$H_5)_2PCl$, 1079-66-9; CH_3PCl_2, 676-83-5; $(C_6H_5)_2POCH_3$, 4020-99-9; $C_6H_5PCl_2$, 644-97-3; $C_6H_4O_2PCl$, 1641-40-3; $(C_6H_5)_2P{-}P(O)(OCH_2)_2C(CH_3)_2$, 54166-37-9; $(CH_3)_2C(CH_2O)_2PCl$, 2428-06-0; $C_6H_4O_2POCH_3$, 20570-25-6; $C_6H_4O_2POPO_2C_6H_4$, 16421-86-6; $(C_6H_5)_2POC_6H_4OPCl_2$, 54166-38-0.

References and Notes

(1) J. R. Van Wazer and K. Moedritzer, *Angew. Chem., Int. Ed. Engl.*, **5**, 341 (1966).
(2) J. R. Van Wazer, *Ann. N.Y. Acad. Sci.*, **159**, Article 1, 5 (1969).
(3) J. R. Van Wazer, *Inorg. Macromol. Rev.*, **1**, 89 (1970).
(4) D. W. Matula, L. C. D. Groenweghe, and J. R. Van Wazer, *J. Chem. Phys.*, **41**, 3105 (1964).
(5) R. M. Levy and J. R. Van Wazer, *J. Chem. Phys.*, **45**, 1824 (1966).
(6) K. M. Abraham and J. R. Van Wazer, *Inorg. Chem.*, **13**, 2346 (1974).
(7) L. Maier, *Helv. Chim. Acta*, **46**, 2667 (1963).
(8) A. E. Arbusov and K. V. Nikonorov, *Zh. Obsch. Chim.*, **18**, 2008 (1948); B. A. Arbusov and G. P. Grechkin, *ibid.*, **20**, 107 (1950).
(9) E. Fluck and H. Binder, *Inorg. Nucl. Chem. Lett.*, **3**, 307 (1967).
(10) D. Grant, J. R. Van Wazer, and C. H. Dungan, *J. Polym. Sci., Part A-1*, **5**, 57 (1967).
(11) E. Fluck, J. R. Van Wazer, and L. C. D. Groenweghe, *J. Amer. Chem. Soc.*, **81**, 6363 (1959).

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The NF_3^+ Radical Cation. Electron Spin Resonance Studies of Radiation Effects in NF_4^+ Salts

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Exposure of $NF_4^+AsF_6^-$ and $NF_4^+SbF_6^-{\cdot}0.8SbF_5$ to ^{60}Co γ rays at 77°K gave two paramagnetic centers, one of which is shown by ESR spectroscopy to contain one nitrogen atom and three equivalent fluorine atoms. Based on its magnetic properties it is identified as pyramidal $\dot{N}F_3^+$, a novel radical cation. The other center exhibits strong interaction of the electron with two fluorine atoms, weaker interaction with the antimony or arsenic central atom, and small interaction with several other fluorine atoms. It is tentatively assigned to the electron-loss species $A\dot{s}F_6$, $Sb\dot{F}_6$, or $Sb_2\dot{F}_{11}$ with the unpaired electron largely confined to two fluorine ligands. Irradiation of $NF_4^+BF_4^-$ did not result in well-defined magnetic centers. An improved synthesis of $NF_4^+BF_4^-$ is reported.

Introduction

Although carbon readily forms tetrahedral molecules with electronegative ligands, such as the halogens, the synthesis of the isoelectronic nitrogen compounds has been achieved only recently.[1] Attempts to prepare NF_4^+ salts had been discouraged by theoretical computations[2,3] showing that these salts should be thermodynamically unstable and by the nonexistence of the parent compound NF_5. Once the principle was recognized[1] that NF_4^+ salts can be prepared from NF_3, F_2, and a strong Lewis acid in the presence of a suitable activation energy source, a number of synthetic methods became available. These involve the use of different activation energy sources such as glow discharge,[4,5] elevated temperature and pressure,[6,7] γ irradiation,[8] and uv photolysis.[9]

On exposure to high-energy radiation, CF_4 undergoes the dissociative electron-capture process

$$CF_4 + e^- \rightarrow \dot{C}F_3 + F^- \tag{1}$$

to give $\dot{C}F_3$ radicals which have been detected both in the liquid[10] and solid[10-12] phase. The fact that no evidence for the existence of the $\dot{C}F_4^-$ radical anion was observed is not surprising in view of the validity of the octet rule for first-row elements of the periodic system. A study of the corresponding NF_4^+ system appeared interesting, particularly in view of the recent suggestion[9] that $\dot{N}F_3^+$ and the radicals derived from the Lewis acid–fluorine interaction, such as $As\dot{F}_6$, are the key intermediates in the formation mechanism of NF_4^+ salts. By analogy with CF_4, one might expect that $\dot{N}F_3^+$ might be prepared by γ irradiation of NF_4^+ salts according to

$$NF_4^+ + e^- \rightarrow \dot{N}F_3^+ + F^- \tag{2}$$

In this paper we report ESR spectroscopic evidence for the existence of the novel radicals $\dot{N}F_3^+$ and $M\dot{F}_6$, in addition to an improved synthesis of $NF_4^+BF_4^-$ by metathesis in HF solution.

Experimental Section

Syntheses of NF_4^+ Salts. A sample of $NF_4^+SbF_6^-{\cdot}0.8SbF_5$ was prepared as previously described[7] by heating a 1:1.2:1 molar mixture of NF_3, F_2, and SbF_5 in a Monel cylinder to 120° for 2 days under an autogenous pressure of 200 atm. The resulting white solid, having the composition $NF_4^+SbF_6^-{\cdot}1.9SbF_5$, was converted to $NF_4^+SbF_6^-{\cdot}0.8SbF_5$ by heating under a dynamic vacuum to 200° for 3 days. The compound was analyzed as previously described.[13] The only detectable impurities were small amounts of Ni (0.066 wt %) and Cu (0.03%) in the form of their salts. The synthesis of $NF_4^+AsF_6^-$ has previously been described.[13] Again, the only detectable impurities were Ni (0.98%) and Cu (0.27%).

For the synthesis of $NF_4^+BF_4^-$ by metathesis, commercial HF was dried by shaking it overnight in a 1-l. Monel cylinder with fluorine (10 l./0.7 kg of HF) after which oxygen and residual fluorine (ca. 210 psi) were removed under vacuum at −78°. The metathesis apparatus, fabricated entirely from Teflon and Kel-F, consisted of four identical 1-l. vessels connected in series through valves and filters with a fitting carrying a vacuum line connection, a 60-psi pressure relief valve, and a compound pressure–vacuum gauge (Kel-F-coated diaphragm) between the last two vessels. In addition, each vessel was stirred with a Teflon-coated magnetic stirring bar and equipped with a valve which by-passed the filter for introduction or removal of gaseous or liquid materials. All manipulations of reagents and products were conducted either in an inert-atmosphere glove box or by standard high-vacuum techniques.

A 251.5-g (1.94-mol) quantity of silver fluoride (Cationic, Inc.), which contained 2.1% HF-insoluble impurities, was loaded into the first vessel and 284 g of HF was added. Into the second vessel were placed 400.5 g (0.822 mol) of $NF_4SbF_6{\cdot}0.8SbF_5$ and 148 g of HF. The $AgHF_2$ solution in the first vessel was pressurized to 30 psi with nitrogen and passed through a filter into the stirred NF_4^+ salt–HF solution under autogenous pressure in the second vessel. The resulting NF_4HF_2 solution was separated from the $AgSbF_6$ precipitate by filtration into the evacuated third reaction vessel. After brief pumping to remove the nitrogen pressurizing gas, BF_3 (68 g, 1.0 mol) was added to the third vessel until the total pressure above the liquid remained constant at 19–20 psi. The NF_4BF_4 solution was separated from the precipitated $AgBF_4$ by filtration into the evacuated fourth vessel. After removal of excess BF_3 and solvent HF the residual solid product (101.9 g) was isolated. The composition of the solid (in mole percent) was NF_4BF_4 (89), $NF_4Sb_2F_{11}$ (7.9), and $AgBF_4$ (3.1).

γ Irradiation and ESR Spectra. The NF_4^+ salts were transferred in the dry nitrogen atmosphere of a glove box into passivated 4-mm o.d. quartz tubes which were flame-sealed in vacuo. For the solution study, a 0.24 *M* solution of $NF_4^+SbF_6^-{\cdot}0.8SbF_5$ in anhydrous HF was heat-sealed in a Teflon FEP tube.

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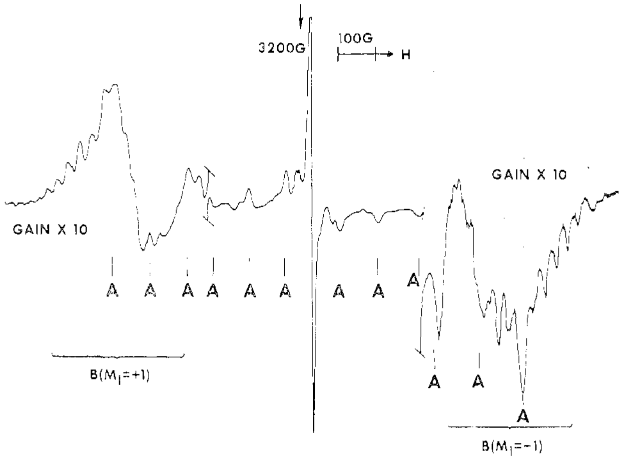


Figure 1. First-derivative X-band ESR spectrum for $NF_4^+SbF_6^-\cdot 0.8SbF_5$ after exposure to ^{60}Co γ rays at 77°K, showing features assigned to species A and B. The intense central component stems in part from paramagnetic centers generated in the quartz tube.

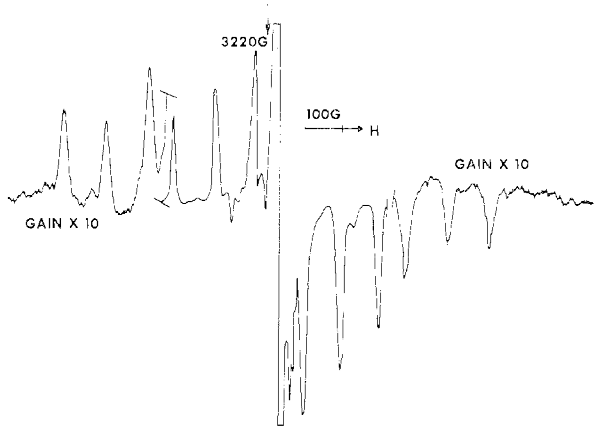


Figure 2. Sample of Figure 1 but after annealing at about 140°K and recooling to 77°K, showing features assigned to radical A.

The sample tubes were cooled to 77°K prior to exposure to ^{60}Co γ rays in a Vickrad cell at a nominal dose rate of about 4 Mrads hr^{-1}. It was necessary to expose samples to high doses (about 10 Mrads) before good ESR signals were obtained.

The ESR spectra were obtained with a Varian E3 spectrometer at 77°K. Samples were annealed by gradual warming to above 77°K and recooling whenever significant changes were observed in the continuously monitored esr signals. Signals were independent of sample tube orientation indicating the absence of sample graining effects.

Results and Discussion

Synthesis. For the preparation of $NF_4^+SbF_6^-\cdot xSbF_5$ and $NF_4^+AsF_6^-$ the previously reported[7] elevated pressure–temperature method was chosen. For that of $NF_4^+BF_4^-$, a metathetical process similar to that of Tolberg, *et al.*[14] was selected which was significantly improved by substituting AgF for the originally used [14]CsF. The reaction sequence is best described by eq 3–5. Since $Ag^+HF_2^-$ was used in excess for

$$AgF + HF \xrightarrow{HF} Ag^+HF_2^- \quad (3)$$

$$Ag^+HF_2^- + NF_4^+SbF_6^- \xrightarrow{HF} AgSbF_6\downarrow + NF_4^+HF_2^- \quad (4)$$

$$NF_4^+HF_2^- + BF_3 \xrightarrow{HF} NF_4^+BF_4^- + HF \quad (5)$$

the precipitation of the fluoroantimonate, the rather insoluble $AgBF_4$ precipitated from the $NF_4^+HF_2^-$ solution upon BF_3 addition. This required an additional filtration step. The level of impurities ($NF_4Sb_2F_{11}$ and $AgBF_4$) in the final crude product is determined by the solubility products of $AgSbF_6$ and $AgBF_4$ in HF.

Since the $NF_4^+SbF_6^-\cdot xSbF_5$ starting material can readily be prepared on a large scale,[7] this metathetical process is well suited for the synthesis of larger amounts of $NF_4^+BF_4^-$. Its main drawback is the relatively low product purity. Using CsF the purity is quite low, but with AgF we have been able to obtain purities as high as 89 mol % of $NF_4^+BF_4^-$. The main impurities could significantly be decreased by subsequent recrystallization[14] of the crude $NF_4^+BF_4^-$ from suitable solvents. Whereas the γ-irradiation[8] and uv-photolysis[9] processes yield purer products, they are at present much less amenable to scale up.

Electron Spin Resonance Spectra. The best defined spectra were obtained from $NF_4^+SbF_6^-\cdot 0.8SbF_5$ and typical spectra, obtained before and after annealing, are given in Figures 1 and 2, respectively. The $NF_4^+AsF_6^-$ salt gave very similar results, but $NF_4^+BF_4^-$ proved to be remarkably resistant to ^{60}Co γ rays. Two radical species, A and B, can be detected in the initial spectra (Figure 1), but radical B decayed rapidly on annealing to about 150°K, leaving a well-defined spectrum of A (Figure 2).

Radical A. Well-defined wing (parallel) triplets characteristic of hyperfine coupling to ^{14}N [$I(^{14}N) = 1$] establish the presence of one strongly coupled ^{14}N nucleus. If the outer sets of triplets are described as the $M_I(^{19}F) = \pm^3/_2$ "parallel" features for $\dot{N}F_3^+$ [$I(^{19}F) = ^1/_2$] for the three equivalent fluorine atoms, then the $\pm^1/_2$ lines are predicted to fall close to the more intense set of six lines in the central region of the spectrum. However, the apparent $A(^{14}N)$ coupling on these inner features has decreased by about 15 G relative to the outer lines, and hence we suggest that these inner lines contain dominant contributions arising from "anisotropic" features.

Interpretation of ESR spectra for pyramidal radicals of this type is complicated by the fact that the principal values for the three ^{19}F hyperfine tensors lie along three different axes, two of which always differ from those for the ^{14}N hyperfine coupling. Also, there should be a relatively large second-order splitting (δ) of the $M_I(^{19}F) = \pm^1/_2$ lines which can be approximately estimated[15] from $\delta_\parallel = ^3/_2A_\perp(^{19}F)/H_\perp$ and $\delta_\perp = ^3/_4(A_\perp + A_\parallel)/H_\parallel$. From the initial approximate data, we find $\delta_\parallel \simeq 3$ G and $\delta_\perp \simeq 23$ G. Thus the former will be barely defined in our spectra, but the latter result is clearly significant. This problem has been discussed in depth by Coope, *et al.*,[11,16] especially for the isoelectronic radical, $\dot{C}F_3$, and we have followed their procedure in arriving at the parameters listed in Table I. The results for $\dot{C}F_3$[10,12] are included for comparison.

The results for ^{19}F of $\dot{N}F_3^+$ are in good agreement with those[12] of $\dot{C}F_3$ but indicate a small increase in spin density on fluorine on going from $\dot{C}F_3$ to $\dot{N}F_3^+$. Since these are not principal values, we make no attempt to estimate the actual spin density on fluorine from these data. However, the data for ^{14}N can be taken as principal values and hence we can deduce approximate spin densities in the 2s and 2p atomic orbitals that nitrogen contributes to the total MO of the unpaired electron. This we do by dividing the A and $2B$ values by the values for $A°$ (550 G) and $2B°$ (33 G) estimated from recent accurate atomic wave functions.[17] (A and $2B$ are the experimental isotropic and traceless parts of the hyperfine tensor components, and $A°$ and $2B°$ are the corresponding computed values for unit population of the 2s and 2p AO's.) The results (Table II) indicate that the total spin density on nitrogen is about 69%, and the 2p:2s ratio is about 2.8. Only the isotropic ^{13}C datum is known[10] for $^{13}CF_3$, and this gives about 24% spin density in the 2s AO on carbon. The latter value might be somewhat high, since the anisotropic components of ^{19}F in $\dot{N}F_3^+$ and $\dot{C}F_3$ are quite similar (133 and 123 G, respectively) implying that the spin densities on F and

Table I. ESR Data for Radical in γ-Irradiated NF_4^+ Salts, Together with Those for $\dot{C}F_3$

	Hyperfine tensor components, $G^{a,b}$								
	^{14}N, ^{13}C, ^{121}Sb			$^{19}F^{c}$			g values		
Radical	∥	⊥	Iso	∥	⊥	Iso	∥	⊥	Av
$\dot{N}F_3^{+\,i}$	115	90	98.3	300	100	167	2.003	2.009	2.007
$\dot{C}F_3^{\,d}$				264	80	141.3			
$\dot{C}F_3^{\,e}$			272			143			
$Sb\dot{F}_6$	~30 or ~60 (see text)			$630^{f,g}$	$420^{f,g}$ $+{\sim}30^{h}$	490		~2.00	

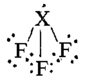
[a] $G = 10^{-4}$ T. [b] Errors ~±3G. [c] Data relate to the C_{3v} axes and therefore are not principal values. [d] Reference 12. [e] Reference 10. [f] For two equivalent fluorine atoms. [g] Approximate since number of subcomponents unknown. [h] Weak coupling to other fluoride ligands. [i] The NF_3^+ signals derived from either NF_4SbF_6 or NF_4AsF_6 had experimentally undistinguishable parameters.

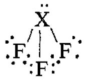
Table II. Estimated Spin Densities (%) for $\dot{N}F_3^+$ and $\dot{C}F_3$ on Central Atom

	a_s^2	a_p^2	Total	2p:2s
$\dot{N}F_3^+$	18	50.5	68.5	2.8
$\dot{C}F_3$	24			

hence also on the central atoms should be similar in both species. An alternate although less plausible, explanation might be that the atomic orbitals of the central atom in $\dot{C}F_3$ have more s character (*i.e.*, a stronger contribution from sp^2 hybridization) than those in $\dot{N}F_3^+$. This would imply that $\dot{C}F_3$ is less pyramidal than $\dot{N}F_3^+$.

The implications from the ESR data that in $\dot{N}F_3^+$ the spin density on F is somewhat higher than in $\dot{C}F_3$ and that the atomic orbitals of the central atom in $\dot{C}F_3$ have more s character than those in $\dot{N}F_3^+$ are in accord with arguments based on consideration of the resonance structures I–III.


I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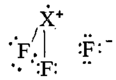
III

In $\dot{N}F_3^+$ the formal positive charge and the higher oxidation state of the central atom should increase the effective electronegativity of the NF_2^+ group when compared to that of CF_2. Therefore, for $\dot{N}F_3^+$ the relative contribution from structure II should be higher than for CF_3 hereby increasing the spin density on F in $\dot{N}F_3^+$. Since with an increasing electronegativity difference between X and F the XF bond becomes more ionic, the contribution from the sp^2-hybridized model III to the bonding should be more significant in $\dot{C}F_3$ than in $\dot{N}F_3^+$. In addition, model III for $\dot{N}F_3^+$ would require an unfavorable double positive charge on the NF_2 part of the molecule.

The failure to observe any evidence for the NF_4 radical is not surprising in view of the above-mentioned strict validity of the octet rule for first-row elements. This is in marked contrast with second-row elements, such as phosphorus for which the corresponding PF_4 has been observed.[18,19] We have also studied the irradiation products from HF solutions of $NF_4^+SbF_6^- \cdot 0.8\ SbF_5$ since it is often found that dissociative reactions, such as the hypothetical process

$$NF_4 \rightarrow \dot{N}F_3^+ + F^- \qquad (6)$$

are solvent dependent. Unfortunately, solutions in HF, the only suitable solvent, gave, after irradiation, only very broad uninformative features.

Radical B. The other species (B), lost during mild annealing, is tentatively identified as $Sb\dot{F}_6$ (or $As\dot{F}_6$) or $Sb_2\dot{F}_{11}$ for the following reasons. (1) $\dot{N}F_3^+$ is undoubtedly formed by electron capture, and the most reasonable initial electron loss center is $Sb\dot{F}_6$. (2) The results indicate the presence of two (or, less reasonably, one) strongly coupled ^{19}F nuclei with very weak coupling to magnetic isotopes of antimony or arsenic and possible further ^{19}F nuclei. Electron loss from SbF_6^- is from one of the nonbonding orbitals on fluorine, and a suitable distortion could well tend to isolate the unpaired electron on just two of the ligands. This model provides a reasonable explanation for the observed data. (3) The broad similarity between the results for the arsenic and antimony salts requires a low spin density on the central atom, in accord with the model. (4) Lack of $\dot{N}F_3^+$ radicals in the BF_4^- salt accord with the apparent inability to form $B\dot{F}_4$ radicals from such salts.[18]

Based on the above arguments, we favor the spectral analysis indicated in Figure 1 rather than the alternative of treating the B features as a doublet, on the basis of the relatively small anisotropy. For a distorted radical with the unpaired electron delocalized between two adjacent fluoride ligands, the apparent anisotropy deduced from the powder spectrum must be greatly reduced compared with the real anisotropy or that to be expected from spin confined to just one ligand.

The superhyperfine coupling present on the $M_I(^{19}F) = \pm 1$ lines must then arise from coupling to ^{121}Sb ($I = {}^5/_2$; 57.25% abundance) and to a lesser extent from ^{123}Sb ($I = {}^7/_2$; 42.75% abundance). This will not explain all the resolved features in Figure 1 and hence extra ^{19}F coupling or interaction with the second antimony atom of Sb_2F_{11} must also be present.

It is interesting to compare these results with those for a species formed in irradiated sodium hexafluoroantimonate, originally thought to be SbF_5^- or SbF_6^{2-} [20] but later assigned to an impurity species, $\dot{O}SbF_4$ or $\dot{O}SbF_5^-$.[21] This center had only very weak coupling to ^{19}F (about 5 G) and a near-isotropic coupling to ^{121}Sb in the 60–70-G region. Our present results indicate a coupling to ^{121}Sb of 30 or 60 G. A reduction of the coupling in SbF_6 or $Sb_2\dot{F}_{11}$, when compared to that for $\dot{O}SbF_5^-$, can be rationalized by electronegativity arguments.[21,22]

Although we have been unable to obtain well-resolved ESR spectra for radical B, we conclude that this center is probably $Sb\dot{F}_6$ or $Sb_2\dot{F}_{11}$, with the unpaired electron largely confined to two adjacent fluoride ligands. Other possible assignments that had occurred to us have been rejected for various reasons. For example, the assignment to F_2^-, weakly interacting with neighboring ions, can be ruled out since the observed hyperfine coupling is too small.

Summary

γ Irradiation of NF_4^+ salts at 77°K produces the novel pyramidal cation $\dot{N}F_3^+$ in addition to a second less stable species which is tentatively assigned to the corresponding anion electron-loss species, $Sb\dot{F}_6$, $Sb_2\dot{F}_{11}$, and $As\dot{F}_6$, respectively. The experimental observation of these species lends further credibility to the reaction mechanism previously suggested[9] for the formation and thermal decomposition of NF_4^+ salts. In this mechanism, the $As\dot{F}_6$ radical was postulated to be the crucial intermediate capable of supplying the energy (ionization potential of NF_3 minus the energy released by the formation of the ion pair) required for the oxidation of NF_3 according to

$$As\dot{F}_6 + NF_3 \rightarrow \dot{N}F_3^+AsF_6^- \qquad (7)$$

Acknowledgment. The group from Rocketdyne is grateful to the Office of Naval Research, Power Branch, for financial support and to Drs. L. R. Grant, C. J. Schack, and I. B. Goldberg for helpful discussions.

Registry No. $NF_4^+SbF_6^-$, 16871-76-4; $NF_4^+AsF_6^-$, 16871-75-3; $NF_4^+BF_4^-$, 15640-93-4; $\dot{N}F_3^+$, 54384-83-7; $Sb\dot{F}_6$, 54384-84-8.

References and Notes

(1) K. O. Christe, J. P. Guertin, and A. E. Pavlath, U.S. Patent 3,503,719 (1970).
(2) W. C. Price, T. R. Passmore, and D. M. Roessler, *Discuss. Faraday Soc.*, **35**, 201 (1963).
(3) J. N. Wilson, paper presented at the Symposium on Advanced Propellant Chemistry, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.
(4) K. O. Christe, J. P. Guertin, and A. E. Pavlath, *Inorg. Nucl. Chem. Lett.*, **2**, 83 (1966).
(5) J. P. Guertin, K. O. Christe, and A. E. Pavlath, *Inorg. Chem.*, **5**, 1921 (1966).
(6) W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, *Inorg. Nucl. Chem. Lett.*, **2**, 79 (1966).
(7) W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, *Inorg. Chem.*, **6**, 1156 (1967).
(8) C. T. Goetschel, V. A. Campanile, R. M. Curtis, K. R. Loos, C. D. Wagner, and J. N. Wilson, *Inorg. Chem.*, **11**, 1696 (1972).
(9) K. O. Christe, R. D. Wilson, and A. E. Axworthy, *Inorg. Chem.*, **12**, 2478 (1973).
(10) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965).
(11) J. Maruani, J. A. R. Coope, and C. A. McDowell, *Mol. Phys.*, **18**, 165 (1970).
(12) J. Maruani, C. A. McDowell, H. Nakajima, and P. Raghunathan, *Mol. Phys.*, **14**, 349 (1968).
(13) K. O. Christe and D. Pilipovich, *Inorg. Chem.*, **10**, 2803 (1971).
(14) W. E. Tolberg, private communication.
(15) R. W. Fessenden, *J. Chem. Phys.*, **37**, 747 (1962).
(16) J. A. R. Coope, *Chem. Phys. Lett.*, **3**, 589 (1969).
(17) Calculated from the data of C. Froese, *J. Chem. Phys.*, **45**, 1417 (1966).
(18) S. P. Mishra and M. C. R. Symons, unpublished results.
(19) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **45**, 1845 (1966).
(20) F. G. Herring, J. H. Hwang, and W. C. Lin, *J. Phys. Chem.*, **71**, 2086 (1967).
(21) M. C. R. Symons, *J. Chem. Soc. A*, 2393 (1971).
(22) S. Subramanian, M. C. R. Symons, and H. W. Wardale, *J. Chem. Soc. A*, 1239 (1970).

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F-N-Isopropylacetimidoyl Chloride: a Precursor to Totally and Partially Fluorinated Imido Esters and Imido Thio Esters [1]

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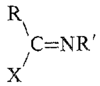
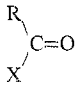
The imidoyl chlorine of $CF_3CCl{=}NCF(CF_3)_2$ is susceptible to base-catalyzed nucleophilic attack by alcohols (ROH; R = $(CF_3)_3C$, $(CF_3)_2CH$, CF_3CH_2) and thiols (R'SH; R' = CF_3, CH_3, C_2H_5) to produce the corresponding imido esters, $CF_3(RO)C{=}NCF(CF_3)_2$, and imido thio esters, $CF_3(R'S)C{=}NCF(CF_3)_2$. Two other imido thio esters, $CF_3(R'S)C{=}NCH(CF_3)_2$ (R' = CH_3, C_2H_5), result in the reaction of the imidoyl chloride with the hydrogenated thiols *via* a complex mechanism. These two imido thio esters exist as a mixture of syn and anti isomers at 30°. Syn and anti conformers of $CF_3(CF_3S)C{=}NCF(CF_3)_2$ and $CF_3(C_2H_5S)C{=}NCF(CF_3)_2$ were resolved at low temperature using ^{19}F nmr spectra. Each of the imido esters exists in the anti configuration with no evidence of stereoisomerization about the C=N bond on the infrared or nmr time scale.

A halo group attached to the carbon atom of >C=N– characterizes a class of reactive compounds known as imidoyl halides. Electronic assistance from a heteroatom attached to the carbon atom bonded to the halo group greatly increases the reactivity of the halide as evidenced by the high reactivity of acid halides where the halo group is attached directly to the carbonyl carbon. In a like manner, the C=N double bond increases the reactivity of an imidoyl halide (I) comparable to that of an acid halide (II).



I



II

Imidoyl halides have been known since 1876 and since that time have proved to be excellent precursors to a wide variety of hydrogenated nitrogen compounds.[2-5] The chloro substituent in hydrogenated imidoyl chlorides is readily displaced by nucleophilic reagents; however, similar reactions of the fluorinated analogs are rare[6-8] or obscured in the literature. We have found that $CF_3CCl{=}NCF(CF_3)_2$ is very susceptible to nucleophilic attack by OR_f^-, SR^-, and SR_f^-. Generally, the imido esters and imido thio esters are formed *via* a straightforward nucleophilic attack at the reactive site by the nucleophile; however, in the case of SR^- a more complex mechanism is operative.

Compounds containing the C=N function may exist as geometrical isomers (syn and anti); however, rotation or inversion about the C=N bond[9] may cause rapid stereoisomerization which renders equivalent the two isomers on the infrared or nmr time scale. By comparison, hydrogenated imines seem to have a much greater configurational stability than similar fluorinated compounds such that the latter often exhibit a temperature-dependent nmr spectrum.[10-15] Stereoisomerism of imines and the possibility of syn and anti isomers is an intriguing subject and both nmr and infrared spectroscopies are useful for the assignment of structure. We have observed *via* ^1H and ^{19}F nmr spectral studies that a mixture of the syn and anti isomers of $CF_3(RS)C{=}NCH(CF_3)_2$ (R = CH_3, C_2H_5) exists at 30°, and through a consideration of peak areas the syn:anti ratios have been determined. None of the other imido thio esters stereoisomerizes at a rate which is slow enough to permit observation of the individual isomers at ambient temperature in the nmr. However, at 25° while $CF_3(CF_3S)C{=}NCF(CF_3)_2$ is just above its nmr coalescence temperature, the individual conformers are observed in the infrared spectra. Low-temperature nmr spectral studies of $CF_3(CF_3S)C{=}NCF(CF_3)_2$ and $CF_3(C_2H_5S)C{=}NCF(CF_3)_2$ showed that the syn and anti conformers could be resolved at low temperature with the major species existing in the anti configuration. A low-temperature nmr spectral study of $CF_3[(CF_3)_2CHO]C{=}NCF(CF_3)_2$ indicated no conformational changes down to –115°. The absence of syn and anti mixtures at low temperature and the nature of the ^{19}F and ^1H nmr coupling patterns suggest that each of the imido esters exist in the anti configuration at ambient temperature with no evidence of stereoisomerization