Correspondence

Hydrolysis and Nuclear Magnetic Resonance Studies of Fluorine Exchange

Sir:

A variety of mechanisms have been suggested to explain nmr studies of fluorine exchange in compounds such as SF_4,[1] PF_5,[2] RPF_4,[3] R_2SeF_2,[4] $RSiF_4^-$, and $R_2SiF_3^-$.[5] The purpose of this correspondence is to emphasize the role of hydrolysis in fluorine exchange processes and to suggest a technique for reducing hydrolysis.

An nmr study of fluorine exchange for the diethylamine catalyzed hydrolysis of trimethylfluorosilane has recently been completed.[6] No exchange occurs in

$$\begin{array}{lr} (CH_3)_3SiF + H_2O \underset{\substack{(C_2H_5)_2NH\ \text{catalyst}\\ CH_3CN\ \text{solvent}}}{\rightleftharpoons} (CH_3)_3SiOH + HF & \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \big\downarrow \text{slow} & (1) \\ \qquad\qquad\qquad\qquad\qquad {}^1/_2(CH_3)_3SiOSi(CH_3)_3 + {}^1/_2H_2O & \end{array}$$

the absence of H_2O; however, addition of H_2O and $(C_2H_5)_2NH$ produces the equilibrium system (1) and the rate of fluorine exchange may be followed by monitoring the collapse of the proton nmr doublet of $(CH_3)_3SiF$ as a function of H_2O, $(C_2H_5)_2NH$, and $(CH_3)_3SiF$ concentration and temperature.[6] Hydrolysis is accompanied by slow condensation of trimethylsilanol to hexamethyldisiloxane.

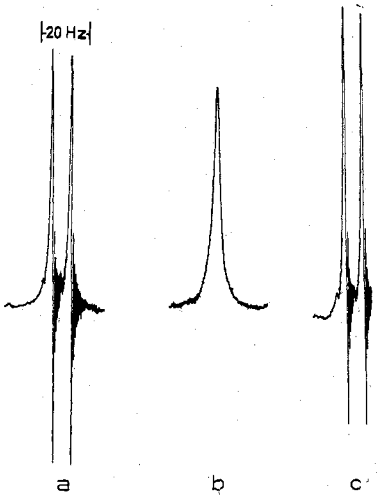

Figure 1.—Proton nmr spectrum at +38° of (a) $(CH_3)_3SiF$ (0.58 mmol) in 0.5 ml of acetonitrile solution, (b) after addition of H_2O (4.5×10^{-4} g, 0.025 mmol) and $(C_2H_5)_2NH$ (0.41 mmol) and (c) after further addition of $(CH_3)_3SiN(C_2H_5)_2$ (7.4×10^{-2} g, 0.51 mmol).

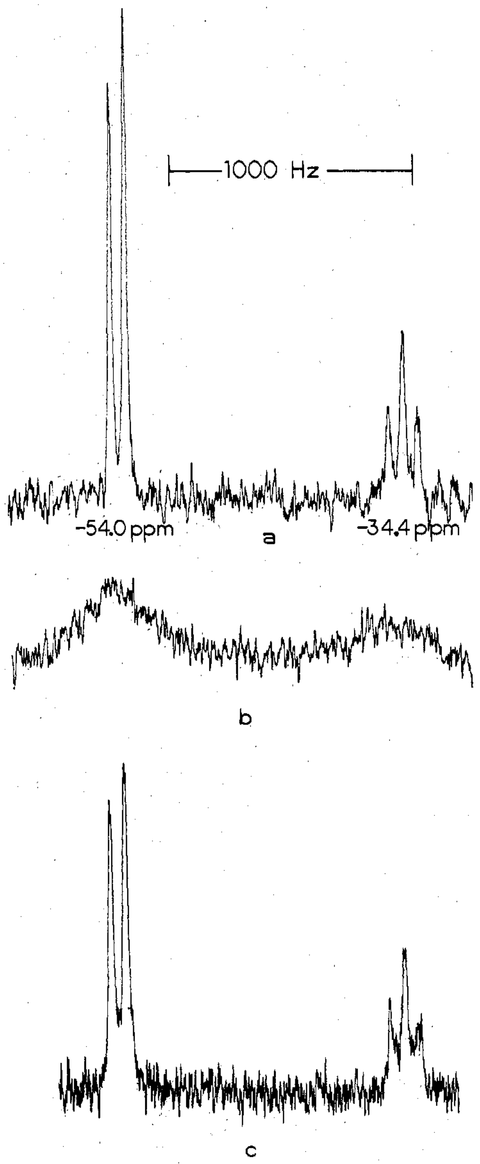

Figure 2.—Fluorine nmr spectrum at −30° of (a) $(C_2H_5)_2NSF_3$ (1.0 mmol) in 0.5 ml of trichlorofluoromethane, (b) after addition of H_2O (5.6×10^{-4} g, 0.031 mmol) and (c) after further addition of $(CH_3)_3SiN(C_2H_5)_2$ (8.4×10^{-2} g, 0.58 mmol). Chemical shift relative to internal $CFCl_3$.

The equilibrium nature of hydrolysis suggests that the rate of fluorine exchange is more a function of the equilibrium constant and the absolute values of the forward and reverse rates than of the amount of moisture present in solution. In other words, traces of moisture or HF, below the usual detection limit, could markedly influence the nmr spectra. With this in mind, we decided to study the nmr spectra of reactive metalloid–fluorine compounds such as *N*,*N*-dlmethylaminosulfur trifluoride and *N*,*N*-diethylaminosulfur trifluoride, which have been prepared by Demitras and MacDiarmid[7] and von Halasz and Glemser[8] but for

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[1] F. A. Cotton, J. W. George, and J. S. Waugh, *J. Chem. Phys.*, **28**, 994 (1958); E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, **81**, 1084 (1958).

[2] E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966); I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Accounts Chem. Res.*, **4**, 288 (1971).

[3] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

[4] K. J. Wynne, *ibid.*, **9**, 299 (1970).

[5] F. Klanberg and E. L. Muetterties, *ibid.*, **7**, 155 (1968).

[6] J. A. Gibson and A. F. Janzen, *Can. J. Chem.*, in press.

[7] G. C. Demitras and A. C. MacDiarmid, *Inorg. Chem.*, **6**, 1903 (1967).

[8] S. P. von Halasz and O. Glemser, *Chem. Ber.*, **103**, 594 (1970).

which only poorly resolved fluorine and proton nmr spectra were obtained.

Under rigorously anhydrous conditions, well resolved fluorine and proton nmr spectra were obtained for $(CH_3)_2NSF_3$ and $(C_2H_5)_2NSF_3$[9] confirming our hypothesis that fluorine exchange due to traces of moisture or HF was responsible for the unresolved nmr spectra.

If an equilibrium of the type represented by eq 1 is responsible for fluorine exchange then it should be possible to stop fluorine exchange by removing H_2O or HF. Since it is well known that HF may react with glass equipment to generate H_2O, it is important that HF be removed. A chemical reagent such as $(CH_3)_3SiN(C_2H_5)_2$ will react with HF and H_2O[10] and the effect of adding $(CH_3)_3SiN(C_2H_5)_2$ to a rapidly exchanging system is shown in Figures 1 and 2.

The anhydrous proton nmr spectrum of $(CH_3)_3SiF$ (Figure 1a) and fluorine spectrum of $(C_2H_5)_2NSF_3$ (Figure 2a) show well resolved multiplets. Addition of H_2O and catalyst $(C_2H_5)_2NH$ to 1a and H_2O to 2a produces collapsed spectra consistent with rapid fluorine exchange (Figures 1b and 2b), however, addition of $(CH_3)_3SiN(C_2H_5)_2$ to 1b and 2b stops fluorine exchange and well resolved spectra reappear (Figures 1c and 2c). The results are entirely consistent with hydrolysis as the mechanism of fluorine exchange.

Unless the presence of traces of H_2O or HF has been rigorously excluded, the possibility that hydrolysis provides a low-energy pathway for fluorine exchange in other reactive metal fluorides must be considered.[11]

Acknowledgments.—We thank the National Research Council of Canada for financial assistance and for a postgraduate scholarship (to J. A. G.).

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RECEIVED APRIL 25, 1972

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[9] D. G. Ibbott and A. F. Janzen, *Can. J. Chem.*, **50**, 2428 (1972).

[10] C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, pp 345–346.

[11] NOTE ADDED IN PROOF.—We have recently obtained the fluorine nmr spectra of $[(CH_3)_2CH]_2NSF_3$ and SF_4. The latter showed resolution 30° higher than reported previously, after treatment with $[(CH_3)_3Si_2]NH$: A. F. Janzen and D. G. Ibbott, submitted to *Can. J. Chem.*