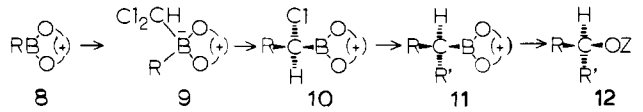
on the basis that nucleophilic displacement of chloride from **3** proceeds with inversion[14] and peroxidic deboronation of **4a** with retention.[15]

To prepare (2*S*,3*S*)-3-phenyl-2-butanol (**7a**), **4a** was homologated with (dichloromethyl)lithium in the same manner as described for **2**, except that the mixture was kept for 7 h at 25 °C before it was cooled and methylmagnesium bromide was added,[9] conditions which permitted completion of the reaction without significant epimerization in this case. The yield of (+)-pinanediol (2*S*,3*R*)-3-phenylbutane-2-boronate (**6a**) was 96%. Oxidation with sodium perborate[10] yielded 88% 3-phenyl-2-butanol, shown to contain 90% (±1%) erythro isomer (**7a**) and 10% threo isomer (**7b** and enantiomer) by ^{1}H NMR analysis with the aid of a shift reagent.[16] The overall yield of contained **7a** is 71%, based on **2**. As a result of the double-homologation sequence, the amount of enantiomer of **7a** present must be very small.[17]

To prepare (2*R*,3*S*)-3-phenyl-2-butanol (**7b**), the (+)-pinanediol ester **4a** was cleaved and the boronic acid was esterified with (−)-pinanediol to form **4b** before the second homologation. Conditions which would hydrolyze most boronic esters failed to affect **4a**, but destructive cleavage of the pinanediol was accomplished with boron trichloride, and the (*S*)-1-phenylethaneboronic acid was isolated as its crystalline diethanolamine ester[18,19] (**4c**) (75%), ee 100%.[20] Treatment of **4c** with 1 M hydrochloric acid regenerated the boronic acid, which was extracted with ether and esterified with (−)-pinanediol[21] to **4b** (79%).[22] Homologation of **4b** as described for **4a** yielded 91% (−)-pinanediol (2*R*,3*R*)-3-phenylbutane-2-boronate (**6b**),[23] which was oxidized[10] to 3-phenyl-2-butanol (93%) containing 94% (±1%) threo isomer (**7b**) and 6% erythro isomer (**7a**).[16,24]

The foregoing results confirm the expected retention of configuration of the migrating alkyl group. In view of the comparable specificities in the routes to **6a** and **6b**, any double-stereodifferentiation effect[25] is small compared to the directing influence of the pinanediol group.

Exploratory preliminary experiments had indicated that (+)-pinanediol boronic esters (**8**) yield dichloromethaneboronate complexes (**9**) which consistently rearrange to αS α-chloro boronic esters (**10**), as shown by reaction with lithium or Grignard reagents (inversion[14]) to form **11**, which were oxidized[10] (retention[15]) and esterified to known derivatives[11] (**12**). Thus, **8** (R = *n*-C_4H_9) homologated under the previously established conditions[1] yielded **10** with 89% diastereoselectivity, as indicated by the rotation of **12** (R′ = CH_3, Z = COPh),[26] or 91% based on an alternative **12** (R′ = Ph, Z = $COCH_3$).[27] An analogous treatment of **8** (R = cyclohexyl) indicated 83% diastereoselectivity, and **8** (R = CH_3) gave 74%. However, all these figures must be regarded as lower limits in view of the long exposure of **10** to chloride ion. The epimerization problem became apparent when **8** (R = Ph) yielded the "wrong" enantiomer of **12** (R′ = CH_3, Z = $COCH_3$) in 8% ee after 20-h exposure of the benzylic **10** (≡**3**) to lithium chloride at 25 °C, which was dramatically changed to 93.7% ee of the "right" isomer when the exposure was reduced to 1 h at 0 °C as outlined in the synthetic directions.



Acknowledgment. We thank the National Science Foundation for support (Grant No. CHE 77-11283).

(14) Midland, M. M.; Zolopa, A. R.; Halterman, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 248–9. Matteson, D. S. *Acc. Chem. Res.* **1970**, *3*, 186–93.
(15) Brown, H. C. "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, N.Y., 1972; pp 317–409. Kabalka, G. W.; Newton, R. J., Jr.; Jacobus, J. *J. Org. Chem.* **1978**, *43*, 1567–9.
(16) Eu(fod)$_3$ shifts the most upfield CH_3 doublet of the threo isomer upfield from that of the erythro isomer. Integrals were evaluated at 60 and 90 MHz.
(17) Calculated enantiomer content is (0.03)(0.07) = 0.21%, too small to measure, if (+)-pinanediol was 100% ee. For our **7a**, obsd $[\alpha]_D$ −2.1° (neat) exceeds lit.[5] $[\alpha]^{25}_D$ −0.69° but is within experimental error of calcd $[\alpha]_D$ −1.9° for a mixture of 90% **7a**, 4% **7b** $[\alpha]^{25}_D$ −30.9°), and 6% racemate. Further confirmation of the predominant isomer as **7a** was provided by the 3-nitrophthalate, crystallized once: mp 138–139 °C; $[\alpha]^{20}_D$ +31.3° (4%, ethanol) (lit.[5] mp 144–145 °C; $[\alpha]^{25}_D$ +34.6°).
(18) Addition of 4 g of **4a** in 20 mL of dichloromethane to ~8 mL of boron trichloride at −78 °C was followed by 2 h at 25 °C, concentration, aqueous workup, and treatment of the crude boronic acid with 1 equiv of diethanolamine in 3 mL of 2-propanol and 10 mL of ether. The **4c** was recrystallized from chloroform/benzene, mp 200–201 °C [lit.[19] (racemate) mp 204 °C].
(19) Korcek, S.; Watts, G. B.; Ingold, K. U. *J. Chem. Soc., Perkin Trans. 2* **1972**, 242–8.
(20) Derived (*S*)-1-phenylethyl acetate, $[\alpha]^{25}_D$ −124.5° (lit.[13] identical).
(21) Benzeneboronate ester $[\alpha]^{19}_D$ −17.6°.
(22) Purified by chromatography on silica with 1:9 ether/petroleum ether.
(23) Simple distillation, bp 115–117 °C (0.03 torr).
(24) The 3-nitrophthalate, purified by way of aqueous extraction of the sodium salt, was obtained as an oil, $[\alpha]^{22}_D$ −30.0° (2%, ethanol); calcd $[\alpha]_D$ −30.1° for 94% **7b** nitrophthalate (lit.[5] $[\alpha]^{25}_D$ −34.2°) with 6% **7a** nitrophthalate (lit.[5] $[\alpha]^{25}_D$ +34.6°).
(25) Heathcock, C. H.; White, C. T. *J. Am. Chem. Soc.* **1979**, *101*, 7076–7.
(26) The starting material was 92% ee (+)-pinanediol boronic ester **12**, $[\alpha]^{21}_D$ +29.9° (lit. $[\alpha]_D$ +31.0°: Kenyon, J.; Pickard, R. H. *J. Chem. Soc.* **1915**, *107*, 115–32).
(27) From 92% ee (+)-pinanediol **12**, $[\alpha]^{20}_D$ +60.1° (lit. $[\alpha]_D$ +80.1°: Levine, P. A.; Marker, R. E. *J. Biol. Chem.* **1932**, *97*, 379–91).

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Superoxide-Ion Oxidation of Hydrophenazines, Reduced Flavins, Hydroxylamine, and Related Substrates via Hydrogen-Atom Transfer

Sir:

Numerous groups have cited evidence that superoxide ion ($O_2^{-}\cdot$) brings about a net oxidation of many substrates.[1-19] However, the direct transfer of an electron to $O_2^{-}\cdot$ is an unlikely process in aprotic media because of the extreme instability of the O_2^{2-} species. Recently, we have shown with acidic reducing substrates such as 3,5-di-*tert*-butylcatechol, α-tocopherol, and ascorbic acid that $O_2^{-}\cdot$ acts as a Brønsted base, and that the reported oxidations of these substrates by $O_2^{-}\cdot$ actually represent an initial proton abstraction to give substrate anion and dismutation species, HO_2^{-} and O_2; the latter oxidizes the substrate anion.[20] This mechanism appears

(1) Mow-oka, Y.; Foote, C. S. *J. Am. Chem. Soc.* **1976**, *98*, 1510.
(2) Dietz, K.; Forno, A. E. J.; Larcombe, B. E.; Peover, M. E. *J. Chem. Soc. B* **1970**, 816.
(3) Stallings, M. D.; Sawyer, D. T., unpublished results (1978).
(4) Lee-Ruff, E.; Lever, A. B. P.; Rigaudy, J. *Can. J. Chem.* **1976**, *54*, 1837.
(5) Afanas'ev, I. B.; Polozeva, H. E. *Zh. Org. Khim.* **1976**, *12*, 1833.
(6) Hisia, H. P.; Fridovich, I. *Biochemistry* **1976**, *15*, 681.
(7) Chern, C. I.; San Filippo, J., Jr. *J. Org. Chem.* **1977**, *42*, 178.
(8) Asada, K.; Kanematsu, S. *Agric. Biol. Chem.* **1976**, *40*, 1891.
(9) Nishikimi, M.; Yagi, K. In "Biochemical and Medical Aspects of Active Oxygen"; Hayashi, O., Asada, K., Eds.; University Park Press: Baltimore, Md., 1977, pp 79–87.
(10) Elster, E. F.; Karamer, R. *Biochim. Biophys. Acta* **1973**, *314*, 340.
(11) Nishikimi, M. *Biochem. Biophys. Res. Commun.* **1975**, *63*, 463.
(12) Nishikimi, M.; Machlin, L. J. *Arch. Biochem. Biophys.* **1975**, *170*, 684.
(13) Matsumoto, S.; Matsuo, M. *Tetrahedron Lett.* **1977**, 1999.
(14) Afanas'ev, I. B.; Polozova, N. I. *Zh. Org. Khim.* **1978**, *14*, 1013.
(15) Afanas'ev, I. B.; Polozova, N. I. *Khim. Pharm. Zh.* **1979**, *No. 4*, 16.
(16) Scully, F. E.; Davis, R. C. *J. Org. Chem.* **1978**, *43*, 1467.
(17) Picot, A.; Milliet, P.; Cherest, M.; LuciuLi, X. *Tetrahedron Lett.* **1977**, 3811.
(18) Sagao, H.; Fujinira, M.; Osa, T.; Lund, H. *Chem. Lett.* **1977**, 798.
(19) Land, E. J.; Swallow, A. J. *Biochim. Biophys. Acta* **1971**, *234*, 34.

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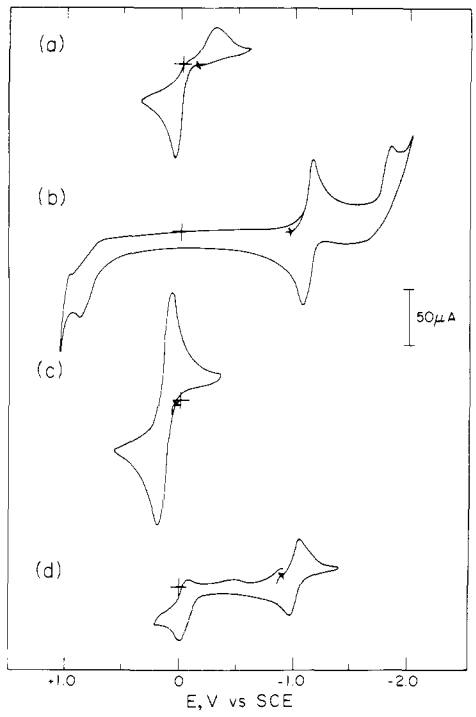


Figure 1. Cyclic voltammograms in dimethylformamide (0.1 M tetraethylammonium perchlorate) of (a) 1 mM *N,N'*-dihydrophenazine (H_2Phen), (b) 1 mM H_2Phen and 1 mM $O_2^{-}\cdot$, (c) 1.3 mM *N*-methyl-*N'*-hydrophenazine (CH_3PhenH), and (d) 1 mM CH_3PhenH plus 1 mM $O_2^{-}\cdot$. Measurements were made with a platinum electrode (area 0.23 cm^2) at a scan rate of 0.1 V s^{-1}; temperature 25 °C.

to account for most of the purported oxidations by $O_2^{-}\cdot$ of acidic substrates.

The half-reactions for one-, two-, and three-electron reductions of $O_2^{-}\cdot$ at pH 14 in aqueous media can be represented by the expressions[21]

$$O_2^{-}\cdot + H_2O + e^- \rightarrow HO_2^- + OH^- \quad (1)$$

$$E_1° = +0.20 \text{ V vs. NHE}$$

$$O_2^{-}\cdot + H_2O + 2e^- \rightarrow 2\ OH^- + \cdot O^- \quad (2)$$

$$E_2° = +0.35 \text{ V vs. NHE}$$

$$O_2^{-}\cdot + 2H_2O + 3e^- \rightarrow 4\ OH^- \quad (3)$$

$$E_3° = +0.65 \text{ V vs. NHE}$$

Incorporation of protons into the redox couples is necessary to stabilize the product species. These redox potentials are believed to be good thermodynamic approximations for the reduction of $O_2^{-}\cdot$ by hydrogen atoms (the thermodynamic equivalent of (H_2O + e^-)) and indicate that one-, two-, and three-hydrogen-atom reductions of $O_2^{-}\cdot$ are energetically favorable. To test this hypothesis we have investigated the reactivity of $O_2^{-}\cdot$ by using reducing substrates that have readily transferable hydrogen atoms but no acidic protons. On the basis of electrochemical and

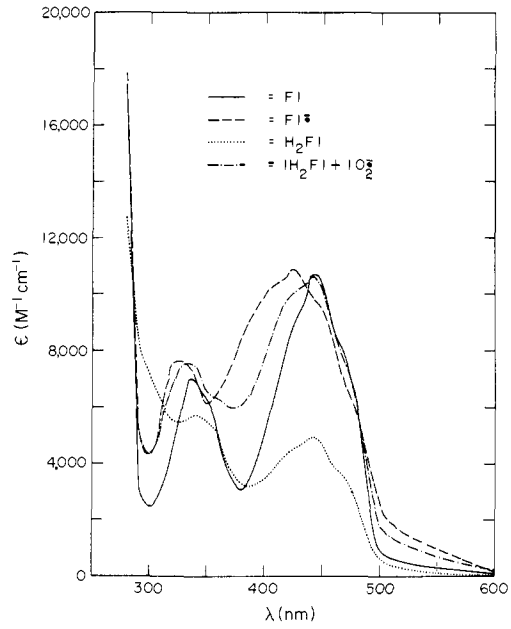
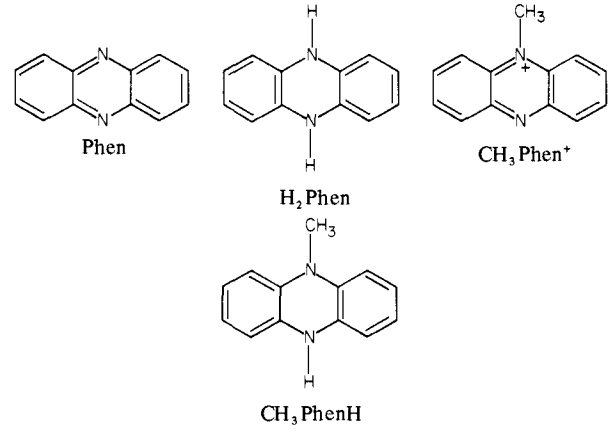


Figure 2. Absorption spectra for dimethylformamide (0.1 M tetraethylammonium perchlorate) solutions of 1 mM *N',N''*-dihydrolumiflavin (H_2Fl) (...), 1 mM Fl (—), 1 mM $Fl^{-}\cdot$ (– – –), and the combination of 1 mM H_2Fl plus 1 mM $O_2^{-}\cdot$ (–·–).

spectroscopic measurements, we report that $O_2^{-}\cdot$ is an effective oxidant of hydrophenazines, reduced flavins and nicotinamides, hydroxylamine, and hydrazine. The absence of acidic protons in these substrates precludes a mechanism that involves the proton-induced dismutation of $O_2^{-}\cdot$.

N,N'-Dihydrophenazine (H_2Phen) and *N*-methyl-*N'*-hydrophenazine (CH_3PhenH) have been synthesized electrochemically by reducing phenazine (Phen) and *N*-methylphenazinium ion (CH_3Phen^+) in the presence of 1 and 2 equiv of HCl, respectively,



in dimethylformamide (DMF).[22] Both reductions require two electrons and result in solutions for which the cyclic voltammograms are presented in Figure 1a,c. When 1 equiv of H_2Phen is added to a sealed cell that contains a DMF solution of $O_2^{-}\cdot$ (electrosynthesized), the voltammetry[23] and spectroscopy[24] illustrate that all of the H_2Phen is oxidized to Phen and that neither $O_2^{-}\cdot$ nor O_2 is present in solution (Figure 1b).

Addition of 1 equiv of CH_3PhenH to a sealed cell of $O_2^{-}\cdot$ results in the red $CH_3Phen\cdot$ radical and a solution that is free of $O_2^{-}\cdot$ and

(20) Nanni, E. J.; Stallings, M. D.; Sawyer, D. T. *J. Am. Chem. Soc.* **1980**, *102*, 4481.

(21) The $E°$ values for the reduction of $O_2^{-}\cdot$ at pH 14 have been calculated with data from: (a) Latimer, W. M. "Oxidation Potentials", 2nd ed.; Prentice-Hall: New York, 1952; pp 38–50. (b) Ilan, Y. A.; Meisel, D.; Czapski, G. *Isr. J. Chem.* **1974**, *12*, 891. (c) George, P. In "Oxidases and Related Redox Systems"; King, T. E., Mason, M. E., Morrison, M., Eds.; Wiley: New York, 1965; pp 3–36. (d) Fee, J. A.; Valentine, J. S. In "Superoxide and Superoxide Dismutases"; Michelsen, A. M., McCord, J. M., Fridovich, I., Eds.; Academic Press: New York, 1977; pp 19–60. (e) Bielski, B. H. J. *Photochem. Photobiol.* **1978**, *28*, 645. (f) Behar, D.; Czapski, G.; Ribini, J.; Dorfmann, L. M.; Schwartz, H. A. *J. Phys. Chem.* **1970**, *74*, 3209. (g) Hoare, J. P. In "Oxidation-Reduction Potentials of Aqueous Solutions: A Selective and Critical Source Book"; Bard, A. J., Parsons, R., Jordan, J., Eds.; International Union of Pure and Applied Chemistry; Chapter 4 (in preparation). (h) Koppenol, W. H. *Nature (London)* **1976**, *262*, 420.

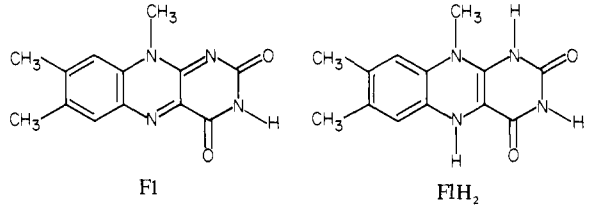
(22) The instrumentation and experimental procedures are summarized in ref 20.

(23) The cyclic voltammetry of Phen is essentially identical with that for the equimolar combination of $O_2^{-}\cdot$ with H_2Phen, i.e., Figure 1b.

(24) The electronic spectrum of this solution is identical with that of Phen and the solution is ESR silent at room temperature. Moreover, the same result is obtained if the conditions are anaerobic, i.e., if the solution is deaerated continuously with argon.

O_2 (Figure 1d). This has been confirmed by cyclic voltammetry, electronic spectroscopy, and ESR (17 lines, $g = 2.00$).[25]

N',N''-Dihydrolumiflavin (FlH_2) has been synthesized elec-



Fl FlH_2

trolytically in a manner analogous to that of the hydrophenazines. Combining 1 equiv of FlH_2 with $O_2^{-}\cdot$ in a sealed cell causes the FlH_2 to be oxidized cleanly to lumiflavin (Fl). Figure 2 illustrates the electronic spectra of (a) Fl, (b) $Fl^{-}\cdot$, (c) FlH_2, and (d) the combination of FlH_2 with $O_2^{-}\cdot$. Note that the electronic spectrum of the FlH_2–$O_2^{-}\cdot$ reaction (Figure 2d) is qualitatively and quantitatively almost the same as that of Fl (Figure 2a). Moreover, the cyclic voltammetry of the product solution closely resembles that of Fl and is ESR silent at room temperature.

N-Benzyl-4,4-dihydronicotinamide (BNH) has been synthesized by established methods.[26,27] The reaction of BNH with $O_2^{-}\cdot$ is slower than that of the reduced phenazines and flavins and requires 4–6 min for completion at millimolar concentrations; the reduced phenazines and flavins react instantaneously. The reaction stoichiometry is 1:1 and the product solution exhibits electrochemistry and spectroscopy which is similar to that for BNH. However, there are distinct differences[28] and no evidence for O_2 or $O_2^{-}\cdot$. The electrochemistry and spectroscopy of BN^{+} is completely different from that of BNH or the product(s) of the $O_2^{-}\cdot$–BNH reaction. Hence, a direct hydride transfer to $O_2^{-}\cdot$ is ruled out. These results confirm that $O_2^{-}\cdot$ reacts with BNH to yield new species, probably derivatives of an unstable primary product such as BN·.

Analogously, the reaction of NH_2OH in basic DMF with $O_2^{-}\cdot$ is complex. Adding 1 equiv of NH_2OH to a sealed cell of $O_2^{-}\cdot$ destroys all of the $O_2^{-}\cdot$, produces no O_2, and yields a bronze-colored solution for 5–10 min before it becomes colorless.[29] Preliminary results also indicate that hydrazine (N_2H_4) is oxidized by $O_2^{-}\cdot$ with an approximate 1:1 stoichiometry (actually 3 N_2H_4 per 4 $O_2^{-}\cdot$ if N_2 and OH^{-} are assumed to be the only products). Additional studies are in progress to elucidate what appears to be a complicated mechanistic pathway.

The results confirm that the two hydrogen atoms of H_2Phen and FlH_2 are oxidized by $O_2^{-}\cdot$ to give Phen and Fl, respectively

$$H_2Phen + O_2^{-}\cdot \rightarrow Phen + \cdot OH + OH^{-} \quad (4)$$

$$FlH_2 + O_2^{-}\cdot \rightarrow Fl + \cdot OH + OH^{-} \quad (5)$$

The single readily oxidizable hydrogen atom of CH_3PhenH is oxidized by $O_2^{-}\cdot$ to yield $CH_3Phen\cdot$

$$CH_3PhenH + O_2^{-}\cdot \rightarrow CH_3Phen\cdot + HO_2^{-} \quad (6)$$

The reactions of $O_2^{-}\cdot$ with BNH and NH_2OH are complicated. We propose that $O_2^{-}\cdot$ oxidizes BNH by a one-hydrogen-atom process[31]

$$BNH + O_2^{-}\cdot \rightleftarrows BN\cdot + HO_2^{-} \quad (7)$$

For NH_2OH, a plausible mechanism for the primary process is a three-hydrogen-atom transfer

$$NH_2OH + O_2^{-}\cdot \rightarrow NO + H_2O + OH^{-} \quad (8)$$

followed by further chemical reactions, such as the combination of NO with solvent or $O_2^{-}\cdot$.[30,32]

In summary, the reduction of $O_2^{-}\cdot$ by nonprotic reducing substrates is controlled by the number of readily oxidizable hydrogen atoms per substrate molecule. Conversion of such hydrogen atoms to protons provides the means to stabilize the reduction products of $O_2^{-}\cdot$ (O_2^{2-}, $\cdot O^{-}$, annd O^{2-}). Hence, $O_2^{-}\cdot$ is a selective oxidant for those substrates that are susceptible to oxidation via a hydrogen-atom transfer mechanism.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. CHE-79-22040.

(25) If CH_3Phen^{+} is reduced electrochemically by one electron to $CH_3Phen\cdot$, the electrochemistry and spectroscopy are nearly identical with that of the equimolar combination of $O_2^{-}\cdot$ and CH_3PhenH. The cyclic voltammetry indicates that minor side products are formed; however, the dominant species is $CH_3Phen\cdot$. That $CH_3PhenH^{+}\cdot$ is not produced is verified by electrochemically reducing CH_3Phen^{+} by one electron in the presence of 1 equiv of HCl; the voltammetry and spectroscopy of $CH_3PhenH^{+}\cdot$ are distinctly different from that of $CH_3Phen\cdot$.

(26) Karrer, P.; Stare, F. J. *Helv. Chim. Acta* **1937**, *20*, 418.

(27) Mauzerall, D.; Westheimer, F. H. *J. Am. Chem. Soc.* **1955**, *77*, 2261.

(28) BNH in DMF has an irreversible oxidation wave at $E_{p_a} = +0.70$ V vs. SCE for an initial anodic scan, which results in three irreversible reduction waves at $E_{p_c} = -0.30$, -0.75, and -1.03 V vs. SCE on the reverse scan; it has no reduction waves for an initial cathodic scan. BNH in DMF also has an absorption band at 346 nm (ϵ 6270 M^{-1} cm^{-1}). The product solution of the $O_2^{-}\cdot$ reaction in DMF has four oxidation waves at $E_{p_a} = -0.10$, $+0.25$, $+0.59$, and $+0.87$ V vs. SCE, which result in only one reduction wave at $E_{p_c} = -1.03$ V on the reverse scan; for an initial cathodic scan reduction waves are not observed. The electronic spectrum of the product solution from the combination of BNH and $O_2^{-}\cdot$ illustrates that the 346-nm band of BNH shifts to 355 nm (ϵ 7190 M^{-1} cm^{-1}) and has two shoulders at 310 (ϵ 3700 M^{-1} cm^{-1}) and 370 nm (ϵ 6790 M^{-1} cm^{-1}) as well as a broad band of low intensity of 470 nm (ϵ 920 M^{-1} cm^{-1}).

(29) Concurrent with the loss of the bronze color is the disappearance of a broad irreversible oxidation wave at $E_{p_a} = -0.12$ V vs. SCE. In addition, two irreversible oxidation waves at $E_{p_a} = +0.13$ and $+0.58$ V vs. SCE occur. The +0.58-V wave can be attributed to the oxidation of NO_2^{-}; however, even under anaerobic conditions the autoxidation of NH_2OH in basic media results in some NO_2^{-}. Furthermore, preliminary results indicate that $O_2^{-}\cdot$ reacts with NO to produce NO_2^{-}.[30]

(30) Roberts, J. L.; Sawyer, D. T., unpublished results (1980).

(31) Presumably, BN· dimerizes, abstracts a solvent hydrogen atom, or is epoxidized by HO_2^{-} to yield a product solution similar to the starting material, BNH.

(32) Although Elstner and Heupel[33] conclude that formation of $O_2^{-}\cdot$ in aqueous media in the presence of NH_2OH yields NO_2^{-} by a primary one-hydrogen-atom transfer to $O_2^{-}\cdot$, the autoxidation of NH_2OH to NO_2^{-} in basic aqueous media is rapid. Thus, the role of $O_2^{-}\cdot$ under aqueous aerobic conditions may be as a Brønsted base rather than an oxidant.[20,34]

(33) Elstner, E. F.; Heupel, A. *Anal. Biochem.* **1976**, *70*, 616.

(34) Sawyer, D. T.; Gibian, M. J. *Tetrahedron* **1979**, *35*, 1471.

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Free Radical and Electron-Transfer Mechanisms for Tertiary Amine Oxidation

Sir:

We recently reported that the photooxidation of nonsymmetrical tertiary amines, e.g., R_2NR', by the singlet state of *trans*-stilbene in acetonitrile solution can result in the formation of two stilbene–amine adducts via the mechanism shown in Scheme I for ethyldimethylamine (**1**, R = CH_3).[1]

These reactions display moderate to high selectivity for formation of the adduct which results from oxidation of the less substituted alkyl group (a > b). Selective oxidation is attributed to a stereoelectronic effect on the deprotonation of an intermediate amine cation radical (aminium radical) and has been reported for chemical[2] and electrochemical[3] as well as photochemical[4] reactions. All of these oxidation reactions are believed to produce an α-amino radical by a sequential electron-transfer, proton-transfer mechanism rather than a one-step hydrogen-atom-transfer mechanism (Scheme I).

(1) Lewis, F. D.; Ho, T.-T. *J. Am. Chem. Soc.* **1980**, *102*, 1751.

(2) Lindsay Smith, J. R.; Mead, L. A. V. *J. Chem. Soc., Perkin Trans. 2* **1973**, 206.

(3) Lindsay Smith, J. R.; Masheder, D. *J. Chem. Soc., Perkin Trans. 2* **1976**, 47.

(4) (a) Lewis, F. D.; Ho, T.-I. *J. Am. Chem. Soc.* **1977**, *99*, 7991. (b) Lewis, F. D. *Acc. Chem. Res.* **1979**, *12*, 152.

0002-7863/80/1502-7593$01.00/0