The Formation of the Superoxide Ion by Electrolysis of Oxygen in Aprotic Solvents

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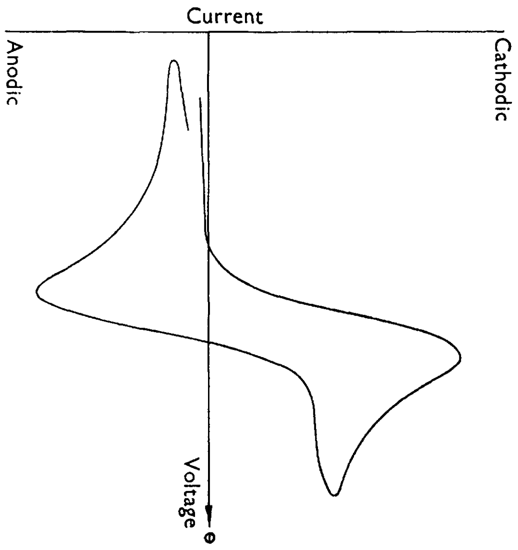
WE find that molecular oxygen is reduced electrolytically to the superoxide ion in a variety of aprotic solvents containing tetrabutylammonium perchlorate (see Table). Studies at the dropping-mercury electrode indicate that the process is mainly diffusion-controlled and that the superoxide ion has considerable stability in these solvents. These conclusions are based on the following observations in each solvent. Oxygen gives a well-defined polarographic wave of slope corresponding closely to one electron/molecule ($n = 0{\cdot}90$—$1{\cdot}00$) with a well-developed A.C. polarogram ($f = 35$ c./sec.; $V = 26{\cdot}5$ mv) of summit potential coincident with half-wave potential. If this were a two-electron process the rate of charge-transfer implied by the D.C. polarogram ($k_s \sim 10^{-4}$ cm.sec.$^{-1}$) would actually eliminate the alternating current. Cyclic polarograms at a stationary mercury drop show reversibility with respect to one-electron transfer and equal cathodic and anodic portions down to at least 0·01 c./sec. (see Figure),

Electrochemical data for oxygen in various solvents

Solvent		$-E_{\frac{1}{2}}$ (v. against s.c.e.)	A*
Dimethylsulphoxide,	0·1M NBu_4ClO_4	0·77	1·3
Dimethylformamide,	0·1M NBu_4ClO_4	0·87	1·6
Acetonitrile,	0·1M NBu_4ClO_4	0·82	1·4
Acetone,	0·2M NBu_4ClO_4	0·88	1·3
Pyridine,	0·2M NBu_4ClO_4	0·89	1·2
Methylene chloride,	0·5M NBu_4ClO_4	0·79	1·2
Water,	pH 5–14	0·1–0·2	—

*$A = i_{AC}/i_{DC}t^{\frac{1}{2}}$, $1{\cdot}8 \geqslant A > 1{\cdot}2$ for diffusion control (M. E. Peover, *J. Chem. Soc.*, 1962, 4540).

thus coupled chemical reactions are slow on this time scale. The further reduction of the superoxide ion presumably to peroxide can be observed as an irreversible process at potentials 1–2 v more negative. Thus the superoxide ion is stable under these conditions with respect to disproportionation to peroxide and oxygen.



Cyclic polarogram of O_2 *in pyridine.* (*Abscissa* $-0{\cdot}6$ *to* $-1{\cdot}05$ v. *against s.c.e.; sweep* 0·1 *c./sec.*)

The electrolysis product of oxygen in dry pyridine was further studied by controlled-potential electrolysis at a stirred-mercury cathode. The resulting yellow solution showed an anodic wave at the position of the cathodic reduction potential of oxygen. With excess of oxygen a single anodic–cathodic wave is found. The anodic limiting current decreases slowly over some hours at room temperature in the absence of light. The solution exhibits an intense e.s.r. signal (*cf.* W. Slough, accompanying communication). Similar results are obtained in dimethylformamide solution.

Reference to the Table shows that the potentials are considerably more negative than the values in water, in which solvent proton-addition accompanies electron transfer. The change in mechanism from hydroxylic to aprotic solvents parallels that found in the reduction behaviour of oxygen-containing aromatic compounds.[1] Deliberate addition of acids to the aprotic solvents results in the replacement of the one-electron wave by a two-electron wave (*i.e.*, double the wave height) at more positive potentials, suggesting reduction of a protonated oxygen molecule. Molecular oxygen is an electron-acceptor of moderate electron affinity compared with common organic electron-acceptors.[2]

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[1] P. H. Given, M. E. Peover, and J. Schoen, *J. Chem. Soc.*, 1958, 2674.

[2] M. E. Peover, *Trans. Faraday Soc.*, 1964, **60**, 479.