Fourth Annual Report

ARPA Order No. 442, Item 3

Program Code No. 5910

New Hypofluorites Containing Nitrogen

University of Idaho
Moscow, Idaho

Jeanne M. Shreeve

1 October 1967

Reproduction in whole or in part is permitted for any purpose of the United States Government.

65

ABSTRACT

Fluorine fluorosulfate, trifluoromethyl hypofluorite, and fluorine have been found to react with fluorosulfuryl isocyanate under the influence of ultraviolet radiation to produce a new class of compounds containing the $FSO_2NC(O)F$ group. Some of the chemical and physical properties of these materials and additional characterization of FSO_2NCO are presented.

Addition across the carbon-carbon double bond in bis(trifluoromethyl)ketene with peroxodisulfuryl difluoride, tetrafluorohydrazine, difluoraminofluorosulfate and fluorine fluorosulfate yield $(CF_3)_2C(OSO_2F)C(O)OSO_2F$, $(CF_3)_2C(NF_2)CFO$, $(CF_3)_2C(NF_2)C(O)OSO_2F$, $(CF_3)_2C(OSO_2F)CFO$, and $(CF_3)_2CFC(O)OSO_2F$, respectively. While in the presence of CsF only, $(CF_3)_2C(NF_2)CFO$ is converted to $(CF_3)_2C{=}NF$. With CsF and F_2, the former and $(CF_3)_2C{=}C{=}O$ give rise to $(CF_3)_2(NF_2)CF_2OF$ and $(CF_3)_2CFCF_2OF$, respectively. These new compounds have been characterized and and structures confirmed by nmr, mass and infrared spectra.

Reactions of NF_2CFO with CF_3OF or with Al_2Cl_6 and HCl yield NF_2OCF_3 or $NF_2C(O)Cl$, respectively. The reactions of NF_2CFO with KF and CsF to give $KOCF_2NF_2$, $KOCN_2F_5$, $KOCN_3F_6$, $CsOCF_2NF_2$, $CsOCN_2F_5$, and $CsOCN_3F_6$ are discussed. Decomposition of $KOCF_2NF_2$ with Cl_2 yields NF_2Cl, and pyrolysis of $KOCN_2F_5$ at 95° yields $(NF_2)_2CO$. Spectra and properties of $(NF_2)_2CO$ and $NF_2C(O)Cl$ are given.

Nitrosyl halides (XNO, X = F, Cl, Br) are easily prepared by the reaction of NO_2 and the respective cesium or potassium halide. In the case of the fluoride, formation of a CsF-hexafluoroacetone salt which is subsequently decomposed seems to enhance the reactivity of the CsF toward NO_2. Careful heating and powdering of CsF have essentially the same effect.

The AgF_2-catalyzed fluorination of CF_3NO with and without fluorine is found to give varying amounts of tris(trifluoromethyl)hydroxylamine. With fluorine, the largest yield (55%) is realized at 24°. While with just the catalyst, maximum yield (23%) is obtained at 129°.

Contribution from the Department of Chemistry
University of Idaho
Moscow, Idaho 83843

ADDITION TO THE CARBON-NITROGEN DOUBLE BOND OF FLUOROSULFURYL ISOCYANATE, FSO_2NCO

by

Ronald E. Noftle and Jean'ne M. Shreeve

Abstract

Fluorine fluorosulfate, trifluoromethyl hypofluorite, and fluorine have been found to react with fluorosulfuryl isocyanate under the influence of ultraviolet radiation to produce a new class of compounds containing the $FSO_2NC(O)F$ group. Some of the chemical and physical properties of these materials and additional characterization of FSO_2NCO are presented.

The chemistry of isocyanates has received much attention in recent years especially that of organic isocyanates and their derivatives[1,2,3,4].

1-2 dipolar addition has been found to occur readily across the C-N

---

[1] H. Ulrich, Chem. Rev., 65, 369 (1965).

[2] R. G. Arnold and J. A. Nelson, ibid., 57, 47 (1957).

[3] C. V. Wilson, Org. Chem. Bull., 35, No. 2 (1963).

[4] Ibid., No. 3 (1963).

double bond in isocyanates. The polarizing effect of the sulfuryl group in sulfuryl isocyanates enhances this tendency[1] However, studies of gas-phase free radical addition to the carbon-nitrogen double bond in sulfuryl isocyanates have not appeared in the literature. This paper reports the reaction of fluorosulfuryl isocyanate with various fluorine-containing free radicals to produce a new class of compounds incorporating the fluorocarbonylfluorosulfurylamino group, ($FSO_2NC(O)F$).

Experimental

Infrared spectra were recorded on a Beckman IR-5A infrared spectrophotometer by using 10 and 13 cm. gas cells equipped with either AgCl or NaCl windows.

^{19}F n.m.r. spectra were obtained using Varian Models HR-60, HA-100, and 4311B high resolution n.m.r. spectrometers.

Chemical analyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium in Max Planck Institut, 433 Mülheim (Ruhr), West Germany and by R. Anderson of Allied Chemical Company.

Vapor pressures were determined by the method of Kellogg and Cady[5] or by direct measurement in a static system employing a Wallace and Tiernan pressure gauge.

Ultraviolet light sources used in this work included a 450 watt lamp (Hanovia L-679A36, Hanovia Lamp Div., Engelhard Hanovia, Inc., 100 Chestnut St., Engelhard, N. J.) and a Hanau 70 watt lamp (Q-81, Brinkman Instruments, Cantiagne Road, Westbury, N. Y.). Corex and Pyrex filters were obtained from Hanovia.

---

[5] K. B. Kellogg and G. H. Cady, J. Am. Chem. Soc., 70, 3986 (1948).

For separation of complex product mixtures, gas chromatography employing a 9.5 ft. x 1/4 in. Al column packed with 20% Kel-F #3 polymer oil on Acid-Washed Chromosorb P was used. He flow rates were 70 cc./min. When circumstances permitted, fractional condensation was used to separate mixtures.

Materials.--Fluorosulfuryl isocyanate was prepared by the method of Appel and Rittersbacher[6] with some important modifications.

a.) Preparation of $SO_2(NCO)_2$. The method of Graf[7] which involves the reaction of solid BrCN with liquid SO_3 was used. The product mixture was first distilled at atmospheric pressure to remove most of the Br_2 and SO_2 formed in the reaction, and then at reduced pressure (1 mm) to distill a mixture of $SO_2(NCO)_2$ and $S_2O_5(NCO)_2$. The product was not fractionated further.

b.) Preparation of FSO_2NCO. The mixture prepared above was placed in a distillation flask and heated under reflux to 170° ($S_2O_5(NCO)_2$ decomposes to $SO_2(NCO)_2$ and SO_3 at 130°) while small aliquots of $HOSO_2F$ (ca. 0.25 ml) were added in the course of a few hr. As soon as FSO_2NCO was formed, it distilled into a collection vessel held at 0°. The crude product was contaminated with SO_3, Br_2 and small amounts of SO_2 and CO_2. SO_3 was removed by passing the crude material under vacuum through a column packed with glass wool saturated with conc. H_2SO_4. (Care must be taken that the column does not heat appreciably because FSO_2NCO reacts

---

[6] R. Appel and H. Rittersbacher, Chem. Ber., 97, 849 (1964).

[7] R. Graf, Ger. Pat. 940, 351 (1956).

with H_2SO_4 at elevated temperature.) Several passes using fresh H_2SO_4 were necessary to completely free the product from SO_3. Traces of CO_2 and SO_2 were removed by pumping at -78°. Finally, Br_2 was removed by shaking the product with dry Hg. (In a separate experiment, it was determined that FSO_2NCO did not react with Hg at 25°.) The final product was clear colorless FSO_2NCO. Calcd. Vapor Density: 125.0 g./g.m.v. Found: 126.0 g./g.m.v. Yield: 29% based on BrCN.

$FOSO_2F$ was collected as a by-product in the preparation of $S_2O_6F_2$[8] and purified by fractional condensation.

Trifluoromethyl hypofluorite was prepared by reaction of CO with F_2 at 350°.[9]

Fluorine was obtained from the General Chemical Div. of Allied Chemical Co. and was passed through a trap held at -183° prior to use.

The sulfur trioxide used was stabilized Sulfan B (Allied Chemical Co., Morristown, N. J.).

Cyanogen bromide was obtained from Matheson, Coleman, and Bell.

Preparation of $FSO_2N(OSO_2F)C(O)F$.--FSO_2NCO (0.1086 g., 0.87 mmole) and $FOSO_2F$ (0.1301 g., 1.10 mmole) were condensed in a 1-l Pyrex vessel equipped with a water-cooled quartz probe. The mixture was allowed to warm to 25° and then photolyzed in the gas phase through a Pyrex filter with light from a 450 watt UV lamp. After 2 hr., the product mixture was examined. No noncondensable gases (-183°) were produced; the mixture

---

[8] J. M. Shreeve and G. H. Cady, Inorg. Syn., 7, 124 (1963).

[9] G. H. Cady, Inorg. Syn., 8, 165 (1966).

contained only unreacted starting materials and the product $FSO_2N(OSO_2F)C(O)F$ as determined by examination of ^{19}F n.m.r. and infrared spectra. The amount of unconsumed $FOSO_2F$ (0.0794 g., 0.67 mmole) indicated that 49.5% conversion was achieved. Other experiments employing larger amounts of reactants and longer irradiation times resulted in different conversion percentages. For example, when a mixture of FSO_2NCO (0.5280 g., 4.22 mmole) and $FOSO_2F$ (0.5957 g., 5.02 mmole) was photolyzed for 6 hr. under the above conditions, the amount of unconsumed $FOSO_2F$ (0.2344 g., 1.99 mmole) indicated that 72.5% conversion had taken place.

If the photolysis was allowed to proceed through quartz in the absence of the Pyrex filter, O_2, SO_2F_2, SiF_4 and a polymeric appearing material were observed to form in addition to $FSO_2N(OSO_2F)C(O)F$.

Separation of the product mixture was accomplished by fractional condensation at -23°, -78°, and -183°C. The unreacted $FOSO_2F$ was easily isolated in the trap held at -183° but repeated passes were necessary to isolate pure $FSO_2N(OSO_2F)C(O)F$ in the trap held at -23°. FSO_2NCO was retained in the trap held at -78°.

Identification and Properties of $FSO_2N(OSO_2F)C(O)F$.--The infrared spectrum of $FSO_2N(OSO_2F)C(O)F$ taken in the gas phase at 5 mm. pressure in a 10 cm. cell with NaCl windows showed absorptions at 1890 (s), 1495 (s), 1250 (s), 1205 (s), 1053 (m), 1021 (m), 854 (s), 827 (s), 788 (ms), and 738 (w) cm^{-1}.

The ^{19}F n.m.r. spectrum consisted of three resonances at +6.58 (-C(O)F), -43.57 ($-OSO_2F$), and -54.69 ($-SO_2F$) ppm. relative to an external reference of CCl_3F. The relative areas under the three peaks were in the ratio of 1.02 : 0.96 : 1.00. Under high resolution these peaks were split into three pairs of doublets of equal intensity ($J_{SO_2F-OSO_2F}$, 4.4 cps; $J_{SO_2F-C(O)F}$, 8.5 cps; $J_{OSO_2F-C(O)F}$, 11.4 cps).

The vapor density was determined by the method of Regnault.-Calcd. for $FSO_2N(OSO_2F)C(O)F$: 243 g./g.m.v. Found: 242 g./g.m.v.

Anal.--Calcd. for $FSO_2N(OSO_2F)C(O)F$: F, 23.44; S, 26.38; N, 5.76; C, 4.94; O, 39.48. Found: F, 24.40; S, 25.84; N, 5.76; C, 5.31; O (diff.), 38.69.

Vapor pressures were measured over the range 325° K to 392° K using the method of Kellogg and Cady.[5] The approximate molar heat of vaporization at the boiling point was calculated to be 8.77 Kcal/mole from the slope of the vapor pressure curve with the aid of the Clausius-Clapeyron equation. The boiling point was estimated to be $121.8^{\circ} \pm 0.4^{\circ}$ by extrapolation of the vapor pressure curve. These values yield a Trouton Constant of 22.2 e.u. Vapor pressure data fit the expression:

$$\log_{10} P_{mm} = 7.6695 - \frac{1895}{T}.$$

All attempts to crystallize the compound resulted in the formation of a glass.

The hydrolysis of $FSO_2N(OSO_2F)C(O)F$ can be easily followed by infrared spectroscopy. When moist air was admitted into an ir cell containing a pure sample of $FSO_2N(OSO_2F)C(O)F$ and the spectrum was rescanned, bands were observed for CO_2 and SiF_4. In addition bands attributed to C=O and C-F stretching modes in the C(O)F group were observed to decrease in intensity with time.

Preparation of $FSO_2N(OCF_3)C(O)F$.--In a typical series of preparations, FSO_2NCO (3.5 mmole) and CF_3OF (3.8 mmole) were photolyzed for 7 hr in the gas phase through a Corex filter with radiation from a 450 watt UV lamp. The Corex filter was found to be important in reducing degradation of the reactants. The product mixture was fractionated at -110° and -183°. A small amount of a noncondensable gas was present. The fraction which condensed at -183° was examined by infrared spectroscopy and shown to consist of CF_3OF, COF_2, SiF_4, CO_2, and traces of SO_2F_2. The fraction which condensed at -110° was separated by gas chromatography and consisted of three major components which were found to be $S_2O_5F_2$ (R_t = 8 min.), unreacted FSO_2NCO (R_t = 11 min.), and $FSO_2N(OCF_3)C(O)F$ (0.2277 g., 0.99 mmole, 28%, R_t = 14 min.) by infrared spectroscopy. In addition to traces of volatile materials (R_t = 4 min.), one other component was observed on the gas chromatogram but was present in amounts too small for identification.

Identification and Properties of $FSO_2N(OCF_3)C(O)F$.--The infrared spectrum of the material in the gas phase at 5 mm. pressure in a 13 cm. cell with AgCl windows showed bands at 1888 (s), 1494 (s), 1308 (s), 1250 (vs), 1206 (vs), 1177 (vs), 1088 (m), 1027 (m), 888 (w), 823 (vs), 776 (w), 747 (w) and 654 (m) cm^{-1}.

Three intense resonances were observed on the ^{19}F n.m.r. spectrogram for $FSO_2N(OCF_3)C(O)F$. Under low resolution, peaks appeared as singlets at +68.4 ($-OCF_3$), +6.6 ($-C(O)F$), and -50.4 ($-SO_2F$) ppm. relative to an external reference of CCl_3F with areas in the ratio of 3 : 1 : 1. Under high resolution fine structure was observed. The first resonance was split into two similar doublets, the second resonance into a broad quintet, and the third resonance into two partially superimposed quartets ($J_{C(O)F-OCF_3}$, 4.3 cps; $J_{OCF_3-SO_2F}$, 1.8 cps; $J_{C(O)F-SO_2F}$, 5.4 cps; J calcd. for two overlapping quartets to form a quintet, 4.6 cps; J obs, 4.6 cps).

The vapor density was calculated to be 229 g./g.m.v. Found: 228±2 g./g.m.v.

Anal.--Calcd. for $FSO_2N(OCF_3)C(O)F$: F, 41.48; S, 13.97; N, 6.11, C, 10.48; O, 27.96. Found: F, 37.59; S, 15.80; N, 6.87; C, 9.78; O (diff.), 29.96.

Vapor pressures were determined in a static system by using cold baths. Data obtained for $FSO_2N(OCF_3)C(O)F$ are: Pmm, T°K; 33.0, 277.0; 39.5, 280.7; 46.0, 284.2; 57.0, 289.0; 60.0, 290.0.

Preparation of $(FSO_2NC(O)F)_2$.--FSO_2NCO (2.99 mmole) and F_2 (3.4 mmole) were photolyzed in a 1-l Pyrex vessel for 20 min. The 70 watt UV lamp was located in a water-cooled quartz probe which fit into the center of the vessel. No filter was used. The product mixture was fractionated at -78° and -183°. A noncondensable gas (F_2) was present and was pumped away through a column packed with soda-lime. The fraction which condensed in the trap held at -183° contained COF_2, SiF_4 and SO_2F_2 identified by infrared analysis. The material which condensed at -78° was refractionated at -23° and -183°. The fraction held in the trap at -23° was $(FSO_2NC(O)F)_2$ (1.02 mmole, 69%). The material volatile at this temperature was $S_2O_5F_2$ (0.28 mmole) contaminated with a trace of FSO_2NCO. A white solid remained in the reaction vessel. When treated with moist air, it evolved a brown gas (NO_2). This result indicated that the white solid was probably $(NO)_2SiF_6$.

Identification and Properties of $(FSO_2NC(O)F)_2$.--The infrared spectrum of $(FSO_2NC(O)F)_2$ at 3 mm. pressure in a 10 cm. cell showed absorptions at 1888 (s), 1494 (s), 1295 (w), 1248 (s), 1225 (s), 1178 (m), 1060 (m), 894 (w), 870 (w), 842 (sh), 829 (s), 727 (vw), and 662 (w) cm^{-1}.

The ^{19}F NMR spectrum exhibited resonances at 9.08 (s) and -57.4 (s) ppm relative to an external standard of CCl_3F. Relative areas of these peaks were in the ratio of 1 : 1. No fine structure was observed under high resolution.

The calculated vapor density for $(FSO_2NC(O)F)_2$ is 288 g./g.m.v. Found: 294±10 g./g.m.v.

Anal.--Calcd. for $(FSO_2NC(O)F)_2$: F, 26.38; S, 22.25; C, 8.34; N, 9.72; O, 33.33. Found: F, 27.0; S, 23.01; C, 8.54; N, 10.85; O (diff.), 30.60.

Vapor pressures were determined in a static system. Pmm, T°K; 1.5, 273.2; 2.8, 282.2; 3.2, 284.7; 4.0, 287.7; 7.5, 296.2.

$(FSO_2NC(O)F)_2$ hydrolyzed in moist air to give CO_2. Bands due to C=O and C-F stretching modes in the C(O)F group were observed to decrease with time.

Reaction of FSO_2NCO with $S_2O_6F_2$.--FSO_2NCO and $S_2O_6F_2$ did not react when allowed to stand together in a glass tube for 2 hr. The mixture was heated to 100°, and after 12 hr., the characteristic yellow-brown color of $\cdot OSO_2F$ radicals[10] was still observed in the reaction vessel.

---

[10] F. B. Dudley and G. H. Cady, J. Am. Chem. Soc., 85, 3375 (1963).

FSO_2NCO (0.6112 g., 4.89 mmole) and $S_2O_6F_2$ (1.0229 g., 5.17 mmole) were condensed in a 1-l Pyrex bulb and irradiated through quartz with UV light from a 450 watt lamp for 5.5 hr. No noncondensable gases (-183°) were observed to form. The product mixture was separated crudely by fractional condensation. The most volatile fraction was SiF_4, the next most volatile fraction consisted of $S_2O_6F_2$ and FSO_2NCO, and the least volatile fraction was mostly $FSO_2N(OSO_2F)C(O)F$ contaminated with FSO_2NCO and $S_2O_6F_2$. In addition, a white, flaky material was isolated and shown to be SO_3 by chemical tests. No evidence was found for the presence of $FSO_2N(OSO_2F)C(O)OSO_2F$, the expected product. Apparently, the reaction followed the equation

$$FSO_2NCO + S_2O_6F_2 \xrightarrow{h\nu} FSO_2N(OSO_2F)C(O)F + SO_3.$$

Further characterization of FSO_2NCO.--The properties reported for FSO_2NCO in the literature include the boiling point (62°,[11] 61.5°[6]) and a chemical analysis. Additional data was obtained in the present work.

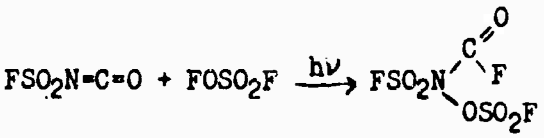
Infrared spectrum (5 mm., 10 cm. cell): 2265 (vs), 1467 (s), 1380 (s), 1235 (s), 833 (s), 763 (s), 649 (s) cm^{-1}.

The ^{19}F NMR spectrum consists of a singlet at -61.1 ppm from an external reference of CCl_3F.

The experimental vapor density was 126.0 g./g.m.v. Calcd.: 125.0 g./g.m.v. The equilibrium vapor pressure at 25° was 155 mm.

Results and Discussion

Fluorine fluorosulfate was found to react with FSO_2NCO in the gas phase under the influence of Pyrex filtered ultraviolet radiation according to the following equation



$$FSO_2N{=}C{=}O + FOSO_2F \xrightarrow{h\nu} FSO_2N(C(O)F)(OSO_2F)$$

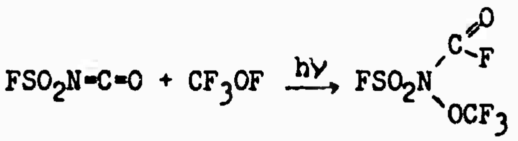
The ^{19}F NMR spectrum of the product showed resonances due $FSO_2N(OSO_2F)C(O)F$ only and suggests that no isomers were formed. Total conversion of the

---

[11] H. Jonas and D. Voigt, Angew. Chem., 70, 572 (1958).

reactants to the product was never achieved but in 7 hr. conversions approached 80% when 4 mmole of each of the starting materials was used. When the irradiation was run in the absence of the Pyrex filter, the product was formed in lower yield and some degradation of the starting materials took place. $FOSO_2F$ is known to produce free radicals under thermal excitation.[10] Heating a mixture of $FOSO_2F$ and $FSO_2N{=}C{=}O$ at 100° for 12 hr. resulted in the formation of the addition product in lower yields with some degradation of the starting materials.

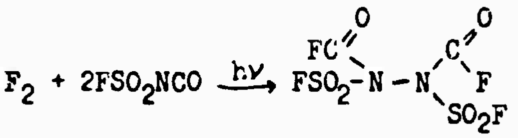
Trifluoromethyl hypofluorite reacted with FSO_2NCO under the influence of ultraviolet radiation to form $FSO_2N(OCF_3)C(O)F$ in 28% yield.



$$FSO_2N{=}C{=}O + CF_3OF \xrightarrow{h\nu} FSO_2N(C(O)F)(OCF_3)$$

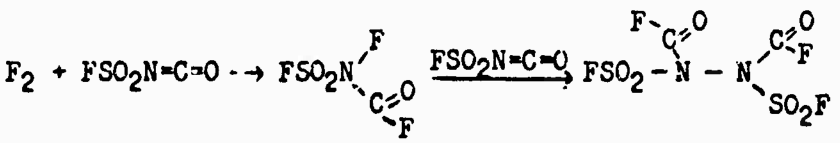
The product mixture was less complex when a Corex glass filter was used than when the UV radiation was allowed to pass directly through quartz. The presence of the other possible isomer, $FSO_2N(F)C(O)OCF_3$, was not detected.

When an equimolar mixture of FSO_2NCO and F_2 was exposed to UV radiation through quartz for 15 min., $(FSO_2NC(O)F)_2$ was isolated in 69% yield. Some degradation products were also observed. The mechanism



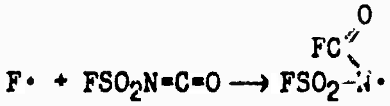
$$F_2 + 2FSO_2NCO \xrightarrow{h\nu} FSO_2{-}N(C(O)F){-}N(C(O)F)(SO_2F)$$

by which this substituted hydrazine is formed may involve the preliminary formation of the F_2 addition product which then adds to FSO_2NCO:

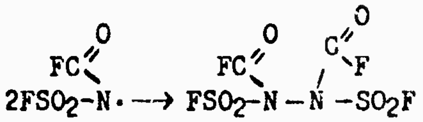


$$F_2 + FSO_2N{=}C{=}O \dashrightarrow FSO_2N(F)(C(O)F) \xrightarrow{FSO_2N{=}C{=}O} FSO_2{-}N(C(O)F){-}N(C(O)F)(SO_2F)$$

or $FSO_2NC(O)F$ radicals may form and recombine:



$$F\cdot + FSO_2N{=}C{=}O \longrightarrow FSO_2\text{-}\overset{FC(O)}{N}\cdot$$



$$2FSO_2\text{-}\overset{FC(O)}{N}\cdot \longrightarrow FSO_2\text{-}\overset{FC(O)}{N}\text{-}\overset{C(O)F}{N}\text{-}SO_2F$$

The infrared spectra of the three derivatives show similarities and comparison with other spectra allows some general assignments to be made. Strong bands in the region 1888 cm^{-1} are assigned to carbonyl stretching of the $-C{\scriptstyle\genfrac{}{}{0pt}{}{\nearrow O}{\searrow F}}$ group.[1] The C-F stretching modes of the $-C{\scriptstyle\genfrac{}{}{0pt}{}{\nearrow O}{\searrow F}}$ group have been found to occur at 1190 cm^{-1} in $FSO_2OC(O)F$[13] and 1221 and 1178 cm^{-1} in $(FC(O)O)_2$[14] which correspond with bands in the region 1177—1205 cm^{-1} in the fluorosulfuryl isocyanate derivatives; these assignments should be regarded as tentative. Absorptions in the region 1494 and 1250 cm^{-1} may be ascribed to asymmetric and symmetric S=O stretching vibrations of the $-SO_2F$ group. These values are in line with those found for similar compounds containing the $-SO_2F$ group, i.e., $-N(SO_2F)_2$[15] and

---

[12] J. H. Simons, "Fluorine Chemistry," Vol. II, Academic Press, Inc., New York, N. Y., 1954, p. 485.

[13] W. B. Fox and G. Franz, Inorg. Chem., 5, 946 (1965).

[14] A. J. Arvia and P. J. Aymonino, Spectrochim. Acta, 18, 1299 (1962).

[15] J. K. Ruff, Inorg. Chem., 5, 732 (1966).

=N-SO_2F.[16] A doublet might be expected to appear for the S=O asymmetric stretching mode in $FSO_2N(OSO_2F)C(O)F$ but none was observed probably due to overlap of the two bands. $CF_3OSO_2OSO_2F$ shows only one band for the S=O asymmetric stretching mode.[17] The strong absorptions at 854 and 827 cm^{-1} are assigned to S-F asymmetric and symmetric stretching modes in $FSO_2N(OSO_2F)C(O)F$.[16,18] Bands at 842--823 cm^{-1} are assigned to S-F stretching modes in $FSO_2N(OCF_3)C(O)F$ and $(FSO_2NC(O)F)_2$.

The ^{19}F n.m.r. spectra of the isocyanate addition products support their proposed structures. $FSO_2N(OSO_2F)C(O)F$ shows three resonances of equal area appearing at +6.6, -43.8, and -54.6 ppm from an external reference of CCl_3F. The first resonance is assigned to the F atom attached to the carbonyl group since other molecules containing a fluorocarbonyl group bonded to nitrogen have been found to absorb near this region.[19,20,21] The resonances at -43.8 and -54.6 ppm are in the regions

---

[16] M. Lustig, C. L. Bumgardner, F. A. Johnson, and J. K. Ruff, Inorg. Chem., 3, 1165 (1964).

[17] W. P. Van Meter and G. H. Cady, J. Am. Chem. Soc., 82, 6005 (1960).

[18] H. C. Clark and H. J. Emeléus, J. Chem. Soc., 190 (1958).

[19] $NF_2C(O)F$: G. W. Fraser and J. M. Shreeve, Inorg. Chem., 4, 1497 (1965).

[20] $(CF_3)_2NC(O)F$: F. S. Fawcett, C. W. Tullock and D. D. Coffman, J. Am. Chem. Soc., 84, 4275 (1962).

[21] SF_2=NC(O)F: A. F. Clifford and C. Kobayashi, Inorg. Chem., 4, 571 (1965).

associated with OSO_2F and SO_2F groups respectively.[22,23,15] Under high resolution each of these singlets was split into a pair of doublets arising from coupling of the two nonequivalent F atoms with the third one. Although no nitrogen coupling was observed, the resonance attributed to the -C(O)F group was broadened indicating that quadrupole interactions may be important. Broadening of n.m.r. signals for F on C(O)F have been observed in compounds containing C(O)F groups bonded to nitrogen.[24] The larger J value observed for coupling of F on OSO_2F with F on C(O)F suggests that through-space interactions may be important since F on OSO_2F is 4 atoms removed from F on C(O)F. Such through-space interactions have been found to be important in the perfluoroalkyl derivatives of sulfur hexafluoride.[25] In the case of $FSO_2N(OCF_3)C(O)F$, three resonances were also observed at +68.3, +6.6, and -50.4 ppm relative to CCl_3F. The areas were in the ratio of 3 : 1 : 1 and are in the regions associated with the $-OCF_3$, -C(O)F, and $-SO_2F$ groups, respectively. The high resolution spectrum showed a high field pair of doublets arising from coupling of two nonequivalent F atoms with those of the $-OCF_3$ group. The resonance at 6.6 ppm was observed as a broadened quintet in the ratio 1 : 4 : 6 : 4 : 1 arising from two overlapping quartets due to coupling of the -C(O)F

---

[22] F. A. Hohorst and J. M. Shreeve, Inorg. Chem., 5, 2069 (1966).

[23] J. K. Ruff, Inorg. Chem., 4, 1446 (1965).

[24] J. K. Ruff, Inorg. Chem., 5, 1787 (1966).

[25] M. T. Rogers and J. D. Graham, J. Am. Chem. Soc., 84, 3666 (1962).

fluorine atom with those of the $-OCF_3$ and $-SO_2F$ groups. The low field resonance appeared as two partially superimposed quartets due to coupling of the F atom on the $-SO_2F$ group with those on the $-C(O)F$ and $-OCF_3$ groups. $(FSO_2NC(O)F)_2$ exhibited two resonances of equal intensity located at +9.08 and -57.4 ppm attributed to F atoms in the $-C(O)F$ and $-SO_2F$ groups, respectively. No fine structure was observed. Although the results of infrared, n.m.r. and chemical analysis indicate that the empirical formula is $(FSO_2NC(O)F)_n$, they do not show that n equals 2. The conclusion that n equals 2 follows after a consideration of rules of chemical valence, comparison of observed with expected volatility, and the fact that the material is uncolored indicating that it is probably not a free radical.[26]

---

[26] R. E. Noftle and G. H. Cady, Inorg. Chem., 4, 1010 (1965).

The compounds are hydrolyzed by traces of moisture. Hydrolytic attack probably occurs first at the fluorocarbonyl group followed by very slow hydrolysis of the fluorosulfuryl group.[23]

Acknowledgment.--The support of the Office of Naval Research is gratefully acknowledged. The authors wish to thank Dr. William B. Fox, Allied Chemical Co., Dr. Friedhelm Aubke, Univ. of British Columbia, and Mr. B. J. Nist, Univ. of Washington, for the ^{19}F NMR spectra.

Contribution from the Department of Chemistry
University of Idaho
Moscow, Idaho 83843

DERIVATIVES OF BIS(TRIFLUOROMETHYL)KETENE WHICH CONTAIN FLUOROSULFATO, DIFLUORAMINO, FLUORIMINO, AND/OR FLUOROXY GROUPS

by

Dayaldas T. Meshri and Jean'ne M. Shreeve

Abstract: Addition reactions across the carbon-carbon double bond in bis(trifluoromethyl)ketene with peroxodisulfuryl difluoride, tetrafluorohydrazine, difluoraminofluorosulfate and fluorine fluorosulfate yield $(CF_3)_2C(OSO_2F)C(O)OSO_2F$, $(CF_3)_2C(NF_2)CFO$, $(CF_3)_2C(NF_2)C(O)OSO_2F$, $(CF_3)_2C(OSO_2F)CFO$, and $(CF_3)_2CFC(O)OSO_2F$, respectively. While in the presence of CsF only, $(CF_3)_2C(NF_2)CFO$ is converted to $(CF_3)_2C{=}NF$. With CsF and F_2, the former and $(CF_3)_2C{=}C{=}O$ give rise to $(CF_3)_2C(NF_2)CF_2OF$ and $(CF_3)_2CFCF_2OF$, respectively. These new compounds have been characterized and structures confirmed by nmr, mass and infrared spectra.

Numerous investigations dealing with the interaction of bis(trifluoromethyl)ketene ($(CF_3)_2C{=}C{=}O$) and organic materials have been reported, e.g., cycloaddition to both the C=C and C=O groups occurs with vinyl benzoate at 100°, and simple alkenes also add to form cyclobutanones and linear adducts.[1] Knunyants and co-workers have published extensively on the reaction chemistry of $(CF_3)_2C=C=O$.[2-11] However, the reactions cf $(CF_3)_2C=C=O$ with typical inorganic fluorine-containing free radical

---

1 D. C. England and C. G. Krespan, J. Am. Chem. Soc., 87, 4019 (1965).

2 I. L. Knunyants, Yu. A. Cheburkov, and M. D. Bargamova, Izv. Aka. Nauk SSSR, Ser. Khim., 1389 (1963). (C.A., 59:15174h)

3 Yu. A. Cheburkov, E. I. Mysov, and I. L. Knunyants, *ibid.*, 1570 (1963). (C.A., 59:15175d)

4 Yu. A. Cheburkov, N. Mukhamadaliev, Yu. E. Arnov, and I. L. Knunyants, *ibid.*, 1478 (1965). (C.A., 63, 16205e)

5 N. Mukhamadaliev, Yu. A. Cheburkov, and I. L. Knunyants, *ibid.*, 1982 (1965). (C.A., 64, 11077c)

6 Yu. A. Cheburkov, N. Mukhamadaliev, and I. L. Knunyants, *ibid.*, 383 (1966). (C.A., 64, 17411d)

7 Yu. A. Cheburkov, N. Mukhamadaliev, and I. L. Knunyants, *ibid.*, 384 (1966). (C.A., 64, 17438a)

8 Yu. A. Cheburkov, Yu. E. Arnov, and I. L. Knunyants, *ibid.*, 582 (1966). (C.A., 65, 8740f)

9 Yu. A. Cheburkov, Yu. E. Arnov, N. S. Mirzabekyants, and I. L. Knunyants, *ibid.*, 773 (1966). (C.A., 65, 8755e)

10 Yu. A. Cheburkov, N. Mukhamadaliev, N. S. Mirzabekyants, and I. L. Knunyants, *ibid.*, 1265 (1966). (C.A., 65, 16852h)

11 Yu. E. Arnov, Yu. A. Cheburkov, and I. L. Knunyants, Abstracts, 4th International Fluorine Symposium, Estes Park, Colorado, July, 1967, p 58.

sources had not been examined. Subsequent fluorination of these addition compounds could lead to new fluoroxy molecules.

Compounds similar to some of those discussed in this paper were reported by Lustig, Ruff and co-workers while this work was underway.[12-15]

Addition of NF_2OSO_2F to perfluoroalkene double bonds, e.g., C_2F_4, C_3F_6, followed by defluorosulfurylation, gives 2-difluoraminoacyl fluorides ($CF_2(NF_2)CFO$, $CF_3CF(NF_2)CFO$). The latter are readily converted via CsF catalyzed fluorination to fluoroxydifluoraminoalkanes.[14,15] Ruff reported a general method for the preparation of 2-haloiminoperfluoropropanes ($(CF_3)_2C{=}NX$) by the catalytic halogenation of $(CF_3)_2C{=}NH$.[13] The highest yield (70%) of the fluorimine was obtained in the presence of potassium fluoride and equimolar amounts of fluorine and the imine. We have found that the new compound $(CF_3)_2C(NF_2)CFO$ may be converted at room temperature in the presence of CsF to $(CF_3)_2C{=}NF$ in yields as high as 96%.

The reactivity of the carbon-carbon double bond in $(CF_3)_2C{=}C{=}O$ has been examined with $S_2O_6F_2$, $FOSO_2F$, NF_2OSO_2F and N_2F_4. Addition compounds are obtained in all cases. For NF_2OSO_2F and N_2F_4, the 2-fluoramino isomers seem to be strongly favored over the 1-fluoramino compounds. When these fluoramino addition compounds are catalytically fluorinated,

---

[12] M. Lustig and J. K. Ruff, Inorg. Chem., 4, 1441 (1965).

[13] J. K. Ruff, J. Org. Chem., 32, 1675 (1967).

[14] J. K. Ruff, A. R. Pitochelli and M. Lustig, J. Am. Chem. Soc., 88, 4531 (1966).

[15] M. Lustig, A. R. Pitochelli and J. K. Ruff, ibid., 89, 2841 (1967).

identical fluoroxy compounds result. Bis(trifluoromethyl)ketene also may be easily fluorinated to give a rather unstable hypofluorite, $(CF_3)_2CFCF_2OF$ which slowly decomposes to C_3F_8 and COF_2.

Experimental Section

Materials: $S_2O_6F_2$,[16] $FOSO_2F$,[17] and NF_2OSO_2F[18] were prepared and purified by the literature methods. Bis(trifluoromethyl)ketene was obtained from E. I. Du Pont de Nemours and Co. and was purified by gas chromatography by using a Kel-F Haloport column. Tetrafluorohydrazine was purchased from Air Products, Inc. Fluorine was obtained from the Allied Chemical Co. and was purified by passing through a sodium fluoride scrubber to remove HF and a trap held at -183°.

Apparatus: A standard Pyrex vacuum system with Teflon stopcocks was employed for material transfer because some compounds dissolved Kel-F stopcock grease. Since the reaction of $S_2O_6F_2$ and $(CF_3)_2C{=}C{=}O$ required a grease-free system, Pyrex storage tubes with Teflon stopcocks which contained the reactants and a Pyrex reaction vessel were sealed to the vacuum line. The ultraviolet irradiation apparatus was a 1-l round bottom Pyrex bulb equipped with a 2 mm vacuum stopcock and a quartz insert (20 cm long and 2.5 cm id) which was sealed into the bulb with a ₮ 45/50 ground glass joint. The lamp (Hanau, Q-81) was inserted so that

---

[16] J. M. Shreeve and G. H. Cady, Inorg. Syn., 7, 124 (1963).

[17] F. B. Dudley, G. H. Cady, and D. F. Eggers, Jr., J. Am. Chem. Soc., 78, 290 (1956).

[18] M. Lustig and G. H. Cady, Inorg. Chem., 2, 388 (1963).

the arc was near the center of the bulb.

Molecular weight: Molecular weights were determined by the method of Regnault and are listed in Table I. A calibrated bulb with a volume of 254.4 ml was used for the determinations. The bulb was fitted with a Teflon 1 1/4 mm stopcock with a Pyrex 10/30 $\$$ inner joint. Pressures were measured with a mercury manometer.

Elemental analysis: 2-Difluoramino-2-trifluoromethylpropionyl fluorosulfate was analyzed by Schwarzkopf Microanalytical Laboratories, Inc., Woodside, New York. Since most of the compounds attacked Pyrex glass slowly at room temperature or decomposed if stored in Pyrex at room temperature for a week or more, they were analyzed in this laboratory. Fluorine was determined by a null point potentiometric method,[19,20] after the compound was fused with sodium metal. Sulfur was determined as BaSO after basic hydrolysis of $(CF_3)_2C(OSO_2F)C(O)OSO_2F$. Elemental analyses results are given in Table I.

Safety precautions: It should be noted that the new hypofluorites are potentially hazardous and proper precautions of shielding and working with small quantities should be observed.

Reaction with $S_2O_6F_2$: After the system was flamed out under vacuum, 2 mmole of $(CF_3)_2C=C=O$ was transferred into the reaction vessel and $S_2O_6F_2$ was added slowly to the reaction vessel in about 0.1 mmole amounts. On occasions when $S_2O_6F_2$ was added too rapidly flashes of light were observed. Addition of $S_2O_6F_2$ was continued until the pressure in the

---

[19] T. A. O'Donnell and D. F. Stewart, Anal. Chem., 33, 337 (1961).

[20] T. A. O'Donnell and D. F. Stewart, ibid., 34, 1347 (1962).

reaction vessel had dropped to about 5 torr (roughly the vapor pressure of the product at room temperature). Colorless droplets of $(CF_3)_2C(OSO_2F)C(O)OSO_2F$ appeared on the inside walls of the reaction vessel. After completion of the reaction, $(CF_3)_2C{=}C{=}O + S_2O_6F_2 \rightarrow (CF_2)_2C(OSO_2F)C(O)OSO_2F$, SiF_4 and traces of $(CF_3)_2C{=}C{=}O$ were removed by pumping on the mixture held at -20°. Further purification was accomplished by passing a stream of dry helium through the liquid. Yields were in excess of 90%.

Reaction with $FOSO_2F$: $(CF_3)_2C{=}C{=}O$ (1 mmole) and dry nitrogen (10 mmole) were added to a 1-l reaction vessel which was held at about -25° in an ethyl alcohol-water slush bath. A total of 1.2 mmole of $FOSO_2F$ was added slowly to react according to $(CF_3)_2C{=}C{=}O + FOSO_2F \longrightarrow (CF_3)_2CFC(O)OSO_2F$ (87%) + $(CF_3)_2C(OSO_2F)CFO$ (13%). These percentages were obtained from nmr data. After 3 hr, N_2, SiF_4, and excess $FOSO_2F$ were pumped off at -25°. Nearly quantitative reaction occurs. Satisfactory separation of the isomers was not realized.

Reaction with NF_2OSO_2F: A 2-l Pyrex bulb with a break-seal and 4 mm quick opening Teflon stopcock was heated to 200—250° under dynamic vacuum. Failure to flame out the vacuum system and reaction vessel decreased the yield of the addition product and increased the yield of nitrogen oxides. When the system was at ambient temperature, 2.6 mmole of $(CF_3)_2C{=}C{=}O$ and 3.2 mmole of NF_2OSO_2F were transferred into the vessel and the stopcock was sealed off. The reaction vessel was heated slowly in an oven over a period of 1 hr until the temperature reached 95°. Heating was continued at this temperature for 7—8 hr. The products were removed from the reaction vessel through the break-seal.

The volatile products, CO_2, SO_2F_2, and SiF_4 were pumped off at -70° and further purification was accomplished by using a Kel-F Haloport column. Typical yields of purified $(CF_3)_2C(NF_2)C(O)OSO_2F$ ranged between 80—94% (2.1—2.5 mmole). No positive evidence for $(CF_3)_2C(OSO_2F)C(O)NF_2$ was found.

Reaction with N_2F_4: A mixture of $(CF_3)_2C{=}C{=}O$ (0.97 mmole) and N_2F_4 (2.1 mmole) was transferred into a vessel equipped with a quartz insert and was subjected to ultraviolet radiation. Tap water (about 20°) was allowed to flow continuously around the lamp and over the reaction vessel. When the ultraviolet lamp was new, irradiation for about an hour was sufficient. Prolonged irradiation resulted in decomposition of the product and increased the yield of nitrogen oxides. In this reaction the major product was $(CF_3)_2C(NF_2)CFO$ and only minor amounts of the isomer, $(CF_3)_2CFC(O)NF_2$, apparently were obtained. This was not positively identified. $(CF_3)_2C(NF_2)CFO$ was purified by pumping off the volatile products, NF_3, N_2F_4, COF_2, CO_2, SiF_4 and lower fluorocarbons. at -78°. Further purification was made by using a Kel-F Haloport column which permitted efficient separation of $(CF_3)_2C(NF_2)CFO$ from NO_2. Typical yields of purified $(CF_3)_2C(NF_2)CFO$ ranged between 0.58--0.88 mmole (59--91%). Lower yields are attributed to the presence of moisture in the system or to inadequate cooling during irradiation.

General procedure for fluoroxy compounds:[14,15] A 1.5 to 3.5 g sample of cesium fluoride was ground to a fine powder with a mortar and pestle and dried in a vacuum oven for 16 hr. The dried cesium fluoride was transferred into a 100 ml Monel Hoke Cylinder or 750 ml nickel vessel prepared by soldering together two nickel crucibles which contained 12 stainless steel balls (3/8 in diam). The reactor was evacuated, filled with fluorine to one atmosphere, and then heated to 200° in the oven for 6 hr. Fluorine was pumped out through a soda lime trap. To ensure the presence of finely ground catalyst, the reactor was shaken manually for half an hour. A 0.25 mmole sample of $(CF_3)_2C(NF_2)CFO$ was condensed into the reactor at -183° and then approximately 2 mmole of purified fluorine, diluted with nitrogen (360 torr F_2 + 320 torr N_2), was added. The reactor was placed in a slush bath (-78°) which was allowed to warm slowly to -20° over a period of 6 to 8 hr. When the temperature of the slush bath reached -20°, the products were transferred into a trap maintained at -183° and nitrogen and unreacted fluorine were pumped off through a soda lime trap. A similar procedure was employed for fluorination of $(CF_3)_2C{=}C{=}O$ except the reactions were carried out with larger quantities. (Typically 3 mmole gave about 2.8 mmole hypofluorite.)

In most runs no further purification was necessary for either compound. Whenever traces of impurities due to the presence of starting materials or decomposition products were observed, the compounds were purified by fractional codistillation or trap-to-trap distillation. In the case of $(CF_3)_2CFCF_2OF$, a trap at -78° retained the hypofluorite and the impurities, C_3F_8, COF_2 and starting material, were found in the trap at -183°.

When the reactions of $(CF_3)_2C(NF_2)CFO$ (0.25 mmole) were carried out at room temperature in the presence of only CsF, 2-fluoroiminoperfluoropropane (0.23 mmole) and carbonyl fluoride (0.21 mole) were obtained. The fluorimine was purified by using a Kel-F Haloport column. A summary of the experimental data is given in Table I.

Infrared spectra: Infrared spectra of new materials were recorded with a Beckman Model IR 5A spectrophotometer (sodium chloride prism, 5000-625 cm^{-1} range, 3 min scan) or a Perkin-Elmer Model 137 infrared spectrophotometer (sodium chloride prism, 4000-667 cm^{-1} range, 12 min scan). The gaseous samples were contained in a 5 cm glass cell with NaCl windows. The following are the frequencies in cm^{-1} for $(CF_3)_2C(OSO_2F)C(O)OSO_2F$: 1836 (s), 1485 (vs), 1290 (vs), 1250 (vs), 1163 (w), 1087 (s), 991 (s), 965 (vs), 873 (s), 842 (s), 805 (w), 773 (m); for a mixture of $(CF_3)_2CFC(O)OSO_2F$ and $(CF_3)_2C(OSO_2F)CFO$: 1872 (ms). 1845 (s), 1492 (vs), 1312 (vs), 1265 (vs) broad, 1192 (ms), 1130 (m), 1095 (m). 990 (vs), 965 (vs), 862 (s), 845 (vs), 808 (m), 778 (m), 748 (w), 708 (w); for $(CF_3)_2C(NF_2)C(O)OSO_2F$: 1824 (s), 1490 (vs), 1280 (vs), 1240 (vs), 1150 (m), 1065 (m), 1010 (s), 980 (vs), 952 (s), 910 (s), 860 (vs), 844 (s), 814 (w), 800 (w), 775 (s), 745 (w); for $(CF_3)_2C(NF_2)CFO$: 1868 (vs), 1260 (s), 1175 (w), 1068 (w), 1008 (vs), 947 (s), 910 (s), 745 (w), 708 (s); for $(CF_3)_2C(NF_2)CF_2OF$: 1280 (s), 1220 (s), 1175 (m), 1130 (w), 1062 (m), 1010 (vs), 953 (vs), 918 (s), 883 (ms), 805 (ms), 735 (s) broad; for $(CF_3)_2CFCF_2OF$: 1282 (vs) broad, 1195 (sh), 1165 (s), 1125 (s), 985 (vs) broad, 882 (s), 808 (s), 750 (s), 727 (s); and for $(CF_3)_2C{=}N{-}F$: 1639 (m), 1350 (vs), [illegible]50 (vs), 1213 (vs), 1181 (sh), 1023 (vs), 940 (sh), 733 (m).

^{19}F NMR spectra: ^{19}F nmr spectra were recorded at room temperature with a Varian Model V 4310 spectrometer operating at 40 Mc, a Varian Model DP-60 spectrometer at 56.4 Mc, a Varian Model 4311 B at 40 Mc or a Varian HA 100 at 91.4 Mc (at -60°). In all cases CCl_3F was used as an external reference and resonances are given in ppm. The chemical shifts and assignments are given in Table II.

Oxidizing equivalent: The oxidizing equivalents of fluoroxy compounds were determined by permitting the weighed sample to react with aqueous acidic iodide solution and titrating the liberated iodine with standard sodium thiosulfate. These are given in Table I.

Mass spectra: Mass spectral cracking patterns were recorded with a Consolidated Engineering Corporation Type 21-103 mass spectrometer. The ionizing potential was 70 volts at ambient temperature. The principal peaks in the spectra of the compounds are given (species, mass number, relative intensity). $(CF_3)_2C(OSO_2F)C(O)OSO_2F$: CO^+, N_2^+, 28, 17; CF^+, 31, 20; O_2^+, SO_2^{++}, 32, 12; CO_2^+, 44, 23; SiF^+, 47, 9; SO^+, 48, 28; SO_2^+, 64, 38; SiF_2^+, 66, 8; FSO^+, 67, 15; CF_3^+, 69, 100; CO_2S^+, 76, 3; FSO_2^+, 83, 57; SiF_3^+, 85, 34; $C_2F_3O^+$, 97, 23; SiF_4^+, 104, 18; $C_2O_3SF^+$, 123, 7; $C_3O_5O^+$, 147, 20; $C_4F_5O^+$, 159, 43; $C_3F_3O_3S^+$, 173, 13; $C_4F_7O_3S^+$, 249, 6; $C_4F_7O_4S^+$, 277, 1; $C_4F_8O_7S_2^+$, 376, 1 (molecule-ion); $(CF_3)_2C(NF_2)C(O)OSO_2F$: CO^+, N_2^+, 28, 9; CF^+, 31, 31; O_2^+, SO_2^{++}, 32, 3; NF^+, 33, 19; C_2F^+, 43, 4; CO_2^+, 44, 17; SiF^+, 47, 2; SO^+, 48, 32; CF_2^+, 50, 8; NF_2^+, 52, 0.6; $C_2F_2^+$, 62, 1; CF_2N^+, SO_2^+, 64, 8; FSO^+, 67, 0.5; CF_3^+, 69, 100; $C_3F_2^+$, 74, 1; CO_2S^+, 76, 3; SO_3^+, 80, 7; $C_2F_3^+$, 81, 3; FSO_2^+, 83, 2; SiF_3^+, 85, 11; $C_3F_3^+$, 93, 4; $C_2F_4^+$, 100, 5;CFO_3S^+, 111, 2; $C_2FNO_4S^+$, 153, 0.9; $C_4F_6^+$, 162, 35; $C_4F_7^+$, 181, 13; $C_3F_7N^+$, 183, 0.6; $C_3F_8N^+$, 202, 0.2; $C_4F_8NO^+$, 230, 0.7; and for $(CF_3)_2C(NF_2)CFO$: CO^+, N_2^+, 28, 0.8; NO^+, 30, 0.9; CF^+, 31, 0.9; O_2^+, 32, 0.5; NF^+, 33, 0.8; CO_2^+, 44, 1; NO_2^+, 46, 2; NF_2^+, 52, 1; CNF_2^+, 64, 0.4; CF_3^+, 100, 69; $^{13}CF_3^+$, 70, 1; $C_2NF_2^+$, 76, 1; $C_2F_3^+$, 81, 0.6; SiF_3^+, 85, 0.3; $C_3F_3^+$, 93, 0.5; $C_2F_3N^+$, 95, 0.5: $C_2F_4^+$, 100, 1; $C_3F_5^+$, 131, 0.3; $C_3F_6^+$, 150, 0.5; $C_3F_7^+$, 169, 0.7; $C_4F_7^+$, 181, 0.6; $C_3F_8N^+$, 202, 0.5.

Table II

^{19}F NMR Spectra (Chemical Shifts in ppm)

Compound	OF	SF	NF_2	CFO	CF_3	CF_2	CF
$(CF_3)_2C(OSO_2F)C(O)OSO_2F$	-	-48.1 septet,1.0* -46.8 singlet,1.0	-	-	72.0 doublet,6.3	-	-
$(CF_3)_2C(OSO_2F)CFO$	-	-47.1 complex	-	-33.7 complex	73.1 2 doublets	-	-
$(CF_3)_2CFC(O)OSO_2F$	-	-46.0 singlet	-	-	76.3 doublet	-	182.7 septet
$(CF_3)_2C(NF_2)C(O)OSO_2F$	-	-48.6 singlet,1.0	-35.5 1.9	-	63.8 triplet,6.1	-	-
$(CF_3)_2C(NF_2)CFO$	-	-	-34.1 1.8	-41.5 septet,1.0	66.1 quintet,6.1	-	-
$(CF_3)_2C(NF_2)CF_2OF$	-151.4 singlet,1.0	-	-35.4 2.3	-	66.7 6.0	82.8 2.0	-
$(CF_3)_2CFCF_2OF$	-144.6 singlet	-	-	-	75.8 br.quartet	90.2 14 lines	179.2 complex

* Hyperfine splitting and relative peak area

Table I

Compound	Reaction Conditions	Mole. Wt.	Anal.
$(CF_3)_2C(OSO_2F)C(O)OSO_2F$	$(CF_3)_2C{=}C{=}O + S_2O_6F_2$, 25°	376±8(376)*	S,16.84(17.02);F,38.92(40.42)
$(CF_3)_2C(NF_2)CFO$	$(CF_3)_2C{=}C{=}O + N_2F_4$, 20°, UV	248.2(249)	F,69.01(68.71)
$(CF_3)_2C(NF_2)C(O)OSO_2F$	$(CF_3)_2C{=}C{=}O + NF_2OSO_2F$, 95°	326.4(329)	S,9.53(9.72);F,51.97(51.98) C,14.88(14.59);N,4.58(4.25)
$(CF_3)_2C(OSO_2F)CFO$	$(CF_3)_2C{=}C{=}O + FOSO_2F$, -25°		
$(CF_3)_2CFC(O)OSO_2F$	$(CF_3)_2C{=}C{=}O + FOSO_2F$, -25°		
$(CF_3)_2C{=}NF$ (0.23 mmole)	$(CF_3)_2C(NF_2)CFO$(0.25 mmole) + CsF + F_2 (0 mmole), 25°	182.8(183)	
$(CF_3)_2C(NF_2)CF_2OF$ (0.248 mmole)	$(CF_3)_2C(NF_2)CFO$(0.25 mmole) + CsF + F_2 (1.9 mmole), -78 to -20°	285.1(287)	Ox.Eq.,1.87(2.0)
$(CF_3)_2CFCF_2OF$ (2.84 mmole)	$(CF_3)_2C{=}C{=}O$(3 mmole) + CsF + F_2 (13.5 mmole), -78 to -15°	248(254)	Ox.Eq.,1.89(2.0)

* Numbers in parentheses are calculated values

Results and Discussion

Infrared spectra of these new compounds have many bands in common and some assignments are possible. Absorbances in the 1872—1824 cm^{-1} region are attributed to C=O stretch. The asymmetric and symmetric S=O stretching frequencies of the OSO_2F group are assigned to bands in the 1492—1485 and the 1265—1240 cm^{-1} regions, respectively.[12] These compounds have typical C-F bands located between 1350—1065 cm^{-1}.[21] N-F vibrations result in bands from 1023—910 cm^{-1}.[15] The bands assigned to S-O-X stretch in numerous fluorosulfate derivatives are found in the vicinity of 790 cm^{-1}.[17] Bands assigned to S-F stretch occur between 873—842 cm^{-1}.[12] The bands at 882 and 883 cm^{-1} in the fluoroxy compounds are attributed to O-F stretch.[17,22] In $(CF_3)_2C{=}NF$, an absorption at 1639 cm^{-1} is assigned to C=N.

As is typical of fluorosulfate-containing compounds,[12,23] all ^{19}F S-F nmr resonances occur from -46.0 to -48.6 ppm. The broaden NF_2 bands occur from -34.1 to -35.5 with the =NF resonance at -46.2 ppm. CF_3, CF_2, and CF resonances fall from 66.1—76.3, 82.8—90.2, and 179.2—182.7 ppm, respectively. Hyperfine splitting has been useful in many cases in making correct assignments. In $(CF_3)_2C(OSO_2F)C(O)OSO_2F$, the septet

---

[21] L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd ed., Methuen and Co., Ltd., London, 1959, p 126.

[22] J. H. Prager and P. G. Thompson, J. Am. Chem. Soc., 87, 230 (1965).

[23] F. A. Hohorst and J. M. Shreeve, Inorg. Chem., 5, 2069 (1966).

(J = 3.6 cps) at -48.1 is assigned to FO_2SOC- since this fluorine would be expected to interact more strongly with the 6 equivalent methyl fluorines than the fluorine of $FO_2SOC{=}O$ which is assigned to the singlet at -46.8. The doublet (J = 3.6 cps) at +72.0 is assigned to CF_3. In the mixture of isomers, $(CF_3)_2C(OSO_2F)CFO$ and $(CF_3)_2CFC(O)OSO_2F$, the relative amounts (13:87) were determined by measuring the areas of the two OSO_2F peaks in the nmr spectrum. Again bands were assigned based on the hyperfine splitting. In the former, the CF_3 groups are split by CFO to a doublet (J = 8 cps) and split again by the OSO_2F (J = 3.2 cps) to a quartet of equally intense peaks. Although in theory the CFO fluorine should be split into 14 peaks, roughly 10 of these are clearly discernible from the background. However, from these it is possible to determine $J_{CFO\text{-}SF}$ = 5.4 cps and to confirm the value of $J_{CFO\text{-}CF_3}$ = 8 cps. Because of the rather small, nearly equivalent values for $J_{SF\text{-}CFO}$ (3.2 cps) and $J_{SF\text{-}CF_3}$ (5.6 cps), the SF region is very complex but 14 lines are observed and the coupling constants are confirmed. The spectrum of $(CF_3)_2CFC(O)OSO_2F$ is much simpler where 6 methyl fluorines couple with CF to give a septet (J_{CF-CF_3} = 7.3 cps), CF splits the CF_3 resonance into a doublet ($J_{CF_3\text{-}CF}$ = 7.5 cps), and the SF resonance is a singlet. Similarly for $(CF_3)_2C(NF_2)C(O)OSO_2F$, where the 2 fluorines of NF_2 couple with the 6 equivalent CF_3 fluorines ($J_{CF_3\text{-}NF_2}$ = 16 cps, 1:2:1), while the NF_2 fluorine resonance is typically broadened with no fine structure. As above, no interaction occurs with the fluorosulfate fluorine. In the $(CF_3)_2C(NF_2)CFO$ spectrum, the septet at -41.5 (J = 9 cps) is assigned to CFO where the fine structure is a result of interaction with the methyl fluorines. Further splitting, apparently from CFO-NF_2 coupling, occurs but J is very small. While NF_2 is a broaden resonance at -34.1, the CF_3 resonance appears to be an ill defined quintet.

It is surprising to note that the OF group in neither of the fluoroxy compounds couples with the remainder of the molecule. In the case of $(CF_3)_2C(NF_2)CF_2OF$, this may be due to the lack of resolution (which precludes the reporting of J values) but for $(CF_3)_2CFCF_2OF$ such is not the case (Varian HA-100). The latter spectrum was determined at -60° since it has been observed that the molecule, although apparently reasonably stable under ambient laboratory conditions, decomposes rather rapidly in the magnetic field. On heating in glass, the decomposition occurs essentially quantitatively to give COF_2 and C_3F_8. The remainder of the spectrum for $(CF_3)_2CFCF_2OF$ seems reasonable. Coupling between CF_3 and CF gives rise to a septet (J_{CF-CF_3} = 7 cps) at 179.2 but further not completely resolved splitting also is observed ($J \cong 3$ cps). Resonance at +75.8 ppm assigned to CF_3 is a broadened quartet which arises from overlap of CF_3-CF_2 ($J_{CF_3-CF_2}{}_{14}$ = 9 cps) and CF_3-CF (J_{CF_3-CF} = 7 cps) interactions. At +90.2 ppm is a/peak multiplet which fits in fairly well with CF_2-CF_3 ($J_{CF_2-CF_3}$ = 9 cps) and CF_3-CF ($J_{CF_3-CF} \cong 3$ cps) interactions. Assigning the resonance at +82.8 to CF_2 in $(CF_3)_2C(NF_2)CF_2OF$ is not out of line since in $CF_3CF(NF_2)CF_2OF$, Lustig[15] has assigned a resonance at +86.1 to CF_2 while in $CF_2(NF_2)CF_2OF$, the CF_2 adjacent to OF is at +92.5. Our value of +82.8 ppm is in keeping with the trend that as fluorines on CF_2 are replaced by CF_3 groups the resonance position of the adjacent CF_2 is shifted downfield. Chemical shifts and coupling constants for $(CF_3)_2C{=}NF$ are essentially the same as those reported by Ruff.[13]

In the reactions of N_2F_4 and NF_2OSO_2F with $(CF_3)_2C=C=O$, little, if any, of the fluoramides, $(CF_3)_2CFC(O)NF_2$ and $(CF_3)_2C(OSO_2F)C(O)NF_2$, was observed during the workup of the product mixture. However, in the latter case the presence of $(CF_3)_2C=O$, SO_2F_2, and CO_2 as minor components suggests that this isomer might have formed but decomposed during the reaction. However, no nitrogen-containing species, other than nitrogen oxides, were isolated. In the case of the former, C_3F_8 as well as nitrogen oxides and NF_3 were often observed as minor products. Possibly this isomer was unstable under the conditions used. The nmr spectrum taken on an unpurified sample gave no indication of two types of NF_2 or OSO_2F groups which should be evident if even small amounts of $(CF_3)_2C(OSO_2F)C(O)NF_2$ were present.

The action of CsF on $(CF_3)_2C(NF_2)CFO$ to abstract COF provides a novel route to $(CF_3)_2C=NF$ in greater than 90% yield. Not even after heating the residual CsF to 200° for several hours is an equivalent amount of COF_2 recovered. However, this was not carried out under conditions of dynamic vacuum. The CsF catalyzed fluorination of $(CF_3)_2C(NF_2)CFO$ and $(CF_3)_2C=C=O$ occurs readily below -20° to give nearly quantitative conversion to the respective fluoroxy compounds. With $(CF_3)_2C(NF_2)C(O)OSO_2F$, fluorination occurs more slowly and is encouraged by slightly higher temperatures (20°). In this case, $(CF_3)_2C(NF_2)CF_2OF$ and decomposition products are obtained. Under no conditions tried was it possible to retain the fluorosulfate moiety in the molecule.[24]

---

[24] M. Lustig and J. K. Ruff, *ibid.*, *3*, 287 (1964).

These fluoroxy compounds are not sensitive to glass or moisture but do attack mercury with vigor. Advantage of their action on acidic iodide solution was taken to determine the number of oxidizing equivalents. The experimental value of about 1.9 agrees fairly well with a theoretical 2 electron change.

As is often typical of fluorosulfate-containing compounds of this type, small amounts of moisture tend to produce a cloudy solution and Kel-F stopcock grease is readily dissolved. It is advantageous to work in glass systems with Teflon stopcocks and without standard taper joints.

The mass spectral data are consistent with the proposed structures, although a molecule ion was obtained only in the case of $(CF_3)_2C(OSO_2F)C(O)OSO_2F$. For every molecule CF_3^+ was the predominant species.

Acknowledgments. The authors are grateful to the Office of Naval Research for their generous support. Our thanks are due Mr. B. J. Nist, University of Washington, Dr. M. Lustig, Rohm and Haas, and Dr. F. Aubke, University of British Columbia for mass and nuclear magnetic resonance spectra. Dr. D. C. England of the E. I. Du Pont de Nemours and Co. graciously supplied the bis(trifluoromethyl)ketene.

Contribution from the Department of Physical Sciences,
University of Idaho, Moscow, Idaho 83843

Some Chemistry of Difluoraminocarbonyl fluoride, NF_2CFO. The Preparation of Perfluorourea, $(NF_2)_2CO$, and Difluoraminocarbonyl Chloride, $NF_2C(O)Cl$. New Preparations for NF_2OCF_3 and NF_2Cl.[1]

by George W. Fraser and Jean'ne M. Shreeve

Reactions of NF_2CFO with CF_3OF or with Al_2Cl_6 and HCl yield NF_2OCF_3 or $NF_2C(O)Cl$, resp. The reactions of NF_2CFO with KF and CsF to give $KOCF_2NF_2$, $KOCN_2F_5$, $KOCN_3F_8$, $CsOCF_2NF_2$, $CsOCN_2F_5$, and $CsOCN_3F_6$ are discussed. Decomposition of $KOCF_2NF_2$ with Cl_2 yields NF_2Cl, and pyrolysis of $KOCN_2F_5$ at 95° yields $(NF_2)_2CO$. Spectra and properties of $(NF_2)_2CO$ and $NF_2C(O)Cl$ are given.

This paper describes some of the chemistry of difluoraminocarbonyl fluoride, NF_2CFO, whose preparation and properties have been reported in a previous note.[2] Reaction of NF_2CFO with trifluoromethyl hypofluorite, CF_3OF, at room temperature yields difluoraminooxyperfluoromethane, NF_2OCF_3, a compound previously prepared by the reaction of tetrafluorohydrazine, N_2F_4, with trifluoromethyl hypofluorite[3,4] and by the basic hydrolysis of

---

[1] Taken from the Ph.D. thesis of G. W. Fraser and presented in part at the 3rd International Symposium on Fluorine Chemistry, Munich, 1965, and at the Symposium on Inorganic Fluorine Chemistry, Ann Arbor, June, 1966.

[2] G. W. Fraser and J. M. Shreeve, Inorg. Chem., 4, 1497 (1965).

[3] W. H. Hale, Jr., and S. M. Williamson, Ibid., 4, 1342 (1965).

difluoraminotrifluoromethoxytetrafluorosulfur(VI), $CF_3OSF_4NF_2$.[4] Several recent reports[5-7] indicate that anhydrous aluminum chloride, with or without a solvent or hydrogen chloride catalyst, is an effective chlorinating agent for replacement of certain labile fluorines in various types of compounds; and by an analogous reaction under mild conditions NF_2CFO is easily converted to the previously-unreported difluoraminocarbonyl chloride, $NF_2C(O)Cl$. Reports of the formation of simple anionic complexes between the alkali metal fluorides and carbonyl fluoride[8,9] or hexafluoroacetone[10,11] suggested the analogous preparation of $KOCF_2NF_2$ from KF and NF_2CFO. This adduct is a useful intermediate for a preparation of chlorodifluoramine, NF_2Cl,[12] and $KOCN_2F_3$. Pyrolysis of the latter is the only known route to

---

[4] J. M. Shreeve, L. C. Duncan, and G. H. Cady, Ibid., 4, 1516 (1965).

[5] [illegible] S. Solomon, L. A. Doe, and D. W. Schults, J. Org. Chem., 31, 1551 (1966).

[6] M. Lustig, Inorg. Chem., 5, 1317 (1966).

[7] D. P. Babb and J. M. Shreeve, Ibid., 6, 351 (1967).

[8] D. C. Bradley, M. E. Redwood, and C. J. Willis, Proc. Chem. Soc., 416 (1964)

[9] M. E. Redwood and C. J. Willis, Can. J. Chem., 43, 1893 (1965).

[10] D. P. Graham and V. Weinmayr, J. Org. Chem., 31, 957 (1966).

[11] A. G. Pittman and D. L. Sharp, Ibid., 31, 2316 (1966).

[12] For other preparations of NF_2Cl, see for example: (a) W. C. Firth, Jr., Inorg. Chem., 4, 254 (1965); and (b) C. B. Colburn, Advances in Fluorine Chemistry, Vol. 3, Butterworths, 1963, pp. 108-9; and references cited therein.

perfluorourea, $(NF_2)_2CO$, some of whose properties have already been described.[13]

Results and Discussion

Trifluoromethyl hypofluorite, CF_3OF, slowly attacks difluoraminocarbonyl fluoride, NF_2CFO, at room temperature in Pyrex glass. After several hours the starting materials initially in equimolar ratio appear to be completely consumed, and while considerable degradation and attack on the glass is evident, difluoraminooxyperfluoromethane, NF_2OCF_3, is easily isolated from the product mixture in yields approaching 40%. The presence of anhydrous CsF does not alter the yield appreciably

$$NF_2CFO + CF_3OF \xrightarrow[\text{Pyrex}]{25°} NF_2OCF_3 + COF_2$$

Difluoraminocarbonyl fluoride reacts very slowly with Al_2Cl_6 at room temperature, but the rate of reaction is greatly increased by the presence of equivalent amounts of anhydrous HCl, whereupon the NF_2CFO is completely consumed within a matter of hours. The disappearance of HCl and the formation of Cl_2 and difluoraminocarbonyl chloride, $NF_2C(O)Cl$, suggest that the two major reactions occur simultaneously.

$$NF_2CFO + Al_2Cl_6\ (xs) \xrightarrow[\text{HCl}]{25°} NF_2C(O)Cl + (\text{solid}) \qquad 75\%$$

$$NF_2CFO + Al_2Cl_6\ (xs) + HCl \xrightarrow{25°} 2Cl_2 + (\text{solid}) \qquad 25\%$$

Side reactions usually lead to the formation of small amounts of SiF_4, COF_2, CClF, and occasionally $COCl_2$. The solid phase has not been characterized, but is generally suitable for subsequent preparation of more $NF_2C(O)Cl$.

---

[13] G. W. Fraser and J. M. Shreeve, Chem. Commun., 532 (1966).

Difluoraminocarbonyl fluoride is completely consumed [illegible] with Al_2Br_6 at room temperature, the only major volatile product being Br_2. The solid product has not been characterized other than to note that it has some tendency to absorb HBr at room temperature. If the reaction is repeated in the presence of two equivalents of HBr, all gases are completely consumed with liberation of nearly the theoretical amount of Br_2. The pink, translucent residue from this reaction has little tendency to absorb more HBr and releases NH_3 upon basic hydrolysis, but has not been otherwise characterized.

$$NF_2CFO + Al_2Br_6\ (xs) \xrightarrow[12\ hr.]{25^\circ} 1.3\ Br_2 + (solid)$$

$$NF_2CFO + Al_2Br_6\ (xs) + 2HBr \xrightarrow[19\ hr.]{25^\circ} 2Br_2 + (solid)$$

Similar reactions at low temperatures lead to the formation of significant amounts of $COBr_2$ along with the Br_2, but under no conditions has there been found evidence of difluoraminocarbonyl bromide, $NF_2C(O)Br$.

First attempts to prepare the adducts $KOCF_2NF_2$ and $CsOCF_2NF_2$ by reactions of anhydrous KF or CsF with equivalents or excesses of NF_2CFO led to little or no reaction at room temperature without solvent, to attack on the solvent in acetonitrile solutions at room temperature, and to partial degradation of the gas to COF_2 in acetonitrile solutions at -40°. If the KF is pretreated with hexafluoroacetone, $(CF_3)_2CO$, however, with the formation and subsequent thermal decomposition of the adduct $KOCF(CF_3)_2$ as outlined below, it will rapidly absorb gaseous NF_2CFO at room temperature or 0° to form a non-volatile product stable in vacuum which releases the NF_2CFO semiquantitatively upon warming. The product appears to be the simple salt $K^+OCF_2NF_2^-$.

$$KF + (CF_3)_2CO\ (xs) \xrightarrow[CH_3CN]{25^\circ} KOCF(CF_3)_2 \xrightarrow{95^\circ} KF + (CF_3)_2CO$$

$$KF + NF_2CFO\ (xs) \xrightarrow[\text{no solvent}]{0^\circ \text{ or } 25^\circ} KOCF_2NF_2 \quad (65\text{-}90\%)$$

$$KOCF_2NF_2 \xrightarrow{80\text{-}100^\circ} KF + NF_2CFO \quad (+ COF_2 + N_2F_2)$$

An analogous reaction with pretreated CsF and NF_2CFO led to partial degradation of the gas to COF_2, and little or no $CsOCF_2NF_2$ was believed to have formed. A solid product insoluble in acetonitrile, thermally stable, and strongly oxidizing, and which may be $CsOCF_2NF_2$, was observed in semi-stoichiometric reaction of the type:

$$CsF + CF_3CFO \xrightarrow[CH_3CN]{25^\circ} CsOC_2F_5$$

$$CsOC_2F_5 + NF_2CFO \xrightarrow[CH_3CN]{-40^\circ} CF_3CFO + \underline{CsOCF_2NF_2}\ (?)$$

The salt $KOCF_2NF_2$ is chemically reactive but has been found to have little synthetic value. Fluorination might be expected to lead to the unreported difluoro(difluoramino)methyl hypofluorite, NF_2CF_2OF, but under all conditions examined leads only to CF_3OF and NF_3. Similarly, chlorination of $KOCF_2NF_2$ in the presence of KF yields chlorodifluoramine, NF_2Cl, in 66% yield, a reaction which has some synthetic interest. The reaction of $KOCF_2NF_2$ with Br_2 yields tetrafluorohydrazine, N_2F_4, instead of the unreported bromodifluoramine, NF_2Br.

$$KOCF_2NF_2 + 2F_2 \xrightarrow{-184^\circ} KF + CF_3OF + NF_3$$

$$KOCF_2NF_2 + KF + Cl_2 \xrightarrow[CH_3CN]{-40^\circ} KCl + NF_2Cl + KOCF_3$$

$$2KOCF_2NF_2 + 2KF + Br_2 \xrightarrow[CH_3CN]{-40^\circ} 2KBr + N_2F_4 + 2KOCF_3$$

Granular anhydrous KF or untreated KF reacts (slowly or rapidly, respectively) with two equivalents of NF_2CFO in acetonitrile solution at -40°, and the salt $KOCF_2NF_2$ reacts rapidly with one equivalent of NF_2CFO under the same conditions. In any case the reaction is usually semi-stoichiometric. From synthetic data the non-volatile product appears to be approximately OCN_2F_5 and is believed to be primarily the salt $K^+OCF(NF_2)_2^-$

$$KF + 2NF_2CFO \xrightarrow[CH_3CN]{-40°} COF_2 + KOCN_2F_5$$

$$KOCF_2NF_2 + NF_2CFO \xrightarrow[CH_3CN]{-40°} COF_2 + KOCN_2F_5$$

The solute ($KOCN_2F_5$) from either of these reactions will react with more NF_2CFO with partial conversion of the gas to COF_2. An equilibrium reaction is indicated, for if the solute is treated several times with NF_2CFO in succession, synthetic data indicate that the nitrogen to carbon and potassium ratio approaches but does not rise significantly above 3:1:1, and the reaction is readily reversible with partial conversion of pure COF_2 to NF_2CFO.

$$KOCN_2F_5 + NF_2CFO \xrightleftharpoons{CH_3CN,\ -40°} COF_2 + KOCN_3F_6 \quad (1)$$

The final product has the approximate empirical formula $KOCN_3F_6$ and is believed to be primarily the salt $K^+OC(NF_2)_3^-$. A cursory examination of the reactions of anhydrous CsF with excess NF_2CFO under the same conditions indicated that the formation of (apparently) $CsOCN_2F_5$ and $CsOCN_3F_6$ is completely analogous.

The postulated salts $M^+OCF_2NF_2^-$, $M^+OCF(NF_2)_2^-$, and $M^+OC(NF_2)_3^-$, where M^+ is K^+ or Cs^+, are all hydrolytically and at least in part thermally unstable, sometimes explosively so. None have been isolated pure, and analytical and spectral data on them are unavailable.

Small samples (less than 0.5 mmole) of $KOCF_2NF_2$ have always decomposed smoothly to KF and NF_2CFO upon heating, but solid samples of (approximately) $KOCN_2F_5$ (0.3 mmole or less) explode violently when heated to 70°, and slow decomposition at lower temperatures does not yield appreciable amounts of perfluorourea, $(NF_2)_2CO$. If, however, the sample of $KOCN_2F_5$ is sufficiently impure with $KOCF_2NF_2$ (the recommended molar ratio of $KOCN_2F_5$ to $KOCF_2NF_2$ being no higher than 1:1), it may usually be decomposed at 95° without exploding. Characterization of the gas mixture thus liberated indicates that approximately 25% of the $KOCN_2F_5$ decomposes to $(NF_2)_2CO$ and KF, while the remainder yields COF_2, N_2F_2, and probably NF_2CFO. The absence of tetrafluorohydrazine, N_2F_4, in this gas mixture indicates that the $(NF_2)_2CO$ probably does not arise from radical recombination, e.g., $NF_2\cdot + \cdot C(O)NF_2$.

$$KOC[illegible]F_5 \xrightarrow{[illegible]°} KF + (NF_2)_2CO$$

Fluorine-19 nuclear magnetic resonance spectra of pure NF_2CFO, $NF_2C(O)Cl$, and $(NF_2)_2CO$, with external CCl_3F reference, were run in sequence under identical conditions. The chemical shifts of the signals assigned to the NF_2 fluorine nuclei were -28.7, -40.4, and -30.8 p.p.m., respectively. Internally referenced NF_2CFO shows the corresponding signal at ϕ^*-33.1. Banks, _et al._,[14] report for N,N-difluorourea, $NF_2C(O)NH_2$, ϕ^* _ca._ -33; Freeman[15] reports for N,N-difluoroacetamide, $NF_2C(O)CH_3$, ϕ^* _ca._ -30; and Koshar, _et al._,[16] report for bis(difluoramino)difluoromethane, $(NF_2)_2CF_2$, ϕ^*-19.0. It is interesting to note that all reported compounds containing the $NF_2C(O)$- structure show the NF_2 resonance in the narrow range of ϕ^* _ca._ -30 to -40.

Experimental Section

Starting Materials.--The preparation and purification of difluoraminocarbonyl fluoride has already been described.[2] Hexafluoroacetone (Pierce Chemical Co.) and anhydrous hydrogen bromide (Matheson Co., Inc.) were used

---

[14] R. E. Banks, R. N. Haszeldine, and J. P. Lalu, J. Chem. Soc., _C_, 1514 (1966).

[15] J. P. Freeman, Advances in Chemistry Series, No. 3 , American Chemical Society, Washington, D. C., 1962, p. 129.

[16] R. J. Koshar, D. R and R. A. Meiklejohn, J. Org. Chem., _31_, 4232 (1966).

without purification. Anhydrous hydrogen chloride was prepared from concentrated sulfuric acid and sodium chloride and was dried by fractional condensation at -80°. Anhydrous aluminum chloride (J. T. Baker Chemical Co.) and anhydrous aluminum bromide (Fisher Scientific Co.) were purified as needed by sealing the desired amount into a sidearm on the reaction bulb, subliming the volatile material into the bulb under dynamic vacuum, and sealing off and removing the nonvolatile residue in the sidearm. Fisher certified reagent acetonitrile was used without purification except to store it at autogenous pressure over calcium hydride (Metal Hydrides, Inc.) at room temperature in a vessel from which it could be taken as needed directly into the vacuum system. Cesium fluoride (anhydrous, 99%, K and K Laboratories) and potassium fluoride (anhydrous granular reagent, Allied Chemical) were dehydrated as needed by stirring in a porcelain crucible over a flame and immediately transferring while hot the desired amount into the clean, tared reaction bulb for weighing. Carbonyl fluoride was prepared from carbon monoxide (Matheson Co., Inc.) and fluorine (Allied Chemical) and was purified by fractional codistillation.[17] It was not completely free of carbon dioxide. Trifluoroacetyl fluoride was prepared by reacting trifluoroacetyl chloride (K and K Laboratories) with an excess of anhydrous cesium fluoride in acetonitrile solution at room temperature. The CF_3CFO was liberated by the decomposition of its adduct, $CsOC_2F_5$, at 95° after evaporation of the solvent, and no purification was necessary. Trifluoromethyl hypofluorite was obtained from Dr. Claude Merrill (Dow Chemical Co.) was was purified by filtration at -184°.

General Procedure.-- Most reactions were run in 25- or 50-ml. Pyrex bulbs which were fitted with a stopcock by means of 14/20 ₷ ground joints. Gases and volatile liquids were handled in conventional glass vacuum apparatus under conditions of high vacuum. A Kel-F oil (Grade KF-3,

---

[17] G. H. Cady and D. P. Siegwarth, Anal. Chem., 31, 618 (1959).

Minnesota Mining and Manufacturing Co.) null-point pressure transducer was used in handling gases highly corrosive to mercury. Gaseous starting materials and purified products were weighed and/or measured quantitatively by P-V-T data. Except where noted, all acetonitrile solutions with nitrogen-fluorine solutes were kept at -35° ± 5° to prevent attack on the solvent. Reactions involving such solutions were worked up by pumping out the gas at -40° through a series of traps at -80° and -184°. Part or all of the solvent was then removed by warming the reaction bulb to 0° while pumping through the traps. For a continuing reaction sequence in solution, the solvent (-80° trap) was then returned to the reaction bulb while the gas (-184° trap) was freed of any remaining solvent by fractional condensation at -80° prior to quantitative measurement. When necessary, gaseous products were separated by fractional codistillation[17] using an unpacked 12-ft., 1/8-in. o.d. aluminum fractionating column coiled to fit into a half-pint Dewar flask.

Infrared spectra (5000-625 cm.$^{-1}$, 3-min. scan) of NF_2CFO, $NF_2C(O)Cl$ and $(NF_2)_2CO$ were obtained on a Beckman IR5A spectrophotometer using a gas cell with NaCl windows and a path length of 50 mm. High-resolution F^{19} nuclear magnetic resonance spectra of these three compounds were taken at room temperature using a modified Varian DP-60 spectrometer (56.4 Mc./sec.) by sealing the pure liquids in capillaries (ca. 1.5 mm. o.d.) which were floated in the external reference, CCl_3F, in standard 5-mm. tubes.

Caution!--Nitrogen-fluorine-containing materials are strong oxidizing agents and in the presence of acetonitrile constitute potential safety hazards. Handling and freezing of such mixtures must always be done with adequate precautions. Solids (e.g., salts) which contain or may contain nitrogen-fluorine groups, or the non-volatile residues from chemical decomposition of such solids, must never be heated indiscriminately, for many have been found to be highly explosive. All pyrolyses must have adequate shielding, and disposal of such solids may be accomplished behind a shield with wet acetonitrile followed with water.

Spectra of NF_2CFO.--The infrared spectrum (10 mm. pressure) is, in cm.$^{-1}$: 1900 (s); 1210 (s); 1035 (m); 960 (m); 835 (w), triplet; 765 (m), triplet. The F^{19} nmr spectrum, referenced externally with CCl_3 , shows: -26.7 p.p.m. (NF_2, broad and unresolved); and +15.1 p.p.m. (CFO, sharp 1:2:1 triplet, J = 19 c.p.s.). The peak area ratio is approximately 3:1. The F^{19} nmr spectrum, referenced internally with CCl_3F solvent, shows (ϕ^*) resonances at -33.1 and + 11.5, but otherwise identical. These data differ slightly from those originally published.[2]

Preparation of NF_2OCF_3.-- To a clean 250-ml. Pyrex reaction bulb were added 0.41 mmole NF_2CFO and 0.41 mmole CF_3OF. After 3 hr. at room temperature the gaseous products (1.00 mmole) were approximately COF_2, NO_2, N_2O_3, SiF_4, and NF_2OCF_3, and considerable white solid (fluorosilicates?) had formed in the bulb. The gaseous products were shaken for a few minutes at room temperature with moist soda-lime pellets to remove acidic gases. Yield of NF_2OCF_3, after drying by fractional condensation at -30°, 0.156 mmole, 38%. It was identified by infrared spectrum, boiling point (-63°), and gas density molecular weight.[3,4]

Preparation of $NF_2C(O)Cl$.--Approximately 1 g. Al_2Cl_6 was sublimed into a 50-ml. Pyrex reaction bulb, and HCl (0.67 mmole) and NF_2CFO (0.70 mmole) were added. After 8 hr. at room temperature, the gaseous products were separated by fractional codistillation. The major components were HCl, Cl_2, and $NF_2C(O)Cl$. [In some preparations, lesser amounts of FC(O)Cl and NF_2CFO were also found. Reaction times of 24 hr. often resulted in the formation of $COCl_2$, which could not be separated from the $NF_2C(O)Cl$.]

Yield: 0.533 mmole (PVT) $NF_2C(O)Cl$, 61.8 mg., m.w. = 116 [calc. for [illegible], [illegible] hr.], [illegible] based on NF_2CFO.

The infrared spectrum (25 mm. pressure) of $NF_2C(O)Cl$ is, in cm.$^{-1}$: 1840 (s); 1300 (ms); 1073 (m); 946 (s); 905 (vs); 770-755 (w), doublet; 645-635 (m), doublet. The F^{19} nmr spectrum shows a single, broad resonance at -40.4 p.p.m. Experimental vapor pressure data are as follows [T (°K), P (mm.)]: 189, 6; 203, 19; 222, 70; 234, 142. These data suggest a Clausius-Clapeyron curve given by: $\log_{10} P \text{ (mm.)} = -1350\, T^{-1} + 7.92$. The extrapolated normal boiling point is -5° C. The corresponding enthalpy of vaporization is 6.17 kcal. mole^{-1}; the entropy of vaporization (-5°C.) is 23.0 e.u. When gaseous $NF_2C(O)Cl$ was held over water at 0°, its infrared bands disappeared from the vapor phase within a matter of minutes with the formation of the well-known absorption bands of HNF_2 and CO_2. The resulting solution gave positive tests for Cl^- and F^-. 10.0 mg. $NF_2C(O)Cl$ was hydrolyzed in acidified aqueous KI solution for 1 hr. at room temperature. Found: 0.0360 oxidizing equivalents (as I_3^-) per gram, calc. for $NF_2C(O)Cl$, 0.0346. At room temperature, $NF_2C(O)Cl$ attacks mercury slowly to form NF_2CFO as the primary volatile product, is stable in Pyrex, and does not react with N_2F_4 or NF_2Cl. Ultraviolet irradiation with N_2F_4 through a Pyrex filter results in slow degradation to FCOCl.

Attempted Bromination of NF_2CFO.--Approximately 1 g. Al_2Br_6 was sublimed into a 50-ml. Pyrex reaction bulb, and HBr (0.58 mmole) and NF_2CFO (0.32 mmole) were added. The color of Br_2 started to develop immediately upon warming. After 19 hr. at room temperature, the volatile material was removed by pumping (1μ) for 10 hr. at room temperature through a U-trap cooled to -134°. Found: 0.02 mmole not condensable at -80° (CO_2 and SiF_4), and 0.101 g. (0.63 mmole) Br_2 containing a trace of $COBr_2$, which was identified by infrared spectrum.[13] The pinkish, translucent residue in the bulb, upon treatment with 0.30 mmole HBr for 38 hr. at room temperature, absorbed 0.04 mmole. It was not characterized.

Pretreatment of KF.--In most reactions a clean, dry 50-ml. Pyrex bulb and 14/20 ₮ stopper were tared and the desired amount of granular dehydrated KF was added and weighed in air. The stopper was then replaced by a stopcock and the KF was re-dehydrated by flaming out under dynamic vacuum. Anhydrous CH_3CN and a molar excess of $(CF_3)_2CO$ were condensed into the bulb. After the KF had completely dissolved (about 8 hr. at room temperature with occasional swirling), all volatile materials were pumped out rapidly at about 50° and the deposited KF was then pumped on for at least 5 min. at 95°. The solvent and $(CF_3)_2CO$ were recovered essentially unchanged and were separable by fractional condensation at -80°. Typically, 21.0 mg. (0.361 mmole) KF, when treated with 0.80 g. CH_3CN and 0.23 g. (1.4 mmole) $(CF_3)_2CO$ for 13 hr., gained 0.4 mg. in weight.

Preparation of $KOCF_2CF_2H$.--The apparatus was a 50-ml. Pyrex bulb with a 1.25-mm. Teflon needle valve (Fischer and Porter Co.) and a small open sidearm. The apparatus was tared, hot dehydrated KF was added through the sidearm, and the latter was pulled off to seal the bulb. Reweighing indicated that 21.0 mg. (0.36 mmole) KF had been added. After pretreatment of the KF with $(CF_3)_2CO$, the apparatus was reweighed and was found to have gained 0.4 mg. HCF_2CFO [52.6 mg., 0.533 mmole (PVT), m.w. = 98.7] was condensed in and allowed to react with the KF (without solvent) for 23.5 hr. at 0°. After removal of unreacted gas [0.23 mmole, m.w. = 97, infrared analysis

---

[13] B. Schneider and J. Štokr, Collection Czech. Chem. Commun., 26, 1221 (1961).

indicated NF_2CFO with a trace of COF_2. Frequently traces of $(CF_3)_2CO$ are also found at this stage.], the apparatus was reweighed. The KF gained [illegible] weight. This solid product was decomposed by heating the bulb to [illegible]° with a water bath (<u>behind a shield!</u>) for 5 min. while pumping the liberated gas through a U-trap cooled to -184°. Reweighing indicated that the solid lost 31.2 mg. during pyrolysis. The liberated gas (0.32 mmole, m.w. = 98) was identified by infrared analysis as NF_2CFO with traces of COF_2 and N_2F_2. These data indicate the formation of 0.31 mmole $KOCF_2NF_2$ (86% conversion of the KF).

$KOCF_2NF_2$ is stable for at least short times under static vacuum at room temperature, but NF_2CFO is rapidly pumped off at 60°. Samples of 0.5 mmole or less have never exploded upon heating. $KOCF_2NF_2$ is immediately hydrolyzed by water to CO_2, HNF_2, H_2F_2, etc. and liberates I_3^- from aqueous solutions of KI. It is highly soluble in acetonitrile at -40°, but such a solution is not stable at room temperature. As a solid at temperatures as low as -184° or in acetonitrile solution at -40°, $KOCF_2NF_2$ is decomposed by F_2 to CF_3OF and NF_3. In acetonitrile solution it yields NF_2Cl or N_2F_4 in good yield when allowed to react with an equivalent of Cl_2 or Br_2, resp. $KOCF_2NF_2$ as a solid at room temperature or in acetonitrile solution at -40° is decomposed by CF_3OF to yield CF_3ONF_2 or NF_3, resp. An acetonitrile solution of $KOCF_2NF_2$ is decomposed by $CF_3C(O)Cl$ at -40° liberating CF_3CFO and NF_2CFO with the precipitation of KCl, or is slowly decomposed by NF_2Cl at room temperature to KCl, N_2F_4, and COF_2.

<u>Preparation of NF_2Cl</u>.--Approximately 0.1 g. dehydrated KF was pretreated with $(CF_3)_2CO$ according to the procedure already described and then allowed to react with 0.92 mmole NF_2CFO at 0° until the gas was absorbed. Approximately 0.5 ml. anhydrous CH_3CN was condensed in, the $KOCF_2NF_2$ was dissolved at -40°,

and 0.[illegible] mmole Cl_2 was frozen onto the solution. After reacting 0.5 hr. at -40°, the residual gas [7[illegible] mg., 0.91 mmole (PVT), m.w. = 86, Cl_2 and NF_2Cl] was removed and separated by fractional codistillation. Yield of NF_2Cl: 0.62 mmole (68%), identified by gas density molecular weight, reactivity to mercury, and infrared spectrum.[19] After 7 hr. at room temperature, the solution in the reaction bulb was evaporated to dryness and 0.14 mmole COF_2 was recovered. The solid residue was not characterized.

$KOCN_2F_5$.--Material of this approximate empirical formula, two preparations of which are given below, may be isolated as a white solid by evaporating its acetonitrile solution at 0° and pumping off the remaining solvent for 1-2 min. at 40°. It is highly soluble in acetonitrile, solutions of which are indefinitely stable at -40° but slowly liberate N_2F_2, etc., with attack on the solvent at room temperature. An acetonitrile solution of $KOCN_2F_5$, when treated with $SiCl_4$ at -40°, liberates NF_2Cl, $NF_2C(O)Cl$, etc., with the precipitation of KCl. Solid $KOCN_2F_5$ slowly decomposes at room temperature to at least NF_2CFO, COF_2, and N_2F_2 and hydrolyzes violently or explosively when placed in water. Most samples explode violently when heated to 70°, but occasionally one will decompose quietly to $(NF_2)_2CO$ (in part) and KF.

Preparation of $KOCN_2F_5$ from Pretreated KF.--The apparatus was similar to that already described for the preparation of $KOCF_2NF_2$. 25.8 mg. (0.44 mmole) KF was pretreated with $(CF_3)_2CO$ and then converted (96%) to $KOCF_2NF_2$ according to the procedures already described. After pyrolysis of the latter to KF, reweighing indicated that the KF was lighter by 0.4 mg. prior to the formation $KOCF(CF_3)_2$. The KF was then treated with NF_2CFO [87.4 mg., 0.880 mmole (PVT), m.w. = 99.3] and 372.3 mg. anhydrous CH_3CN

---

[19] See note 12 (b), p. 113.)

for 51.5 hr. at -35° ± 5°. The residual gas was removed at -40° (20 min.) and the solvent was pumped off at 0° (15 min.). After separation were recovered 362.6 mg. CH_3CN and 33.8 mg. gas [0.477 mmole (PVT), m.w. = 70.9]. The latter was identified by infrared analysis as COF_2 containing a small amount of unreacted NF_2CFO, and on the basis of its molecular weight was estimated to be 0.41 mmole (27 mg.) COF_2 and 0.07 mmole (7 mg.) NF_2CFO. Thus the gas had decreased in mass by 53.6 mg. during reaction and 0.7 mg. CH_3CN were not recovered. By direct weighing of the residue (partially crystallized to a white solid) in the apparatus, the KF had gained in weight by 65.5 mg. From the observed composition of the residual gas in the reaction, the composition of the solid product appeared to be (element, mmole): K, 0.44; O, 0.40; C, 0.40; N, 0.81; F, 2.05; and 0.24 mmole CH_3CN; corresponding to the empirical formula $K_{1.1}O_{1.0}C_{1.0}N_{2.0}F_{5.1}$. This $KOCN_2F_5$ readily dissolved in a small amount of CH_3CN at 0°. About 0.5 ml. H_2O was frozen onto the solution and upon warming to room temperature, no visible reaction occurred. (Previous experiments showed that solid $KOCN_2F_5$ hydrolyzes violently or explosively in water to HNF_2, N_2F_2, CO_2, etc.). All volatile material in the reaction bulb was then transferred <u>in vacuo</u> to a bulb containing acidified aqueous KI solution, and the I_3^- liberated at room temperature was titrated with standard thiosulfate solution. Found: 3.01 mequiv. [Calc. for 0.44 mmole $KOCN_2F_5$, 3.52 mequiv.; calc. for 0.40 mmole $KOCN_2F_5$, 3.20 mequiv.].

<u>Preparation of $KOCN_2F_5$ from untreated KF</u>.--In a 25-ml. reaction bulb 15.3 mg. (0.26 mmole) dehydrated granular KF was weighed out and treated with 0.52 mmole (PVT) NF_2CFO and 421.5 mg. anhydrous CH_3CN for 26 hr. at -35° ± 5°, by which time the KF had completely dissolved. The residual gas was removed, measured, and returned to the reaction. After an additional 21 hr. it was again removed and measured, and there was found no appreciable

change in its quantity or composition (0.30 mmole, COF_2 with a small amount of unreacted NF_2CFO). The solvent was pumped off for 20 min at -35°, and all but 28 mg. was recoverd. After sitting 30 min. at room temperature, the solid product in the reaction bulb released 21 mg. CH_3CN and 0.02 mmole gas (COF_2, N_2F_2, and NF_2CFO). An additional 25 hr. at room temperature released 0.035 mmole gas of similar composition, and 0.015 mmole gas was pumped off when the solid was then warmed to 60° for a few minutes. In a few minutes at 75° the solid released ca. 3 mg. CH_3CN and 0.20 mmole gas [COF_2, N_2F_2, NF_2CFO, and $(NF_2)_2CO$], and subsequent heating to 95° liberated 0.08 mmole gas of similar composition.

Preparation of $KOCN_3F_6$(?).--In a typical reaction 42.3 mg. (0.73 mmole) KF was pretreated with $(CF_3)_2CO$ according to the procedure already described and was then treated with 0.79 mmole NF_2CFO at 0° for 12.5 hr. Characterization of the residual gas indicated the formation of 0.65 mmole $KOCF_2NF_2$ (89% conversion). This product was treated in situ with 1.58 mmole NF_2CFO and 756.3 mg. anhydrous CH_3CN for 52 hr. at -35° ± 5°. The residual gas in the system, after 28 and 52 hr., respectively, was: 119 mg., 1.53 mmole, m.w. = 77.8; 118 mg., 1.54 mmole, m.w. = 76.6. On the basis of molecular weight, this gas mixture was estimated to be 1.03 mmole (68 mg.) COF_2 and 0.51 mmole (50 mg.) NF_2CFO; this was qualitatively confirmed by infrared analysis. Consequently the solute (which was not isolated) has the apparent composition (element, mmole): K, 0.73; O, 0.69; C, 0.69; N, 1.72; F, 3.83; corresponding to the empirical formula $K_{1.1}O_{1.0}C_{1.0}N_{2.5}F_{5.6}$. These data are consistent with the assumption that the solute is 0.4 mmole $KOCN_2F_5$ and 0.3 mmole $KOCN_3F_6$.

When this solution was treated with 0.9 mmole NF_2CFO for 24 hr., the residual gas was found to be 0.3 mmole COF_2 and 0.5 mmole NF_2CFO. Treatment of the resulting solution with 0.9 mmole COF_2 for 23 hr. yielded 0.7 mmole COF_2 and 0.3 mmole NF_2CFO, and subsequent treatment of the solution with 0.8 mmole NF_2CFO for 72 hr. yielded 0.3 mmole COF_2 and 0.5 mmole NF_2CFO. These values are approximate and were determined by fractional codistillation of the residual gas. This solution of (approximately) $KOCN_3F_6$ was then treated with 1.48 mmole CF_3CFO for 25.5 hr. at -35° ± 5°. The residual gas, after separation by fractional codistillation, was 1.47 mmole pure CF_3CFO.

$KOCN_3F_6$ is deposited as a white solid by evaporation of its acetonitrile solution. It is highly soluble in acetonitrile at -40° and neither the solid nor solution are stable at room temperature. Its chemistry has not been studied other than to note that in acetonitrile solution at -40° it reacts rapidly with Cl_2 and liberates NF_2Cl, NF_2CFO, $NF_2C(O)Cl$, and probably $(NF_2)_2CO$, although the latter could not be isolated from the gas mixture for positive identification.

Preparation of $(NF_2)_2CO$.--In a 50-ml. Pyrex reaction bulb 20.0 mg. KF (0.34 mmole) was pretreated with $(CF_3)_2CO$ according to the procedure already described. It was then treated with 0.39 mmole NF_2CFO at 0° (no solvent) for 13 hr. and the residual gas, 0.08 mmole [essentially $(CF_3)_2CO$

and COF_2], was removed. [illegible] mmole NF_2CFO and about 1.2 ml. anhydrous CH_3CN were condensed onto the solid ($KOCF_2NF_2$) and the reaction was kept at -40° for 2 hr. The residual gas (after removal from CH_3CN, 0.16 mmole [illegible]) was pumped off at -40° and the solvent was pumped off at 0° (ca. 10 min.). The residue in the bulb was pumped on for 2 min. at 40°, whereupon it crystallized to a white solid and liberated 0.02 mmole of gas (NF_2CFO and COF_2) and 0.13 mmole CH_3CN. The solid was then pyrolyzed by heating the bulb to 95° with a water bath for 2-3 min. while pumping the liberated gases through a U-trap cooled with liquid nitrogen. (Caution! Adequate shielding is necessary, as such a solid occasionally explodes violently when heated). The trap was then warmed to -80° and volatile material was distilled out into a storage tube, leaving 0.09 mmole CH_3CN.

The residual KF in the bulb was then used directly for several subsequent one-step preparations. Typically, 0.50-0.55 mmole NF_2CFO and 0.5 ml. CH_3CN were condensed in, and after a reaction time of 3-5 hr. at -40° the product was worked up and pyrolyzed exactly as described above. Pretreatment of the KF with $(CF_3)_2CO$ and preliminary formation of $KOCF_2NF_2$ [to insure adequate removal of residual $(CF_3)_2CO$ from the system] was used only for "new" KF.

The gas mixtures from two or three pyrolyses were combined for separation by fractional codistillation. Generally, first a small sample of NF_2CFO was put through the apparatus to dry the column, etc. The gaseous products from a typical pyrolysis were: 0.15 mmole low-boiling fraction (primarily cis-N_2F_2, COF_2, and CO_2); 0.17 mmole NF_2CFO; a trace of HNF_2; and 0.05 mmole $(NF_2)_2CO$. Based on the estimated content of $KOCF(NF_2)_2$ in the solid, the yield of $(NF_2)_2CO$ appeared to be 25-30%.

The infrared spectrum (20 mm. pressure) of $(NF_2)_2CO$ is, in cm.$^{-1}$. 1860 (s); 1150 (m); 970 (s); 926 (vs); 885 (m); 848 (m), doublet; 720 ([illegible]), broad. The F^{19} nmr spectrum shows a single, broad resonance at -30.8

[illegible] The gas density molecular weight was 131 ± 1 (calc. 132). Infrared analysis indicated that the gas reacts instantly with water vapor at room temperature to form only CO_2 and HNF_2. 13.4 mg. $(NF_2)_2CO$ was hydrolyzed in acidified aqueous KI solution at room temperature. Found: 0.0592 oxidizing equivalents (as I_3^-) per gram, calc. for $(NF_2)_2CO$, 0.0606. The pure compound forms a cracked glass at -196° and boils near -20° (estimated by fractional codistillation^{17}). It may be handled in conventional glass vacuum apparatus and does not attack mercury at room temperature.

Preparation of $CsOCF_2NF_2$(?).--60.0 mg. (0.39 mmole) dehydrated CsF was allowed to react with 0.64 mmole CF_3CFO and 1.85 g. CH_3CN at room temperature for 24 hr. The unreacted gas was 0.30 mmole CF_3CFO, indicating the formation of 0.34 mmole $CsOC_2F_5$. 0.39 mmole NF_2CFO was frozen onto this solution, and after reacting 25 hr. at -40°, the solvent was pumped off completely at -25°. The gas recovered from the reaction (0.40 mmole), after separation by fractional codistillation, was found to be 0.11 mmole of (essentially) COF_2 and 0.27 mmole CF_3CFO. The solid product was slowly heated to 100° while pumping but liberated only micromolar amounts of COF_2, N_2F_2, CF_3CFO, and CH_3CN. It was apparently insoluble in CH_3CN and liberated considerable I_3^- from aqueous KI solution.

Reaction of NF_2CFO with CsF.--64.3 mg. (0.42 mmole) dehydrated CsF was allowed to react with NF_2CFO [106.7 mg., 1.09 mmole (PVT), m.w. = 97.9] and 291.2 mg. anhydrous CH_3CN. After 4 hr. at -40° the CsF had completely dissolved and after 5.5 hr. the gas was removed. On the basis of infrared analysis and molecular weight [46.4 mg., 0.639 mmole (PVT), m.w. = 72.6] it was found to be approximately 0.51 mmole (34 mg.) COF_2 and 0.13 mmole (13 mg.) NF_2CFO. Consequently the composition of the non-volatile solute appeared to be (element, mmole): Cs, 0.42; O, 0.44; C, 0.44; F, 0.95;

F, 2.25; corresponding to the empirical formula $Cs_{1.0}O_{1.0}C_{1.0}H_{2.[illegible]}F_{[illegible]}$. After this solution was treated with 0.66 mmole (PVT) HF_2CFO for 20 hr. at -40°, the residual gas was separated and found to be a mixture of COF_2 and HF_2CFO [33.1 mg., 0.390 mmole (PVT), m.w. = 84.9] and was estimated to be 0.17 mmole (11 mg.) COF_2 and 0.22 mmole (22mg.) HF_2CFO. The net reaction to this point was therefore the consumption of 1.09 mmole HF_2CFO by 0.42 mmole CsF with the formation of 0.67 mmole COF_2. Consequently the composition of the solute now appeared to be (element, mmole): Cs, 0.42; O, 0.42; C, 0.42; H, 1.09; F, 2.35; corresponding to the empirical formula $Cs_{1.0}O_{1.0}C_{1.0}H_{2.6}F_{5.6}$.

Acknowledgments.--This work was supported in part by the Advanced Research Projects Agency through a contract monitored by the Office of Naval Research. G.W.F. was a National Science Foundation predoctoral fellow during 1965-67. The authors wish to thank Mr. B. J. Nist of the University of Washington for some of the nuclear magnetic resonance spectra.

A SIMPLE METHOD FOR THE PREPARATION OF NITROSYL FLUORIDE

by Charles T. Ratcliffe and Jean'ne M. Shreeve

(Department of Physical Sciences, University of Idaho, Moscow, Idaho 83843)

An easy, straight-forward method for the synthesis of nitrosyl fluoride has been discovered which requires only simple laboratory entities compared to more difficult methods previously reported.[1]

The preparation consists of the reaction of nitrogen dioxide with either KF or CsF to give essentially pure ONF as the only volatile product. The solid residue remaining is the alkali metal nitrate. The reaction proceeds smoothly at room temperature in either a Pyrex glass or metal reaction vessel. Temporary storage of the product in the reaction vessel without noticeable decomposition is possible.

In a typical run, 5 g. (33 mmoles) of 99% CsF was dried at 300° for two hours, powdered under vacuum conditions, and placed in a 150 ml. prefluorinated Monel vessel. 2.85 mmoles of NO_2 were condensed into the vessel at -78° and allowed to warm to ambient temperature. The volatile material was removed after 5 days and found to contain 1.37 mmoles of nitrosyl fluoride as the only gaseous product. The reaction time varied from one to five days in several runs and is dependent on the particle size and anhydrous nature of the salt.

The rate of preparation of ONF can be enhanced by allowing the reaction to occur in a prefluorinated metal vessel above 90°. 2.47 mmoles of NO_2 and an excess of KF were heated to 90° for 2.5 hours. Total reaction had occurred and 1.19 mmoles of ONF were recovered corresponding to 48.2% conversion based on the NO_2 added. At 300° the reaction occurred within 15 minutes with a slightly lower yield of ONF. Both metal fluorides react to give only ONF in about the same yield.

Identification of the volatile product was carried out by molecular weight determination and infrared spectra.[2] Gravimetric determination and x-ray powder pattern analysis were used to identify the solid residue as the alkali metal nitrate.

The reaction can be carried out in all Pyrex equipment with similar experimental results as listed above. Storage of the ONF in a Pyrex bulb over CsF was found satisfactory for at least a week with no SiF_4 observed in any of the preparations of the product.

The reactivity of CsF and KF has been found to be greatly enhanced by first forming the hexafluoracetone adduct of the metal fluoride in acetonitrile solution.[3] The compound $MF \cdot OC_3F_6$ can then be decomposed by removing the solvent and hexafluoracetone at 100° under dynamic vacuum.

When mmole samples of NO_2 were condensed on the salt at -78°, the reaction was found to go to completion upon warming to room temperature with quantitative yields of ONF as the only volatile product. It was found that the metal fluoride must be present in excess to allow complete reaction to occur, and attempts to react NO_2 and CsF in stoichiometric amounts gave a mixture of NO_2 and ONF.

If excess hexafluoroacetone is added to CsF in acetonitrile to give a clear solution and the solvent is removed under vacuum at room temperature, the salt, $CsFOC_3F_6$ is found to be stable. Addition of NO_2 to the latter causes an immediate reaction to occur giving $CF(CF_3)_2ONO$ as the major product with ONF present in only minor amounts.[4]

Based on the above evidence the reaction appears to proceed according to

$$2NO_2 + MF \rightarrow ONF + MNO_3$$

$$M = K \text{ or } Cs$$

1. C. Woolf, Advances in Fluorine Chemistry. Ed. M. Stacey et. al. Vol. 5, pp. 1-30, 1965. Washington; Butterworths.
2. P. J. H. Woltz, E. A. Jones, and A. H. Nielsen, J. Chem. Phys., 20 (1952) 378.
3. G. W. Fraser and J. M. Shreeve, In Press.
4. S. Andreades, J. Org. Chem., 27 (1962) 4157.

Contribution from the

Department of Physical Sciences
University of Idaho
Moscow, Idaho
83843

THE SILVER(II) FLUORIDE-CATALYZED FORMATION OF TRIS(TRIFLUOROMETHYL)HYDROXYLAMINE, $(CF_3)_2NOCF_3$

by

Daniel P. Babb and Jean'ne M. Shreeve

Both direct and catalytic fluorinations of trifluoronitrosomethane have been examined under a variety of conditions, and the latter has been found to provide a route to tris(trifluoromethyl)hydroxylamine, $(CF_3)_2NOCF_3$.[1,2] The data in Table I show the yields of $(CF_3)_2NOCF_3$ obtained without and with fluorine in the presence of the AgF_2 catalyst.

In the absence of fluorine, but in the presence of an excess of AgF_2 (at least a molar ratio of 10:1), the percentage yield of $(CF_3)_2NOCF_3$ increases with temperature from 0 at 28° to a maximum of 23 in the vicinity of 130°. Although AgF_2 is thermodynamically stable with respect to AgF and F_2 at 25°[3], as the temperature increases, decomposition of AgF_2 may provide a source of fluorine which seems to be necessary for the formation of $(CF_3)_2NOCF_3$.

Table I

AgF_2 Catalyst Only

mmoles CF_3NO	T, °C	%$(CF_3)_2NOCF_3$
5.9	28	0
3.0	111	15
5.0	129	23
8.0	146	19
10.0	172	15

AgF_2 Catalyst and F_2

mmoles CF_3NO	T, °C	%$(CF_3)_2NOCF_3$
5.5	24	55
6.0	62	37
3.7	125	17
13.1	177	7

The yield of the latter increases until such a temperature where the CF_3• radicals which are formed are consumed in the formation of CF_4. It is found that the amounts of CF_4 and C_2F_6 produced increase with temperature. At 2[illegible]°, the trifluoronitrosomethane is essentially recovered unchanged except for small amounts of NO_2 and CF_4. When CF_3NO was heated in a Monel tube at 125-130° for one hour, essentially no reaction took place.

In the presence of AgF_2 and excess fluorine, yields of $(CF_3)_2NOCF_3$ in excess of 50% are realized at 25°. The amounts of $(CF_3)_2NOCF_3$ produced fall off with temperature while CF_4 and C_2F_6 increase much more rapidly than in the absence of fluorine. Without the catalyst, fluorine and CF_3NO react at room temperature to give the expected fluorination products, but no $(CF_3)_2NOCF_3$.

Experimental Section

Materials. Elemental fluorine was passed through NaF to remove HF before use. Trifluoronitrosomethane was prepared by a literature method.[4] After separation using a ten-foot column (No. 3 Kel-F oil on Chromasorb P) at -21° or a 25-foot column of the same material at room temperature, identification of the products was made by infrared spectra.

Direct fluorination. Reaction of CF_3NO with elemental fluorine was observed to occur above -78°, but infrared analysis indicated the formation of only CF_4, COF_2, CO_2, N_2O, and traces of C_2F_3 and NO_2 in prefluorinated Monel tubes.

Catalytic Fluorination. In catalytic fluorination, the CF_3NO was frozen into a glass trap at -183° and nitrogen was caused to flow through the trap as it gradually warmed in a dewar. The nitrogen carried the CF_3NO into a well-fluorinated silver(II) fluoride catalytic reactor[5] which was maintained at the desired temperature. The residence time was about one hour and the products were trapped at -183°.

The reactor is a copper tube 100 cm. long and 7 cm. in diameter which contains silver-plated copper turnings ("chore girls") and is insulated and wound with Nichrome wire to permit heating. Inlet and exit tubes were made of 1/4 in. copper tubing soldered to the ends of the reactor. Prior to use the catalyst is prepared by passing fluorine over the chore girls at temperatures exceeding 200°C until no fluorine appears to be absorbed. Fluorination of the catalyst was carried out prior to each pass of CF_3NO and the residual fluorine gas was flushed from the reactor with dry nitrogen.

Fluorination of CF_3NO was attempted in two ways: 1) CF_3NO was carried by nitrogen flowing at a rate of 3.5-4 liters/hour into and through the reactor; and 2) CF_3NO was carried by the nitrogen flowing at a rate of 2.5-3 liters/hour into the reactor where it was mixed with fluorine gas entering at the rate of 1.2 liters/hour and allowed to pass through the reactor. Both fluorinations were carried out at several temperatures. A variety of compounds, in addition to $(CF_3)_2NOCF_3$, obtained in amounts which varied with the temperature include: CF_4, C_2F_6, COF_2, $(CF_3)_2NF$, $(CF_3)_3N$, $(CF_3)_2NN(CF_3)_2$, NF_3, CF_3NO_2, as well as SiF_4, NO_2, CO_2, and N_2O plus traces of other compounds. Except at 28° in the absence of fluorine, no unreacted CF_3NO was recovered. The yield of $(CF_3)_2NOCF_3$ was found to vary with temperature as is indicated in Table 1.

Mass spectrum. A weak peak attributed to the molecule-ion is observed in the mass spectrum run at 70 v. Species found in order of increasing mass to charge ratio include (mass, species, relative abundance): 64, CF_2N^+, 3.5; 66, CF_2O^+, 0.61; 69, CF_3^+, 100; 83, CF_3N^+, 0.13; 85, CF_3O^+, 0.07; 95, $C_2F_3N^+$, 0.26; 114, $C_2F_4N^+$, 0.09; 130, $C_2F_4NO^+$, 6.15; 152, $C_2F_6N^+$, 0.10; 218, $C_3F_8NO^+$, 1.5; 237, $C_3F_9NO^+$, 0.36.

The infrared spectrum[1] and nuclear magnetic resonance spectrum[6] as well as boiling point[5] agree with values previously reported.

Acknowledgments. This work was supported in part by the Advance Research Projects Agency through a contract administered by the Office of Naval Research. The authors are indebted to Mr. B. J. Nist of the University of Washington for the mass and nuclear magnetic resonance spectra.

(1) A. M. Dinwoodie and R. N. Haszeldine, J. Chem. Soc., 1681 (1965). Also R. E. Banks, M. G. Barlow, R. N. Haszeldine, M. K. McCreath, and H. Sutcliffe, Ibid., 7209 (1965).

(2) A. Ya. Yakubovich, S. P. Makarov, V. A. Ginsburg, N. F. Privezentseva, and L. L. Martynova, Dokl. Akad. Nauk SSSR, 141, 125 (1961).

(3) D. F. C. Morris, J. Phys. Chem. Solids, 7, 214 (1958).

(4) C. W. Taylor, T. J. Brice, and R. L. Wear, J. Org. Chem., 27, 1064 (1962).

(5) K. B. Kellogg and G. H. Cady, J. Am. Chem. Soc., 70, 3986 (1948).

(6) W. D. Blackley and R. R. Reinhard, J. Am. Chem. Soc., 87, 802 (1965).

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
University of Idaho
Moscow, Idaho 83843

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP
NA

3. REPORT TITLE
NEW HYPOFLUORITES CONTAINING NITROGEN

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Annual 1 October 1966 - 30 September 1967

5. AUTHOR(S) (First name, middle initial, last name)
Jean'ne M. Shreeve

6. REPORT DATE
1 October 1967

7a. TOTAL NO. OF PAGES
61

7b. NO. OF REFS
79

8a. CONTRACT OR GRANT NO.
Nonr-4217(00)

b. PROJECT NO.
ARPA Order No. 442, Item 3

c. Program Code No. 5910

d. None

9a. ORIGINATOR'S REPORT NUMBER(S)
Fourth Annual Report - October 1, 1967

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
None

10. DISTRIBUTION STATEMENT
Distribution of this document is unlimited

11. SUPPLEMENTARY NOTES
None

12. SPONSORING MILITARY ACTIVITY
Office of Naval Research
Power Branch (Code 429)
Washington, D. C.

13. ABSTRACT

Fluorine fluorosulfate, trifluoromethyl hypofluorite, and fluorine have been found to react with fluorosulfuryl isocyanate under the influence of ultraviolet radiation to produce a new class of compounds containing the $FSO_2NC(O)F$ group. Some of the chemical and physical properties of these materials and additional characterization of FSO_2NCO are presented. (U)

Addition across the carbon-carbon double bond in bis(trifluoromethyl)ketene with peroxodisulfuryl difluoride, tetrafluorohydrazine, difluoraminofluorosulfate and fluorine fluorosulfate yield $(CF_3)_2C(OSO_2F)C(O)OSO2F$, $(CF_3)_2C(NF_2)CFO$, $(CF_3)_2C(NF_2)C(O)OSO_2F$, $(CF_3)_2C(OSO_2F)CFO$, and $(CF_3)_2CFC(O)OSO_2F$, respectively. While in the presence of CsF only, $(CF_3)_2C(NF_2)CFO$ is converted to $(CF_3)_2C{=}NF$. With CsF and F_2, the former and $(CF_3)_2C{=}C{=}O$ give rise to $(CF_3)_2C(NF_2)CF_2OF$ and $(CF_3)_2CFCF_2OF$, respectively. These new compounds have been characterized and structures confirmed by nmr, mass and infrared spectra. (U)

Reactions of NF_2CFO with CF_3OF or with Al_2Cl_6 and HCl yield NF_2OCF_3 or $NF_2C(O)Cl$, respectively. The reactions of NF_2CFO with KF and CsF to give $KOCF_2NF_2$, $KOCN_2F_5$, $KOCN_3F_6$, $CsOCF_2NF_2$, $CsOCN_2F_5$, and $CsOCN_3F_6$ are discussed. Decomposition of $KOCF_2NF_2$ with Cl_2 yields NF_2Cl, and pyrolysis of $KOCN_2F_5$ at 95° yields $(NF_2)_2CO$. Spectra and properties of $(NF_2)_2CO$ and $NF_2C(O)Cl$ are given. (U)

Nitrosyl halides (XNO, X = F, Cl, Br) are easily prepared by the reaction of NO_2 and the respective cesium or potassium halide. In the case of the fluoride, formation of a CsF-hexafluoroacetone salt which is subsequently decomposed seems to enhance the reactivity of the CsF toward NO_2. Careful heating and powdering of CsF have essentially the same effect. (U)

(Continued on next page)

DD Form 1473 (Page 1 continued)

The AgF_2-catalyzed fluorination of CF_3NO with and without fluorine is found to give varying amounts of tris(trifluoromethyl)hydroxylamine. With fluorine, the largest yield (55%) is realized at 24°. While with just the catalyst, maximum yield (23%) is obtained at 129°. (U)

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Compounds containing the $FSO_2NC(O)F$ group						
Addition reactions with $(CF_3)_2C=C=O$						
Fluoroxy compounds						
Reactions of NF_2CFO						
Preparation of tetrafluorourea						
Salts containing difluoramino groups						
Difluoraminocarbonyl chloride						
Preparation of nitrosyl halides						
AgF_2-catalyzed fluorination of CF_3NO						
Tris(trifluoromethyl)hydroxylamine						