gradually diminished, CoPcTs bands predominating. When oxygen pressure was high, the reaction was so fast that it could not be followed. After the $CoPcTs^-$ band disappeared, the ambient gas was evacuated, and the CoPcTs bands became weak as those of $CoPcTs^-$ reappeared. Isosbestic points were observed at 575 and 685 nm (Figure). After 2 h only $CoPcTs^-$ bands were observed. When oxygen was readmitted a change from $CoPcTs^-$ to CoPcTs was observed, and this oxygen uptake was reversible for >20 cycles. The isosbestic points show that the complex was not decomposed during the reaction, but electrochemically prepared $CoPcTs^-$ (II) was oxidized to $CoPcTs{\cdot}O_2^-$ (IV) irreversibly. All reactions were carried out at room temperature. CoPc anions did not exhibit reversible oxygen uptake with alkali metals.

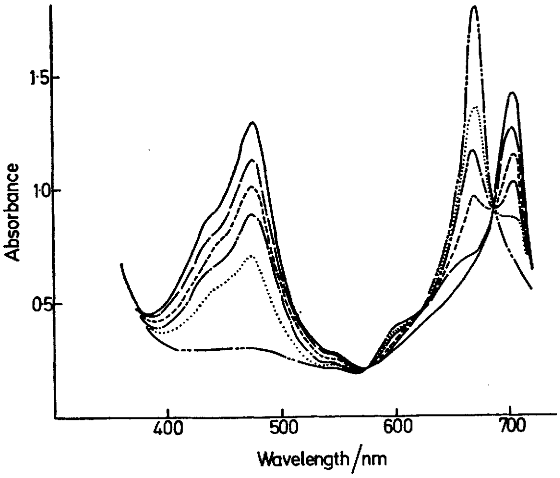
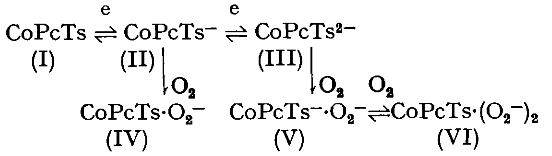


FIGURE 1. Changes in absorption spectra in the 380—720 nm region during the reaction and after evacuation of the ambient oxygen; the band at 667 nm decreases with a corresponding increase at 475 and 704 nm.

The e.s.r. spectra of oxygen adducts of CoPc and CoPcTs have been studied before, when O_2^- signals were observed. When oxygen was admitted into the DMF solution of $CoPcTs^{2-}$, a signal (g 2·00, line width 14 G) appeared in place of the $CoPcTs^{2-}$ signal, and as clear hyperfine structures have not been observed at liquid nitrogen temperature, it was thought to be the O_2^- signal (*cf.* previous spectra[7]). The peak-to-peak height of the O_2^- signal decreased upon evacuation of the ambient oxygen, finally being about half the height of that from the fully oxygenated complex solution, but was restored by readmission of oxygen. The change in absorption and e.s.r. spectra demonstrated that two molecules of oxygen were attached to $CoPcTs^{2-}$, one of which could be released reversibly by evacuation. Volumetric measurements of oxygen absorption showed that the ratio of CoPcTs: O_2 was *ca.* 1:2 at full oxidation. The reactions of electrochemically reduced CoPcTs with an oxygen molecule are shown in Scheme 1. The oxidation states and visible spectra of the phthalocyanines are similar in complexes (I), (IV), and (VI), as are those in complexes (II) and (V). Although the visible absorption bands of phthalocyanines are assigned to $\pi\pi$ transitions,[8] the π electronic states seemed little changed by the exchange of axial ligand.



$$\begin{tikzcd}
\underset{\text{(I)}}{\text{CoPcTs}} \arrow[r, shift left, "e"] \arrow[r, leftarrow, shift right] & \underset{\text{(II)}}{\text{CoPcTs}^-} \arrow[r, shift left, "e"] \arrow[r, leftarrow, shift right] \arrow[d, "O_2"] & \underset{\text{(III)}}{\text{CoPcTs}^{2-}} \arrow[d, "O_2"] & \\
 & \underset{\text{(IV)}}{\text{CoPcTs}{\cdot}O_2^-} & \underset{\text{(V)}}{\text{CoPcTs}^-{\cdot}O_2^-} \arrow[r, shift left, "O_2"] \arrow[r, leftarrow, shift right] & \underset{\text{(VI)}}{\text{CoPcTs}{\cdot}(O_2^-)_2}
\end{tikzcd}$$

SCHEME 1

The absorption and e.s.r. spectral changes were also examined for $CoPcTs^-$ and $CoPcTs^{2-}$ films, prepared by evaporation of the DMF solutions. $CoPcTs^-$ was oxidized by oxygen to CoPcTs, while $CoPcTs^{2-}$ was oxidised only to $CoPcTs^-$ but no further (Scheme 2). The spectra were unchanged on evacuation showing that only one oxygen molecule was irreversibly taken up by each CoPcTs anion in the films.

$$\text{CoPcTs}^- \xrightarrow{O_2} \text{CoPcTs}{\cdot}O_2^-$$

$$\text{CoPcTs}^{2-} \xrightarrow{O_2} \text{CoPcTs}^-{\cdot}O_2^-$$

SCHEME 2

In catalytic oxidations, oxygen is usually activated by the catalysts, and we have carried out catalytic oxidations using the oxygen activated in these systems. Oxygen was admitted into the DMF solution of (III), and the substrate was incubated. Reactions were followed by measurements of the O_2 uptake. Polyhydric phenols such as catechol, hydroquinone, and pyrogallol were oxidized catalytically at room temperature, but the products could not be analysed because of polymerization of the oxidized species, except for trimethylhydroquinone which led to trimethylbenzoquinone. Phenol and substituted phenols such as xylenol were not oxidized, (the amount of O_2 needed for oxidation was *ca.* 100 times the catalytic amount), these compounds were not oxidized in the presence of complexes (I) or (II) or Co_2^+ ions either. The reduced state of the metal complex and its activation of oxygen are essential for this catalytic system. Electrochemically reduced NiPcTs provides a similar catalytic system.

(*Received*, 16*th December* 1974; *Com.* 1515.)

---

[1] J. H. Wang, *Accounts Chem. Res.*, 1970, **3**, 90; R. J. P. Williams, *Inorg. Chim. Acta, Rev.*, 1971, **5**, 137; G. W. R. Canham and A. B. P. Lever, *J. Chem. Educ.*, 1972, **49**, 656; G. Henrici-Olivé and S. Olivé, *Angew. Chem.*, 1974, **13**, 29.

[2] J. S. Valentine, *Chem. Rev.*, 1973, **73**, 235.

[3] D. V. Stynes, H. C. Stynes, J. A. Ibers, and B. R. James, *J. Amer. Chem. Soc.*, 1973, **95**, 1142; F. A. Walker, *ibid.*, 1973, **95**, 1154; A. L. Crumbliss and F. Basolo, *ibid.*, 1970, **92**, 55; J. H. Bayston, N. K. King, F. D. Looney, and M. E. Winfield, *ibid.*, 1969, **91**, 2775.

[4] Y. Bansho, K. Kuwahara, T. Sekiguchi, and K. Yamashiro, *Nippon Kagaku Kashi*, 1972, 1712.

[5] L. D. Rollmann and R. T. Iwamoto, *J. Amer. Chem. Soc.*, 1968, **90**, 1455.

[6] Y. Bansho, T. Shimura, O. Ueda, H. Tanzaki, and K. Takei, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1971, **74**, 1870.

[7] Y. Ogata, K. Marumo, and T. Kwan, *Chem. Pharm. Bull. Japan*, 1969, **17**, 1194; E. W. Abel, *Chem. Comm.*, 1971, 449.

[8] A. Henriksson, B. Roos, and M. Sundbom, *Theor. Chim. Acta*, 1972, **27**, 303; A. M. Schaffer and M. Gouterman, *ibid.*, 1972, **25**, 62.