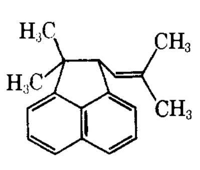
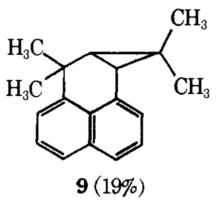
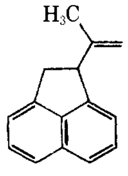


8 (74%)

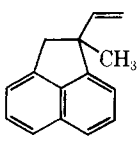


9 (19%)

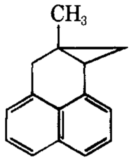
Regioselectivity similar to that shown in eq 1 was also observed with 2-methylbutadiene. 1,2-Addition was again favored at the less substituted double bond, and the only 1,3-adduct found was 6-methylnaphtho[1′,8′]bicyclo[4.1.0]-hept-2-ene (**12**), whose structure was confirmed by synthesis from 2-methylphenalene.[6-8] Diene **13** was isolated as a minor product. The reaction of **2** with 2,3-dimethylbutadiene also yielded a dienic adduct (**16**) along with the expected products (**14** and **15**). The formation of dienes **13** and **16** can be considered to occur via a hydrogen atom transfer reaction in an initially formed diradical intermediate (eq 2).



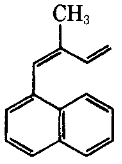
10 (18%)



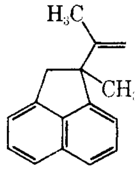
11 (10%)



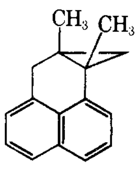
12 (68%)



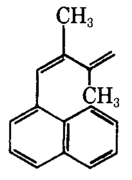
13 (4%)



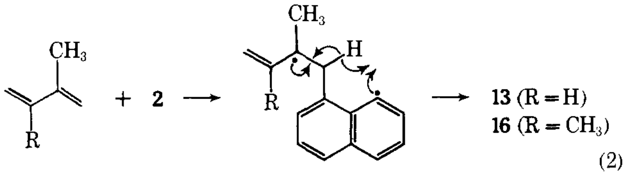
14 (46%)



15 (26%)

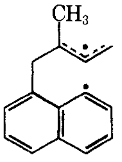


16 (28%)

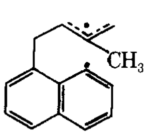


(2)

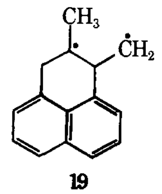
Since 1,2-additions are favored at the less substituted double bond of a diene, a concerted process which does not involve an intermediate diradical (and which does not reflect the ability of substituents to stabilize such a species) is implied. Singlet 1,8-dehydronaphthalene might well be the attacking reagent. On the other hand, the selectivity of the 1,3-additions can be rationalized best on the basis of a stepwise process, involving the formation of a single bond at one end of the diene to give the more stable of the two possible diradical intermediates (e.g., **17** rather than **18** from 2-methyl-1,3-butadiene). If a species such as **17** were produced by attack of triplet 1,8-dehydronaphthalene on 2-methyl-1,3-butadiene, it might then proceed to form a new diradical (**19**) by bonding of the aryl radical site to the central atom in the allylic system, since formation of a five- or seven-membered ring would be unlikely for triplet **17**. Finally, collapse of **19** to the corresponding cyclopropane would give the observed 1,3-adduct. The important feature of this hypothesis for 1,3-addition is that, in contrast to the 1,2-addition, it involves a stepwise process. It should be noted that instead of triplet 1,8-dehydronaphthalene, some other (nitrogen- or lead-containing) reactive intermediate which could bond selectively to one end of the diene might be involved. Further work to elucidate the many questions raised by these reactions is now in progress.



17



18



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References and Notes

(1) C. W. Rees and R. C. Storr, *J. Chem. Soc. C*, 765 (1969).
(2) J. Meinwald and G. W. Gruber, *J. Am. Chem. Soc.*, **93**, 3802 (1971).
(3) Each product mixture was purified by chromatography on basic alumina, followed by separation of the products using preparative GLPC. All products were shown to be stable under the separation and purification conditions. Yields of individual products throughout this paper are expressed as percentages of the total monomeric hydrocarbon fraction isolated. Structural and stereochemical assignments for new compounds are based chiefly on mass spectra, 60-MHz ^{1}H NMR spectra, and infrared spectra.
(4) R. M. Pagni and C. R. Watson, *Tetrahedron Lett.*, 59 (1973).
(5) R. M. Pagni and C. R. Watson, *Tetrahedron*, **29**, 3807 (1973).
(6) H. E. Simmons, T. L. Cairns, S. A. Vladuchick, and C. M. Hoiness, *Org. React.*, **20**, 1 (1973).
(7) I. T. Harrison and R. J. Rawson, *J. Org. Chem.*, **35**, 2057 (1970).
(8) V. Boekelheide and C. E. Larrabee, *J. Am. Chem. Soc.*, **72**, 1240 (1950).

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Concerning the Oxygen Electrodes in Nitrate Melts

Sir:

In nitrate melts, nitronium ion, NO_2^+, has often been assumed as an intermediate to explain kinetic processes[1] as well as nitration reactions of aromatic organic compounds.[2-4] It was generally thought that there should be an equilibrium of the sort, $NO_3^- = NO_2^+ + O^{2-}$, quite analogous to the dissociation of water. As a result, the first "oxide ion" electrode in nitrate melts was reported by Kust and Duke,[5] and subsequent publications[6-10] have confirmed that this electrode responds to Lux-Flood acids and bases yielding Nernst slopes which correspond to a two-electron process, $O^{2-} = \frac{1}{2}O_2 + 2e^-$.

Later, however, Zambonin and Jordan[11] reported that addition of O^{2-} to nitrate melts resulted in its oxidation by nitrate to peroxide and superoxide if the melt is free of acidic species such as silica and water. They therefore questioned the validity of the oxide ion electrode first proposed by Kust and Duke. Subsequently, Zambonin and his colleagues[12] have shown that oxide ion cannot exist in nitrate melts in any appreciable concentration, and that the "true" oxygen electrode is one which responds to the redox couple, $O_2^- = O_2 + e^-$, having a Nernst slope which corresponds to a one-electron transfer.

I propose that the oxygen electrode reported by Kust and Duke[5] does respond to oxide ion and that the oxygen electrode reported by Zambonin and Signorile[12] does respond to superoxide ion. Also, addition of relatively large amounts of Na_2O to a nitrate melt free of *silica and water* ultimately yields a solution in which an oxygen electrode responds to a redox couple characteristic of the superoxide-oxygen electrode couple reported by Zambonin and Signorile.[13] The important observation to be made is that those authors who report an oxygen electrode which responds to Lux-Flood bases publish potential vs. log (base) plots having *positive* slopes equal to $RT/2F$ (two-electron transfer), and, those authors who report an oxygen electrode which responds to superoxide ion publish potential vs. log (O_2^-) plots having *negative* slopes equal to RT/F (one-electron transfer). Furthermore, an equilibrium constant for the reaction

$$O^{2-} + \tfrac{3}{2}O_2 = 2O_2^- \qquad (1)$$

can be obtained from potentiometric and voltametric studies, and the value obtained compares very well with an equilibrium constant for this reaction obtained from other independent methods.

A recent publication by Burke and Kerridge[14] presents a convincing argument that in nitrate melts oxide ion, O^{2-}, is stabilized and controlled through an equilibrium

$$(SiO_2)_x + O^{2-} = (SiO_2)_x{\cdot}O^{2-} \qquad K_2 = 10^{16} \qquad (2)$$

They conclude that this equilibrium reaction should be considered when reactions and galvanic cells are studied in Pyrex vessels. Assuming that the potential determining ion in Duke and Kust's cell is O^{2-} whose concentration is controlled through equilibrium 2, the Nernst expression for the O_2/O^{2-} couples can be written

$$E = E^0_{O_2/O^{2-}} - \frac{RT}{2F} \ln \frac{(O_2)^{1/2}(SiO_2)_x K_2}{(SiO_2)_x{\cdot}O^{2-}}$$

Assigning unit activities to $(SiO_2)_x$ and $(SiO_2)_x{\cdot}O^{2-}$, species which are incorporated in the Pyrex vessel and are not soluble in the melt, one obtains in an atmosphere of oxygen

$$E_{O_2/O^{2-}} = E^0_{O_2/O^{2-}} - \frac{RT}{2F} \ln K_2$$

Since $E_{O_2/O^{2-}}$ is the value reported by Kust and Duke,[5] the standard emf vs. 1 *m* Ag^+ concentration in the reference cell is equal to 1.437 at 230°.

Zambonin[15] performed some potentiometric studies and reported a standard emf of $E^0 = -0.645$ for $O_2 + e^- = O_2^-$. A close look at Figure 2 in his paper reveals that this value for the standard emf was incorrectly obtained. The correct value is $E^0 = -1.185$. This value is very close to the half-wave potential reported by Zambonin and Jordan[16] for the reduction of superoxide $O_2^- = e^- = O_2^{2-}$. Clearly Zambonin's indicator electrode in his potentiometric studies is not responding to the O_2/O_2^- couple but to the O_2^-/O_2^{2-} couple. Oxygen gas does influence the potential but indirectly through the equilibrium reaction

$$O_2 + O_2^{2-} = 2O_2^-, \qquad K_3 = 10^{6.3} \qquad (3)$$

The Nernst equation for the O_2^-/O_2^{2-} couple is

$$E = E^0_{O_2^-/O_2^{2-}} - \frac{2.3RT}{F} \log \frac{(O_2^{2-})}{(O_2^-)}$$

The oxygen dependence is incorporated into this expression by substituting $(O_2^{2-}) = (O_2^-)^2/(O_2)K_3$ to obtain

$$E = E^0_{O_2^-/O_2^{2-}} - 0.10 \log \frac{(O_2^-)}{(O_2)K_3}$$

where 2.3 $RT/F = 0.100$ V at 230°. The solubility of O_2 in nitrate melts at 230° is $10^{-5.8}$. Substituting this value and the value for K_3 into the above relationship yields −1.265 V for $E^0_{O_2^-/O_2^{2-}}$. The half-wave potential for this couple reported by Zambonin and Jordan[16] is −1.28. The very good agreement between the potentiometric value and the value obtained from voltammetric studies is convincing evidence to allow the use of half-wave potentials to evaluate standard reduction potentials in nitrate melts. Assuming that the RDE theory applies to the O_2/O_2^- redox couple, a standard emf can be obtained from the half-wave potential and the diffusion coefficients for O_2 and O_2^-. $E^0_{O_2/O_2^-}$ is calculated to be −0.64 V vs. their reference electrode. This value becomes −0.76 V when normalized to 1 *m* concentration of Ag^+ in the reference electrode.

$E^0_{O_2/O_2^-}$ and $E^0_{O_2^-/O_2^{2-}}$ may be used to calculate an equilibrium constant for reaction 1, $K = 10^{2F(\Delta E^0)/2.3RT} = 10^{13.6}$. The equilibrium constant for reaction 1 can also be obtained independently using the equilibrium constants of two reactions,

$$O_2^{2-} + O_2 = 2O_2^-, \; K = 2 \times 10^6$$

$$2O^{2-} + O_2 = 2O_2^{2-}, \; K = 10^{16}$$

The equilibrium constant for the first reaction has been well established by two independent methods;[16,17] however, the equilibrium constant for the second reaction is an approximation extrapolated from hydroxide melts.[16] Nevertheless, an appropriate combination of these two equilibrium reactions and their corresponding equilibrium constants yields reaction 1 above with an equilibrium constant of 2×10^{14}.

The agreement between these two values is remarkably good when one considers that one of the above equilibrium constants is an approximation. There is no question that the redox couples reported by the various authors cited above are correct under the conditions reported by them. The sign and value of the slopes of the Nernst plots confirm this conclusion.

References and Notes

(1) B. R. Sundheim, Ed., "Fused Salts," McGraw-Hill, New York, N.Y., 1964.
(2) R. B. Temple, C. Fay, and J. Williamson, *Chem. Commun.*, 966 (1967).
(3) R. F. Bartholomew and H. M. Garfinkel, *J. Inorg. Nucl. Chem.*, **31**, 3655 (1969).
(4) J. Schlegel and J. Robinson, *J. Am. Chem. Soc.*, **95**, 665 (1973).
(5) R. N. Kust and F. R. Duke, *J. Am. Chem. Soc.*, **85**, 3338 (1963).
(6) R. N. Kust, *Inorg. Chem.*, **6**, 157 (1967).
(7) J. Schlegel and R. Bauer, *Chem. Commun.*, 483 (1971).
(8) J. Schlegel and R. Bauer, *Inorg. Chem.*, 11, 909 (1972).
(9) J. Schlegel and D. Uhr, *Inorg. Chem.*, **12**, 595 (1973).
(10) A. M. Shams El Din and A. A. El Hosary, *Electrochim. Acta*, **13**, 135 (1968).
(11) J. Jordan and P. Zambonin, *J. Am. Chem. Soc.*, **89**, 6365 (1967).
(12) P. Zambonin and G. Signorile, *J. Electroanal. Chem.*, **35**, 251 (1972).
(13) Private communication.
(14) J. Burke and D. Kerridge, *Electrochimica Acta*, **19**, 251 (1974).
(15) P. Zambonin, *J. Electroanal. Chem.*, **33**, 243 (1971).
(16) P. Zambonin and J. Jordan, *J. Am. Chem. Soc.*, **91**, 2225 (1969).
(17) J. Schlegel and D. Priore, *J. Phys. Chem.*, **20**, 2841 (1972).

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