22 *Inorg. Chem.* **1983**, *22*, 22-25

Contribution from Rocketdyne,
A Division of Rockwell International Corporation, Canoga Park, California 91304

# Reactions of Azidotrifluoromethane with Halogen-Containing Oxidizers

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*Received April 13, 1982*

Azidotrifluoromethane reacts readily with halogen fluorosulfates and peroxydisulfuryl difluoride to form the new compounds $CF_3NX(OSO_2F)$, X = F, Cl, Br, $OSO_2F$, in high yield. These materials were characterized, and their thermal reactions in the presence of CsF were studied. The reactions of ClF and BrF with $CF_3N_3$ at ambient temperature furnish $CF_3NFCl$ and $CF_3N{=}NCF_3$, respectively, in high yield. Under similar conditions $CF_3N_3$ did not react with $Cl_2$, $Br_2$, HF, or HCl. Photochemical activation of $CF_3N_3$ resulted in a rapid, controlled decomposition leading to the formation of $CF_3N{=}CF_2$ and $(CF_3)_2NN(CF_3)_2$ as major products.

## Introduction

Highly fluorinated organonitrogen species are of continuing interest particularly with respect to their interactions with simple inorganic moieties.[1-4] A basic member of this class of materials is azidotrifluoromethane. However, despite its existence having been known for some 20 years,[5] the chemistry of $CF_3N_3$ has remained virtually unexplored. Recently[6] we reported on the physicochemical properties of $CF_3N_3$. In this paper, its chemical reactions with halogen-containing oxidizers and photochemical reactions are summarized.

## Experimental Section

*Caution*! Although no explosions were encountered in this study, covalent azides are in general explosive.[7] Makarov and co-workers reported that $CF_3N_3$ explodes at 330 °C.[8] Appropriate safety precautions should be taken when working with $CF_3N_3$ and *N*-halo amines, especially in larger amounts.

**Apparatus and Materials**. The apparatus employed in this work has previously been described.[6] Literature methods were used to prepare $CF_3N_3$,[6] $CF_3NF_2$,[9] $FOSO_2F$,[10] $ClOSO_2F$,[11] $BrOSO_2F$,[12] $S_2O_6F_2$,[13] ClF,[14] and BrF.[15] Cesium fluoride was fused in platinum and then cooled and powdered in a glovebox. Other chemicals were purchased and used as received.

**General Procedure**. Typically a 30-mL stainless steel Hoke cylinder was cooled at −196 °C and measured amounts of reactants were successively condensed into the cylinder from the vacuum line. Bromine monofluoride was an exception, and it was formed in the cylinder prior to admitting $CF_3N_3$. The closed cylinder was allowed to warm to the desired temperature slowly, in either a cold empty Dewar or one partially filled with dry ice. Quantitative information on the $CF_3N_3$–oxidizer reaction parameters is shown in Table I.

After the desired reaction time the reactor was recooled to −196 °C and the noncondensable gas, presumed to be $N_2$, was removed and measured. The condensable products were separated by fractional condensation in a series of U-traps on the vacuum line. In general a lower temperature trap and a higher temperature trap were used to remove minor byproducts or unreacted material. The primary products were retained at the temperatures shown in Table I. One or more repetitions of the fractionation procedure were used to complete the purification. Product identification was based on the observed material balance of the synthetic reaction and $^{19}F$ NMR, infrared, Raman, and mass spectroscopy. For the new compounds, $CF_3NXOSO_2F$, vapor density molecular weight data and vapor pressure–temperature data were collected. This information and the derived thermodynamic relations are summarized in Table II. Known compounds were identified by comparison of their properties with published properties. Measured vapor pressure–temperature points for individual compounds are given below. Also included is a listing of infrared and Raman bands and the observed ions from the mass spectra. $^{19}F$ NMR data are presented in Table III.

**$CF_3NF(OSO_2F)$.** *T* (°C), *P* (mm): −78.4, 3; −63.5, 9; −46.0, 27; −31.9, 56; −23.4, 89; −7.5, 184. IR, $cm^{-1}$ (intensity): 1500 (s), 1285 (vs), 1254 (s), 1220 (s), 997 (m), 924 (m), 885 (m), 828 (s), 717 (mw), 609 (m), 568 (ms). Raman, $cm^{-1}$ (intensity polarization): 1500 (0.7, dp), 1285 (0.2), 1256 (8.6, p), 1220 (0.2), 998 (1.6, p), 947 (2.4, p, impurity?), 922 (1.4, dp), 890 (5.7, p), 835 (10, p), 820 (sh), 720 (6.0, p), 613 (1.5, p), 608 (1.7, dp), 569 (1.3), 548 (1.0, dp), 522 (1.4, dp), 488 (2.3, p), 431 (1.2, dp), 418 (1.3, p), 321 (8.1, dp), 310 (sh, dp), 272 (2.3, dp), 217 (4, p), 202 (2.5, dp). Mass spectrum, *m/e* assignments: $CF_3NSO_3F^+$, $CF_3NO^+$, $CF_3N^+/SO_2F^+$, $CF_2NO^+$, $CF_3^+$ (base), $SOF^+$, $CF_2N^+/SO_2^+$, $CF_2^+$, $SO^+$.

**$CF_3NCl(OSO_2F)$.** *T* (°C), *P* (mm): −30.2, 8; −8.1, 30; 0.0, 49; 11.3, 85; 25.5, 154. IR, $cm^{-1}$ (intensity): 1490 (s), 1280 (s), 1248 (s), 1197 (s), 928 (m), 873 (m), 839 (s), 822 (sh), 760 (w), 694 (w), 600 (w), 572 (w), 541 (m). Raman, $cm^{-1}$ (intensity, polarization): 1485 (0.5, dp), 1280 (sh), 1248 (6.5, p), 1198 (0+), 930 (0.9, dp), 879 (1.3, dp), 840 (sh, dp), 827 (7.3, p), 770 (10, p), 760 (sh, p), 699 (1.4, p), 608 (0.9, p), 577 (1.4, dp), 548 (2.9, p), 542 (2.0, dp), 514 (1.9, dp), 444 (2.7, p), 432 (1.3, dp), 382 (8.6, p), 323 (9.2, p), 277 (2.5, p), 268 (3.8, p), 248 (2.5, p), 238 (sh), 200 (2.1, dp), 155 (2.2, dp). Mass spectrum, *m/e* assignments: $CF_3NCl(SO_3F)^+$, $CF_3NCl(SO_3)^+$, $CF_3NCl^+$, $CF_3NO^+$, $CF_3N^+/SO_2F^+$; $CF_2NO^+$, $CF_3NO^+$, $CF_3^+$ (base), $SOF^+$, $CF_2N^+/SO_2^+$, $CF_2^+$, $SO^+$.

**$CF_3NBr(OSO_2F)$.** *T* (°C), *P* (mm): −30.3, 3; 0.0, 18; 11.1, 31; 21.4, 51. IR, $cm^{-1}$ (intensity): 1492 (s), 1276 (s), 1250 (s), 1240 (s), 1195 (s), 923 (m), 874 (m), 836 (s), 819 (sh), 725 (w), 688 (w), 602 (w), 570 (w), 534 (w). Raman, $cm^{-1}$ (intensity): 1248 (3), 925 (1), 880 (1.5), 828 (6), 730 (10), 575 (2), 538 (4), 512 (3), 435 (4), 338 (5), 317 (9.5), 242 (5), 230 (5), 178 (1), 133 (1.5). Mass spectrum, *m/e* assignments: $CF_3NSO_3F^+$, $CF_3NBrO^+$, $CF_3NBr^+$, $CF_3NOF^+$, $CF_3NO^+$, $CF_3N^+/SO_2F^+$, $CF_2NO^+$, $Br^+$, $CF_3^+$ (base), $SOF^+$, $CF_2N^+/SO_2^+$, $CF_2^+$, $SO^+$.

**$CF_3N(OSO_2F)_2$.** IR, $cm^{-1}$ (intensity): 1501 (s), 1300 (s), 1276 (s), 1253 (s), 1208 (s), 979 (mw), 908 (m), 850 (sh), 838 (s), 767 (s), 606 (m), 579 (m), 538 (w), 516 (w). Raman, $cm^{-1}$ (intensity), polarization): 1502 (0.5, dp), 1261 (10, p), 982 (0.7, dp), 913 (2.0, p), 860 (5.3, p) 843 (6.5, p), 770 (0.7, p), 728 (4.7, p), 612 (1.1, p), 583 (0.7, dp), 544 (1.1, dp), 525 (1.5, dp), 458 (1.0 p), 450 (0.8 dp), 432 (1.5, p), 385 (0.8, p), 337 (2.6, dp), 318 (5.5, p), 269 (4.2, p), 252 (8.8, p), 210 (0.5, dp), 185 (0.7, dp), 125 (0.8, p). Mass spectrum, *m/e* assignments: $CF_3NO(SO_3F)^+$, $CF_3NSO_3F^+$ $CF_3NOF^+$, $CF_3NO^+$, $CF_3N^+/SO_2F^+$, $CF_2NO^+$, $CF_3^+$ (base), $SOF^+$, $CF_2N^+/SO_2^+$, $CF_2^+$, $SO^+$.

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Table I. Reaction Parameters

| reactants (mmol) | conditions | trapping temp, °C[a] | products (% yield)[b] |
|---|---|---|---|
| $CF_3N_3$ (1.42), ClF (2.75) | 25 °C, 4 h | −142 | $CF_3NFCl$ (98), $N_2$ (93), ClF, $Cl_2$ |
| $CF_3N_3$ (1.53), BrF (~3) | 25 °C, 16 h | −196 | $CF_3N{=}NCF_3$ (99), $N_2$ (91), BrF |
| $CF_3N_3$ (1.70), $FOSO_2F$ (2.31) | 25 °C, 4 days | −112 | $CF_3NF(OSO_2F)$ (96), $N_2$ (103), $FOSO_2F$, $CF_3N(OSO_2F)_2$ |
| $CF_3N_3$ (2.50), $ClOSO_2F$ (2.27) | 25 °C, 16 h | −112 | $CF_3NCl(OSO_2F)$ (89), $N_2$(97), $CF_3OSO_2F$, $CF_3N_3$ |
| $CF_3N_3$ (3.15), $BrOSO_2F$ (3.13) | −45 °C, 3 weeks | −78 | $CF_3NBr(OSO_2F)$ (88), $N_2$ (102), $CF_3OSO_2F$, $CF_3N{=}NCF_3$, $CF_3N_3$, $Br_2$ |
| $CF_3N_3$ (1.74), $(-OSO_2F)_2$ (1.62) | 25 °C, 2 days | −78 | $CF_3N(OSO_2F)_2$ (77), $N_2$ (102), $CF_3OSO_2F$, $CF_3N_3$ |
| $CF_3NF(OSO_2F)$ (1.09), CsF (13.4) | 90 °C, 20 h | −196 | $CF_3NO$ (100), $SO_2F_2$ (100) |
| $CF_3N(OSO_2F)_2$ (0.86), CsF(13.4) | 90 °C, 16 h | −196 | $CF_3NO$ (100), $SO_2F_2$ (100), $CsSO_3F$ (88) |
| $CF_3NBr(OSO_2F)$ (1.09), CsF (8.75) | 90 °C, 6 h | −142 | $CF_3N{=}N(O)CF_3$ (86), $SO_2F_2$ (98), $CsSO_3F$ (67), $Br_2$, $CF_3NO$ |
| $CF_3NCl(OSO_2F)$ (0.71), CsF (8.75) | 90 °C, 10 h | −142 | $CF_3N{=}N(O)CF_3$ (61), $CF_3NO$, $SO_2F_2$, $Cl_2$, $CsSO_3F$ |

[a] Temperature at which first listed product was retained during fractional condensation under a dynamic vacuum. [b] Yield based on the limiting reagent. The $N_2$ percent yield is based on 1 mol of $N_2$ per mole of $CF_3N_3$ reacted. If the C–N bond is also broken, the evolved $N_2$ yield may be higher than 100%.

Table II. Properties of $CF_3NX(OSO_2F)$

| X[a] | vapor dens |  | bp, °C | $\Delta H_v$, kcal/mol | $\Delta S_v$, eu | log [$P$ (mm)] = $A - B/[T$ (K)] |  |  |
|---|---|---|---|---|---|---|---|---|
|  | obsd | calcd |  |  |  | $A$ | $B$ | $T$, °C |
| F | 200 | 201 | 31.1 | 5.95 | 19.5 | 7.152 | 1300 | −78 to −7 |
| Cl | 225 | 227.5 | 66.4 | 7.71 | 22.7 | 7.845 | 1686 | −30 to +25 |
| Br | 260 | 262 | 96.8 | 7.77 | 21.0 | 7.473 | 1699 | −30 to +21 |
| $OSO_2F$ | 278 | 281 | 24 (36 mm) |  |  |  |  |  |

[a] Colorless liquids except for X = Br, which is pale yellow.

Table III. $^{19}F$ NMR Data[a]

| compd | $CF_3$ | NF | $OSO_2F$ | $J_{F\text{-}CF}$, Hz |
|---|---|---|---|---|
| $CF_3NF(OSO_2F)$ | 80.8 d | −11.2 bq | −40.3 dq | 1.1<br>4.6 ($J_{NF\text{-}SF}$) |
| $CF_3NCl(OSO_2F)$ | 76.4 d |  | −37.6 q | 2.6 |
| $CF_3NBr(OSO_2F)$ | 74.8 d |  | −36.7 q | 2.9 |
| $CF_3N(OSO_2F)_2$ | 78.3 t |  | −42.7 q | 3.0 |
| $CF_3N_3$ | 57.6 s |  |  |  |
| $CF_3OSO_2F$ | 57.0 d |  | −46.8 q | 6.5 |
| $CF_3NFCl$ | 79.9 d | 7.0 b |  | 9.8 ($J_{F\text{-}F}$) |

[a] Chemical shifts in ppm, positive values being upfield from internal $CFCl_3$. Abbreviations: d, doublet; q, quartet; s, singlet; t, triplet, b, broad.

**Photolysis of $CF_3N_3$.** A 150-mL quartz bulb fitted with a Teflon stopcock was charged at −196 °C with $CF_3N_3$ (2.00 mmol). Upon removal of the cold bath the bulb was irradiated while it was warmed and while it was kept at ambient temperature for a total of 3 h with use of a Hanovia 100-W lamp at a distance of about 5 cm. After the bulb was recooled to −196 °C, the generated noncondensable gas, presumed to be $N_2$, was removed and measured (2.58 mmol). The remaining products were separated by vacuum fractionation through traps cooled at −112, −142, and −196 °C. Retained at −112 °C was $(CF_3)_2NN(CF_3)_2$ (0.205 mmol), identified by its reported[16,17] properties. The yield was 41 mol %. The fraction obtained at −142 °C was found to be $CF_3N{=}CF_2$[18-20] (0.415 mmol) in 41% yield. A minor amount of $(CF_3)_2NH$[18,21] was present in this fraction and probably arose by scavenging of HF by $CF_3N{=}CF_2$ from the metal vacuum system. The remainder of the $CF_3N{=}CF_2$ was converted to $(CF_3)_2NH$ by treatment was HF, which further confirmed its identity.[18] The −196 °C trap contained mainly $CF_4$ and some $C_2F_6$ (0.246 mmol total) together with traces of $CF_2{=}NF$.[22] No unreacted $CF_3N_3$ was observed. If the lamp was placed closer (2.5 cm) to the quartz bulb and photolysis was carried out for only 1.5 h, the yield of $CF_2{=}NF$ was increased to about 2%.

A similar reaction in a steel cell 7.5 cm in length with a 5-cm diameter sapphire window gave comparable results after a 4-h photolysis: $(CF_3)_2NN(CF_3)_2$, 33%; $CF_3N{=}CF_2$, 43%. In a Pyrex bulb after 80 h, 6% of the $CF_3N_3$ was recovered, but the same products were formed in about the same proportions.

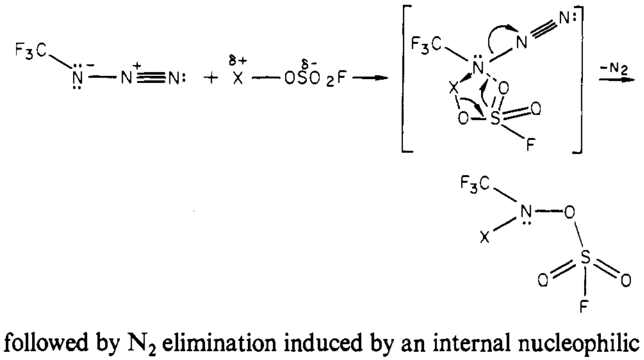
## Results and Discussion

**Synthesis of $CF_3NX(OSO_2F)$ Compounds.** The reaction of azidotrifluoromethane with the halogen fluorosulfates and peroxydisulfuryl difluoride can be described by the equation

$$CF_3N_3 + XOSO_2F \rightarrow N_2 + CF_3NX(OSO_2F)$$
$$X = F, Cl, Br, OSO_2F$$

These reactions proceed at or below room temperature to provide the new group of compounds *N*-fluorosulfato *N*-halo amines in excellent yield. The synthetic data are summarized in Table I. The course of the reaction is easily followed by monitoring the amount of nitrogen evolved.

A plausible mechanism for the reaction of $CF_3N_3$ with halogen fluorosulfates involves the attack of the positive halogen of the fluorosulfate on the negatively charged nitrogen adjacent to the $CF_3$ group of $CF_3N_3$ in its most important resonance structure[6]



followed by $N_2$ elimination induced by an internal nucleophilic substitution ($S_Ni$) reaction involving the fluorosulfate group.

**Properties of $CF_3NX(OSO_2F)$ Compounds.** All of the new compounds are stable at ambient temperature and have been stored in stainless steel vessels. A sample of $CF_3NCl(OSO_2F)$ in a stainless steel cylinder was heated at 90 °C for 1 month without evidence of decomposition. Some of the properties of the $CF_3NX(OSO_2F)$ compounds are given in Table II. In the case of $BrOSO_2F$ and $CF_3N_3$ a reaction temperature of −45 °C was used to minimize a side reaction giving 30% or

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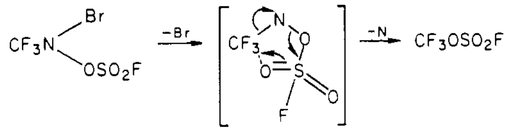
Table IV. Assignment of Fundamental Vibrations (cm$^{-1}$) of $CF_3NX(OSO_2F)$ Compared to Those of Related Molecules

| assignt | | $CF_3NF_2$ | $CF_3NFCl$ | $CF_3NF(OSO_2F)$ | $CF_3NCl(OSO_2F)$ | $CF_3NBr(OSO_2F)$ | $CF_3N(OSO_2F)_2$ | $CF_3NO$[a] |
|---|---|---|---|---|---|---|---|---|
| $\nu_{as}(SO_2)$ | | | | 1500 | 1490 | 1492 | 1501 | |
| $\nu_s(SO_2)$ | | | | 1254 | 1248 | 1250 | 1261 | |
| $\nu(SF)$ | | | | 835 | 839 | 836 | 838 | |
| $\nu(SO)$, $\nu(ON)$ | $\nu_{as}(SON)$ | | | 924 | 928 | 923 | 908 | |
| | $\nu_s(SON)$ | | | 890 | 873 | 880 | 980, 770<br>($\nu(NO_2)$) | |
| $\nu_s(CF_3)$ | | 1290 | 1268 | 1285 | 1280 | 1276 | 1300 | 1291 |
| $\nu_{as}(CF_3)$ | | 1242 | 1215 | (1254) | (1248) | 1240 | 1276 | 1230 |
| | | 1218 | | 1220 | 1197 | 1195 | 1208 | 1175 |
| $\nu(CN)$ | | 854 | 892 | 828 | 827 | 828 | 860 | 810 |
| $\nu(NX)$ | | 1018 | 951 | 997 | 770 | 730 | | |
| | | 951 | 752 | | | | | |
| $\delta(CF_3)$ | | 720 | 695 | 720 | 699 | 688 | 728 | 730 |

[a] Reference 28.

more $CF_3OSO_2F$[23] when conducted at ambient temperature. A plausible path for the formation of this derivative might involve rupture of the N–Br bond, followed by stabilization of the resulting $CF_3NOSO_2F$ radical by nitrogen elimination:



Much smaller amounts of $CF_3OSO_2F$ were encountered in the $ClOSO_2F$ and the $S_2O_6F_2$ reactions, indicating that the well-known weakness of N–Br bonds facilitates their decomposition reaction.

In addition to the good material balances obtained in the syntheses, the observed spectroscopic properties agreed fully with their formulation as $CF_3NX(OSO_2F)$ species.

**$^{19}F$ NMR Spectra.** The $^{19}F$ NMR spectra of the $CF_3NX(OSO_2F)$ compounds (Table III) were particularly definitive. All the observed chemical shifts,[24] coupling constants, multiplicities, and peak area ratios are consistent with the designations given.

**Vibrational Spectra.** Table IV contains a summary of the fundamental vibrations for the $CF_3NX(OSO_2F)$ molecules and a comparison of those of related molecules. The infrared and Raman spectra, respectively, of gaseous and liquid $CF_3NX(OSO_2F)$ show the bands characteristic for a monodentate $OSO_2F$ group. Thus all have strong infrared bands at about 1500 and 1250 cm$^{-1}$ attributable to $\nu_{as}$ and $\nu_s$ of the $SO_2$ group and a strong band at 835 cm$^{-1}$ due to the S–F stretching mode.[25,26] In the Raman spectra the 1500-cm$^{-1}$ $\nu_{as}$ band is very weak as expected. Also, as expected, the intense C–F stretching bands noted in the infrared spectra at about 1280 and 1220 cm$^{-1}$ are very weak in the Raman spectrum.[6,27] The N–O–S linkage gives rise to two medium-intensity bands in the infrared spectra at about 920 and 880 cm$^{-1}$ arising from asymmetric and symmetric stretches for this group. For the C–N stretching mode an assignment of the band at about 825 cm$^{-1}$ in both the infrared and the Raman spectra is made on the basis of the assignment for $CF_3NO$, which was established by $^{15}N$ isotopic shifts and the results from a normal-coordinate analysis.[28] This band often appears as a shoulder on the very intense S–F band. The remaining important stretching vibration arises from the N–X bond and is expected to be of medium to weak intensity in the infrared spectra and weak to strong in the Raman spectra for the series X = F, Cl, Br. Accordingly the N–X stretching mode in these compounds is attributed to the following bands: X = F, 997; X = Cl, 770; X = Br, 730 cm$^{-1}$. These bands have the anticipated intensities in the infrared and Raman spectra, and their frequency trend agrees with that given in the literature[29] for the following series of $XN_3$ compounds: X = F, 869; X = Cl, 719; X = Br, 687 cm$^{-1}$.

Trifluoromethyl compounds normally exhibit a weak $CF_3$ deformation mode at about 700 cm$^{-1}$, and such a band is present in all these spectra. For $CF_3NF(OSO_2F)$, the 947-cm$^{-1}$ Raman band, which lacks an infrared counterpart, is attributed to an impurity band.

**Mass Spectra.** The mass spectra of the $CF_3NX(OSO_2F)$ compounds do not contain parent ion peaks except for the chlorine compound, where it is very weak. Loss of X or F gives rise to the highest *m/e*. Intense $CF_3NO^+$ and $CF_3N^+$ and $CF_3N^+/SO_2F^+$ peaks (both *m/e* 83) are always present, and $CF_3^+$ is the base peak in all cases. A similar mass spectrum has been reported for the related moiety $(CF_3)_2NOSO_2F$.[30] For the chlorine and bromine compounds the correct isotope ratios were obtained for those ions containing those elements. The peak for the parent minus $OSO_2F$ was of low intensity for all, and no $OSO_2F^+$ ion was observed, as is normal for covalent fluorosulfates.[30,31]

**CsF-Catalyzed Decomposition.** As an aid in the characterization of the fluorosulfate amines their reaction with CsF under thermal conditions was investigated. The results are tabulated in Table I and are described by eq 1–3. The N–Cl

$$CF_3NF(OSO_2F) \xrightarrow{CsF} CF_3NO + SO_2F_2 \quad (1)$$

$$CF_3N(OSO_2F)_2 + CsF \rightarrow CF_3NO + SO_2F_2 + CsSO_3F \quad (2)$$

$$2CF_3NBr(OSO_2F) + CsF \rightarrow CF_3N(O){=}NCF_3 + SO_2F_2 + CsSO_3F + Br_2 \quad (3)$$

compound reacted according to both (3) and (4). In all the

$$CF_3NCl(OSO_2F) + CsF \rightarrow CF_3NO + SO_2F_2 + CsCl \quad (4)$$

examples the susceptibility of the $OSO_2F$ group to attack by the strong base CsF is confirmed. While eq 1 and 2 proceeded as expected for a CsF-induced displacement, the N–Br compound behaved quite differently. Here only a trace of $CF_3NO$ was formed and the primary product involved a coupling re-

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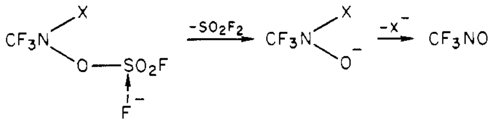
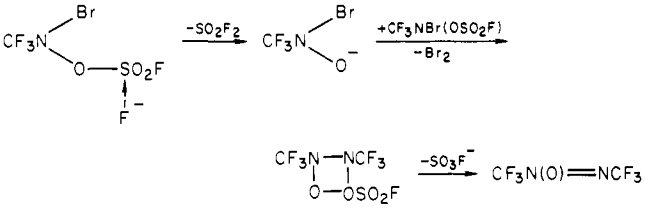
action furnishing the known[32-34] $CF_3N(O){=}NCF_3$. This difference in reactivity is probably attributable to the weak N–Br bond, which permits facile coupling with $Br_2$ elimination. A plausible mechanism for the above reactions involves fluoride ion attack on sulfur, followed by $SO_2F_2$ elimination with $CF_3N(X)O^-$ formation. The latter anion can readily undergo $X^-$ elimination with formation of $CF_3NO$:



For X being Br, the observed coupling reaction (eq 3) could be explained by the weak and highly polarizable N–Br bond, which might undergo the $Br_2$-elimination reaction



This $Br_2$ elimination might be explained by the negative charge in $CF_3N(Br)O^-$ permitting the bromine to become negatively polarized, which could then undergo a facile $Br_2$ elimination with the positively polarized Br of the neutral $CF_3N(Br)OSO_2F$ molecule. The fact that the N–Cl compound reacted with CsF by both (3) and (4) can be ascribed to the N–Cl bond being intermediate between the N–Br and N–F bonds.

**Reactions of $CF_3N_3$ with Halogens and Halide Molecules.** Previously we had reported on the fluorination of $CF_3N_3$ to furnish $CF_3NF_2$ in high yield.[9] At ambient temperature this reaction required a catalyst, and thus it is not surprising that $Cl_2$, $Br_2$, HCl, and HF do not react with $CF_3N_3$ at ambient temperature. However, the interhalogen fluorides ClF and BrF react readily and disparately (Table I):

$$CF_3N_3 + ClF \rightarrow CF_3NFCl + N_2$$

$$2CF_3N_3 \xrightarrow{BrF} CF_3N{=}NCF_3 + 2\ N_2$$

The ClF example parallels the $XOSO_2F$ systems described above, and the chlorofluoramine produced is well-known.[35-37] The high yield and simplicity of this reaction render it an attractive synthetic method for $CF_3NFCl$. In contrast to the ClF case, BrF and $CF_3N_3$ did not result in any N–Br derivative, although $CF_3NBrF$ is a known stable compound.[38] Instead, an excellent conversion to hexafluoroazomethane[33,39,40] ensued in a BrF-catalyzed reaction. Again, this is attributed to the low N–Br bond strength of the expected $CF_3NFBr$ intermediate, which leads to further reaction producing the much more stable end product. Again this facile, high-yield process makes it a potentially useful synthesis for $CF_3N{=}NCF_3$. The azomethane did not react with BrF even at 90 °C. Indeed it a has been reported not to react with $F_2$ at 400 °C.[41]

**UV Photolysis of $CF_3N_3$.** Azidotrifluoromethane has a UV absorption spectrum typical of covalent azides[6] and thus is capable of photochemical excitation and transformation. This behavior was examined at ambient temperature in Pyrex, quartz, and sapphire-steel vessels. Two predominant compounds were obtained, $CF_3N{=}CF_2$[18-20] and $(CF_3)_2NN(CF_3)_2$,[16,17] each in about 40% yield. Additional products were $CF_4$ and $C_2F_6$ together with large quantities of $N_2$. All of the products can be accounted for by the generation, combination, and rearrangement of $CF_3N$ and $CF_3$ radicals (Scheme I). A very low yield of perfluoro(methanimine), $CF_2{=}NF$,[22] was noted in these photolysis experiments and is attributed to fluorine rearrangement in the nitrene, $CF_3\dot{N}\cdot$.

**Scheme I**

$$CF_3N_3 \rightarrow CF_3\dot{N}\cdot + N_2$$

$$CF_3\dot{N}\cdot \rightarrow CF_3\cdot + 0.5N_2$$

$$CF_3\dot{N}\cdot \rightarrow CF_3\cdot \rightarrow CF_3\dot{N}CF_3$$

$$2CF_3\dot{N}CF_3 \rightarrow (CF_3)_2NN(CF_3)_2$$

$$CF_3\dot{N}CF_3 \rightarrow CF_3N{=}CF_2 + F\cdot$$

$$CF_3\cdot\ F\cdot \rightarrow CF_4$$

$$2CF_3\cdot \rightarrow CF_3CF_3$$

**Summary.** It has been found that azidotrifluoromethane is a reactive compound capable of furnishing a wide variety of $CF_3N$-containing products. It is anticipated that many other useful derivatives can be prepared from this azide.

**Acknowledgment.** The authors gratefully acknowledge support for this work by the U. S. Air Force Office of Scientific Research under Contract F49620-81-C-0020. We are also grateful to Dr. L. R. Grant for helpful discussions.

**Registry No.** $CF_3NF(OSO_2F)$, 83292-18-6; $CF_3NCl(OSO_2F)$, 83292-19-7; $CF_3NBr(OSO_2F)$, 83292-20-0; $CF_3N(OSO_2F)_2$, 83292-21-1; $CF_3N_3$, 3802-95-7; $(CF_3)_2NN(CF_3)_2$, 383-96-0; $CF_3N{=}CF_2$, 371-71-7; ClF, 7790-89-8; BrF, 13863-59-7; $CF_3NFCl$, 13880-72-3; $CF_3N{=}NCF_3$, 372-63-4; $FOSO_2F$, 13536-85-1; $ClOSO_2F$, 13997-90-5; $BrOSO_2F$, 13997-93-8; $(-OSO_2F)_2$, 13709-32-5.

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