Reduction of Sulphur Dioxide with Superoxide Ion

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Summary Combination of superoxide ion with sulphur dioxide in aprotic media results in a stoicheiometric yield of dithionite ion.

THE chemistry of superoxide ion has been extensively studied since $O_2^{\cdot -}$ was discovered to be a respiratory intermediate in aerobes.[1] Several of these investigations have confirmed that $O_2^{\cdot -}$ is a moderate one-electron reducing agent[2,3] for manganese(III)tetraphenylporphyrin,[4] ferricytochrome c,[5] quinones,[6–8] and nitrosubstituted aromatics.[9]

When electro-synthesized superoxide ion is combined with sulphur dioxide in dimethylformamide (or other aprotic solvents) a stoicheiometric yield of dithionite ion is obtained. Previous electrochemical studies of molecular oxygen[10,11] and of sulphur dioxide[12,13] in aprotic media, as well as the data of the Figure, indicate that $O_2^{\cdot -}$ has a sufficiently negative redox potential to reduce sulphur dioxide, but only to a limited extent [equations (1) and (2)].

$$O_2 + e^- \rightleftharpoons O_2^{\cdot -} \qquad E' = -0{\cdot}87\ \text{V}\ vs.\ \text{S.C.E.} \qquad (1)$$

$$SO_2 + e^- \rightleftharpoons SO_2^{\cdot -} \qquad E' = -0{\cdot}83\ \text{V}\ vs.\ \text{S.C.E.} \qquad (2)$$

On the basis of these redox potentials the equilibrium constant for reaction (3) has a value of 4·8 in dimethylformamide.

$$O_2^{\cdot -} + SO_2 \rightleftharpoons SO_2^{\cdot -} + O_2 \quad K_3 \qquad (3)$$

However, the Figure (c) indicates that the reaction goes to completion. Apparently, this results from the previously observed[12–14] complexation of $SO_2^{\cdot -}$ by sulphur dioxide, equation (4), and its dimerization to dithionite

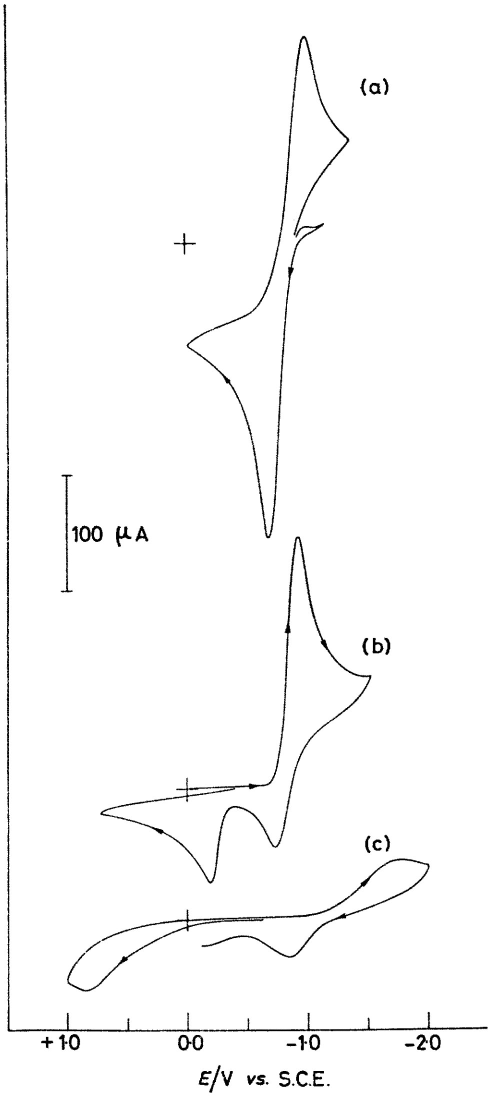

FIGURE. Cyclic voltammograms at a platinum electrode (area, 0·23 cm^2) in dimethylformamide (0·1 M tetraethylammonium perchlorate); scan rate 0·1 V s^{-1}. (a), 5 mM $O_2^{-\cdot}$ (prepared by controlled potential coulometric reduction of O_2); (b), 5 mM SO_2 (prepared from gaseous SO_2); (c), product solution from the combination of 5 mM $O_2^{-\cdot}$ and 5 mM SO_2 (followed by deaeration with argon).

$$SO_2^{-\cdot} + 2SO_2 \rightleftharpoons (SO_2)_2SO_2^{-\cdot} \quad K_4 = 1{\cdot}9 \times 10^6\ l^2\ mol^{-2} \quad (4)$$

ion, equation (5). The product of reaction (4) results in the anodic peak at −0·20 V of the Figure (b), while the stoicheiometric reduction of SO_2 by $O_2^{-\cdot}$ [reaction (3)] followed by

$$2\ SO_2^{-\cdot} \rightleftharpoons S_2O_4^{2-} \quad K_5 = 4{\cdot}8 \times 10^3\ l\ mol^{-1} \quad (5)$$

removal of O_2 with argon deaeration yields a solution with the cyclic voltammogram of the Figure (c). The latter is identical to the voltammogram for electro-synthesized $S_2O_4^{2-}$.[12] (The values for the standard potentials and equilibrium constants are based on the molar concentrations of the dissolved reactant and product species at 25 °C in dimethylformamide that contains 0·1 M tetraethylammonium perchlorate.)

The product solution of reaction (3) (after deaeration with argon) exhibits a u.v. absorption maximum at 295 nm, which is identical to that for dithionite ion.[13] If additional SO_2 is added to this solution it changes to a deep blue colour (λ_{max} 580 nm) which is characteristic of the $(SO_2)_2$-$SO_2^{-\cdot}$ complex [reaction (4)].[11–16] This same complex is observed in dimethylacetamide, but not in dimethyl sulphoxide.[17] An e.s.r. spectrum of the deaerated product solution of reaction (3) yields a spectrum with a g-value of 2·006, which is identical to that for the $SO_2^{-\cdot}$ radical anion.[15,18] Such an observation is consistent with the dissociation of dithionite ion [reaction (5)].

In summary, electrochemical, spectroscopic, and chemical evidence confirms that superoxide ion efficiently reduces sulphur dioxide to dithionite ion in aprotic solvents. The results of such studies provide convincing support for the conclusion that $O_2^{-\cdot}$ is a significantly stronger and more effective reducing agent than dithionite ion. This capacity of $O_2^{-\cdot}$ to act as a strong one-electron reducing agent ($E^{0\prime}$, −570 mV *vs.* normal hydrogen electrode, N.H.E.) may represent its most serious biological hazard. For example, the reduction of ferricytochrome c by $O_2^{-\cdot}$ [equation (6)]

$$\text{cyt c}(Fe^{3+}) + O_2^{-\cdot} \rightleftharpoons \text{cyt c}(Fe^{2+}) + O_2 \quad K_6 \quad (6)$$

has an equilibrium constant, K_6, with a value of $3{\cdot}67 \times 10^4$ in aqueous media.[5] Incomplete removal of $O_2^{-\cdot}$ from a biological matrix by superoxide dismutase could result in similar reductions of biological oxidants. The standard redox potential for the O_2–$O_2^{-\cdot}$ couple in aqueous solutions is shifted to −330 mV *vs.* N.H.E.,[19] which precludes the effective reduction of SO_2 by $O_2^{-\cdot}$ in such media.

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