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Some Chemistry of Difluoraminocarbonyl Chloride. A New Route to Perfluorourea

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Improved yields of $NF_2C(O)Cl$ are obtained by short-term (4-6 hr) photolysis of N_2F_4 with oxalyl chloride. Reactions of $NF_2C(O)Cl$ with AgCN, AgNCS, AgNCO, $Hg(SCF_3)_2$ and $Hg(ON(CF_3)_2)_2$ give the new difluoraminocarbonyl pseudohalides $NF_2C(O)CN$, $NF_2C(O)NCS$, $NF_2C(O)NCO$, $NF_2C(O)SCF_3$, and $NF_2C(O)ON(CF_3)_2$. With excess of either Ag_2O at 0° or HgO at −78°, $NF_2C(O)Cl$ is converted to $(NF_2)_2CO$ and CO_2 in nearly quantitative yield. Chlorocarbonyl fluorosulfate results when $NF_2C(O)Cl$ is mixed with $S_2O_6F_2$ or $BrOSO_2F$.

This work concerns a modified preparation[2,3] of difluoraminocarbonyl chloride, $NF_2C(O)Cl$, and some of its chemistry on which a preliminary report has recently appeared.[4] It is now possible to prepare the compound in amounts which make studying its chemistry feasible. Only with AgNCS and $Hg(ON(CF_3)_2)_2$ does $NF_2C(O)Cl$ undergo metathetical reactions at or below 25°. With AgCN, AgNCO, and $Hg(SCF_3)_2$, higher temperatures, longer reaction times, and, in some cases, recycling of unreacted $NF_2C(O)Cl$ are necessary to ensure yields greater than 50%. It is likely that perfluorourea arises *via* decarboxylation of an unstable symmetrical anhydride intermediate formed when $NF_2C(O)Cl$ reacts with either HgO or Ag_2O. This provides a facile, much less hazardous route to $(NF_2)_2CO$ than the original method of pyrolyzing $KOCN_2F_5$.[2,5] Reactions of $NF_2C(O)Cl$ with several other silver, mercury, and alkali metal salts which do not result in new compounds are also described.

Surprisingly, both peroxydisulfuryl difluoride, $S_2O_6F_2$, and bromine fluorosulfate, $BrOSO_2F$, form chlorocarbonyl fluorosulfate, $ClC(O)OSO_2F$,[6] at 25° with $NF_2C(O)Cl$. Other methods for preparing $ClC(O)OSO_2F$, as well as some of its reaction chemistry, are detailed below.

Experimental Section

Caution! Nitrogen–fluorine-containing compounds are strong oxidizing agents and should be handled with proper shielding and other safety precautions. Although we experienced no difficulty in handling these materials, it should be reported that the analyst was injured when a sample of $NF_2C(O)NCO$ exploded in his hand. These difluoraminocarbonyl compounds are very sensitive to hydrolysis and can be handled successfully only under highly anhydrous conditions.

Starting Materials. Most reagents used are available from standard chemical supply houses. AgNCO,[7] $Hg(ON(CF_3)_2)_2$,[8] $Hg(SCF_3)_2$,[9] $(CF_3)_2NOH$,[10] $Hg(OSO_2F)_2$,[11] $S_2O_6F_2$,[12] $BrOSO_2F$,[13] and $(CF_3)_2C{=}NLi$[14] were synthesized *via* literature methods.

Preparation of Difluoraminocarbonyl Chloride, $NF_2C(O)Cl$. There are two methods available for the synthesis of $NF_2C(O)Cl$: (1) chlorination of $NF_2C(O)F$ with Al_2Cl_6 [2] and (2) photolysis of a mixture of $Cl(CO)_2Cl$ and N_2F_4.[3] The former method requires first the preparation of $NF_2C(O)F$ (15% yield) and then its subsequent conversion to $NF_2C(O)Cl$ which occurs in rather high yield (76%) when millimolar amounts are used. However, when the conversion reaction is scaled up by 16-fold, none of the carbonyl chloride is obtained. Therefore, we have modified the latter method to increase the conversion of $Cl(CO)_2Cl$ from 20 to 40% thus making it a method by which preparative amounts of $NF_2C(O)Cl$ can be realized.

In a typical preparation, 112 Torr (30 mmol) of $Cl(CO)_2Cl$ is placed in a 5-l. Pyrex bulb equipped with a water-cooled quartz finger. An additional 168 Torr (45 mmol) of N_2F_4 is added to the bulb. The mixture is irradiated for 6 hr with a Pyrex-filtered, medium-pressure, 450-W ultraviolet lamp (Hanovia L-679 A36, Engelhard Hanovia, Inc.), and a crude separation is effected by fractional condensation. Approximately 18% of the complex product mixture is not condensable at −183° (O_2). The fraction stopped at −183° consists of ~37 mmol of highly volatile material, mostly N_2F_4, N_2F_2, FCOCl, SiF_4, and NF_2Cl. The trap at −139° contains ~10 mmol of a nearly equal mixture of $NF_2C(O)Cl$ and $COCl_2$ plus other minor impurities. The trap at −108° contains ~31 mmol of a similar mixture. The fractions at −108 and −139° are recombined and separated by gas chromatography using a 19 ft × 0.25 in. o.d. aluminum column packed with 20% Kel-F-3 oil on Chromasorb P. Two-millimole samples can be successfully separated without flooding the column. $NF_2C(O)Cl$ elutes before phosgene. Great care must be taken to keep the column and collection system completely anhydrous.

Reactions of $NF_2C(O)Cl$ with Pseudohalide Salts. A similar method is used for the preparation of all the new difluoraminocarbonyl pseudohalides. A measured amount of $NF_2C(O)Cl$ is condensed into a reaction vessel containing an excess of the dry silver or mercury salt. The reaction is allowed to proceed at a suitable temperature for an appropriate length of time depending upon the reactivity of the salt. The volatile products are removed, separated by fractional condensation, and any unreacted $NF_2C(O)Cl$ is recycled to the vessel for additional reaction. Both Pyrex flasks with Teflon valves and stainless steel Hoke bombs can be used successfully (see Table I). All react extremely rapidly with water by the general reaction

$$NF_2C(O)X + H_2O \rightarrow HNF_2 + CO_2 + HX$$

where X = CN, NCO, NCS, $(CF_3)_2NO$, or CF_3S. At 25°, these compounds are colorless, with the exception of yellow $NF_2C(O)NCS$, volatile liquids which are stable in glass and in contact with mercury (except $NF_2C(O)SCF_3$). $NF_2C(O)NCS$ exhibits some thermal instability at 25° to form a yellow polymeric material. The rate of decomposition becomes very rapid above 60°.

Reactions with Salts Which Did Not Produce New Compounds. In most cases, the C–N bond of the $NF_2C(O)Cl$ is cleaved with concomitant loss and/or destruction of the NF_2 group. In some cases, especially where considerable heating is required to produce reaction, the solid seems to catalyze the decomposition of $NF_2C(O)Cl$ to yield the self-fluorination product $NF_2C(O)F$. Compounds reacting with $NF_2C(O)Cl$, reaction temperature(s), and volatile products are as follows: (a) CF_3CO_2Ag, −78 to +25°, $(CF_3CO)_2O$; (b) AgBr or KBr, >100°, Br_2, $NF_2C(O)F$, $NF_2C(O)NCO$; (c) AgI, 25°, I_2, $NF_2C(O)F$, $NF_2C(O)NCO$; (d) $AgClO_4$, 25°, hydrolysis products of $NF_2C(O)Cl$; (e) AgO, 25°, CO_2, NF_3, SiF_4, noncondensable gas; (f) Ag_2S, 25°, $NF_2C(O)F$, $NF_2C(O)NCO$, COS; (g) $NaOCH_3$, −106°, $(CH_3O)_2CO$, trace of N_2F_4; (h) NaN_3 or KN_3, 40°, CO_2, 4%

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(1) (a) NDEA Fellow. (b) Alfred P. Sloan Foundation Fellow.

(2) G. W. Fraser and J. M. Shreeve, *Inorg. Chem.*, 6, 1711 (1967).

(3) R. L. Cauble and G. H. Cady, *ibid.*, 6, 2117 (1967).

(4) K. J. Wright and J. M. Shreeve, *Chem. Commun.*, 649 (1971).

(5) G. W. Fraser and J. M. Shreeve, *Chem. Commun.*, 532 (1966).

(6) R. Cauble and G. H. Cady cited by D. D. Des Marteau, *Inorg. Chem.*, 7, 434 (1968).

(7) R. G. Neville and J. J. McGee, *Inorg. Syn.*, 8, 23 (1966).

(8) H. J. Emeleus, J. M. Shreeve, and P. M. Spaziante, *J. Chem. Soc. A*, 431 (1969).

(9) G. R. A. Brandt, H. J. Emeleus, and R. N. Haszeldine, *J. Chem. Soc.*, 2198 (1952).

(10) S. P. Makarov, A. Ya. Yukubovich, S. S. Dubov, and A. N. Medvedev, *Dokl. Akad. Nauk SSSR*, 160, 1319 (1965).

(11) J. E. Roberts and G. H. Cady, *J. Amer. Chem. Soc.*, 82, 353 (1960).

(12) J. M. Shreeve and G. H. Cady, *Inorg. Syn.*, 7, 124 (1963).

(13) J. E. Roberts and G. H. Cady, *J. Amer. Chem. Soc.*, 82, 352 (1960).

(14) R. F. Swindell, T. J. Ouellette, D. P. Babb, and J. M. Shreeve, *Inorg. Nucl. Chem. Lett.*, 7, 239 (1971).

Table I. Properties of $NF_2C(O)X$ Compounds

Salt (mmol of $NF_2C(O)Cl$)	Temp, °C (time, hr)	Product (% yield)	Elemental analyses, %								A^d	B^d	ΔH_v, kcal/mol	ΔS_v, eu	Mp, °C	Bp, °C
			C		F		N		S							
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found						
AgSCN (2.0)	25 (0.7)	$NF_2C(O)NCS$ (94)	17.40	17.28	27.5	28.0	20.28	20.75	23.22	23.53					−92	
AgNCO (2.0)	40-70 (8)	$NF_2C(O)NCO$ (60)^a	19.68	19.51	31.1	31.4	22.96	23.10			8.26	1762	8.1	24.6	−99	54.4
AgCN (2.0)	110 (7 + 8)^b	$NF_2C(O)CN$ (66)			35.8	35.3^c					8.33	1544	7.1	24.9	−101	10.2
$Hg(SCF_3)_2$ (1.0)	65 (5)^b	$NF_2C(O)SCF_3$ (80)	13.27	13.16	52.5	52.2	7.73	7.74	17.71	17.66	6.72	1213	5.5	17.6	−119	42.5
$Hg(ON(CF_3)_2)_2$ (1.0)	−95 (10)^b	$NF_2C(O)ON(CF_3)_2$ (69.5)	14.53	14.01	61.3	60.4	11.29	11.33			8.19	1645	7.5	24.3	−103	36.8

[a] Yields were significantly larger when AgNCO was freshly prepared. [b] Recycle. [c] Determined from ^{19}F nmr data. [d] For the expression $\log P_{Torr} = A - B/T$.

Table II.

Compd	ϕ(N-F)	ϕ(C-F)	J_{NF-CF}, Hz
$NF_2C(O)F$[2]	−33.1 s	11.5 t	19
$NF_2C(O)Cl$[3]	−41.8 s		
$NF_2C(O)CN$	−30.8 s		
$NF_2C(O)NCO$	−35.4 s		
$NF_2C(O)NCS$	−36.0 s		
$NF_2C(O)SCF_3$	−37.4 s	40.7 t	3.6
$NF_2C(O)ON(CF_3)_2$	−34.8 s	68.4 s	
$(NF_2)_2CO$	−33.4 s		

$NF_2C(O)N_3$;[15] (i) $Hg(OSO_2F)_2$, 100°, CO_2, N_2O, $NF_2C(O)F$, SO_2, SiF_4, FCOCl, NF_2OSO_2F.

Nmr Spectra of $NF_2C(O)X$ Compounds. The ^{19}F nmr spectra consist of broadened resonances for the fluorine bonded to nitrogen but no coupling between fluorine and nitrogen is observed. High-resolution ^{19}F nmr spectra were obtained with a Varian Model HA-100 spectrometer operating at 94.1 MHz with an internal reference of CCl_3F. (See Table II.)

Infrared Data for $NF_2C(O)X$ Compounds. The infrared spectra, recorded with a Perkin-Elmer Model 621 grating spectrometer using a 5-cm cell equipped with KBr windows, for these five new $NF_2C(O)X$ compounds are as follows (cm^{-1}): $NF_2C(O)CN$, 2243 s, 1805 vs, 1796 vs, 1151 s, 988 vs, 789 w, 698 m, 687 m, 481 w, 470 w; $NF_2C(O)NCO$, 2281 vvs, 2220 m, sh, 1835 vs, 1814 s, sh, 1804 s, sh, 1443, 1415 m, sh, 1137 m, 1093 mw, 988 s, 820 mw, 774 m, 613 mw; $NF_2C(O)NCS$, 2035 m, sh, 1970 vs, br, 1958 s, sh, 1816 s, 1240 ms, 1206 m, 949 mw, 898 m, 888 m, 864 ms, 733 m; $NF_2C(O)SCF_3$, 1956 vs, 1816 ms, 1787 ms, 1197 s, 1145 m, 1120 s, 1064 m, 938 m, 904 s, 765 m; $NF_2C(O)ON(CF_3)_2$, 1885 s, 1384 w, 1322 vs, 1270 vs, 1238 vs, 1221 s, 1191 m, 1158 s, 1060 s, 1013 m, 981 ms, 960 mw, sh, 885 m, 794 w, 716 m, 713 m, 659 w. On the basis of literature assignments for SCN *vs.* NCS[16,17] and NCO *vs.* OCN,[18] we conclude that both $NF_2C(O)NCS$ and $NF_2C(O)NCO$ are the iso compounds.

Preparation of Perfluorourea, $(NF_2)_2CO$. In a typical preparation of perfluorourea, 1 mmol of $NF_2C(O)Cl$ is condensed into a 65-ml Pyrex flask containing 15.6 mmol of dry, unused yellow HgO and the reaction proceeds for 2.5 hr at −78°. The volatile products (1.12 mmol) are $(NF_2)_2CO$, CO_2, and traces of $NF_2C(O)F$ and HNF_2. In a two-stage purification, the products are separated first by fractional condensation in traps at −110 or −118° ($NF_2C(O)Cl$), at −138° ($(NF_2)_2CO$ contaminated with the hydrolysis product HNF_2), and at −183° (CO_2 and $NF_2C(O)F$). Final purification of perfluorourea is attained by removal of HNF_2 using 5A molecular sieves (30-60 granular, Wilkins Instrument and Research, Inc.). The sieves are carefully predried by strong heating under dynamic vacuum. The best results are obtained by condensing the perfluorourea-difluoramine mixture onto the sieves at −183°, warming the flask to 25° over a 5-min period, and then immediately removing the volatile material. The yield of $(NF_2)_2CO$ is >95%. Contact times longer than 10 min result in poor recovery of $(NF_2)_2CO$ as well as the formation of some noncondensable gas.

Silver(I) oxide may also be used to prepare $(NF_2)_2CO$ but longer reaction time and higher temperature are required. In a typical preparation, 0.5 mmol of $NF_2C(O)Cl$ is allowed to react with 11 mmol of dry Ag_2O in a 65-ml Pyrex flask. After 21 hr at 0°, the volatile products were fractionated with traps at −183 (0.346 mmol of CO_2 and $NF_2C(O)F$), −138 (0.21 mmol of nearly pure $(NF_2)_2CO$), −120, and −110°. The latter two traps are essentially empty. The yield of $(NF_2)_2CO$ is ~82%.

Spectral Properties of $(NF_2)_2CO$. Infrared bands appear at 1866 s, 1859 s, 1806 w, sh, 1151 m, 979 ms, 931 vs, 847 m, tr, 721 m, br, 472 w, 331 m, and 255 cm^{-1} w. The **ultraviolet** spectrum was recorded on a Perkin-Elmer Model 202 spectrophotometer using a sample at 0.7 Torr in a 10-cm quartz cell. In the range from 190 to 390 nm, one broad absorption was observed with a maximum at 202 nm. The ^{19}F **nmr** spectrum was obtained on a 20 mol % solution in $CFCl_3$ as a single broad resonance at ϕ −33.4 (*vs* −30.8 ppm with external reference). The **mass** spectrum which was recorded at 70 eV shows no molecular ion but fragments of hydrolysis products are present. The base peak is NF_2^+ and the spectrum includes the following peaks (*m/e*, species, relative percentage): 18, H_2O^+, 25.3; 20, HF^+, 7.0; 28, CO^+, N_2^+, 61.3; 30, NO^+, 6.4; 32, O_2^+, 11.7; 33, NF^+, 49.6; 34, HNF^+, 20.6; 42, NCO^+, 14.6; 43, $HNCO^+$, 6.0; 44, CO_2^+, 78.2; 47, COF^+, 22.3; 52, NF_2^+, 100; 53, HNF_2^+, 29.8; 61, $FNCO^+$, 52.8; 63, FCO_2^+, 6.7; 66, COF_2^+, 4.5; 69, CF_3^+, 7.9; 80, F_2NCO^+, 54.6; 113, F_2NCONF^+, trace.

Preparation of Chlorocarbonyl Fluorosulfate. There are four methods by which this compound can be prepared but the first two are impractical on the preparative scale. Method four is the most useful. (1) $NF_2C(O)Cl + S_2O_6F_2$, in equimolar amounts (0.5 mmol), are held in a Pyrex tube for 10 hr at 25° and give equal

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(15) R. J. Shozda, U. S. Patent 3,418,341 (1968); *Chem. Abstr.*, 70, 57199 (1969).

(16) E. Lieber, C. N. R. Rao, and J. Ramachandran, *Spectrochim. Acta*, 13, 296 (1959).

(17) D. W. Emerson, *J. Chem. Educ.*, 48, 81 (1971).

(18) F. A. Miller and G. L. Carlson, *Spectrochim. Acta*, 17, 977 (1961).

quantities of NF_2OSO_2F[19] and $ClC(O)OSO_2F$. (2) $NF_2C(O)Cl$ + $BrOSO_2F$, in equimolar amounts (0.5 mmol), are held in a Pyrex tube for 1 hr at 25° and react according to $NF_2C(O)Cl + BrOSO_2F \rightarrow ClC(O)OSO_2F + N_2F_4 + Br_2$. (3) $BrOSO_2F$ (1 mmol) + $COCl_2$ (7.3 mmol), after 16 hr at −65°, gave $ClC(O)OSO_2F$ (0.54 mmol, 54% yield) and BrCl. (4) The thermal reaction between $(COCl)_2$ and $S_2O_6F_2$ gives yields of $ClC(O)OSO_2F$ which are superior to those obtained *via* photolysis, but each method has an advantage.

(a) In a typical thermal reaction, 2.1 mmol each of $(COCl)_2$ and $S_2O_6F_2$ are heated slowly to 43° for 30 hr in a 150-ml Pyrex glass tube. The products are separated by use of traps at −183° (1.3 mmol of $COCl_2$, CO_2, and Cl_2), −95° (0.1 mmol of $S_2O_5F_2$), −78° (2.46 mmol of impure $ClC(O)OSO_2F$, 58% yield), and −47° (trace of $Cl(CO)_2OSO_2F$).[6] Carbon monoxide formed passed a trap at −183°.

When equimolar amounts of $(COCl)_2$ and $S_2O_6F_2$ are thermolyzed, the $ClC(O)OSO_2F$ which is trapped is contaminated with unreacted $S_2O_6F_2$ from which it cannot be easily separated by fractional condensation. The best procedure is to use an excess of $(COCl)_2$ (30–50%) and, since it cannot be separated efficiently from the product by fractional condensation, to destroy the unreacted $(COCl)_2$ in the product mixture by photolysis through Pyrex.

(b) In a typical photochemical preparation, 1.0 mmol each of $(COCl)_2$ and $S_2O_6F_2$ are irradiated through Pyrex for 4.5 hr in a Srinivasan–Griffin reactor equipped with sixteen 21-W 3000 Å uv lamps. Fractional condensation of the products used traps at −183° (1.33 mmol of $COCl_2$ and Cl_2), at −78° (0.74 mmol of $ClC(O)OSO_2F$, ~37% yield), and at −47° (trace $ClC(O)OSO_2F$).

Chlorocarbonyl fluorosulfate of good purity was then obtained by allowing the product from section (a) or (b) to pass slowly a trap at −47° and to stop in a trap at −64°. Final purification was achieved by gas chromatography using a 3 ft × 0.25 in. 20% FS-1265 on Anakrom Tee-Six column at 25°.

Properties of Chlorocarbonyl Fluorosulfate. $ClC(O)OSO_2F$ is a colorless, viscous liquid with a vapor pressure of about 100 Torr at 25°. It dissolves readily in Halocarbon greases to give a characteristic brown viscous mess which makes handling it in gear with Teflon or metal valves necessary. A glass is formed when $ClC(O)OSO_2F$ is cooled. An experimental molecular weight of 161.8 (162.5, *PVT*) was obtained. *Anal.* Calcd for $ClC(O)OSO_2F$: Cl, 21.81; F, 11.7; S, 19.73. Found: Cl, 21.55; F, 11.5; S, 19.97. **Infrared** spectral bands occur at 1830 s, 1492 s, 1257 s, 1016 vs, 871 m, 841 s, 782 m, 657 w, and 577 cm^{-1} s. The **^{19}F nuclear magnetic resonance** spectrum consists of a single peak at ϕ −44.7. In the mass spectrum no molecular ion occurs, but a fragment $M-Cl^+$ is observed.

Reactions of Chlorocarbonyl Fluorosulfate. The reactants and conditions used and and products formed are as follows (invariably, the C–O bond is broken): (a) NH_3 (N_2 diluent), 0°, CO_2, $COCl_2$, COFCl, COF_2, HNCO, SO_2F_2, NH_4^+ salt; (b) $(CH_3)_2NH$, 25°, CO_2, $COCl_2$, SO_2F_2, SiF_4, white solid; (c) AgNCO, −78°, CO_2, $COCl_2$, SiF_4; (d) $(CF_3)_2C{=}NLi$, −78°, $COCl_2$, unidentified isocyanate; (e) KF, 50°, no reaction; (f) CsF, 50°, $COCl_2$, CO_2, COF_2, SO_2F_2, COClF; (g) AgF_2, 25°, CO_2, COF_2, COClF, SiF_4, $S_2O_5F_2$.

Results and Discussion

Oxalyl chloride when photolyzed with an excess of N_2F_4 through Pyrex glass for several hours is more than 40% converted to $NF_2C(O)Cl$ and, while large quantities of other volatile products are formed, preliminary trap-to-trap separation followed by gas chromatography permits good separation of the $NF_2C(O)Cl$. Phosgene is the contaminant most difficult to remove. Higher energy radiation allows

$$N_2F_4 + (COCl)_2 \xrightarrow[\text{Pyrex, } h\nu]{25^\circ} NF_2C(O)Cl, N_2F_2, FCOCl, COCl_2$$

generation of a higher concentration of $\cdot C(O)Cl$ radicals but no $NF_2C(O)Cl$ can be isolated under these conditions probably due to photolytic decomposition of the product. In Pyrex glass, there is no evidence of decomposition of $NF_2C(O)Cl$ below 180° at which temperature, after 12 hr, traces of $NF_2C(O)F$ and CO begin to appear. At 240°, complete degradation occurs to produce CO_2, SiF_4, N_2F_4, $COCl_2$, COClF, and Cl_2. At intermediate temperatures, the decomposition appears to proceed initially *via* a self-fluorination reaction

$$4NF_2C(O)Cl \rightarrow 2NF_2C(O)F + NF_2C(O)NCO + 2Cl_2$$

Hydrolysis occurs very readily with only traces of moisture making anhydrous conditions an absolute necessity.

$$NF_2C(O)Cl + H_2O \rightarrow HNF_2 + HCl + CO_2$$

Difluoraminocarbonyl chloride is completely consumed after 40 min upon contact with carefully dried AgSCN at 25°, the major product being $NF_2C(O)NCS$ (94% yield). Some $NF_2C(O)F$ and COF_2 are also formed; the respective amounts increase with reaction time and at the expense of the $NF_2C(O)NCS$. This compound is a faintly yellow liquid which freezes to a white solid and which at 25° commences to decompose slowly to a yellow polymeric material. Decomposition becomes appreciable above 60° and precludes the determination of a normal boiling point although the vapor pressure is about 29 Torr at 25°.

Recycling of difluoraminocarbonyl chloride is necessary after initial contact with AgCN, $Hg(SCF_3)_2$, and $Hg(ON(CF_3)_2)_2$ at various temperatures for several hours in order to consume the $NF_2C(O)Cl$ completely. Although prevention of the hydrolysis of these compounds is difficult, it is imperative with $NF_2C(O)CN$ because one of the hydrolysis products, HCN, is impossible to remove by fractional condensation and attempts to remove it with 4A molecular sieves or gas chromatography were unsuccessful.

For the mercury salt reactions, temperature control as well as temperature range is important since altering the temperature by a few degrees can cause the reaction to proceed to an entirely different set of products. When $NF_2C(O)Cl$ was treated with mercury(II) bis(trifluoromethyl) nitroxide, $Hg(ON(CF_3)_2)_2$, at 0°, $((CF_3)_2NO)_2CO$[20] and N_2F_4 were the only volatile products. After lowering the reaction temperature to −78°, $NF_2C(O)ON(CF_3)_2$ was obtained in 19% yield but $((CF_3)_2NO)_2CO$ was by far the major component (71%). However, at −95°, the yield of $((CF_3)_2NO)_2CO$ falls to ~25%, and $NF_2C(O)ON(CF_3)_2$ increases to 69.5% after a single recycle to utilize the $NF_2C(O)Cl$ completely. While other examples of displacement of $\cdot NF_2$ by $(CF_3)_2NO\cdot$ or $Hg(ON(CF_3)_2)_2$ are not known, $Hg(ON(CF_3)_2)_2$ can, at low temperatures, cause H or X (F, Cl, Br, I) to be displaced or replaced in a variety of organic and inorganic materials. Although $NF_2C(O)ON(CF_3)_2$ is stable at least to its boiling point (36.8°), whether or not it is stable to further attack by $Hg(ON(CF_3)_2)_2$ at 25 or 0° is unknown. This would be helpful in understanding the production of $((CF_3)_2NO)_2CO$.

An alternate synthesis of $NF_2C(O)ON(CF_3)_2$ is provided not unexpectedly by the reaction between $NF_2C(O)F$ and $(CF_3)_2NOH$ at −50 to −78° in the presence of excess dry CsF for several hours. Some $((CF_3)_2NO)_2CO$ is formed also which makes this reaction analogous to that of $(CF_3)_2NOH$ with COF_2 or $COCl_2$[20] using the same conditions where the majority of product is the mono- or disubstituted carbonyl depending on the relative amounts of reactants.

Reaction temperatures in excess of 65° result in the production of large amounts of $NF_2C(O)F$, SiF_4, COF_2, and CO_2 at the expense of $NF_2C(O)SCF_3$ in the reaction of $(CF_3S)_2Hg$ with $NF_2C(O)Cl$. After 5-hr contact of $NF_2C(O)Cl$ with $Hg(SCF_3)_2$ at 65° and a single recycle of the unreacted $NF_2C(O)Cl$, an 80% yield of $NF_2C(O)SCF_3$ is realized. In order to free $NF_2C(O)SCF_3$ from the small

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(19) M. Lustig and G. H. Cady, *Inorg. Chem.*, **2**, 388 (1963).

(20) D. P. Babb and J. M. Shreeve, *Inorg. Chem.*, **6**, 351 (1967).

quantity of CF_3SSCF_3 formed in the reaction, gas chromatographic separation is necessary.

Photolysis or thermolysis of $NF_2C(O)ON(CF_3)_2$ does not result in decarboxylation to form an unsymmetrical hydrazine, but rather, *e.g.*, after 9 hr at 140°, all has been converted to $FC(O)ON(CF_3)_2$, $CF_3N{=}CF_2$, CF_3NCO, SiF_4, NO, $(CF_3)_2NH$, and noncondensable gases, N_2 and CO. No attack was observed by photolysis through a Vycor filter while irradiation through quartz produced approximately the same products as thermal decomposition although at a faster rate.

Molecular ions are not observed in the mass spectra for any of the $NF_2C(O)X$ compounds and fragments arising from hydrolysis products are present in all spectra. For compounds in which the CF_3 moiety occurs, the CF_3^+ ion is the base peak, whereas in $NF_2C(O)CN$ and $NF_2C(O)NCS$, M-NF_2^+ is the base peak.

Although perfluorourea, $(NF_2)_2CO$, does not result from the pyrolysis at 95° of $KOCN_2F_5$, this method is involved and hazardous and the yield is low.[2] We find that while both Ag_2O and yellow HgO will convert $NF_2C(O)Cl$ to $(NF_2)_2CO$, probably through an anhydride intermediate which rapidly decarboxylates, the product is formed at lower temperature and nearly quantitatively with HgO.

$$NF_2C(O)Cl \xrightarrow[-78^\circ]{HgO} (NF_2C(O)O(O)CNF_2) \rightarrow (NF_2)_2CO + CO_2$$

Difluoraminocarbonyl chloride with an excess of Ag_2O gives $(NF_2)_2CO$ in yields exceeding 80% when the reaction is carried out at 0° for 20 hr, whereas $(NF_2)_2CO$ is produced essentially quantitatively at −78° after 2-3 hr with yellow HgO. The amount of $NF_2C(O)F$ formed at the expense of the $(NF_2)_2CO$ may be reduced by limiting the contact time of $(NF_2)_2CO$ with the solid. Tetrafluorourea is extremely water sensitive, even more so than $NF_2C(O)Cl$ or $NF_2C(O)F$, and can be handled successfully only under "bone-dry" conditions. The reactivity of HgO is greatly reduced after one reaction and for greatest efficiency should be fresh for each reaction.

Perfluorourea appears to be thermally stable in Pyrex to 80° where self-fluorination begins to produce $NF_2C(O)F$ and noncondensable products (N_2 by mass spectrum). At 140°, the rate of thermal decomposition becomes appreciable, and the first trace of SiF_4 appears. The quantity of $NF_2C(O)F$ diminishes at 160°, until finally at 180° the condensable pyrolysis products consist of SiF_4, COF_2, and N_2F_4. When equimolar amounts of $(NF_2)_2CO$ and FNO are combined in a 95-ml Monel bomb at 25° and at −78°, the products are N_2F_4, COF_2, NO, and some $NF_2C(O)F$ with no evidence for a nitrite as is observed for the analogous reaction between $(CF_3)_2CO$ and FNO.[21]

Chlorocarbonyl fluorosulfate can be prepared in fair yields by photolysis or thermolysis of a mixture of $S_2O_6F_2$ and $(COCl)_2$ which suggests combination of $FSO_2O\cdot$ and $\cdot C(O)Cl$ radicals. It undergoes slow hydrolysis *via*

$$ClC(O)OSO_2F + H_2O \rightarrow HCl + CO_2 + HOSO_2F$$

$ClC(O)OSO_2F$ is stable in Pyrex glass up to 100° where it slowly commences to give traces of $COCl_2$, CO_2, and noncondensable gas. At 160°, thermal decomposition is complete, *i.e.*

$$ClC(O)OSO_2F \xrightarrow[SiO_2]{160^\circ} CO_2 + COCl_2 + SiF_4 + SO_2$$

Although not the best preparative methods, the more interesting chemically are the reactions of $NF_2C(O)Cl$ with $S_2O_6F_2$ and with $BrOSO_2F$ where, in each case, the production of $ClC(O)OSO_2F$ is not the one predicted based on the previous chemistry of $S_2O_6F_2$ or $BrOSO_2F$ where chlorine would invariably be attacked or, as above with $Hg(ON(CF_3)_2)_2$, at higher temperatures, where both the C-N and C-Cl bonds would be severed.

The unexpected reaction behavior of $ClC(O)OSO_2F$ in which the C-O bond is apparently the weakest may arise from the extreme stability of the fluorosulfate radical, but whatever the cause, this fact precludes its use as a synthetic reagent under the conditions tried here.

Registry No. $NF_2C(O)Cl$, 16847-30-6; $NF_2C(O)NCS$, 32837-65-3; $NF_2C(O)NCO$, 32837-64-2; $NF_2C(O)CN$, 32837-63-1; $NF_2C(O)SCF_3$, 32837-66-4; $NF_2C(O)ON(CF_3)_2$, 32837-67-5; $(NF_2)_2CO$, 10256-92-5; $ClC(O)OSO_2F$, 36341-79-4.

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(21) S. Andreades, *J. Org. Chem.*, **27**, 4157 (1962).