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The Reaction of Difluoramine–Potassium Fluoride Adduct with Perfluoroacyl Fluorides

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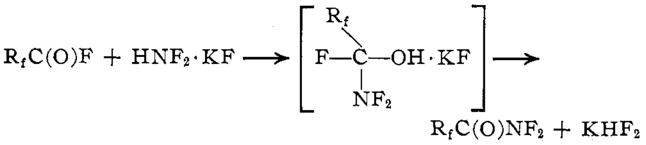
The reaction of the $HNF_2\cdot KF$ molecular complex with various fluorinated acyl fluorides gives a new class of compounds, $R_fC(O)NF_2$. The totally fluorinated amides $CF_3C(O)NF_2$, $C_2F_5C(O)NF_2$, $C_3F_7C(O)NF_2$, and $F_2N(O)C(CF_2)_3C(O)NF_2$ as well as the ester $CF_3CO_2C(NF_2)_2CF_3$ are reported and characterized. Also, the previously reported amides $FC(O)NF_2$ and $CH_3C(O)NF_2$ are easily prepared by this method.

The synthetic applications of difluoramine have received considerable attention in the recent literature. These reactions have included the preparation of poly(difluoramino)alkanes, difluoraminoalkanols, and diazirines from aldehydes, ketones, alkynes, alkenes, ethers, esters, and imines.[1-5] The reaction conditions employed generally involved the presence of a strong acid or Lewis base such as fuming H_2SO_4, FSO_3H, $ClSO_3H$, $BF_3\cdot H_3PO_4$, BF_3, or SO_3. These reactions have also been limited to nonfluorinated compounds and it is reported that the difluoraminoalkanol of hexafluoroacetone could not be made.[6]

Although fluorinated acylamides and *N*,*N*-difluoroamides have been prepared by various methods,[7-9] *N*,*N*-difluoroperfluoroamides had not been. The seemingly straightforward reaction of N_2F_4 and perfluoroacyl fluorides[10] did not yield these compounds but rather perfluoroalkyldifluoramines. The ease with which perfluoroacyl radicals eliminate CO requires that a nonradical pathway be used in synthesizing these amides.

In an attempt to facilitate reactions of difluoramine with perfluoroacyl fluorides *via* a nonradical mechanism, use was made of the $HNF_2\cdot KF$ adduct[11] rather than the previously employed conditions. This investigation has shown that the use of this adduct provides a simple route to substitute the NF_2 group into perfluoroacyl fluorides under mild conditions. The reaction of this adduct with $CF_3C(O)F$, $C_2F_5C(O)F$, $C_3F_7C(O)F$, $F(O)C(CF_2)_3C(O)F$, F_2CO, and $CH_3C(O)F$ yielded *N*,*N*-difluoroperfluoroamides in all cases. In the reaction of $CF_3C(O)F$ with this adduct, the amide $CF_3C(O)NF_2$ was formed at −23, −78, and −105° in essentially the same yield.

A possible pathway for the formation of the fluorinated amides can be considered to be



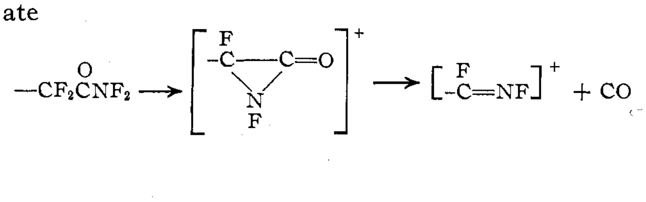
$$R_fC(O)F + HNF_2\cdot KF \longrightarrow \left[F-\overset{R_f}{\underset{NF_2}{C}}-OH\cdot KF \right] \longrightarrow R_fC(O)NF_2 + KHF_2$$

The formation of the amide at −105° indicates that the reaction proceeds through the complexed HNF_2 since the extrapolated dissociation pressure[11] of $HNF_2\cdot KF$ at this temperature is negligible. Also, when NaF, which does not form an adduct with HNF_2,[11] was used, no reaction occurred. These eliminate mechanistic considerations based on noncomplexed HNF_2 since the difluoraminoalkanol intermediate would eliminate HF, especially in the presence of a base such as NaF. Also removed from consideration would be an initial elimination of HF followed by difluoramino nucleophilic attack either in solution or in the vapor phase since the NaF would again function as a base in this system. Additional work presently being carried out seems to indicate that the fluoride reactant must be able to form adducts with KF or no reaction will occur. This again is suggestive of an initial carbonyl attack rather than an initial loss of the fluoride.

Although these reactions are generally free of side products, the reaction with $CF_3C(O)F$ gives rise to the ester $CF_3CO_2C(NF_2)_2CF_3$ as a major product. Attempts to isolate the bis(difluoramino) alcohol intermediate under these reaction conditions by the reaction of $CF_3C(O)NF_2$ with HNF_2 or the $HNF_2\cdot KF$ adduct were unsuccessful. This is not surprising since the difluoraminoalkanol of hexafluoroacetone could not be isolated.[6]

While attempting to isolate the proposed bis(difluoramino) alcohol, slight decomposition of $CF_3C(O)NF_2$ to $CF_3C(O)F$ was noted but no ester was isolated. Formation of analogous esters with other perfluoroacyl fluorides in isolable quantities is not observed. If attempts are made to rationalize this by a steric blocking of the carbonyl by larger perfluoroacyl groups and the difluoramino group, then it seems reasonable still to expect to isolate $(F_2N)_2CO$ or the ester arising from the hypothetical alcohol $FC(NF_2)_2OH$ in the F_2CO reaction. Neither of these products was isolated from this reaction.

Spectral data for the products are found in the tables. There is a characteristic shift toward lower energy in the infrared spectra for the carbonyl frequency of ~57 cm^{-1} for the monosubstituted amides compared to those of the corresponding fluorides. The mass spectra of these compounds are primarily due to perfluoroacyl ($M-NF_2$) and perfluoroalkyl cleavage. The other peaks are generally <3% of the base peak which is due to the perfluoroalkyl group or CF_3. The spectrum of each amide contains peaks of lesser intensity which lack oxygen and may be explained in terms of an aziridinone intermediate



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The mass spectrum of the ester is also primarily due to trifluoroacetyl and CF_3 cleavage but contains small peaks at *m/e* 278 and 185 due to M–F and $CF_3C(NF_2)_2^+$. The ^{19}F nmr spectra show little variance for the NF_2 chemical shift and are characteristic for these compounds. The high-resolution spectra are typically first order except for that of $F_2N(O)C(CF_2)_3C(O)NF_2$ which, because of magnetic nonequivalence of the α-CF_2 and NF_2 groups, is complex. A complex spectrum is also obtained for $C_3F_7C(O)NF_2$. The nmr integration and chemical shifts for these compounds are consistent with the proposed structures.

Experimental Section

Starting Materials.—Difluoramine was prepared from trityldifluoramine[12] (Peninsular Chemresearch, Inc.) and was used without purification. Acyl fluorides were purchased from Peninsular Chemresearch, Inc., or prepared from the corresponding acyl chloride (Peninsular Chemresearch, Inc.) and cesium fluoride (American Potash and Chemical Corp.), which was dried *in vacuo* at 170°. Potassium fluoride dihydrate (J. T. Baker) was dehydrated at 450°. Molecular sieves, 5A (30–60 mesh, Wilkens Instrument and Research, Inc.), were dried *in vacuo* prior to use.

Apparatus.—The reactions were carried out in 10–50-ml Pyrex flasks fitted with a Fischer-Porter Teflon stopcock and a side arm for the introduction of anhydrous KF. Volatile liquids and gaseous materials were handled in a standard glass vacuum line equipped with a Heise-Bourdon gauge. The products were purified by fractional condensation, fractional codistillation, or gas chromatography. For fractional codistillation, a 15 ft × 0.25 in. o.d. unpacked aluminum column coiled to fit a 1-l. dewar flask was used and for gas chromatography a 22 ft × 0.25 in. o.d. copper column packed with F.S. 1265 on Chromasorb P was used.

Analysis.—Infrared spectra (Table I) were taken with Beckman IR-5A and Perkin-Elmer 621 spectrophotometers in a 10-cm stainless steel gas cell equipped with AgCl windows. High-resolution ^{19}F nmr (Table II) were obtained using a Varian Model HA-100 spectrometer operating at 94.1 Mc. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6E mass spectrometer at an ionizing potential of 70 eV. Fluoride analyses were done by sodium fusion and the fluoride ion was determined by the use of an Orion specific fluoride ion electrode, Model 94-09, or by Beller Mikroanalytisches Laboratorium, Göttingen, Germany. Boiling points, vapor pressure data, molecular weights, and analyses are found in Table III.

TABLE I
INFRARED SPECTRA (CM^{-1})

$CF_3C(O)NF_2$	1835 d, ms, 1295 m, 1240 s, 1208 s, 1107 mw, 948 s, 754 m, 652 w, 583 w, 500 w
$C_2F_5C(O)NF_2$	1832 ms, 1340 m, 1241 s, 1210 m, 1130 m, 1049 mw, 953 mw, 845 m, 822 m, 745 m
$C_3F_7C(O)NF_2$	1830 ms, 1356 ms, 1280 sh, 1250 s, 1208 sh, 1144 s, 1096 w, 1075 w, 1000 m, 959 mw, 887 m, 865 m, 748 m, 731 ms, 635 w, 535 w, 507 w
$F_2N(O)C(CF_2)_3C(O)NF_2$	1859 ms, 1340 mw, 1312 mw, 1277 mw, 1236 sh, 1201 s, 1150 s, 1069 s, 1045 sh, 975 sh, 945 m, 901 m, 874 sh, 730 w, 590 w
$CF_3CO_2C(NF_2)_2CF_3$	1856 ms, 1330 m, 1281 sh, 1250 s, 1202 s, 1158 sh, 1145 s, 1098 s, 1080 s, 984 sh, 970 sh, 940 m, 911 sh, 868 w, 760 sh, 744 m, 728 m, 500 vw

General Procedure. A. Complexation of Difluoramine.—The complexation of HNF_2 was varied from the method reported previously.[11] In a typical reaction, 3–6 mmol of HNF_2 was condensed onto a threefold excess of anhydrous KF in a 25-ml vessel at −145°. The vessel was then warmed to −78° for 2 hr to allow complexation to occur. After this period a dissociation pressure of <5 mm was generally noted at −78°.

TABLE II
^{19}F NMR

Compound	φ,[a] ppm		J,[b] cps	Rel area (calcd)[c]
$CF_3C(O)NF_2$	CF_3	74.5 (t)	$J_{1,3} = 7.9$	1.54 (1.50)
	NF_2	−25.4 (b)		1
$C_2F_5C(O)NF_2$	CF_3	82.8 (tt)	$J_{1,4} = 2.9$, $J_{3,4} = 1.3$	1.48 (1.50)
	CF_2	120.0 (tq)	$J_{1,3} = 9.6$	1.09 (1.00)
	NF_2	−26.4 (b)		1
$CF_3CO_2C(NF_2)_2$-CF_3	$\overset{O}{CF_3C-}$	74.9 (s)		0.78 (0.75)
	$\geqslant CCF_3$	69.0 (p)	$J_{2,1} = 10.9$	0.81 (0.75)
	NF_2	−25.3 (b)		1
$C_3F_7C(O)NF_2$	CF_3	81.1 (t)	$J_{3,5} = 9.4$	1.64 (1.50)
	β-CF_2	125.9 (complex)		1.06 (1.00)
	α-CF_2	117.1 (complex)		1.05 (1.00)
	NF_2	−26.8 (b)		1
$F_2N(O)C(CF_2)_3$-$C(O)NF_2$	α-CF_2	120.0 (complex)		1.05 (1.00)
	β-CF_2	133.0 (complex)		0.53 (0.50)
	NF_2	−25.2 (b)		1

[a] Relative to $CFCl_3$ internal reference. [b] The NF_2 group is numbered 1 and the skeletal atoms are numbered successively in the amides.[2] The alkyl CF_3 is numbered 1 in the ester. [c] Integration was done by planimetry and the area ratios were determined relative to the NF_2 group.

B. General Reactions with the $HNF_2 \cdot KF$ Adduct.—The complexed HNF_2 was cooled to −145° and a 4-5-fold excess of acyl fluoride, relative to HNF_2, was condensed into the vessel. The vessel was then warmed to −23° for 4 hr. (Perfluoroglutaryl fluoride was run at −23° for 4 hr and then at −12° for approximately 8 hr.) Volatile materials were slowly removed under static vacuum at −23° and then the vessel was pumped on for 1 hr at −23°. The amides isolated are colorless, water sensitive, and thermally stable compounds which freeze to a glass.

Warning! Care should be exercised in handling difluoramine since it is known to exhibit explosive properties especially when frozen at −183 or −196°. In addition to explosions occurring during complexation, explosions occurred while removing the volatiles from the vessel and in one instance while cleaning a reaction vessel.

1. **Reaction of $CF_3C(O)F$.**—The reaction mixture was separated by fractional condensation using traps at −78, −128, and −196°. The −78° trap contained $CF_3CO_2C(NF_2)_2CF_3$ which was further purified by gas chromatography (40% yield). Due to the ease of hydrolysis, complete characterization could not be accomplished. The molecular weight was determined to be 300.5 (calcd 298) and hydrolysis of 0.05 mmol with excess water gave 0.10 mmol of HNF_2. The −128° trap contained a mixture of $CF_3C(O)F$, $CF_3C(O)NF_2$, and HNF_2. The HNF_2 was removed by condensing the mixture onto 5A molecular sieves at −196° and slowly allowed to warm to room temperature. The residual $CF_3C(O)F$ was removed by fractional condensation using −125 and −196° traps. The pure $CF_3C(O)NF_2$ (15% yield) was condensed in the −125° trap.

2. **Reaction of $C_2F_5C(O)F$.**—Separation of the reaction mixture using −107 and −196° traps resulted in isolation of $C_2F_5C(O)NF_2$ contaminated with $C_2F_5C(O)F$ in the −107° trap. The product was purified by fractional codistillation (58% yield).

3. **Reaction of $C_3F_7C(O)F$.**—Fractional condensation of the reaction mixture using −70 and −196° traps resulted in impure product in the −70° trap. The $C_3F_7C(O)F$ impurity was removed by fractional codistillation (42% yield).

4. **Reaction of $F(O)C(CF_2)_3C(O)F$.**—Separation was afforded by fractional condensation using −47 and −196° traps. The impure product was isolated in the −47° trap and further purified by fractional distillation (75% yield).

5. **Reaction of F_2CO.**—The reaction mixture was separated by fractional condensation using −128, −137, and −196° traps. Unreacted HNF_2 was found in the −128° trap and $F_2NC(O)F$ contaminated with some F_2CO was found in the −137° trap. A second separation of this sample using the same traps resulted in essentially pure product (63% yield). The product was identified by ir analysis.[13]

6. **Reaction of $CH_3C(O)F$.**—Fractional condensation of the

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TABLE III

ELEMENTAL ANALYSES AND VAPOR PRESSURE DATA

	$CF_3C(O)NF_2$	$C_2F_5C(O)NF_2$	$C_3F_7C(O)NF_2$	$F_2N(O)C(CF_2)_3C(O)NF_2$
Log $P_{mm} = a - b/T$ a	7.80	7.96	7.91	7.95
b	1240	1418	1540	1865
Analysis	F, 64.6 (63.7)[a]	F, 66.8 (66.8)	F, 68.6 (68.7)	F, 61.3 (61.4) C, 19.4 (19.2) N, 9.0 (9.1)
Bp, °C	−21.1	6.2	33.1	94.8
ΔH_{vap}, kcal/mol	5.7	6.5	7.1	8.5
ΔS_{vap}, eu	22.5	23.2	23.0	23.2
Mol wt	150.8(149.2)	203.8(199.0)	248.6(249.0)	312.9(310)

[a] Calculated values in parentheses.

reaction mixture using −91, −131, and −196° traps resulted in an impure product in the −91° trap. Pumping on this sample at −78° gave essentially pure product (35% yield). Identification was made by ir analysis.[9]

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Studies on the Chemistry of Halogens and Polyhalides.
XXXIII. Spectroscopic and Electrical Conductance Studies of the Bromine Trifluoride–Chlorine Trifluoride Systems[1,2]

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Raman, infrared, and electrical conductance studies were carried out on liquid mixtures of bromine trifluoride with chlorine trifluoride. The experimental data reveal the existence of a fluoride ion transfer equilibrium $ClF_3 + BrF_3 \rightleftharpoons ClF_2^+ + BrF_4^-$. The equilibrium constant for the above reaction was calculated to be $\sim 10^{-4}$.

Introduction

In connection with a detailed investigation of the chemistry of liquid halogen fluorides[3–6] carried out in this laboratory, it was decided to study the equilibria existing in the liquid mixtures of bromine trifluoride and chlorine trifluoride by spectroscopic and conductometric techniques. These techniques have been shown to be very useful in the identification and quantitative estimation of species present in halogen fluorides.[3]

The exchange of radioactive ^{18}F isotope between BrF_3 and ClF_3 in binary mixtures of these compounds was studied by Rogers and Katz.[7] They found that the exchange was complete in 10 min at 27° and concluded that this exchange was due to the existence of a fluoride ion transfer equilibrium, probably

$$BrF_3 + ClF_3 \rightleftharpoons ClF_2^+ + BrF_4^- \qquad (1)$$

This would imply that in these mixtures chlorine trifluoride behaves as a base (fluoride ion donor). It was of interest to us, therefore, to determine the magnitude of the interaction between the two halogen fluorides.

Experimental Section

Chemicals.—Bromine trifluoride, chlorine trifluoride, and arsenic pentafluoride were obtained from the Matheson Co. and were purified by previously described methods.[3]

Apparatus.—The vacuum line used for the handling of the halogen fluorides as well as the conductivity cells have also been described in previous publications.[3,4] The conductance measurements were made with an Industrial Model RC-18 conductivity bridge at 25°. The precision of the conductivity measurements was ±1%.

Raman spectra were obtained on a Cary Model 81 Raman spectrometer using previously described cells.[3] Infrared measurements were made on a Beckman IR-12 recording spectrophotometer with a specially constructed cell with diamond windows.[5] In general, Raman and infrared measurements were made in the 200–900-cm^{-1} spectral region, although some measurements were carried out to 2000 cm^{-1}. The spectra were resolved on a Du Pont Model 310 curve resolver.

Preparation of Solutions.—Bromine trifluoride–chlorine trifluoride solutions were prepared on a vacuum system using the same technique as was described for the hydrogen fluoride–bromine trifluoride mixtures.[6]

Results and Discussion

Chlorine Trifluoride Spectra.—The Raman spectrum of liquid chlorine trifluoride is shown in Figure 1 and the bands are listed in Table I. In general, the results

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Abstracted in part from the Ph.D. thesis of T. Surles, Michigan State University, 1970.

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