Electrocatalytic Formation of Superoxides in the Presence of Cobalt Chelates

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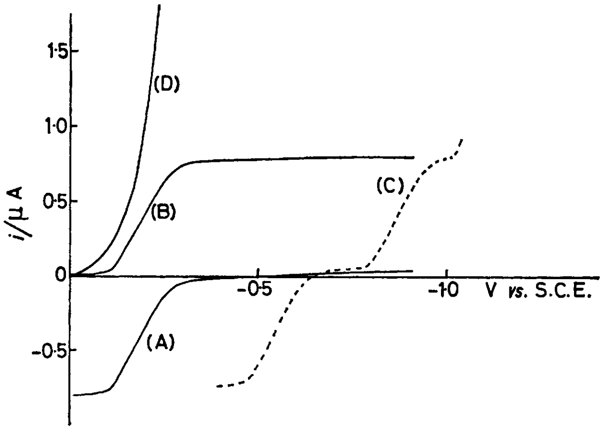
Summary Controlled potential reduction of the *NN*-ethylenebis(salicylideneaminato)dipyridinecobalt(III) cation in pyridine in the presence of lithium perchlorate and oxygen leads to the electrocatalytic formation of LiO_2.

Investigation of the electrochemical reduction of molecular oxygen in the presence of transition metal compounds is relevant to an understanding of catalytic oxygen reduction in biological and non-biological systems. The increase in reactivity of the oxygen molecule is attributed to co-ordination to the metal and formation of oxygen adducts as intermediates.[1] Electrochemical reduction of dioxygen in aprotic solvents in the presence of oxygen carrier cobalt chelates has been shown to occur at less negative potentials compared with the non-co-ordinated molecule.[2] We now report that the electrochemical one-electron reduction of dioxygen occurs catalytically, in the presence of cobalt chelates and Li^+ in pyridine (py), with formation of lithium superoxide. *NN'*-Ethylenebis(salicylideneaminato)cobalt(II), $[Co^{II}(salen)]^{\circ}$, and the corresponding Co^{III} chelate $[Co^{III}(salen)(py)_2]^+$ in deoxygenated pyridine solution containing $(NEt_4)ClO_4$ (0·1 mol dm^{-3}) as supporting electrolyte show respectively, diffusion controlled reversible polarographic anodic and cathodic waves with half-wave potential $E_{\frac{1}{2}}$ — 0·54 V *vs.* S.C.E. When $LiClO_4$ is used as supporting electrolyte the only difference in the polarographic behaviour is a shift of $E_{\frac{1}{2}}$ to −0·2 V *vs.* S.C.E. (Figure, A and B).



The displacement of the $E_{\frac{1}{2}}$ value is attributed to the electrostatic interaction between the oxygen atoms of the ligand in the cobalt chelates and Li^+, which increases the electron affinity of the cobalt atom, as already reported for the reduction of several Co^{II} chelates.[3]

In O_2-containing solutions of $[Co^{II}(salen)]^\circ$ ($0{\cdot}5 \times 10^{-3}$ mol dm^{-3}) and $(NEt_4)ClO_4$ ($0{\cdot}1$ mol dm^{-3}) the adduct $[Co^{II}(salen)(O_2)]^\circ$ is present and two polarographic waves are observed: the anodic wave is due to the oxidation of the $[Co^{II}(salen)]^\circ$ and the cathodic wave to the reduction of co-ordinated oxygen[2] ($E_{\frac{1}{2}} - 0{\cdot}87$ V *vs.* S.C.E.) (Figure, C).

When $LiClO_4$ is used as supporting electrolyte under the same conditions the diffusion-controlled anodic wave is replaced by a catalytic cathodic wave (Figure, D) at potentials corresponding to the $E_{\frac{1}{2}}$ of the Co^{II}–Co^{III} couple. The latter potential is significantly more positive than that of non-co-ordinated oxygen in the same solvent and with the same supporting electrolyte. This wave is attributed to the catalytic one-electron reduction of $[Co^{III}(salen)(py)_2]^+$ which is formed from $[Co^{II}(salen)(O_2)]^\circ$ in the presence of Li^+.

In fact by bubbling N_2 through $[Co^{II}(salen)(O_2)]^\circ$ solutions containing $[NEt_4][ClO_4]$ the $[Co^{II}(salen)]^\circ$ is regenerated as shown by an anodic wave with $E_{\frac{1}{2}} - 0{\cdot}54$ V *vs.* S.C.E. In the presence of $LiClO_4$ the formation of $[Co^{III}(salen)(py)_2]^+$ is proved by a cathodic wave with $E_{\frac{1}{2}}$ $-0{\cdot}20$ V *vs.* S.C.E. Electrolysis in an oxygen-saturated solution of $[Co^{III}(salen)(py)_2]^+$ at $-0{\cdot}27$ V *vs.* S.C.E. in the presence of Li^+ gave rise to a yellowish precipitate of LiO_2 at the Hg cathode. LiO_2 was identified by the 'nitroblue tetrazolium' test.[4] Treatment with water led to disproportionation and formation of H_2O_2.

From the above results the catalytic mechanism in reactions (1)—(3) is proposed. The overall reaction is the

$$[\mathrm{Co^{III}(salen)}]^+ \xrightarrow[\mathrm{O_2}]{\mathrm{e}} [\mathrm{Co^{II}(salen)(O_2)}] \qquad (1)$$

$$[\mathrm{Co^{II}(salen)(O_2)}] \longleftrightarrow [\mathrm{Co^{III}(salen)(O_2)^-}] \qquad (2)$$

$$\begin{aligned}[\mathrm{Co^{III}(salen)(O_2)^-}] + \mathrm{M}^+ &\rightleftharpoons [\mathrm{Co^{III}(salen)(O_2 \ldots . M)^+}] \\ &\rightarrow [\mathrm{Co^{III}(salen)}]^+ + \mathrm{MO_2} \qquad (3)\end{aligned}$$

one-electron reduction of O_2 to lithium superoxide and the catalytic process is the electrochemical reduction of the Co^{III} chelate regenerating as oxygen carrier the Co^{II} chelate. The essential step of the catalytic mechanism is ion pair formation and transfer of O_2^- from cobalt to lithium within the ion pair. Formation of an oxygen adduct from electrogenerated O_2^- in dimethylformamide and a cobalt(III) chelate (aquocobalamin) has also been observed.[5]

The stabilization of O_2^- by formation of LiO_2 may also explain the inhibition of the metal-dependent catalysis of Bu_3P oxidation by bis(acetylacetonato)cobalt(II) which was observed when Li^+ is added to the system.[6]

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[1] H. Alt, H. Binder, W. Lindner, and G. Sandstade, *Electroanalyt. Chem. Interfacial Electrochem.*, 1971, **31**, App. 19—22.

[2] G. Costa, A. Puxeddu, and L. Nardin Stefani, *Inorg. Nucl. Chem. Letters*, 1970, **6**, 191.

[3] E. Reisenhofer and G. Costa, *J.C.S. Dalton*, 1976, 521.

[4] J. S. Valentine and A. B. Curtis, *J. Amer. Chem. Soc.*, 1975, **97**, 224.

[5] R. P. Hanzlik and D. Williamson, *J. Amer. Chem. Soc.*, 1976, **98**, 6570.

[6] I. Ellis, I. M. Pratt, and M. Green, *J.C.S. Chem. Comm.*, 1973, 781.