References and Notes

(1) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution", Academic Press, New York, N.Y., 1970.
(2) D. A. Aikens and J. W. Ross, *J. Phys. Chem.*, **65**, 1213 (1961).
(3) J. G. Jones and F. C. Anson, *Anal. Chem.*, **36**, 1137 (1964).
(4) J. Jones Ulrich and F. C. Anson, *Inorg. Chem.*, **8**, 195 (1969).
(5) D. C. Barclay, E. Passeron, and F. C. Anson, *Inorg. Chem.*, **9**, 1024 (1970).
(6) F. C. Anson and R. S. Rodgers, *J. Electroanal. Chem.*, **47**, 287 (1973).
(7) M. J. Weaver and F. C. Anson, *J. Electroanal. Chem.*, **58**, 95 (1975).
(8) H. Taube, H. Myers, and R. L. Rich, *J. Am. Chem. Soc.*, **75**, 4118 (1953).
(9) D. M. Mohilner in "Electroanalytical Chemistry", Vol. 1, A. J. Bard, Ed., Marcel Dekker, New York, N.Y., 1966, p 243.
(10) P. Delahay, "Double Layer and Electrode Kinetics", Interscience, New York, N.Y., 1965, Chapter 9.
(11) M. J. Weaver and F. C. Anson, submitted to *J. Electroanal. Chem.*
(12) R. Parsons, *Trans. Faraday Soc.*, **51**, 1518 (1955).
(13) C. V. D'Alkaine, E. R. Gonzalez, and R. Parsons, *J. Electroanal. Chem.*, **32**, 57 (1971).

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Concerning the Superoxide Electrodes in Nitrate Melts

Sir:

This note is written in the hope of preventing confusion that may be caused by an error in a recent communication[1] by Schlegel, concerning oxygen electrode in molten nitrates.

Work in this laboratory has shown[2] that the potential of the superoxide/oxygen electrode in molten (sodium, potassium) nitrate at 503 K can be described by the half-reaction

$$O_2 + e = O_2^- \qquad (1)$$

and that its standard potential, E_1^0 in the equation

$$E = E_1^0 - (RT/F) \ln [O_2^-]/[O_2] \qquad (2)$$

can be deduced both from potentiometric[2] data and from the reversible[2-5] voltammetric half-wave potential of the redox couple O_2/O_2^-: $E_1^0 = E^0{}_{O_2/O_2^-} = -0.645$ V vs. a Ag/Ag$^+$ (0.07 *m*) reference electrode.

Schlegel[1] used our data[2] to obtain a different value of the standard potential, $E_2^0 = -1.185$ V, by the unstated assumption that

$$E = E_2^0 - (RT/F) \ln [O_2^-]/p_{O_2} \qquad (3)$$

where p_{O_2} is the partial pressure (atm) of oxygen in equilibrium with the melt. Neither E_1^0 nor E_2^0 is incorrect per se, and both pertain to the redox couple O_2/O_2^-, but they do differ in the choice of the standard state for oxygen, which is a 1 *m* solution (as for superoxide) for E_1^0 and a partial pressure of 1 atm for E_2^0. Because of this difference it is impossible to compare E_2^0 directly with the voltammetric half-wave potential, as Schlegel attempted to do. At the half-wave potential of any couple, ox + *n*e = red, the activities of ox and red are equal if both are contained in the same phase, but *only if they are expressed in the same units.* For the O_2/O_2^- couple the potential at which $p_{O_2} = m_{O_2^-}$ is very different from the half-wave potential.

Schlegel was apparently misled by the fact that the difference between E_1^0 and E_2^0, which involves the Henry's law coefficient[5] for oxygen ($K_H = 4.10^{-6}$ mol kg^{-1} atm^{-1})

$$E_1^0 - E_2^0 = -(RT/F) \ln K_H \qquad (4)$$

is fortuitously almost equal to the difference between the standard[2] (and half-wave[4]) potentials of the O_2/O_2^- and O_2^-/O_2^{2-} couples, which involves the disproportionation constant[2] of superoxide ion

$$2O_2^- = O_2 + O_2^{2-};\ K_5 = 5.10^{-7} \qquad (5)$$

so that

$$E^0{}_{O_2/O_2^-} - E^0{}_{O_2^-/O_2^{2-}} = -(RT/F) \ln K_5 \qquad (6)$$

Schlegel[1] concluded that the potential of an oxygen electrode under these conditions is governed by the O_2^-/O_2^{2-} couple rather than by the O_2/O_2^- couple. This is not proven by his argument, could not be proven by any purely thermodynamic argument, and has no real meaning at the present time. A potential determining process can be identified only with the aid of kinetic data. At present it is known only that the rate constants for electron transfer at the standard potentials are high enough so that both couples are voltammetrically reversible,[3,6] and they are interrelated through reaction 5, for which both the forward and backward rate constants are also high.[7] Hence it is as yet possible only to identify the half-reaction responsible for the two voltammetric waves and to evaluate their standard potentials, and this was correctly done in our previous studies. The standard potentials (vs. Ag/Ag$^+$, 0.07 *m*) for the oxygen/superoxide and superoxide/peroxide couples in a (Na, K)NO_3 equimolar melt at 503 K are the following: $E^0{}_{O_2/O_2^-} = -0.645 \pm 0.005$ V (from both potentiometric[2] and RDE voltammetric[8] data); $E^0{}_{O_2^-/O_2^{2-}} = -1.26 \pm 0.01$ V (from RDE voltammetric[8] data).

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Reference and Notes

(1) J. M. Schlegel, *J. Am. Chem. Soc.*, **97**, 682 (1975).
(2) P. G. Zambonin, *J. Electroanal. Chem.*, **33**, 243 (1971).
(3) P. G. Zambonin and J. Jordan, *J. Am. Chem. Soc.*, **89**, 6365 (1967).
(4) P. G. Zambonin and J. Jordan, *J. Am. Chem. Soc.*, **91**, 2225 (1969).
(5) E. Desimoni, F. Paniccia, and P. G. Zambonin, *J. Electroanal. Chem.*, **38**, 373 (1972).
(6) L. Meites, "Polarographic Techniques", 2nd ed, Interscience, New York, N.Y., 1965, p 203.
(7) P. G. Zambonin, F. Paniccia, and A. Bufo, *J. Phys. Chem.*, **76**, 422 (1969).
(8) The standard potentials can be obtained from the half-wave values of the proper[4] rotating disk electrode (RDE) voltammograms via the general relationship[9,10]

$$E^0 = E_{1/2} - (RT/nF) \ln (D_{red}/D_{ox})^{2/3}$$

The diffusion coefficients data for oxygen, superoxide, and peroxide are given in ref 2 and 4.
(9) J. Heyrovsky and J. Kuta, "Principles of Polarography", Academic Press, New York, N.Y., 1966.
(10) B. Levich, "Physicochemical Hydrodynamics", Prentice-Hall, Englewood Cliffs, N.J., 1962.

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One-Step Preparation of Metacyclophanes and (2,6)Pyridinophanes by Nickel-Catalyzed Grignard Cyclocoupling

Sir:

There is much current interest in the chemistry of cyclophanes and heterophanes;[1] however, the overall product yields in the wide variety of synthetic methods so far developed generally suffer from the multistep sequences involved.[1a,2] We report here a one-step preparation of [*n*]metacyclophanes and [*n*](2,6)pyridinophanes by the cyclocoupling of di-Grignard reagents with aromatic dihalides in the presence of catalytic quantities of a nickel-phosphine complex