hydrofluoric acid would have a single $F^{19}$ resonance displaced only slightly from that of hydrofluoric acid. Consistent with our interpretations, the n.m.r. spectra of these solutions show no significant temperature dependence. Changes in cation can also markedly affect relaxation times. The $F^{19}$ spectrum of $AgNbF_6$ in acetonitrile is a single, broad resonance.

We conclude from our data that there is no fast ($k \sim 10^8$) interaction of $NbF_6^-$ with $F^-$ since the $F^{19}$ decet and the $Nb^{93}$ septet are maintained in the presence of $F^-$ and HF. This is consistent with the general behavior of fluoroanions of $O_h$ symmetry[5] in that exchange through a seven-coordinate intermediate appears to be of significantly higher energy than exchange through a dissociative process.

The heptafluoroniobate anion $NbF_7^{2-}$ cannot be present in significant concentration ($>5\%$) in these previously described solutions. Moreover, $48\%$ hydrofluoric acid seems to have no effect on $NbF_6^-$. Hoard[6] has established the existence of a discrete $NbF_7^{2-}$ ion in the solid state ($K_2NbF_7$). Therefore, there must be either a small but finite $NbF_7^{2-}$ concentration in hydrofluoric acid solutions of $NbF_6^-$ with preferential precipitation of $NbF_7^{2-}$ salts or formation of $NbF_7^{2-}$ in the actual process of nucleation.

(5) E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **81**, 1084 (1959).

(6) J. L. Hoard, *ibid.*, **61**, 1252 (1939).

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## Electron-Transfer Reactions of Aromatic Thiolate Anions with Organic Oxidizing Agents

*Sir:*

While the oxidation of mercaptans with inorganic oxidizing agents is a well known reaction,[1] the corresponding reaction utilizing organic oxidizing agents has received relatively little study[2a,b] exclusive of quinoid systems.[3a–c]

We have found the oxidation of aromatic thiolate anions with organic oxidizing agents to be a reaction whose generality heretofore has not been realized. Thus, aromatic thiolate anions in the solvent mixture dimethyl sulfoxide–*t*-butyl alcohol undergo electron transfer with organic electron acceptors to give aromatic disulfides and the corresponding reduction products.

$$ArS^- + \underset{Z}{=\!\!<} \longrightarrow ArS\cdot + \underset{I^-}{\overset{Z}{=\!\!<}} \longrightarrow \longrightarrow$$

$$ArSSAr + \text{reduction products}$$
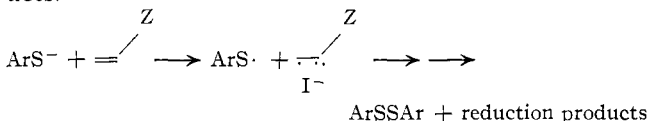
For example, in an inert atmosphere 2-naphthalenethiol with catalytic amounts of sublimed potassium *t*-butoxide in dimethyl sulfoxide–*t*-butyl alcohol (2:1) is oxidized by less than molar amounts of nitrosobenzene to the disulfide in $79\%$ yield. Azobenzene and azoxybenzene are found as the reduction products. The reaction conducted without nitrosobenzene leads to complete recovery of the thiol. A basic medium is ad-

(1) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 1, Chemical Publishing Co., Inc., New York, N. Y., 1958.

(2) (a) H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *J. Am. Chem. Soc.*, **84**, 4772 (1962); (b) A. Schriesheim, *et al.*, *Chem. Eng. News*, Feb. 11, 1963, p. 41.

(3) (a) H. I. Hadler, M. J. Erwin, and H. A. Lardy, *J. Am. Chem. Soc.*, **85**, 458 (1963); (b) C. G. Overberger and P. V. Bonsignore, *ibid.*, **80**, 5431 (1958); (c) L. F. Fieser and R. B. Turner, *ibid.*, **69**, 2335 (1947).
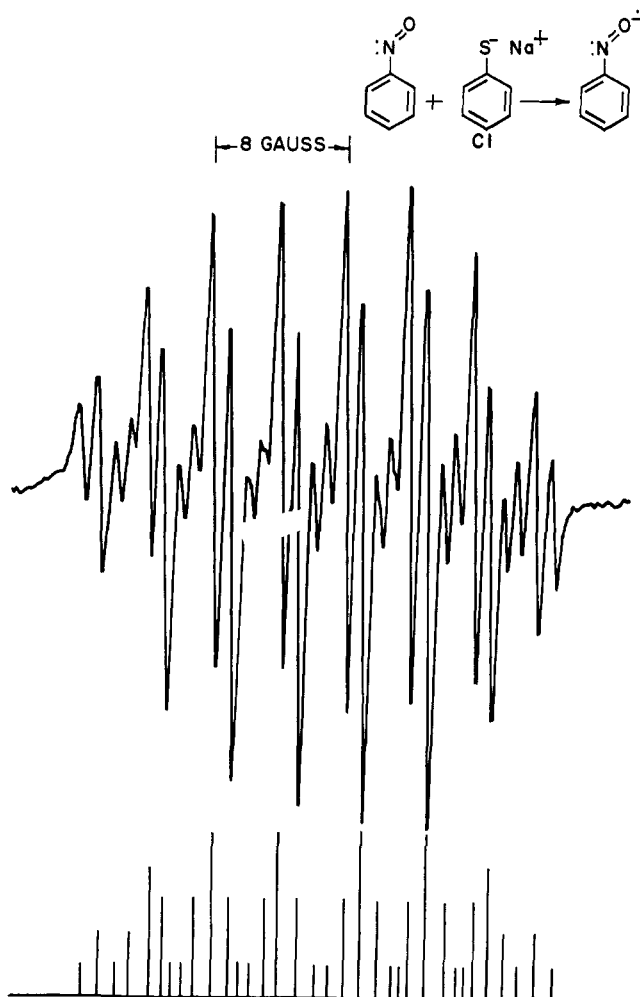


Fig. 1.—Radical anion produced by electron transfer between nitrosobenzene and sodium *p*-chlorobenzenethiolate in dimethyl sulfoxide–*t*-butyl alcohol (2:1).

vantageous if high yields of the disulfide are to be realized.

It is also found that reasonably stable radical anions(I) can be detected as intermediates as determined by e.s.r. measurements.[4] Thus, in dimethyl sulfoxide–*t*-butyl alcohol (2:1) nitrosobenzene with sodium *p*-chlorobenzenethiolate[5,6] leads to a 34-line spectrum, Fig. 1, with a line width (between centers of two extreme components) of 28.7 gauss. (Nitrobenzene radical anion in this solvent system, dimethyl sulfoxide–*t*-butyl alcohol (2:1), leads to a 48-line spectrum with a line width of 33.7 gauss.[7]) The measured coupling constants are: $a_N = 8.0$, $a_{H_p} = 3.9$, $a_{H_o} = 2.9 \pm 0.1$, $a_{H_m} = 1.1 \pm 0.1$ gauss.[8] The radical anion is tentatively identified as nitrosobenzene radical anion.[9]

(4) Experiments were performed using a Varian V-4500 100 kc. e.p.r. spectrometer equipped with a flow system.

(5) The salt was prepared by a method similar to the preparation of sodium phenoxide by N. Kornblum and A. P. Lurie, *J. Am. Chem. Soc.*, **81**, 2705 (1959). *Anal.* Calcd. for $C_6H_4ClSNa$: S, 19.25. Found: S, 19.62. In the dry state the salt is rather stable to air oxidation.

(6) The salt and nitrosobenzene were dissolved in deoxygenated solvent before mixing.

(7) Line widths were determined by comparison with *p*-benzosemiquinone (E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **36**, 1944 (1962); J. Gendell, J. H. Freed, and G. K. Fraenkel, *ibid.*, **37**, 2832 (1962)).

(8) The assignment of the coupling constants to the protons in the various positions is based on the general behavior of the splitting constants in benzene anion radicals with a single electron-withdrawing substituent. (J. C. Schug, T. H. Brown, and M. Karplus, *J. Chem. Phys.*, **37**, 330 (1962), and references therein.) Absolute assignment of the coupling constants could be obtained by use of deuterium labeling.

(9) The same radical anion has been obtained by two other methods: (1) The reaction of two moles of potassium *t*-butoxide with 1:1 molar

The following experiment is typical of the electron-transfer reaction. To 25 ml. of dimethyl sulfoxide-*t*-butyl alcohol (2:1) (all solutions degassed and the reaction conducted under 47 mm. nitrogen pressure), 0.003 $M$ in potassium *t*-butoxide, was added 2.01 mmoles of benzenethiol. Nitrosobenzene (1.43 mmoles) was then added, giving a red-brown solution. After stirring magnetically for 35 min., the reaction was quenched with salt solution, then acidified to pH 2 and filtered. Recrystallization of the precipitate from ethanol gave a 70% yield of diphenyl disulfide, m.p. 61°. Other aromatic thiols which undergo oxidation with nitrosobenzene to the disulfide are: (yields in parentheses) *p-t*-butylbenzenethiol (48), thiosalicylic acid (55), *p*-chlorobenzenethiol (60), and *p*-nitrobenzenethiol (58). It is interesting to note that it is conceivable for *p*-nitrobenzenethiol to act as its own electron-transfer agent analogous to the oxidation of *p*-nitrotoluene.[10] It was found that *p*-nitrobenzenethiol and base without any nitrosobenzene gave negligible yields of disulfide utilizing normal (35 min.) reaction times. However, with deficient amounts of base and long reaction times small amounts of disulfide (18% yield in 4 hr.) were formed. If mole to mole amounts of *p*-nitrobenzenethiol and base were used, no disulfide was formed, even with long reaction times. Thus, *p*-nitrobenzenethiol is a poor electron-transfer agent, while its conjugate base undergoes no electron transfer at all.

Our success with nitrosobenzene led us to seek other compounds as electron-transfer agents. Thus it was found that dienophiles such as maleic anhydride and azodicarbonamide with potassium 2-naphthalenethiolate gave high yields of the disulfide. Other possible electron-transfer reagents such as nitrobenzene, acrylonitrile, and acrylamide gave poor yields of the disulfide. The relative electron-transfer ability of these reagents can be determined. Potassium 2-naphthalenethiolate was oxidized with the electron-transfer agent (in the same manner as described for oxidation of potassium benzenethiolate by nitrosobenzene) and the reaction quenched after 1 hr. Ordering the electron-transfer agents in their ability to dimerize potassium 2-naphthalenethiolate we have (yields of the disulfide in parentheses) azodicarbonamide (88) > nitrosobenzene (79) > maleic anhydride (56) >> acrylonitrile (7) > nitrobenzene (6) > acrylamide (0).

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## Synthesis of Boron Chloroperchlorates and Boron Triperchlorate[1]

*Sir:*

We have synthesized the compounds $BCl_2ClO_4$, $BCl(ClO_4)_2$, and $B(ClO_4)_3$ by the reaction of boron trichloride and anhydrous perchloric acid. At −78° the reaction proceeds smoothly with evolution of hydrogen chloride to give a quantitative yield of product and the compound formed is governed by the ratio of boron trichloride to perchloric acid used in the reaction. The

boron chloroperchlorates have also been prepared by an alternative reaction involving boron trichloride and anhydrous silver perchlorate[2] and both methods give identical compounds. These compounds are temperature and moisture sensitive, undergoing hydrolysis and decomposition reactions, but under anhydrous conditions they are stable at low temperatures. Decomposition is accompanied by the eventual evolution of chlorine with the chloroperchlorates of boron losing their chlorine to give compounds containing boron, perchlorate, and oxygen. There is a possibility that in some instances a boroxole triperchlorate is formed as a decomposition product.

Infrared spectra of the boron chloroperchlorates in carbon tetrachloride were obtained and give spectra with sharp, well defined absorption bands corresponding to B–Cl, B–O, and Cl–O bonds. Spectra obtained at −16° and at room temperature on the same solution show no significant change, indicating that these materials are relatively stable in dilute solutions of carbon tetrachloride even at room temperature. In contrast, boron triperchlorate is unstable in carbon tetrachloride at −16°, and as a result a spectrum has not been obtained as yet on this material. Sensitivity of these compounds has made handling tedious, but a low temperature drybox has allowed analytical data and physical properties of these compounds to be measured. These data are summarized in the following sections.

**Boron Dichloroperchlorate.**—A liquid at −78.5° solidifies to a glassy solid at lower temperatures. *Anal.* Calcd. for $BCl_2ClO_4$: B, 5.97; Cl, 38.14; $ClO_4$, 54.89; mol. wt., 181. Found: B, 5.91; Cl, 38.93; $ClO_4$, 55.15; mol. wt., 180; $d^{-16}{}_4$ 1.728; $n^{-16}$D 1.4288. Infrared: B–Cl at 948 and 1002 cm.$^{-1}$.

**Boron Chlorodiperchlorate.**—A crystalline solid which melts at −15 to −17°: once the compound has melted, recooling results in solidification either to a glassy or a crystalline solid depending on the purity of the compound. *Anal.* Calcd. for $BCl(ClO_4)_2$: B, 4.41; Cl, 14.46; $ClO_4$, 81.13; mol. wt., 245. Found: B, 4.32; Cl, 14.84; $ClO_4$, 80.85; mol. wt., 242; $d^{-16}{}_4$ 1.872; $n^{-16}$D 1.4348. Infrared: B–Cl band at 1001 cm.$^{-1}$.

**Boron Triperchlorate.**—A white crystalline solid which does not melt at temperatures up to −5° and undergoes decomposition reactions before its melting point is reached. *Anal.* Calcd. for $B(ClO_4)_3$: B, 3.50; $ClO_4$, 96.50. Found: B, 3.48; $ClO_4$, 96.52.

The chloroperchlorates of boron, in addition to being sensitive to heat and moisture, have also shown another type of instability. These compounds readily undergo exchange reactions similar in nature to those observed for the alkyl chloroborinates ($ROBCl_2$ and $(RO)_2BCl$) formed by the reaction of alcohols or phenols with boron trichloride, but exchange is less facile with the perchlorate compounds:

$$2BCl_2ClO_4 \rightleftharpoons BCl_3 + BCl(ClO_4)_2$$
$$3BCl(ClO_4)_2 \rightleftharpoons BCl_3 + 2B(ClO_4)_3$$
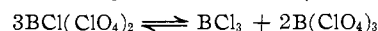
This property makes the purification of the chloroperchlorates by vacuum distillation difficult, since the loss of volatile boron trichloride is a driving force for the reaction. Disproportionation is slow at − 78° under 2–3 mm. pressure, but at 0.1 mm. pressure it proceeds at a measurable rate. Under the latter conditions distillation proceeds rapidly enough so that boron dichloroperchlorate can be distilled leaving behind any boron chlorodiperchlorate formed by the exchange reaction.

Complex formation is a common phenomenon of boron compounds and one case is reported with an organic