$Me_3P\cdot BH_3$ over an extended period of time. Thus, under the conditions of our competition studies, displacement reactions are not important.

Experimental Section

All experimental manipulations were carried out in a standard high-vacuum line and a Vacuum Atmosphere HE-43 Dri-Lab equipped with an He-493 Dri-Train. The NMR data were obtained by using a Nicolet 300-MHz multinuclear Fourier Transform NMR Spectrometer operating at 75.5 MHz for ^{13}C, 300.1 MHz for ^1H, 121.5 MHz for ^{31}P, 96.3 MHz for ^{11}B, and 59.6 MHz for ^{29}Si. The ^{11}B and ^{31}P chemical shift values were measured relative to external $BF_3\cdot OEt_2$ and 85% H_3PO_4, respectively, high-field shifts being taken as negative. δ_H, δ_C, and δ_{Si} were measured by using Me_4Si as an internal standard. THF-d_8 and toluene-d_8 were purchased from Aldrich and stored over molecular sieves (note: use of fresh THF-d_8 is recommended). Low-resolution EI-MS data were recorded on a HP 5986A GC/MS/DS mass spectrometer operated at 70 eV, 2400-V electron multiplier, and with a direct-insert probe. The source temperature was maintained at 200 °C, and the probe temperature, at 25 °C.

Diborane(6) was synthesized by the reaction of $NaBH_4$ and I_2 in $(MeOCH_2CH_2)_2O$ and purified by trap-to-trap fractionation.[33] The aminophosphines, R_2PNR_2, were synthesized by two general methods: (a) the reaction of Me_2NPCl_2 with $EtMgX$[34–36] and (b) the reaction of Me_2PCl with the corresponding secondary amine, R'_2NH (R' = Me, Et, Pr^n, Pr^i).[35] Method b was also used for the preparation of Ph_2PNMe_2. $(Me_3Si)_2NPMe_2$ was synthesized by reacting $(Me_3Si)_2NLi$ with PCl_3 and subsequently using MeMgBr via a Grignard reaction.[37] Me_2AsNMe_2 was synthesized by the aminolysis of Me_2AsCl.[38] The reaction of Me_3Al with As_2O_3 yielded Me_3As.[39]

$Me_2\overline{PNMe_2\cdot B}H_3$ (I) and $H_3BP(\overline{NMe_2\cdot B}H_3)Me_2$ (II) were synthesized as previously reported.[25] Satisfactory elemental analyses of II (mp 117 °C) were obtained from Schwarzkopf Microanalytical laboratory. Calcd: C, 36.23; H, 13.74; B, 16.29. Found: C, 36.92; H, 13.57; B, 16.96. The EI–MS data (greater than 20% abundance) of II suggest the following peak assignments {[species], *m/z* (relative abundance)}: $[Me_2PNMe_2\cdot 2BH_3]^+$, 133 (22); $[Me_2NPH_3]^+$, 78 (100); $[Me_2NPH_2]^{\bullet+}$, 77 (22); $[Me_2PB]^{\bullet+}$, 72 (21); $[Me_2PH_2]^+$, 63 (88); $[Me_2PH]^{\bullet+}$, 62 (54); $[Me_2NBH_2]^{\bullet+}$, 57 (29); $[Me_2NBH]^+$, 56 (52); $[MePH]^+$, 47 (25); $Me_2NH]^{\bullet+}$, 45 (45); $[Me_2N]^+$, 44 (47).

All aminophosphines were purified by distillation on a spinning-band column: Me_2PNMe_2 (100 °C), Me_2PNEt_2 (136–138 °C), $Me_2PNPr^n_2$ (172–174 °C), $Me_2PNPr^i_2$ (166 °C), $(Me_3Si)_2NPMe_2$ (55–60 °C/4 Torr), Et_2PNMe_2 (86 °C/146 Torr), Ph_2PNMe_2 (96 °C/0.1 Torr), Me_2NPCl_2 (150 °C). $(Me_2N)_2PMe$, $(Me_2N)_3P$, and Me_3P were obtained from Strem Chemicals Co., and Me_3N was obtained from Matheson. The purity of these compounds was checked by ^1H and ^{13}C NMR spectroscopy.

$Me_3N\cdot BH_3$, $Me_3P\cdot BH_3$, and $Me_3As\cdot BH_3$ were synthesized by the direct reaction of B_2H_6 with the respective Lewis base in the vacuum line. The purity of these adducts was determined from their ^{11}B, ^{13}C, and ^{31}P NMR spectra in toluene-d_8 at room temperature (all δ values in ppm): $Me_3N\cdot BH_3$ [δ_B, −7.53; δ_C, 53.54], $Me_3P\cdot BH_3$ [δ_B, 36.71 (d), $^1J_{PB}$ = 58.0 Hz; δ_C, 12.38 (d), $^1J_{PC}$ = 36.7 Hz; δ_P, −1.28 (q)], $Me_3As\cdot BH_3$ [δ_B, −33.18; δ_C, 8.48].

General Reaction of $R_2PNR'_2$ with $BH_3\cdot THF$. A Pyrex NMR tube (10 mm × 22.5 cm) equipped with a greaseless vacuum adapter and stopcock containing 3.0 mL of toluene-d_8, 0.5 mL of THF-d_8, and 1 drop of TMS was degassed on the vacuum line by using freeze-and-thaw cycles. The appropriate amount of B_2H_6 was condensed into it at −196 °C. The reaction mixture was allowed to warm to 20 °C to ensure complete formation of $BH_3\cdot THF$. The NMR tube was recooled to −196 °C, and the appropriate amount of $R_2PNR'2$ was condensed (or added by using an addition tube) into it. The NMR tube was sealed, agitated at −95 °C (toluene/liquid N_2 slush), and inserted into the precooled probe of the NMR spectrometer. The ^1H, ^{11}B, ^{13}C, and ^{31}P NMR spectra of the reaction mixture were recorded at different temperatures. The NMR data for all the adducts formed in these reactions are listed in Tables I–III.

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Insertion of Nitriles into the Nitrogen–Chlorine Bond. Synthesis of Polyfluoro- and (Perfluoroalkyl)tetrazanes

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Photolysis of $CF_3N(CF_2CFXCl)Cl$ with ClCN leads to $CF_3N(CF_2CFXCl)N{=}CCl_2$ (X = Cl, F). Similarly, RCN (R = CF_3, Cl) with $CF_3(C_2F_5)NCl$ forms $CF_3(C_2F_5)NN{=}C(Cl)R$. Chlorine fluoride adds readily to the carbon–nitrogen double bond in $CF_3(C_2F_5)NN{=}C(Cl)R$ to give $CF_3(C_2F_5)NN(Cl)CClFR'$ (R′ = F, CF_3). While photolysis of $CF_3(C_2F_5)NN(Cl)CF_2Cl$ results in a tetrazane, $[CF_3(C_2F_5)NNCF_2Cl]_2$, under analogous conditions chlorine is eliminated from $CF_3(C_2F_5)NN(Cl)CClFCF_3$ to form $CF_3(C_2F_5)NN{=}CFCF_3$. Addition of chlorine fluoride to the latter compound followed by photolysis produces a tetrazane with perfluorinated alkyl substituents, $[CF_3(C_2F_5)NNCF_2CF_3]_2$. With CsF, $CF_3(C_2F_5)NN{=}CCl_2$ gives a rearranged perfluoro dimer, $CF_3(C_2F_5)NN{=}CFN(CF_3)N(C_2F_5)CF_3$. Photolysis of the product obtained after reacting the latter with ClF results in a highly substituted tetrazane, $[CF_3(C_2F_5)NN(CF_3)CF_2NN(C_2F_5)CF_3]_2$. These highly catenated nitrogen compounds are thermally and hydrolytically stable.

Introduction

The study of the chemistry of nitrogen–halogen bonds in fluorinated compounds has been ongoing for nearly 35 years, but heretofore the reactivity of these bonds has not been utilized in the preparation of fluorinated, highly catenated nitrogen-containing compounds. It has been shown that both fluorinated and nonfluorinated olefins can be inserted with ease into the nitrogen–halogen bond, e.g., hexafluoropropane or ethylene into the nitrogen–halogen bond of bromo- or iodobis(trifluoromethyl)amine[1–5] or olefins into chlorobis(trifluoromethyl)amine.[6–7] More recently we reported the stepwise insertion of $CF_2{=}CFX$ (X = Cl, F) into the N–Cl bonds of dichloro(perfluoroalkyl)amines.[8] Insertions of cyanogen chloride and/or trifluoroacetonitrile into nitrogen–chlorine bonds, e.g., in chlorobis(trifluoromethyl)amine,[9]

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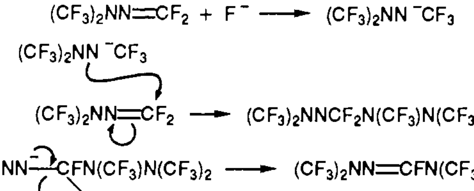
and into sulfur–chlorine bonds, e.g., SF_5Cl[10] and CF_3SF_4Cl,[11] via photolysis, gives $(R_f)_2NN{=}CClR_f'$ or $XSF_4N{=}NCClR_f'$ (R_f = perfluoroalkyl; R_f' = Cl or *F*-alkyl; X = F, CF_3). The products that are formed when these compounds that contain $-N{=}CClR_f'$ are reacted with fluoride ion are rearranged dimers.[12,13] It is very likely that the first step is the fluorination of the C–Cl bonds followed by the subsequent dimerization, viz.[9]



Some (perfluoroalkyl)- or (polyfluoroalkyl)tetrazanes that have been reported have been obtained in low yields from the photolysis at 2537 Å of the respective diazenes.[14,15] The formation of tetrazane may result from reaction of the methyl group formed in the initial decomposition of the diazene with the parent compound,[14] i.e.

$$R_fN{=}NR_f \xrightarrow{h\nu} 2R_f^{\bullet} + N_2$$

$$R_f = \text{polyfluoro- or perfluoromethyl}$$

$$R_f^{\bullet} + R_fN{=}NR_f \rightarrow (R_f)_2N\dot{N}R_f$$

followed either by dimerization of the hydrazo radical

$$2(R_f)_2N\dot{N}R_f \rightarrow [(R_f)_2NN(R_f)]_2$$

or reaction of the hydrazo radical with the starting diazene to form a tetrazo radical, which would react subsequently with $R_f^{\bullet}$

$$(R_f)_2N\dot{N}(R_f) + R_fN{=}NR_f \rightarrow$$
$$(R_f)_2NN(R_f)N(R_f)\dot{N}R_f \xrightarrow{R_f^{\bullet}} [(R_f)_2NNR_f]_2$$

Emeléus and Dobbie also identified $[(CF_3)_2NN(CF_3)]_2$ as a minor product from the reaction of $[(CF_3)_2NN(CF_3)]_2Hg$ with bromine or chlorine.[9] The formation of the tetrakis(trifluoromethyl)tetrazane very likely results from the decomposition of the photolytically or thermally sensitive halo compounds even in diffuse light at 20 °C.

$$(CF_3)_2NN(CF_3)X \xrightarrow[-X_2]{h\nu \text{ or } \Delta} [(CF_3)_2NN(CF_3)]_2$$
$$X = Cl, Br$$

The reported thermal stability of these tetrazanes is surprisingly high.

In this study we have taken advantage of the ready insertion of ClCN and CF_3CN into the nitrogen–chlorine bonds of bis(polyfluoroalkyl)- or bis(perfluoroalkyl)chloroamines, followed by the facile addition of chlorine fluoride to the carbon–nitrogen double bond. Photolysis of the resulting nitrogen–chlorine bonds gives rise to tetrazanes that are highly stable and insensitive to water, air, heat, and shock.

Results and Discussion

The bond energies of the nitrogen–chlorine and the oxygen–chlorine bonds in (perfluoroalkyl)chloroamines or -dichloroamines and perfluoroalkyl hypochlorites are very similar and their chemistries are not greatly different. However, it is interesting to compare relative reactivities and the effect of greater charge separation in chloroamines than hypochlorites; e.g., when insertion of either $CF_2{=}CF_2$ or $CF_2{=}CFCl$ into $CF_3O{-}Cl$ or CF_3NCl_2 occurs, it is seen that more forcing conditions are required for N–Cl insertion, viz.

$$CF_3N(Cl)CF_2CF_2Cl^{8} \xleftarrow[65\text{–}70\ °C]{CF_3NCl_2} F_2C{=}CF_2 \xrightarrow[-111\text{ to }-145\ °C]{CF_3OCl} CF_3OCF_2CF_2Cl^{16}$$

$$CF_3N(Cl)CF_2CCl_2F \xleftarrow[65\text{–}70\ °C]{CF_3NCl_2} F_2C{=}CClF \xrightarrow[-80\ °C]{CF_3OCl} \underset{2.5}{CF_3OCFClCClF_2} + \underset{3.0}{CF_3OCF_2CCl_2F}$$

With the exception that a higher temperature is required for insertion into the N–Cl bond, the products obtained with $CF_2{=}CF_2$ in either case are analogous and are found in high yield. It should be noted that with the unsymmetric olefin, the temperature differential still exists, but also only one isomer is formed with CF_3NCl_2 where the sole product of interest is the one where the positive chlorine of the CF_3NCl_2 is found on the olefinic carbon with the greatest electron density. While this, too, is the normal mode of behavior for CF_3OCl, in some cases where the difference in electron density between the two carbons of the olefin is small, significant amounts of each isomer are found.[16] In our recent studies[8] with $R_fR_f'NCl$, we also observe that a temperature of about 100 °C is required for olefin insertion reactions to proceed and only one isomer is obtained as is the case for R_fNCl_2.

Insertion of olefins into sulfur–chlorine bonds, e.g., SF_5Cl + >=<, requires photolysis, and both possible adducts are obtained with unsymmetric olefins. Synthesis of new substituted carbimides by insertion of nitriles into the element–chlorine bond of –O–Cl,[17] >N–Cl,[9] and S^{VI}–Cl[10] proceeds readily with the latter two usually via photolysis, but for –O–Cl, heating in the presence of an acid catalyst is necessary for the insertion reaction to occur.

On the basis of an early study on the reactions of SF_5Cl with nitriles,[10] other workers demonstrated that $(CF_3)_2NCl$ could be reacted in a similar manner.[9]

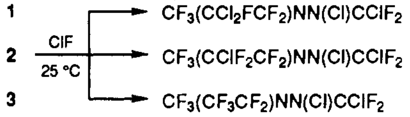
$$(CF_3)_2NCl + ClCN \xrightarrow{h\nu} (CF_3)_2NN{=}CCl_2$$

We now have taken advantage of this method to prepare similar carbimides, which are reactive precursors to a variety of new compounds. Thus, when mixtures of the *N*-chloro compounds $CF_3N(Cl)CF_2CXClF$ (X = Cl, F) or $CF_3(C_2F_5)NCl$ and RCN (R = Cl, CF_3) are photolyzed for 6–8 h, the insertion of $-C{\equiv}N$ into the N—Cl bond occurs readily to form the carbimide in high yields.

$$R_f(CF_3)NCl + RC{\equiv}N \xrightarrow{h\nu} \underset{\mathbf{1\text{–}4}}{R_f(CF_3)NN{=}CClR}$$

$$R_f = CCl_2FCF_2,\ R = Cl\ (\mathbf{1});\ R_f = CClF_2CF_2,\ R = Cl\ (\mathbf{2});$$
$$R_f = CF_3CF_2,\ R = Cl\ (\mathbf{3});\ R_f = CF_3CF_2,\ R = CF_3\ (\mathbf{4})$$

Advantage has been taken of the polar nature of the $-N{=}C<$ bonds to form new chloroamines with the addition of ClF at 25 °C. With **1**, **2**, and **3** both addition of ClF and partial fluorination take place



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Chlorine fluoride adds to the double bond in **4** without concomitant

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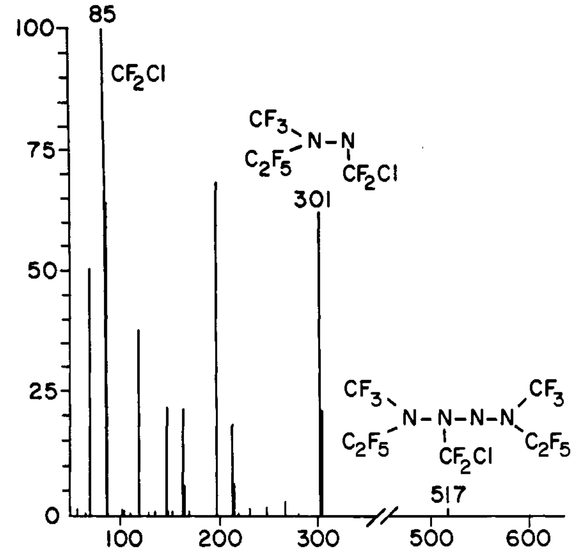


Figure 1. Electron-impact mass spectrum of $[CF_3(C_2F_5)NN(CF_2Cl)]_2$.

fluorination to form $CF_3(CF_2CF_3)NN(Cl)CClFCF_3$ (**6**). Subsequent photolysis of **5** results in the formation of a stable tetrazane, **7**. The properties and characterization of these new compounds are discussed later in this section.

$$\mathbf{5} \xrightarrow{h\nu} \underset{\mathbf{7}}{[CF_3(CF_3CF_2)NN(CClF_2)]_2} + Cl_2$$

Surprisingly, the photolysis of **6** results in the loss of chlorine to form a new perfluorinated carbimide, **8**. However, chlorine

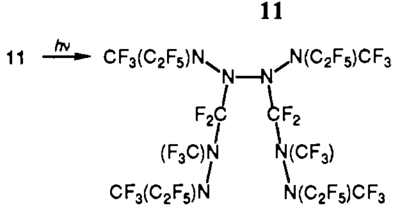
$$\mathbf{6} \xrightarrow[-Cl_2]{h\nu} \underset{\mathbf{8}}{CF_3(CF_3CF_2)NN{=}CFCF_3}$$

fluoride can be reacted readily with **8** to give $CF_3(CF_3CF_2)NN(Cl)CF_2CF_3$, which when photolyzed results in the totally fluorinated tetrazane **9**.

$$\mathbf{8} + ClF \rightarrow CF_3(CF_3CF_2)NN(Cl)CF_2CF_3 \xrightarrow{h\nu} \underset{\mathbf{9}}{[CF_3(CF_3CF_2)NN(CF_2CF_3)]_2}$$

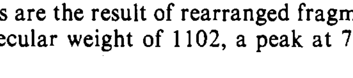
In an effort to replace all of the chlorine in **3** and **4**, each was reacted with CsF. Simple fluorination of **4** gives $CF_3(C_2F_5)NN{=}CFCF_3$ (**8**). However with **3**, fluorination first occurs to form $CF_3(C_2F_5)NN{=}CF_2$ with dimerization occurring by the same route as suggested in the Introduction for $(CF_3)_2NN{=}CF_2$[9] to give $CF_3(C_2F_5)NN(CF_3)CF{=}NN(C_2F_5)CF_3$ (**10**). Chlorofluorination with ClF to form **11**, followed by photolysis gives rise to a more complex tetrazane, **12**.

$$\mathbf{10} + ClF \rightarrow \underset{\mathbf{11}}{CF_3(C_2F_5)NN(CF_3)CF_2N(Cl)N(C_2F_5)CF_3}$$



12

Each of the new compounds has been characterized by infrared, NMR and mass spectral measurements. Mass spectra are particularly helpful, as is shown in the spectrum of **7** in Figure 1 where $M^+ - CF_2Cl$ plus other appropriate fragments are visible. In some cases, the peaks are the result of rearranged fragments, e.g., for **12** with a molecular weight of 1102, a peak at 734 that is attributed to



$$CF_3(C_2F_5)NN[CF_2\underset{\displaystyle N(C_2F_4)CF_3}{\underset{|}{N}}(CF_3)N(C_2F_5)CF_3]$$

where the N(2)–N(3) bond in the tetrazane backbone breaks with concomitant shifting of the $N(C_2F_5)CF_3$ group minus fluorine from N(3) to N(2). This redistribution process is also observed with other of the catenated species. Detailed NMR assignments are being studied further. In most cases elemental analyses have been utilized to confirm the structural assignments. The tetrazanes are stable thermally; e.g., **7** and **9** are stable at 100 °C (in Pyrex glass) while **12** is stable to 80 °C. None are attacked by water or are shock sensitive.

Conclusion

Insertion of nitriles into the nitrogen–chlorine bond of chlorobis(perfluoroalkyl)amines with subsequent chlorofluorination with chlorine fluoride provides precursors that lead to highly fluorinated alkyl-substituted tetrazanes. These compounds are stable fluids with densities of about 2 g/mL. We are continuing our efforts toward additional high nitrogen compounds.

Experimental Section

Materials. Chlorine fluoride (Ozark-Mahoning), cyanogen chloride (K & K Laboratories, Inc.), trifluoroacetonitrile (PCR), and cesium fluoride (American Potash) were used as received. $CF_3N(CF_2CFXCl)Cl$ (X = Cl, F),[8] $C_2F_5N{=}CF_2$,[8] and $CF_3(C_2F_5)NCl$[8] were prepared according to the literature methods.

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex glass vacuum system equipped with a Heise Bourdon tube and Televac thermocouple gauges. Products were purified by fractional condensation (trap-to-trap distillation). Volatile starting materials and products were quantitated by using standard *PVT* techniques. Infrared spectra were recorded on a Perkin-Elmer 1710 infrared Fourier transform spectrometer with a 10-cm gas cell equipped with KBr windows. ^{19}F NMR spectra were recorded on a JEOL FX-90Q Fourier transform nuclear magnetic resonance spectrometer with CCl_3F as reference and $CDCl_3$ as solvent. Mass spectra were obtained with a VG 7070 mass spectrometer operating at an ionization potential of 17 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany. Photolysis reactions were carried out in quartz reaction vessels irradiated in a Rayonet photochemical reactor with 3000-Å UV lamps.

Reactions of Nitriles. ClCN with $CF_3N(CF_2CFXCl)Cl$ (X = Cl, F) and RCN (R = Cl, CF_3) with $CF_3(C_2F_5)NCl$. The *N*-chloro compound $CF_3N(CF_2CFXCl)Cl$ or $CF_3(C_2F_5)NCl$ (5 mmol) and 30-35 mmol of nitrile (CF_3CN or ClCN) were condensed at −196 °C in a 2-L quartz vessel fitted with a Kontes Teflon stopcock. After the vessel reached 25 °C, it was exposed to UV radiation (3000 Å) for 6–7 h. The products were separated and purified by trap-to-trap distillation.

Properties of $CF_3(CF_2CF_2Cl)NN{=}CCl_2$. This compound was isolated in the trap at −30 °C, having passed through a trap at −10 °C. It was obtained in ~45–50% yield as a colorless liquid. Spectral data were as follows. MS (EI) [*m*/*e* (species), intensity]: 316/314 (M^+), 3.41/3.86; 297/295 ($M^+ - F$), 1.38/1.18, 281/279 ($M^+ - Cl$), 6.56/9.51; 231/229 ($M^+ - CF_2Cl$), 26.91/40.56; 137/135 ($C_2F_4Cl^+$), 7.12/29.22; 98/96 ($CNCl_2^+$), 12.82/22.20; 87/85 (CF_2Cl^+), 9.83/42.50; 84/82 (CCl_2^+), 7.68/8.99; 69 (CF_3^+), 100; 50 (CF_2^+), 11.32. IR (gas): 1586 vs (C═N), 1313 vs, 1280 vs, 1235 vs, 1209 vs, 1177 vs, 1115 s, 997 vs, 876 s, 833 s, 782 s, 749 w, 661 w, 650 w cm^{-1}. ^{19}F NMR: ϕ −59.77 (CF_3, tt), −69.26 (CF_2Cl, hextet), −101.24 NCF_2CF_2Cl, qt); $J_{CF_3-NCF_2} = 12.45$ Hz, $J_{CF_3-CF_2Cl} = 2.97$ Hz, $J_{CF_2-CF_2} = 2.8$ Hz. Anal. Calcd for $C_4F_7Cl_3N_2$: C, 15.29; F, 42.36; N, 8.92. Found: C, 14.81; F, 41.7; N, 8.89.

Properties of $CF_3(CF_2CFCl_2)NN{=}CCl_2$. This compound was found in the trap at −10 °C. It was obtained in ~30% yield as a colorless liquid. Spectral data were as follows. MS (EI) [*m*/*e* (species), intensity]: 332/330 (M^+), 1.5/1.4; 297/295 ($M^+ - Cl$), 5.8/6.6; 231/229 ($M^+ - CFCl_2$), 39.2/61.7; 164 ($C_3F_6N^+$), 24.5; 159 ($C_3F_5N_2^+$), 6.6; 153/151 ($C_2F_3Cl_2^+$), 36.9/58.0; 103/101 ($CFCl_2^+$), 58.4/88; 98/96 (CCl_2N^+), 16/25.6; 84/82 (CCl_2^+), 17.3/26.4; 69 (CF_3^+), 100; 63/61 ($CClN^+$), 6.8/11.4. IR (liquid): 1511 s (C═N), 1332 w, 1299 w, 1247 vs, 1215 w, 1190 s, 1122 s, 913 s, 845 s, 816 w, 795 w, 737 s cm^{-1}. ^{19}F NMR: ϕ −59.60 (CF_3, td), −72.86 ($CFCl_2$, tq), −99.33 (CF_2CFCl, qd); $J_{CF_3-CF_2} = 13.43$ Hz, $J_{CF_3-CF} = 2.44$ Hz, $J_{CF_2-CF} = 7.93$ Hz.

Properties of $CF_3(C_2F_5)NN{=}CCl_2$. This compound was found in the trap at −50 °C. It was obtained as a colorless liquid in ~60% yield. Spectral data were as follows. MS (EI) [*m*/*e* (species), intensity]: 300/298 (M^+), 4.90/6.93; 281/279 ($M^+ - F$), 1.99/2.37; 265/263 ($M^+ - Cl$), 3.34/11.38; 231/229 ($M^+ - CF_3$), 11.25/16.93; 181/179 ($M^+ - C_2F_5$), 2.07/3.39; 177/175 ($C_3F_4N_2Cl^+$), 1.20/4.10; 119 ($C_2F_5^+$), 26.75; 84/82 (CCl_2^+), 4.01/6.33; 69 (CF_3^+), 100. IR (gas): 1586 s (C═N), 1382 w, 1291 vs, 1241 vs, 1211 w, 1180 s, 1097 s, 990 vs, 899 s, 792 w, 747 w, 706 w, 675 w cm^{-1}. ^{19}F NMR: ϕ −60.52 (CF_3N, tq), −82.41 (CF_3CF_2, q), −103.38 (CF_2, q); $J_{CF_3N-CF_3C} = 3.18$ Hz, $J_{CF_3N-CF_2} = 11.84$

Hz. Anal. Calcd for $C_4F_8N_2Cl_2$: C, 16.11; N, 9.39. Found: C, 16.30; N, 9.22.

Properties of $CF_3(C_2F_5)NN{=}C(Cl)CF_3$. This compound was found in the trap at −65 °C, having passed through a trap at −40 °C. It was obtained in ~55% yield as a colorless liquid. Spectra data were as follows. MS (EI) [*m/e* (species), intensity]: 334/332 (M^+), 1.67/5.15; 315/313 ($M^+ - F$), 0.43/1.54; 297 ($M^+ - Cl$), 7.31; 265/263 ($M^+ - CF_3$), 3.05/9.74; 215/213 ($M^+ - C_2F_5$), 0.47/1.58; 177/175 ($C_3F_4N_2Cl^+$), 0.93/2.73; 159 ($C_3F_5N_2^+$), 5.21; 119 ($C_2F_5^+$), 31.05; 69 (CF_3^+), 100. IR (gas): 1641 s (C=N), 1380 m, 1295 vs, 1251 vs, 1193 vs, 1098 s, 1001 s, 926 w, 902 s, 752 m, 707 w, 674 w, 522 w cm^{-1}; ^{19}F NMR: ϕ −58.90 (CF_3N, tq), −70.36 (CF_3CCl, s), −82.30 (CF_3CF_2, q), −103.44 (CF_2, q); $J_{CF_3N-CF_3CF_2}$ = 2.98 Hz; $J_{CF_3N-CF_2}$ = 12.09 Hz. Anal. Calcd for $C_5F_{11}ClN_2$: C, 18.07; N, 8.43. Found: C, 18.19; N, 8.40.

Reaction of Chlorine Fluoride with $CF_3(C_2F_5)NN{=}C(Cl)CF_3$. Five millimoles of $CF_3(C_2F_5)NN{=}C(Cl)CF_3$ and 6 mmol of ClF were condensed at −196 °C into a 75-mL stainless-steel vessel fitted with a Whitey high-pressure stainless-steel valve. The reactions were allowed to warm from −196 °C to room temperature and held there for 8−10 h. The contents of the vessel were purified by trap-to-trap distillation. The compound found at −60 °C was $CF_3(C_2F_5)NN(Cl)CFClCF_3$. Spectral data were as follows. MS (EI) [*m/e* (species), intensity]: 316 ($M^+ - Cl_2$), 15.99; 297 ($C_5F_{11}N_2^+$), 52.78; 247 ($C_4F_9N_2^+$), 17.40; 228 ($C_4F_8N_2^+$), 2.55; 209 ($C_4F_7N_2^+$), 4.39; 164 ($C_3F_6N^+$), 4.35; 159 ($C_3F_5N_2^+$), 9.4; 119 ($C_2F_5^+$), 35.65; 114 ($C_2F_4N^+$), 5.2; 69 (CF_3^+), 100. IR (gas): 1468 w, 1313 vs, 1250 vs, 1229 vs, 1190 w, 1163 w, 1100 s, 1042 m, 991 m, 934 w, 912 w, 781 w cm^{-1}. ^{19}F NMR: ϕ −56.24 (NCF_3, qq, $J_{CF_3N-CF_3C}$ = 2.0 Hz, $J_{CF_3N-CF_3CF}$ = 12 Hz), −56.64 (NCF_3, mult), −78.53 (CF_3CFCl, dq, $J_{CF_3CF-CF_3CF_2}$ = 4.15 Hz, J_{CF_3CF-CF} = 8.42 Hz), −78.82 (CF_3CFCl, mult), −82.01 (CF_3CF_2, dq, J_{CF_3C-CF} = 7.32 Hz), −82.18 (CF_3CF_2, dq, $J'_{CF_3-CF_3N}$ = 2.07 Hz, J'_{CF_3C-CF} = 4.15 Hz), −94.17 (CFCl, mult), −99.04 (CF_2CF_3, dqq, $J_{CF_2-CF_3N}$ = 7.5 Hz, J_{CF_2-CF} = 18.56 Hz, $J_{CF_2-CF_3}$ = 3.54 Hz), −100.7 (CF_2CF_3, dq, $J'_{CF_3N-CF_2}$ = 9.28 Hz, J'_{CF_2-CF} = 18.19 Hz), −101.9 (CF_2CF_3, qd, $J''_{CF_2-CF_3N}$ = 11.85 Hz, J''_{CF_2-CF} = 1.95 Hz).

Photolysis of $CF_3(C_2F_5)NN(Cl)CF_2Cl$. Three millimoles of $CF_3(C_2F_5)NN(Cl)CF_2Cl$ was condensed at −196 °C into a 2-L quartz vessel. After warming to room temperature over a period of 1 h, the contents of the quartz vessel were photolyzed for 1 h at 3000 Å. The contents of the vessel were then distilled. The slightly volatile product, $[CF_3(C_2F_5)NN(CF_2Cl)]_2$ was found in ~90% yield. All of the volatile materials were removed under dynamic vacuum to leave the pure tetrazane. Spectral data were as follows. MS (EI) [*m/e* (species), intensity]: 517 ($M^+ - CF_2Cl$), 0.59; 303/301 ($C_4F_{10}ClN_2^+$), 21.13/62.77; 266 ($C_4F_{10}N_2^+$), 3.49; 247 ($C_4F_9N_2^+$), 1.79; 215/213 ($C_3F_6ClN_2^+$), 6.77/18.8; 197 ($C_3F_7N_2^+$), 68.34; 165/163 ($C_2F_4ClN_2^+$), 6.27/21.46; 147 ($C_2F_5N_2^+$), 22.47; 119 ($C_2F_5^+$), 37.67; 85 (CF_2Cl^+), 100; 69 (CF_3^+), 50.75. IR (liquid): 1303 w, 1230 vs, 1139 w, 1082 s, 1007 m, 974 m, 925 s, 820 s, 801 m, 768 m, 751 s, 735 vs, 708 s, 655 w, 634 w, 533 w cm^{-1}. ^{19}F NMR: ϕ −32.72 to −41.06 (CF_2Cl, two sets of four mult), −56.18 and −57.05 (CF_3N, two mult), −80.51 and −82.12 (CF_3C, two mult), −93.59 and −95.67 (CF_2C, two mult). Anal. Calcd for $C_8F_{20}Cl_2N_4$: C, 15.95; N, 9.30; Cl, 11.77. Found: C, 16.03; N, 9.30; Cl, 11.84. Density: 1.995 g/mL at 23 °C.

Photolysis of $CF_3(C_2F_5)NN(Cl)CFClCF_3$. Three millimoles of $CF_3(C_2F_5)NN(Cl)CFClCF_3$ was condensed at −195 °C into a 2-L quartz vessel. After the vessel was warmed to room temperature over a period of 1 h, the contents were photolyzed for 1 h (3000 Å). When the contents of the vessel were distilled, chlorine (~3 mmol) and $CF_3(C_2F_5)NN{=}CFCF_3$ were found in a trap at −80 °C in ~90% yield. Spectra data were as follows. MS (EI) [*m/e* (species), intensity]: 316 (M^+), 4.49; 297 ($M^+ - F$), 3.07; 247 ($M^+ - CF_3$), 10.42; 159 ($C_3F_5N_2^+$), 8.08; 119 ($C_2F_5^+$), 38.46; 100 ($C_2F_4^+$), 4.86; 69 (CF^+_3), 100. IR (gas): 1729 m (C=N), 1380 s, 1305 vs, 1255 vs, 1196 vs, 1142 w, 1099 s, 934 w, 920 m, 754 w, 710 m, 522 w cm^{-1}. ^{19}F NMR: ϕ −53.17 (CF, mult), −59.88 (CF_3N, q tr d), −72.57 (CF_3CFN, d), −82.53 (CF_3CF_2, dq), 100.7 (CF_2, qd); $J_{CF_3N-CF_2}$ = 13.55 Hz, J_{CF_2-CF} = 5.89 Hz, J_{CF_3CF-CF} = 5.01 Hz, $J_{CF_3N-CF_3CF_2}$ = 3.06 Hz, J_{CF_3N-CF} = 20.14 Hz, $J_{CF_3CF_2-CF}$ = 4.72 Hz.

Photolysis of $CF_3(C_2F_5)NN(Cl)C_2F_5$. Three millimoles of $CF_3(C_2F_5)NN(Cl)C_2F_5$ was condensed into a 2-L quartz vessel at −196 °C. After the vessel was allowed to warm to 25 °C over a period of 1 h, the contents were photolyzed for 1 h (3000 Å), and the mixture was distilled. The compound that stopped at −10 °C was found to be the tetrazane $[CF_3(C_2F_5)NN(C_2F_5)]_2$, in ~90% yield. Spectral data were as follows. MS (CI^+) [*m/e* (species), intensity]: 435 ($C_7F_{17}N_2^+$, rearranged), 24.41; 385 ($C_6F_{15}N_2^+$, rearranged), 19.70; 335 ($C_5F_{13}N_2^+$), 4.03; 316 ($C_5F_{15}N_2^+$), 0.73; 297 ($C_5F_{11}N_2^+$), 17.65; 247 ($C_4F_9N_2^+$), 8.18; 197 ($C_3F_7N_2^+$), 8.36; 119 ($C_2F_5^+$), 63.06; 100 ($C_2F_4^+$), 3.05; 69 (CF_3^+), 100. IR (liquid): 1357 w, 1305 w, 1224 vs, 1180 w, 1139 s, 1110 m, 1070 s, 994 w, 934 s, 840 w, 821 w, 737 s, 709 m, 650 w, 538 w cm^{-1}. ^{19}F NMR: ϕ −55.66, −57.74 (NCF_3, br), −79.86, −81.89 (CF_3CF_2, br), −92.72, −94.92 (CF_3CF_2, br). A suitable solvent could not be found. Thus, the spectrum is low resolution only. Anal. Calcd for $C_{10}F_{26}N_4$: C, 17.91; F, 73.73; N, 8.36. Found: C, 18.02; F, 73.8; N, 8.46. Density: 2.1 g/mL at 23 °C.

Reaction of $CF_3(C_2F_5)NN{=}CCl_2$ with Cesium Fluoride. Five millimoles of $CF_3(C_2F_5)NN{=}CCl_2$ was condensed into a stainless-steel vessel, which was fitted with a Whitey high-pressure stainless-steel valve and contained 15 mmol of CsF. After being allowed to warm to 25 °C, the contents of the vessel were heated at 70–75 °C for 24−30 h. The vessel was agitated periodically to renew the surface area of CsF. After 30 h, the contents of the vessel were separated by fractional distillation with traps at −20, −30, −50, and −80 °C. The compound in the trap at −30 °C was found to be $CF_3{}^ACF_2{}^B(CF_3{}^C)NN{=}CFN(CF_3{}^D)N(CF_3{}^E)CF_2{}^GCF_3{}^H$, in ~65% yield. Spectral data were as follows. MS (EI) [*m/e* (species), intensity]: 532 (M^+), 14.68; 513 ($M^+ - F$), 14.42; 463 ($M^+ - CF_3$), 16.66; 425 ($C_7F_{15}N_4^+$), 4.20; 375 ($C_6F_{13}N_4^+$), 3.41; 311 ($C_5F_{11}N_3^+$), 0.96; 247 ($C_4F_9N_2^+$), 4.39; 197 ($C_3F_7N_2^+$), 3.74; 159 ($C_3F_5N_2^+$), 3.77; 119 ($C_2F_5^+$), 72.08; 114 ($C_2F_4N^+$), 14.08; 69 (CF_3^+), 100. IR (gas): 1713 vs, 1338 s, 1294 vs, 1251 vs, 1211 w, 1097 s, 1004 w, 927 m, 904 m, 730 s cm^{-1}. ^{19}F NMR: ϕ −50.39 (CF, mult), −58.15 ($CF_3{}^D$, br), −60.06 ($CF_3{}^E$, br), −62.55 ($CF_3{}^C$, br), −82.82 ($CF_3{}^H$, s) −84.09 ($CF_3{}^A$, s), −99.96, −101.41 ($CF_2{}^G$, 2 mult), −103.9, −104.02 ($CF_2{}^B$, qd); $J_{CF_3{}^C-CF_2{}^B}$ = 12.67 Hz, J_{CF_3C-CF} = 2.84 Hz. Integration of peaks gave 1:3:3:3:3:3:2:2. Anal. Calcd for $C_8F_{20}N_4$: C, 18.04; N, 10.53. Found: C, 18.49; N, 10.71.

Reaction of Chlorine Fluoride with $CF_3(C_2F_5)NN{=}CCl_2$. Five millimoles of $CF_3(C_2F_5)NN{=}CCl_2$ and 6 mmol of ClF were condensed at −196 °C into a 75-mL stainless-steel vessel fitted with a Whitey high-pressure stainless-steel valve. The reactants were allowed to warm to and were held at 25 °C for 8−10 h. The contents of the vessel were purified by trap-to-trap distillation. The compound found at −50 °C was $CF_3(C_2F_5)NN(Cl)CF_2Cl$. Spectral data were as follows. MS (EI) [*m/e* (species), intensity]: 301 ($M^+ - Cl$), 0.36; 266 ($M^+ - Cl_2$), 6.38; 247 ($C_4F_9N_2^+$), 5.84; 197 ($C_3F_7N_2^+$), 22.58; 119 ($C_2F_5^+$), 39.66; 114 ($C_2F_4N^+$), 2.48; 109 ($C_2F_3N_2^+$), 3.90; 100 ($C_2F_4^+$), 3.74; 85 (CF_2Cl^+), 3.41; 69 (CF_3^+), 100. IR (gas): 1380 w, 1317 vs, 1250 vs, 1200 w, 1163 s, 1113 m, 1101 m, 1058 w, 1036 s, 906 s, 791 w, 738 m, 714 m cm^{-1}; ^{19}F NMR: ϕ −40.89 (CF_2Cl, qq), −41.58 (CF_2Cl', qq), −56.82 (CF_3N, pq), −82.64 (CF_3C, q), −101.6 (CF_2, mult); $J_{CF_3N-CF_3C}$ = 2.57 Hz, $J_{CF_3N-CF_2Cl'}$ = 9.84 Hz, $J_{CF_2Cl'-CF_3C}$ = 3.41 Hz, $J_{CF_3N-CF_2Cl}$ = 6.95 Hz, $J_{CF_2Cl-CF_3C}$ = 2.2 Hz, $J_{CF_2-CF_3N}$ = 9.64 Hz, $J_{CF_3C-CF_3N}$ = 2.57 Hz.

Reaction of Chlorine Fluoride with $CF_3(C_2F_5)NN{=}CFCF_3$. Five millimoles of $CF_3(C_2F_5)NN{=}CFCF_3$ and 6 mmol of ClF were condensed at −196 °C into a 75-mL stainless-steel vessel fitted with a Whitey high-pressure stainless-steel valve. The reactants were allowed to warm to 25 °C and remain there for 8−10 h. The contents of the vessel were separated by trap-to-trap distillation. The compound in a trap at −60 °C was found to be $CF_3{}^A(CF_3{}^BCF_2{}^C)NN(Cl)CF_2{}^DCF_3{}^E$. Spectral data were as follows. MS (EI) [*m/e* (species), intensity]: 370 (M^+), 0.4; 351 ($M^+ - F$), 0.45, 335 ($M^+ - Cl$), 4.34; 316 ($M^+ - ClF$), 2.83; 297 ($C_5F_{11}N_2^+$), 1.82; 247 ($C_4F_9N_2^+$), 5.92; 159 ($C_3F_5N_2^+$), 3.84; 119 ($C_2F_5^+$), 46.52; 100 ($C_2F_4^+$), 2.86; 69 (CF_3^+), 100. IR (gas): 1362 w, 1317 vs, 1268 vs, 1197 w, 1167 m, 1131 m, 1100 s, 1066 vs, 937 w, 912 s, 875 w, 799 w, 759 w, 728 s, 713 s, 531 w, 502 w cm^{-1}. ^{19}F NMR: ϕ −57.39 ($CF_3{}^A$, complex mult), −81.95 ($CF_3{}^B$, br q, J_{A-B} = 4.27 Hz), −83.22 ($CF_3{}^E$, $CF_3{}^{E'}$, overlapping quartets, J = 2.93 Hz), −98.51, ($CF_2{}^C$, q, J = 2.44 Hz; q, J = 14.44 Hz), −99.15 ($CF_2{}^{C'}$, q, J = 6.47 Hz; q, J = 3.91 Hz), −102,34 ($CF_2{}^D$, q, J = 13.31 Hz; $CF_2{}^{D'}$, q, J = 10.0 Hz; $CF_2{}^{D''}$, q, J = 10.0 Hz). Integration of the peak areas A:B:C:D:E = 3:3:2:2:3.

Reaction of Chlorine Fluoride with $CF_3(CF_3CF_2)NN{=}CFN(CF_3)N(CF_3CF_2)CF_3$. Five millimoles of $CF_3(C_2F_5)NN{=}CFN(CF_3)N(C_2F_5)CF_3$ and 6 mmol of ClF were condensed into a stainless-steel vessel, fitted with a Whitey high-pressure stainless-steel valve, at −196 °C. After warming to 25 °C, the vessel was held for 6−8 h. The contents were purified by trap-to-trap distillation by using traps at −20, −30, and −50 °C. The compound found at −20 °C was $CF_3(CF_3CF_2)NN(Cl)CF_2N(CF_3{}^A)N(CF_2CF_3{}^B)CF_3{}^C$ in ~90% yield. Spectral data were as follows. MS (EI) [*m/e* (species), intensity]: 532 ($M^+ - ClF$), 6.78; 513 ($C_8F_{19}N_4^+$), 5.73; 463 ($C_7F_{17}N_4^+$), 7.24; 425 ($C_7F_{15}N_4^+$), 1.48; 335 ($C_5F_{13}N_2^+$), 6.02; 266 ($C_4F_{10}N_2^+$), 9.80; 247 ($C_4F_9N_2^+$), 17.01; 197 ($C_3F_7N_2^+$), 36.25; 159 ($C_3F_5N_2^+$), 6.49; 119 ($C_2F_5^+$), 91.67; 114 ($C_2F_4N^+$), 8.18; 100 ($C_2F_4^+$), 5.17; 69 (CF_3^+), 100. IR (liquid): 1234 b, vs, 1118 w, 1083 s, 973 vs, 945 m, 915 s, 889 w, 831 s, 783 s, 762 s, 738 s, 727 vs, 662 w, 514 m cm^{-1}. ^{19}F NMR: ϕ −57.22, −57.92, −58.55 (NCF_3, 3 peaks, br mult), −73.20 ($N-CF_2-N$, br, mult), −83.63 ($CF_3{}^{\prime B}$, br mult), −84.21 ($CF_3{}^B$, qq, $J_{CF_3{}^B-CF_3{}^C}$ = 7.0 Hz, $J_{CF_3{}^B-CF_3{}^A}$ = 3.42 Hz), −99.04 to −103.84 (CF_3CF_2, many mult).

Photolysis of $CF_3(C_2F_5)NN(Cl)CF_2N(CF_3)N(C_2F_5)CF_3$. Two millimoles of $CF_3(C_2F_5)NN(Cl)CF_2N(CF_3)N(C_2F_5)CF_3$ was condensed at

−196 °C into a 200-mL quartz vessel. After it was warmed from −196 to +25 °C over a period of 1 h, the quartz vessel was photolyzed for 1 h at 3000 Å. The quartz vessel was evacuated, leaving a nonvolatile viscous liquid. This viscous compound on analysis was found to be $[CF_3(C_2F_5)NN(CF_3)CF_2NN(C_2F_5)CF_3]_2$ in ~93% yield. Spectral data were as follows. MS (CI^+) [*m/e* (species), intensity]: 734 ($C_{11}F_{28}N_5^+$), 0.59; 651 ($C_{10}F_{25}N_4^+$), 4.92; 601 ($C_9F_{23}N_4^+$), 3.93; 563 ($C_9F_{21}N_4^+$), 0.26; 513 ($C_8F_{19}N_4^+$), 2.38; 413 ($C_6F_{15}N_4^+$), 5.17; 385 ($C_6F_{15}N_2^+$), 9.02; 335 ($C_5F_{13}N_2^+$), 41.88; 285 ($C_4F_{11}N_2^+$), 6.82; 247 ($C_4F_9N_2^+$), 17.34; 119 ($C_2F_5^+$), 21.57; 114 ($C_2F_4N^+$), 18.89; 69 (CF_3^+), 100. IR (liquid) 1229 b, vs, 1098 w, 1077 s, 972 w, 954 s, 805 m, 739 s, 664 w, 534 w cm^{-1}; ^{19}F NMR: ϕ −55.71 to −63.94 (NCF_3, mult), −67.18 (NCF_2N, mult), −83.86, −85.54 (CF_3CF_2, mult), −96.14 to −100.9 (CF_3CF_2, mult). Density: 2.14 g/mL at 23 °C. Anal. Calcd for $C_{16}F_{42}N_8$: C, 17.42; F, 72.41; N, 10.16. Found: C, 17.55; F, 72.7; N, 10.21.

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Oxidation of Trivalent Plutonium in Acid Solution by Xenon Difluoride and by the Fluoroxysulfate Ion, SO_4F^- [1]

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Stopped-flow spectrophotometry was used to study the oxidation of plutonium(III) to plutonium(IV) in 1 M $HClO_4$ by XeF_2 and by the fluoroxysulfate ion, SO_4F^-. In both reactions, 2 mol of Pu(III) is oxidized per 1 mol of oxidant consumed, and neither Pu(V) or Pu(VI) appears to be formed either as an intermediate or as an initial product, although an excess of XeF_2 does slowly oxidize the Pu(IV) product to Pu(VI). At 2 °C the reactions have respective bimolecular rate constants of 1160 ± 70 and 120 ± 9 $M^{-1}\ s^{-1}$, expressed in terms of $-d[Pu(III)]/dt$. Over the temperature range 2–24 °C, the activation parameters for the XeF_2 reaction are $\Delta H^{\ddagger} = 39.5 \pm 8.6$ kJ/mol and $\Delta S^{\ddagger} = -48.3 \pm 29$ J/(mol K), while those for the SO_4F^- reaction are $\Delta H^{\ddagger} = 30.8 \pm 2.3$ kJ/mol and $\Delta S^{\ddagger} = -98.5 \pm 7.8$ J/(mol K). Mechanisms are postulated that invoke a sequence of two one-electron-oxidation steps.

Introduction

Molecular fluorine has a standard electrode potential in aqueous solution of 3.1 V, and many of its compounds have potentials well in excess of 2 V. Their reactions with reducing substrates are therefore highly exoergic, and such reactions may at least in principle proceed by pathways that are inaccessible to milder oxidants. While fluorine itself has a limited solubility and vanishingly short liftime in aqueous solution,[2] some reactive fluorine compounds are both substantially soluble and reasonably long-lived in water. Two such compounds are xenon difluoride, XeF_2, and the fluoroxysulfate ion, SO_4F^-.

Xenon difluoride dissolves in water to the extent of about 0.15 M at 0 °C, apparently as the unchanged molecule, and it oxidizes water with a half-time of about 7 h at the ice point,[3] the half-time decreasing to about 30 min at room temperature.[4] Aqueous XeF_2 is estimated to have a standard electrode potential of 2.7 V for the half-reaction[5]

$$XeF_2 + 2H^+ + 2e^- \rightleftarrows Xe + 2HF$$

Although the kinetics of the reaction of XeF_2 with water itself have been studied,[4,6] and qualitative reports of its behavior as an aqueous oxidant have been published,[7] only a relatively limited number of kinetic investigations of its reactions with aqueous reductants have been reported.[8]

The fluoroxysulfate ion is usually prepared in the form of its cesium salt, $CsSO_4F$, which is soluble in water to the extent of about 0.5 M at room temperature.[9] The half-time for oxidation of water by the fluoroxysulfate ion increases from about 15 min at room temperature to about 3.6 h at the ice point.[10] The half-reaction

$$SO_4F^- + 2H^+ + 2e^- \rightleftarrows HSO_4^- + HF$$

has a standard electrode potential of 2.47 V,[11] making fluoroxysulfate thermodynamically a somewhat less potent oxidant than XeF_2. The kinetics of reactions of fluoroxysulfate with several aqueous reductants have been reported in two papers.[10,12]

Of particular interest concerning the reactions of these powerful oxidizing agents is the question of whether they act as one- or two-electron oxidants. Trivalent plutonium can potentially be oxidized to Pu(IV), Pu(V), and Pu(VI), and all four of these plutonium oxidation states are interrelated by electrode potentials around 1 V.[13] Furthermore, the interconversion of these states by way of reactions among themselves generally takes place relatively slowly,[13] making it feasible to draw conclusions about the mechanism of oxidation of Pu(III) from the identity of the initial products. With these considerations in mind, we have undertaken the present kinetic study of the reaction of Pu(III) with xenon difluoride and with the fluoroxysulfate ion.

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