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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]

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Received March 1, 1967

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 $NF_2(O)Cl$ 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 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 $KOCN_2F_5$. Pyrolysis of the latter is the only known route to 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

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

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

$$NF_2CFO + Al_2Cl_6\,(\text{excess}) \xrightarrow[\text{HCl}]{25^\circ} NF_2C(O)Cl + \text{solid} \quad 75\%$$

$$NF_2CFO + Al_2Cl_6\,(\text{excess}) + HCl \xrightarrow{25^\circ} 2Cl_2 + \text{solid} \quad 25\%$$

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

Difluoraminocarbonyl fluoride is completely consumed within 12 hr upon contact 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 2 equiv 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. Similar reactions at low

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

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

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[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, Mich., 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).

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

[5] W. S. Solomon, L. A. Dee, 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); (b) C. B. Colburn, *Advan. Fluorine Chem.*, **3**, 108 (1963), and references cited therein.

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

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 nonvolatile product stable under vacuum which releases the NF_2CFO semiquantitatively upon warming. The product appears to be the simple salt $K^+OCF_2NF_2^-$.

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

$$KF + NF_2CFO\text{ (excess)} \xrightarrow[\text{no solvent}]{0\text{ or }25^\circ} KOCF_2NF_2\ (85\text{–}90\%)$$

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

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, which may be $CsOCF_2NF_2$, was observed in semistoichiometric reactions 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 68% 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 pretreated KF reacts (slowly or rapidly, respectively) with 2 equiv of NF_2CFO in acetonitrile solution at −40°, and the salt $KOCF_2NF_2$ reacts rapidly with 1 equiv of NF_2CFO under the same conditions. In any case the reaction is usually semistoichiometric. From synthetic data the nonvolatile product appears to be approximately $KOCN_2F_5$ and is believed to be primarily the salt $K^+OCF(NF_2)_2^-$

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

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

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

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

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 has 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.*, $NF_2\cdot + \cdot C(O)NF_2$.

$$KOCN_2F_5 \xrightarrow{95^\circ} KF + (NF_2)_2CO$$

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 ppm, 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 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 side arm on the reaction bulb, subliming the volatile material into the bulb under dynamic vacuum, and sealing off and removing the nonvolatile residue in the side arm. 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 & 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 allowing trifluoroacetyl chloride (K & K Laboratories) to react 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.) and 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 $\mathbb{\$}$ 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, 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 *PVT* 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 nonvolatile 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_3F, shows: −28.7 ppm (NF_2, broad and unresolved) and +15.1 ppm (CFO, sharp 1:2:1 triplet, J = 19 cps). 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 is 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 of NF_2CFO and 0.41 mmole of 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. The yield of NF_2OCF_3, after drying by fractional condensation at −80°, was 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 of 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 FCOCl 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 $NF_2C(O)Cl$.] The yield was 0.533 mmole (*PVT*) of $NF_2C(O)Cl$, 61.7 mg, mol wt = 116 [calcd for $NF_2C(O)Cl$, 115.5], 76% based on NF_2CFO.

The infrared spectrum (25 mm pressure) of $NF_2C(O)Cl$ is (in cm^{-1}): 1840 (s), 1800 (ms), 1073 (m), 948 (s), 905 (vs), 770–755 (w), doublet, 645–635 (m), doublet. The F^{19} nmr spectrum shows a single, broad resonance at −40.4 ppm. Experimental vapor pressure data are as follows [T (°K), P (mm)]: 189, 6; 213, 19; 222, 70; 234, 142. These data suggest a Clausius–Clapeyron curve given by: $\log P(\text{mm}) = -1350T^{-1} + 7.92$. The extrapolated normal boiling point is −5°. The corresponding enthalpy of vaporization is 6.17 kcal $mole^{-1}$; the entropy of vaporization (−5°) is 23.0 eu. 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^-. $NF_2C(O)Cl$ (10 mg) was hydrolyzed in acidified aqueous KI solution for 1 hr at room temperature. *Anal.* Found: 0.0360 oxidizing equiv (as I_3^-)/g. Calcd 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.

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

[15] J. P. Freeman, Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p 129.

[16] R. J. Koshar, D. R. Husted, and R. A. Meiklejohn, *J. Org. Chem.*, **31**, 4232 (1966).

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

Attempted Bromination of NF_2CFO.—Approximately 1 g of 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 (1 μ) for 10 hr at room temperature through a U trap cooled to −184°. The yield was 0.02 mmole not condensable at −80° (CO_2 and SiF_4) and 0.101 g (0.63 mmole) of Br_2 containing a trace of $COBr_2$, which was identified by its infrared spectrum.[18] The pinkish, translucent residue in the bulb, upon treatment with 0.90 mmole of 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 redehydrated 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) of KF, when treated with 0.80 g of CH_3CN and 0.23 g (1.4 mmoles) of $(CF_3)_2CO$ for 13 hr, gained 0.4 mg in weight.

Preparation of $KOCF_2NF_2$.—The apparatus was a 50-ml Pyrex bulb with a 1.25-mm Teflon needle valve (Fischer and Porter Co.) and a small, open side arm. The apparatus was tared, hot dehydrated KF was added through the side arm, and the latter was pulled off to seal the bulb. Reweighing indicated that 21.0 mg (0.36 mmole) of 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. NF_2CFO [52.6 mg, 0.533 mmole (PVT), mol wt = 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, mol wt = 97, infrared analysis indicated NF_2CFO with a trace of COF_2; frequently traces of $(CF_3)_2CO$ are also found at this step], the apparatus was reweighed. The KF gained 30.4 mg in weight. This solid product was decomposed by heating the bulb to 85° with a water bath (*behind a shield!*) 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, mol wt = 97) 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 of $KOCF_2NF_2$ (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 80°. 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, N_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 amount of Cl_2 or Br_2, respectively. $KOCF_2NF_2$ 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, respectively. 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.

Preparation of NF_2Cl.—Approximately 0.1 g of dehydrated KF was pretreated with $(CF_3)_2CO$ according to the procedure already described and then allowed to react with 0.92 mmole of NF_2CFO at 0° until the gas was absorbed. Approximately 0.5 ml of anhydrous CH_3CN was condensed in, the $KOCF_2NF_2$ was dissolved at −40°, and 0.91 mmole of Cl_2 was frozen onto the solution. After being allowed to react for 0.5 hr at −40°, the residual gas [78.4 mg, 0.91 mmole (*PVT*), mol wt = 86, Cl_2 and NF_2Cl] was removed and separated by fractional codistillation. The yield of NF_2Cl was 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 of 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 $KOCF_2NF_2$. KF (25.8 mg, 0.44 mmole) was pretreated with $(CF_3)_2CO$ and then converted (86%) 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*), mol wt = 99.3] and 372.3 mg of anhydrous CH_3CN for 31.5 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 of CH_3CN and 33.8 mg of gas [0.477 mmole (*PVT*), mol wt = 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) of COF_2 and 0.07 mmole (7 mg) of NF_2CFO. Thus the gas had decreased in mass by 53.6 mg during reaction and 9.7 mg of CH_3CN was 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, mmoles): K, 0.44; O, 0.40; C, 0.40; N, 0.81; F, 2.05; and 0.24 mmole of CH_3CN; this corresponds 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 of 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 *in vacuo* to a bulb containing acidified aqueous KI solution, and the I_3^- liberated at room temperature was titrated with standard thiosulfate solution. *Anal.* Found: 3.01 mequiv. Calcd for 0.44 mmole of $KOCN_2F_5$: 3.52 mequiv; calcd for 0.40 mmole of $KOCN_2F_5$: 3.20 mequiv.

Preparation of $KOCN_2F_5$ from Untreated KF.—In a 25-ml reaction bulb 15.3 mg (0.26 mmole) of dehydrated granular KF was weighed out and treated with 0.52 mmole (*PVT*) of NF_2CFO and 421.5 mg of 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 −25°, and

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

[19] See ref 12b, p 113.

all but 26 mg was recovered. After sitting 30 min at room temperature, the solid product in the reaction bulb released 21 mg of CH_3CN and 0.02 mmole of gas (COF_2, N_2F_2, and NF_2CFO). An additional 25 hr at room temperature released 0.035 mmole of gas of similar composition, and 0.015 mmole of 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 of CH_3CN and 0.20 mmole of gas [COF_2, N_2F_2, NF_2CFO, and $(NF_2)_2CO$], and subsequent heating to 95° liberated 0.08 mmole of gas of similar composition.

Preparation of $KOCN_3F_6$(?).—In a typical reaction 42.3 mg (0.73 mmole) of KF was pretreated with $(CF_3)_2CO$ according to the procedure already described and was then treated with 0.79 mmole of NF_2CFO at 0° for 12.5 hr. Characterization of the residual gas indicated the formation of 0.65 mmole of $KOCF_2NF_2$ (89% conversion). This product was treated *in situ* with 1.58 mmoles of NF_2CFO and 756.3 mg of anhydrous CH_3CN for 52 hr at $-35 \pm 5°$. The residual gas in the system, after 28 and 52 hr, respectively, was: 119 mg, 1.53 mmoles, mol wt = 77.8; 118 mg, 1.54 mmole, mol wt = 76.6. On the basis of molecular weight, this gas mixture was estimated to be 1.03 mmoles (68 mg) of COF_2 and 0.51 mmole (50 mg) of NF_2CFO; this was qualitatively confirmed by infrared analysis. Consequently the solute (which was not isolated) has the apparent composition (element, mmoles): K, 0.73; O, 0.69; C, 0.69; N, 1.72; F, 3.83; this corresponds 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 of $KOCN_2F_5$ and 0.3 mmole of $KOCN_3F_6$.

When this solution was treated with 0.9 mmole of NF_2CFO for 24 hr, the residual gas was found to be 0.3 mmole of COF_2 and 0.5 mmole of NF_2CFO. Treatment of the resulting solution with 0.9 mmole of COF_2 for 23 hr yielded 0.7 mmole of COF_2 and 0.3 mmole of NF_2CFO, and subsequent treatment of the solution with 0.8 mmole of NF_2CFO for 72 hr yielded 0.3 mmole of COF_2 and 0.5 mmole of 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 mmoles of CF_3CO for 25.5 hr at $-35 \pm 5°$. The residual gas, after separation by fractional codistillation, was 1.47 mmoles of 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 is 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 of KF (0.34 mmole) was pretreated with $(CF_3)_2CO$ according to the procedure already described. It was then treated with 0.39 mmole of 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. NF_2CFO (0.16 mmole) and about 0.5 ml of 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 of COF_2) 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 of 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 of CH_3CN.

The residual KF in the bulb was then used directly for several subsequent one-step preparations. Typically, 0.50–0.55 mmole of NF_2CFO and 0.5 ml of 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 ensure 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 fron a typical pyrolysis were: 0.15 mmole of a low-boiling fraction (primarily *cis*-N_2F_2, COF_2, and CO_2), 0.17 mmole of NF_2CFO, a trace of HNF_2, and 0.05 mmole of $(NF_2)_2CO$. 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), 978 (s), 926 (vs), 885 (m), 848 (m), doublet, 720 (m), broad. The F^{19} nmr spectrum shows a single, broad resonance at −30.8 ppm. The gas density molecular weight was 131 ± 1 (calcd, 132). Infrared analysis indicated that the gas reacts instantly with water vapor at room temperature to form only CO_2 and HNF_2. $(NF_2)_2CO$ (13.4 mg) was hydrolyzed in acidified aqueous KI solution at room temperature. *Anal.* Found: 0.0592 oxidizing equiv (as I_3^-)/g. Calcd 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 $CsOCF_2NF_2$(?).—Dehydrated CsF (60.0 mg, 0.39 mmole) was allowed to react with 0.64 mmole of CF_3CFO and 1.85 g of CH_3CN at room temperature for 24 hr. The unreacted gas was 0.30 mmole of CF_3CFO, indicating the formation of 0.34 mmole of $CsOC_2F_6$. NF_2CFO (0.39 mmole) was frozen onto this solution, and after being allowed to react 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 of 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.—Dehydrated CsF (64.3 mg, 0.42 mmole) was allowed to react with NF_2CFO [106.7 mg, 1.09 mmoles (*PVT*), mol wt = 97.9] and 291.2 mg of 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*), mol wt = 72.6], it was found to be approximately 0.51 mmole (34 mg) of COF_2 and 0.13 mmole (13 mg) of NF_2CFO. Consequently, the composition of the nonvolatile solute appeared to be (element, mmoles): Cs, 0.42; O, 0.44; C, 0.44; N, 0.95; F, 2.25; this corresponds to the empirical formula $Cs_{1.0}O_{1.0}C_{1.0}N_{2.2}F_{5.2}$. After this solution was treated with 0.36 mmole (*PVT*) of NF_2CFO for 20 hr at −40°, the residual gas was separated and found to be a mixture of COF_2 and NF_2CFO [33.1 mg, 0.390 mmole (*PVT*), mol wt = 84.9] and was estimated to be 0.17 mmole (11 mg) of COF_2 and 0.22 mmole (22 mg) of NF_2CFO. The net reaction to this point was therefore the consumption of 1.09 mmoles of NF_2CFO by 0.42 mmole of CsF with the formation of 0.67 mmole of COF_2. Consequently the composition of the solute now appeared to be (element, mmoles): Cs, 0.42; O, 0.42; C, 0.42; N, 1.09; F, 2.35; this corresponds to the empirical formula $Cs_{1.0}O_{1.0}C_{1.0}N_{2.6}F_{5.6}$.

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 1965–1967. The authors wish to thank Mr. B. J. Nist of the University of Washington for some of the nuclear magnetic resonance spectra.