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Nature of Niobium(V) Fluoride Species in Solution

Sir:

We have unequivocally established the existence of the NbF_6^- ion in solution and find that it shows little tendency to interact with F^- to generate the seven coordinate NbF_7^{2-} anion in solution.¹

The Nb^{93} n.m.r. spectrum of NbF_6^- , the first high resolution niobium spectrum, consists of a septet showing that six equivalent fluorine atoms are bound to the niobium atom (Fig. 1). Consistently, the F^{19} spectrum

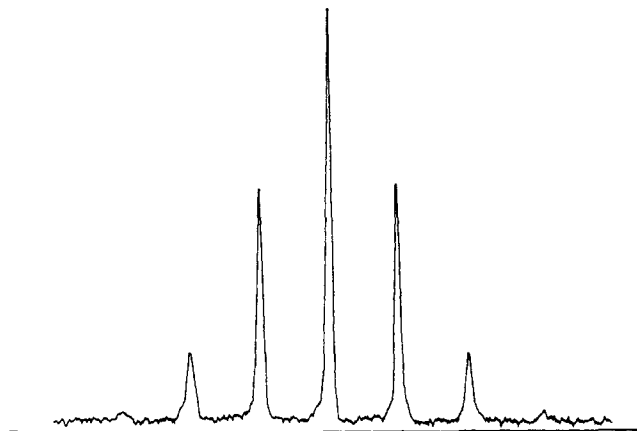


Fig. 1.—The Nb^{93} n.m.r. spectrum of the NbF_6^- ion at 14.2 Mc.

is a decet; the ten lines arise from coupling with the niobium nucleus which has a spin quantum number of $9/2$. There is a symmetrical variation in the line widths in this spectrum (Fig. 2). This is a consequence of the predominant relaxation process for the Nb^{93} nucleus, namely, the interaction of its quadrupole moment with the fluctuating electric field gradients in the ion. The theoretical spectrum for a nucleus of spin $1/2$ coupled to a nucleus of spin $9/2$ was calculated, using the treatment of Pople.² The agreement between the observed and calculated line intensities is very good, as shown in Fig. 2.

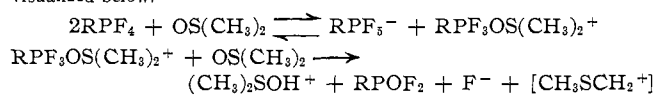
The n.m.r. spectra of NbF_6^- were obtained from acetonitrile solutions of the reaction product (A) of NbF_5 with dimethylformamide.³ Previously characterized metal salts of NbF_6^- are too insoluble for n.m.r. solution studies (AgNbF_6 , *vide infra*, is an exception).

The following observations bear on the reactivity of the NbF_6^- anion. Addition of water, saturated

(1) O. L. Keller, Jr., in an article (*Inorg. Chem.*, **2**, 783 (1963)) appearing after submission of this manuscript, reports on a Raman study of hydrofluoric acid solutions of Nb^V and concludes that NbF_7^{2-} is not an important species in solution.

(2) J. A. Pople, *Mol. Phys.*, **1**, 168 (1958).

(3) Another niobium species must be formed and is identified with a very broad resonance in the F^{19} spectrum of A in acetonitrile. Water rapidly hydrolyzes this species; thus an F^{19} spectrum (Fig. 2) free of this resonance can be obtained. In related work, we have established that RPF_4 compounds react with $(\text{CH}_3)_2\text{SO}$ to give RPF_5^- , RPOF_2 , and Me_2SOH^+ as visualized below.



and a similar sequence is suggested for the NbF_5 system.

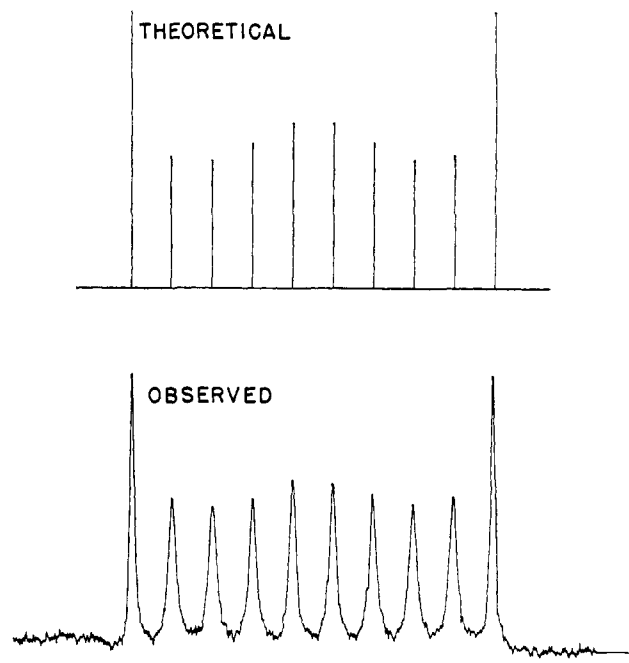


Fig. 2.—Comparison of the theoretical F^{19} n.m.r. spectrum of NbF_6^- with that observed at 56.4 Mc. $J_{\text{NbF}} = 334$ c.p.s. and $\delta_{\text{F}} = -178$ p.p.m. (CF_3COOH reference).

aqueous ammonium fluoride, or 48% hydrofluoric acid to the acetonitrile solution of A caused some broadening of the Nb^{93} septet but no shift or collapse. A solution of A in water gave a single broad Nb^{93} resonance unshifted from the resonance observed for the acetonitrile solution.

Dissolution of A in water or in 48% hydrofluoric acid followed by rapid evaporation and then redissolution in acetonitrile yielded the F^{19} decet in the n.m.r. experiment. The F^{19} spectrum of A in 48% hydrofluoric acid was identical with that of A in acetonitrile except that there was a high field fluoride ion resonance and sufficient broadening that the decet fine structure for NbF_6^- was not discernible. Addition of water, saturated aqueous ammonium fluoride, or 48% hydrofluoric acid to the acetonitrile solution of A resulted in a broadening, but no collapse, of the $\text{NbF}_6^- \text{F}^{19}$ decet and the slow appearance of two overlapping broad resonances at higher field. The intensities of the two higher field peaks increased with time showing a slow irreversible hydrolysis of NbF_6^- to $\text{NbO}_x\text{F}_y^{2-}$ species. Even after several hours, an aqueous acetonitrile solution of NbF_6^- still showed the $\text{NbF}_6^- \text{F}^{19}$ decet although increase in intensity of the higher field peaks was observable indicating continuing hydrolysis. The hydrolyzed species eventually separate from solution; these show strong OH infrared stretching absorption and are rich in oxygen by analyses.

The line-width dependence of the Nb^{93} and F^{19} spectra of NbF_6^- on medium is ascribed to a solvent dependence of nuclear relaxation times and not to an exchange process.⁴ Exchange is ruled out by the observations that additions of 48% hydrofluoric acid to acetonitrile solutions of A cause broadening of the F^{19} and Nb^{93} spectra, yet solutions of A in 48% hydrofluoric acid show a resonance which, although broad, occurs at precisely the same position as for the acetonitrile solutions. If fluorine exchange were responsible for the initial broadening, then the solution of A in 48%

(4) We have found another example of this dependence of quadrupole relaxation on medium in the F^{19} n.m.r. spectrum for the hexafluoroarsenate anion; line width and shape are grossly altered by large changes in dielectric constant and the nature of the cation.

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 symmetry⁵ 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^- . Hoard⁶ 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. Muettterties and W. D. Phillips, *J. Am. Chem. Soc.*, **81**, 1084 (1959).

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

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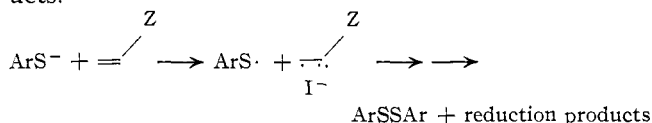
RECEIVED AUGUST 1, 1963

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.



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).

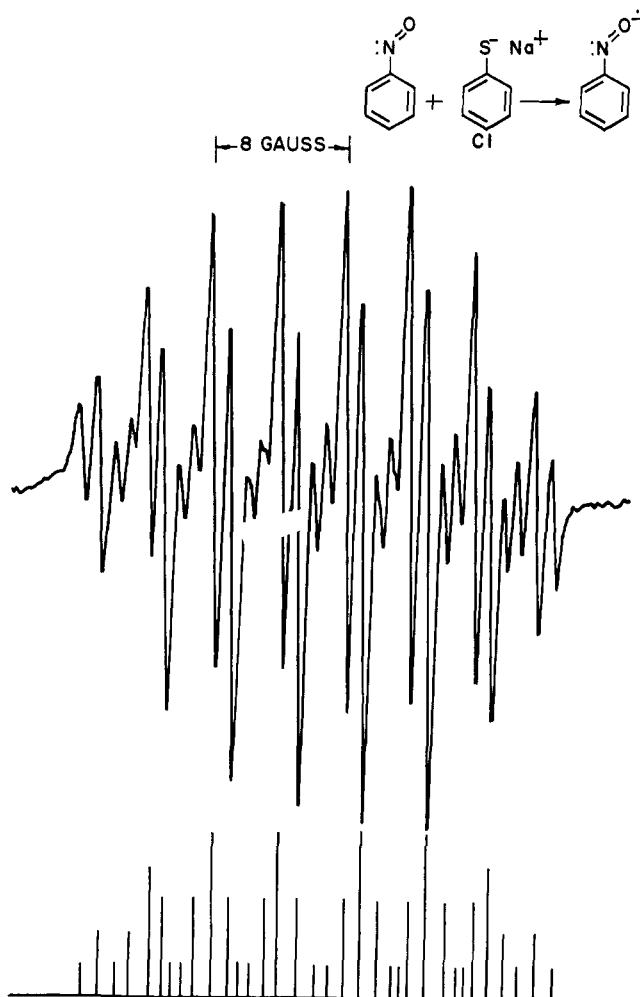


Fig. 1.—Radical anion produced by electron transfer between nitrosobenzene and sodium *p*-chlorobenzenethiolate in dimethyl sulfoxide-*t*-butyl alcohol (2:1).

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. (Nitrosobenzene 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