THIRD ANNUAL REPORT

Nonr 4217(00)

ARPA Order No. 442, Item 3 Program Code No. 5910

NEW HYPOFLUORITES CONTAINING NITROGEN

University of Idaho
Moscow, Idaho

Jean'ne M. Shreeve

October 1966

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

Third Annual Report

Abstract

Difluoroaminocarbonyl fluoride, which is easily prepared by the ultraviolet irradiation of N_2F_4 and CO, is readily absorbed by anhydrous KF to form compounds of the nature $KOCF_2NF_2$, $KOCF(NF_2)_2$, and $KOC(NF_2)_3$. If 1.5 equivalents of NF_2CFO is allowed to react with a single equivalent of KF to form what is likely mixture of $KOCF_2NF_2$ and $KOCF(NF_2)_2$, this mixture may be thermally decomposed without explosion to yield perfluorourea. It has not been possible to prepare the hypofluorite, NF_2CF_2OF. When $KOCF(NF_2)_2$ is reacted with $SiCl_4$, a new volatile compound, $NF_2C(Cl)O$ is obtained. $NF_2C(F)O$ gives $NF_2C(Cl)O$ with $AlCl_3$.

N,N-bis(trifluoromethyl)hydroxylamine forms a solid adduct with either CsF or KF. The adduct will react at room temperature with perfluoroacyl and carbonyl halides to give the corresponding bis(trifluoromethyl)nitroxo-compounds. These compounds are stable, volatile liquids with characteristic nmr and ms spectra. The solid adduct seems to be $2(CF_3)_2NOH \cdot CsF$ which when reacted is converted to the residue, $CsF \cdot 2HX$.

Bis(trifluoromethyl)ketene is highly reactive with compounds that ordinarily add across olefinic double bonds, e.g., $S_2O_6F_2$, N_2F_4, and NF_2OSO_2F. With the latter two, two isomers are obtained. Only fair separation of these has been realized. Treatment with fluorine at -20° in the presence of CsF yields hypofluorites as indicated by the nmr. The ketene isomer, $(CF_3)C(=CF_2)C(O)F$, also will react with the above compounds and hypofluorites should arise.

A simple preparation of FNO has been found which involves the reaction of nitrogen dioxide with KF or CsF. The conversion based on NO_2 consumed is about 48+%. This reaction may be carried out in metal or Pyrex glass vessels and the conversion rate is increased by heating. It has been found that if the KF is pretreated with hexafluoroacetone the much greater surface area remaining apparently causes reaction even at room temperature to be essentially instantaneous. The solid remaining is KNO_3 as determined by x-ray powder patterns.

Third Annual Report

A. The synthesis of difluoroaminocarbonyl fluoride[1] and its subsequent volatile and nonvolatile reaction products formed with a variety of compounds has resulted in some very interesting chemistry.

Difluoraminocarbonyl fluoride will not react with gross-crystalline anhydrous potassium fluoride at room temperature in the absence of a solvent; however, if the salt is first treated by the formation and subsequent decomposition of its adduct with hexafluoroacetone, $KOCF(CF_3)_2$, it will readily absorb gaseous NF_2CFO to form the adduct $KOCF_2NF_2$ in good yield. If the latter salt is dissolved in anhydrous acetonitrile and treated with an equivalent of NF_2CFO at about -35°, there is formed in good yield a nonvolatile product corresponding to the empirical formula $KOCN_2F_5$ which is probably the salt $K^+OCF(NF_2)_2^-$. The latter is not stable at room temperature and has not been isolated completely free of acetonitrile. Although $KOCF_2NF_2$ decomposes rapidly and nearly quantitatively at 80° to KF and NF_2CFO, $KOCF(NF_2)_2$ generally explodes violently when heated under vacuum. A sample of about 0.2 mmol. completely demolished a heavy-walled glass bulb when placed in a water bath at 95°. If the solid, however, is diluted about 1:1 with $KOCF_2NF_2$, it may usually be pyrolysed without explosion, yielding perfluorourea in about 30% yield[2].

The preparation must be done under strictly anhydrous conditions and whenever possible under high vacuum. In a typical experiment, 0.5 mmol.of anhydrous KF was weighed out in a small Pyrex bulb which could be fitted with a stopcock. It was then treated with an excess of hexafluoroacetone in acetonitrile solution at room temperature until completely dissolved. The solution was evaporated in vacuo from a warm water bath and pumped on at 95° to leave the deposited KF as pure as possible. It was then treated with an excess of gaseous NF_2CFO at 0° for 12 hr. The KF was about 90% converted to $KOCF_2NF_2$, and any residual hexafluoroacetone was liberated and removed with the unreacted NF_2CFO. The salt was dissolved in acetonitrile at -35° and 0.25 mmol. of NF_2CFO was frozen in. After reacting 6 hr. at -35°, the residual gas (COF_2) was removed at this temperature and the solvent was pumped off as completely as possible at 0°. Most of the remaining solvent was removed by pumping for 3 min. at 40°, although slight decomposition of the solid resulted. The decomposition products included NF_2CFO and COF_2, but not $(NF_2)_2CO$. The bulb was then immersed in a water bath at 95° while volatile materials liberated were removed by pumping through a trap at -183°. The solid decomposed rapidly yielding at least cis-N_2F_2, COF_2, NF_2CFO, $(NF_2)_2CO$, and small amounts of HNF_2 and CH_3CN. The gases were distilled out of the trap at -79° and separated by fractional codistillation using an unpacked 10-ft., 1/8-in. o.d. copper column.

Pure perfluorourea is stable in Pyrex at 25° for at least short periods. It is instantly and completely hydrolysed when it contacts water. The only volatile infrared-active hydrolysis products are CO_2 and HNF_2. Since the reaction of HNF_2 with I^- is quantitative[3], a weighed sample of $(NF_2)_2CO$ was hydrolysed in 0.2 M HI solution for analysis. Found 20.7% N, calculated for CF_4N_2O, 21.2% N. Its vapor-density molecular weight was found to be 132, 130, and 131; calculated for CF_4N_2O, 132. It condenses to a colorless glass at -183° and its boiling point, estimated from the fractional codistillation, is near -35°

The fundamental bands in the infrared spectrum are, in cm.$^{-1}$: 1860 s, carbonyl stretch; 1150 m; 978 s; 926 vs; 885 m (trace HNF_2?); 848 m, doublet; 720 m, broad. The F^{19} nuclear magnetic resonance spectrum was obtained at 56.4 mc. using a modified Varian DP-60 instrument. The spectrum was scanned from -210 to +135 ppm. relative to an external CCl_3F reference. The only resonance detected for $(NF_2)_2CO$ was a broad peak at -30.8 ppm. Under these conditions NF_2CFO gives a similar resonance at -28.7 ppm.

Preparation and properties of a series of solids which are probably the ionic salts, $M^+OCF_2NF_2^-$, $M^+OCF(NF_2)_2^-$, and $M^+OC(NF_2)_3^-$, where M is K or Cs, have been examined. $KOCF_2NF_2$ is easily prepared in a solid-gas reaction if the crystalline, anhydrous KF is first pretreated as for production of perfluorourea above. The finely-divided KF will readily absorb gaseous NF_2CFO at room temperature or 0° and conversion to $KOCF_2NF_2$ is 90% complete after 12 hours. The unreacted NF_2CFO contains only small amounts of degradation products, COF_2 and N_2F_2, and hexafluoroacetone. Analogous reactions with CsF result in degradation of at least part of the gas to COF_2. The solid which may be $CsOCF_2NF_2$ is easily prepared as a precipitate when an acetonitrile solution of $CsOC_2F_5$ (CsF + $CF_3C(O)F$) is reacted with an equivalent of NF_2CFO at -40°. It is stable at least for short periods at 95° and liberates I_2 from a solution of KI. Conversely, while $KOCF_2NF_2$ is stable for at least short periods under static vacuum at room temperature, it is very rapidly decomposed to KF and NF_2CFO in high yield under dynamic vacuum at 80 or 90° and is highly soluble in acetonitrile at -40°. It is immediately hydrolyzed by water to CO_2, HNF_2, and N_2F_2 and liberates I_2 from a solution of KI. Although its acetonitrile solution is not stable at room temperature, F^{19} nmr studies of $KOCF_2NF_2$ in this solvent suggest chemical shifts of +47.0 and -21.1 ppm. relative to an external reference of CCl_3F.

We have looked at the chemistry of $KOCF_2NF_2$ to some extent. All attempts to prepare the unreported hypofluorite, pentafluoro(1-aza,3-oxa)-propane, NF_2CF_2OF by the fluorination of $KOCF_2NF_2$ have been unsuccessful. Treatment of the solid with pure fluorine or fluorine diluted with nitrogen at temperatures as low as -183° yields only NF_3 and CF_3OF as the volatile products.

$KOCF_2NF_2$, in the presence of excess KF, has also been allowed to react with the halogens in acetonitrile solution at -35°. Fluorine liberates NF_3 and CF_3OF as the major products. An equivalent of chlorine yields NF_2Cl as the primary product which is easily separated from unreacted Cl_2 and other contaminants by fractional codistillation. This preparation of NF_2Cl is one of the safest and most convenient of those yet reported as it requires no specialized apparatus or tedious separation. An equivalent of bromine yields N_2F_4 in high yield as the only gaseous product. CF_3OF will rapidly decompose solid $KOCF_2NF_2$ at room temperature yielding CF_3ONF_2; an analogous reaction in acetonitrile solution at -40° yields NF_3. $KOCF_2NF_2$, in acetonitrile solution at -40°, does not react appreciably with NF_2Cl after several days; at room temperature, however, KCl slowly precipitates with the liberation of N_2F_4 and COF_2.

$KOCF_2NF_2$ reacts rapidly with an equivalent of NF_2CFO in acetonitrile solution at -40°. Since the only volatile product is an equivalent of COF_2, this would seem to indicate that the salt $KOCF(NF_2)_2$ is formed according to

$$KOCF_2NF_2 + NF_2CFO = KOCF(NF_2)_2 + COF_2.$$

$KOCF(NF_2)_2$ is not stable at room temperature and has not been isolated completely free of acetonitrile. The solid will not crystallize completely by pumping off the solvent at 0°. Although most of the remaining solvent may be removed by pumping at 40° for a few minutes, the solid then slowly decomposes to COF_2, N_2F_2, and NF_2CFO, and when heated to 70° under vacuum, it generally explodes violently. F^{19} nmr studies of $KOCF(NF_2)_2$ in acetonitrile solution at room temperature suggest chemical shifts of +69.4 and -18.4 ppm. relative to CCl_3F as an external reference. The solid, when allowed to react with $SiCl_4$, yields at least NF_2Cl and a compound identified as $NF_2C(O)Cl$; when treated with fluorine, yields at least CF_3OF; and decomposes slowly at room temperature. As stated above, if a solution of $KOCF_2NF_2$ in acetonitrile is treated with half an equivalent of NF_2CFO at -40°, the products are presumably a mixture of $KOCF_2NF_2$ and $KOCF(NF_2)_2$. This mixture, after evaporation of the solvent, may generally be pyrolyzed at 95° without explosion to yield $(NF_2)_2CO$ in about 30% yield based on the estimated content of $KOCF(NF_2)_2$.

When $KOCF(NF_2)_2$ is treated with NF_2CFO in acetonitrile solution at -40°, the gas is partially converted to COF_2. The initial reaction proceeds rapidly but will not go to completion during extended reaction time at this temperature. There seems to be an equilibrium established since if NF_2CFO is added to $KOCF(NF_2)_2$, COF_2 is produced. On the other hand, if the solid is treated with COF_2, NF_2CFO is produced.

$$KOCF(NF_2)_2 + NF_2C(O)F \rightleftharpoons KOC(NF_2)_3 + COF_2$$

Some perhaps meaningful equilibrium constants have been determined.

$KOC(NF_2)_3$ is deposited as a white solid upon evaporation of the solvent and slowly decomposes at room temperature, liberating at least

COF_2, N_2F_2, and NF_2CFO. The above equation would seem to suggest that $KOC(NF_2)_3$ might be useful as a difluoroaminating agent for acyl fluorides. However, when the reaction $KOC(NF_2)_3 + CF_3CFO = KOCF(NF_2)_2 + CF_3CONF_2$ was attempted, no appreciable reaction was observed.

Work is being continued here to try to more thoroughly characterize these solids and to st y the $KOCF(NF_2)_2$-$KOC(NF_2)_3$ equilibrium more extensively.

B. N,N-bis(trifluoromethyl)hydroxylamine ($(CF_3)_2NOH$) reacts with either CsF or KF to form a solid adduct. As the hydroxylamine is taken up by the anhydrous salt at room temperature, its physical appearance changes and when two moles of the former have been added, the solid is fluffy and non-crystalline looking. This is the maximum amount of material to be absorbed by the solid and at room temperature the CsF adduct has an equilibrium vapor pressure of $(CF_3)_2NOH$ of about 1 mm. while the KF adduct has about 4 mm. The solid ($2(CF_3)_2NOH\cdot CsF$) melts at about 70° with the evolution of $(CF_3)_2NOH$. Examination of the proton and F^{19} nmr. shifts of the adduct relative to the unreacted hydroxylamine both in acetonitrile solvent indicates the formation of an addition compound rather than one of an ionic nature since the shifts of the former are both to lower field.

This adduct has been found to react with a variety of perfluoroacyl and carbonyl halides at room temperature--with COF_2 to form carbonyl bis(trifluoromethyl)nitroxide, $((CF_3)_2NO)_2CO$, and bis(trifluoromethyl)nitroxocarbonyl fluoride, $(CF_3)_2NOC(O)F$; with $COCl_2$ to form bis(trifluoromethyl)nitroxocarbonyl chloride, $(CF_3)_2NOC(O)Cl$[4]. Trifluoromethylcarbonyl bis(trifluoromethyl)-nitroxide, $(CF_3)_2NOC(O)CF_3$, and heptafluoropropylcarbonyl bis(trifluoromethyl)nitroxide, $(CF_3)_2NOC(O)C_3F_7$, are obtained with the perfluoroacyl chlorides, $CF_3C(O)Cl$ and $C_3F_7C(O)Cl$, respectively. These reactions are run neat and the yields are respectable ($>50\%$ conversion) with the exception of the reaction with $COCl_2$ to obtain $(CF_3)_2NOC(O)Cl$. Here it is found that both chlorides are readily replaced and about 10% yield is the best realized for this method. However, if $(CF_3)_2NOC(O)F$ is allowed to contact $AlCl_3$ in the presence of a slight excess of anhydrous gaseous HCl, considerably larger yields of $(CF_3)_2NOC(O)Cl$ may be obtained.

The F^{19} nmr's are as one would predict--the CF_3 groups in $(CF_3)_2NO$- are relatively invariant in the 69 ϕ region and the other CF groups are in their characteristic shift positions.

It is interesting to note that the mass spectra of these compounds, without exception, have as the second most abundant peak the $C(O)X^+$ group from $(CF_3)_2NOC(O)X$ which would indicate that one of the primary processes occurring is $(CF_3)_2NOC(O)X + e^- = (CF_3)_2NO\cdot + C(O)X^+ + 2e^-$. This infers that the O-C bond is comparatively easily ruptured and perhaps is not unexpected since the bis(trifluoromethyl)nitroxide radical is very stable^5. Infrared spectra are also consistant with postulated structures.

All of the compounds are volatile liquids and are stable in glass at room temperature. However, $(CF_3)_2NOC(O)F$, $(CF_3)_2NOC(O)Cl$, and $(CF_3)_2NOC(O)CF_3$ are hydrolytically unstable while $((CF_3)_2NO)_2C(O)$ and $(CF_3)_2NOC(O)C_3F_7$ are both stable toward water. This indicates that steric hindrance may be an important factor in their relative reactivities.

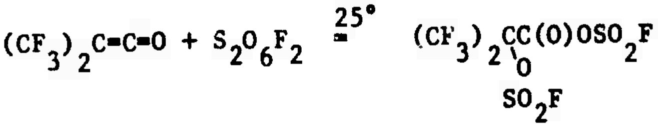
The solid remaining after reaction of the adduct with an acyl halide has been found to be thermally stable but not further reactive with more of the halide. The solid may be $CsF\cdot 2HX$. The preparation of the new nitroxo-compounds may best be described by the following:

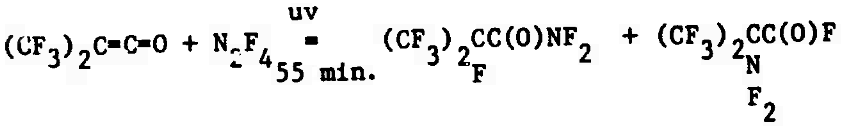
$$2(CF_3)_2NOH + CsF \rightleftharpoons ((CF_3)_2NOH)_2\cdot CsF$$

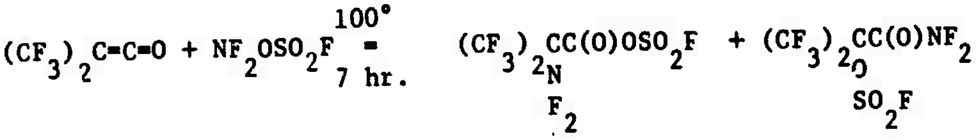
$$((CF_3)_2NOH)_2\cdot CsF + 2R_fC(O)X = 2(CF_3)_2NOC(O)R_f + CsF\cdot 2HX$$

Since this seems to be a general method for the compounds here described, we are expanding our efforts to examine reactions of inorganic halides, e.g., $SOCl_2$, SOF_2, PF_2Cl, etc., with the solid adduct in order to prepare analogous inorganic derivatives.

C. Bis(trifluoromethyl)ketene, $(CF_3)_2C{=}C{=}O$, has a relatively reactive olefinic bond. We have taken advantage of this to prepare several new compounds including several new hypofluorites. Characterization of these compounds is currently under way.

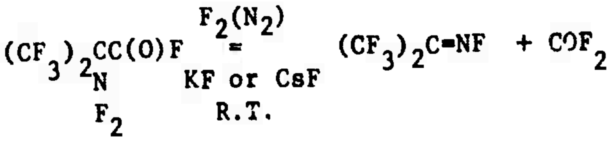
a)

$(CF_3)_2C{=}C{=}O + S_2O_6F_2 \xrightarrow{25°} (CF_3)_2\underset{\underset{SO_2F}{O}}{C}C(O)OSO_2F$

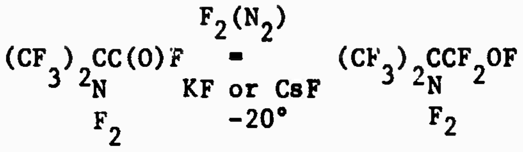
b)

$(CF_3)_2C{=}C{=}O + N_2F_4 \xrightarrow[55\ min.]{uv} (CF_3)_2\underset{F}{C}C(O)NF_2 + (CF_3)_2\underset{\underset{F_2}{N}}{C}C(O)F$

c)

$(CF_3)_2C{=}C{=}O + NF_2OSO_2F \xrightarrow[7\ hr.]{100°} (CF_3)_2\underset{\underset{F_2}{N}}{C}C(O)OSO_2F + (CF_3)_2\underset{\underset{SO_2F}{O}}{C}C(O)NF_2$

d) $(CF_3)_2C{=}C{=}O + NF_2Cl \xrightarrow[1\ hr.]{100°}$ unstable addition compounds

Separation of the isomers obtained in these reactions is wrought with difficulty and we still have not been entirely successful in this undertaking. However, we have taken what we consider fairly pure samples and subjected them to the following:

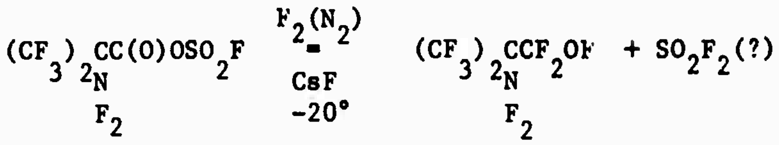

$(CF_3)_2\underset{\underset{F_2}{N}}{C}C(O)F \xrightarrow[\substack{KF\ or\ CsF\\ R.T.}]{F_2(N_2)} (CF_3)_2C{=}NF + COF_2$



$$\underset{\underset{F_2}{N}}{(CF_3)_2C}C(O)F \underset{\substack{\text{KF or CsF}\\ -20^\circ}}{\overset{F_2(N_2)}{=}} \underset{\underset{F_2}{N}}{(CF_3)_2C}CF_2OF$$

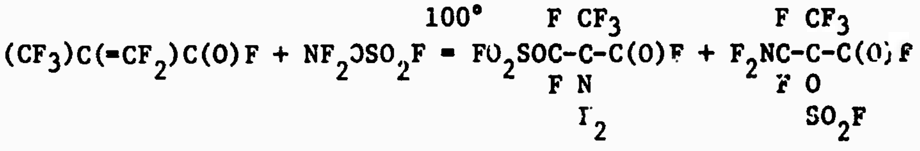
(ca 100%)

This hypofluorite has been confirmed by nmr.



$$\underset{\underset{F_2}{N}}{(CF_3)_2C}C(O)OSO_2F \underset{\substack{CsF\\ -20^\circ}}{\overset{F_2(N_2)}{=}} \underset{\underset{F_2}{N}}{(CF_3)_2C}CF_2OF + SO_2F_2(?)$$

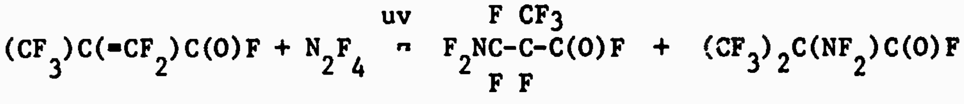
Since in the $(CF_3)_2C=C=O$, there is considerable quantity of its isomer $(CF_3)C(=CF_2)C(O)F$, we are looking at some of the reactions of the latter:



$$(CF_3)C(=CF_2)C(O)F + NF_2OSO_2F \overset{100^\circ}{=} FO_2SOC\text{-}\overset{F}{\underset{F}{C}}\text{-}\overset{CF_3}{\underset{\underset{F_2}{N}}{C}}\text{-}C(O)F + F_2NC\text{-}\overset{F}{\underset{F}{C}}\text{-}\overset{CF_3}{\underset{\underset{SO_2F}{O}}{C}}\text{-}C(O)F$$

I II

$$\text{I and II} + F_2(N_2) \underset{-20^\circ}{\overset{CsF}{=}} 2 \text{ hypofluorites}$$



$$(CF_3)C(=CF_2)C(O)F + N_2F_4 \overset{uv}{=} F_2NC\text{-}\overset{F}{\underset{F}{C}}\text{-}\overset{CF_3}{\underset{F}{C}}\text{-}C(O)F + (CF_3)_2C(NF_2)C(O)F$$

III IV

$$\text{III and IV} + F_2(N_2) \underset{-20^\circ}{\overset{CsF}{=}} 2 \text{ hypofluorites}$$

Much work remains to be done on this entire series of reactions.

D. An easy, straight-forward method for the synthesis of nitrosyl fluoride which involves the reaction of nitrogen dioxide with either KF or CsF has been well-worked out.[6] The synthesis proceeds smoothly at room temperature in either a Pyrex glass or metal reaction vessel.

In a typical run, 5 g. (33 mmoles) of 99% CsF were 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.

Reactions have been carried out in prefluorinated vessels of Monel, stainless steel, and nickel without noticeable decomposition or decrease in yield of ONF at temperatures below 300°. Infrared spectra of ONF taken in Pyrex cells with NaCl windows agree with published data[7] with only a trace of impurity present.

Molecular weight determination using a nickel weighing vessel and gas density method gave satisfactory results. Identification of the ONF was made by infrared analysis and molecular weight determinations in all cases.

The reaction can also be carried out using all Pyrex glass equipment. It can be followed by the decrease in the red-brown color of the unreacted NO_2. The ONF can easily be removed from an incomplete reaction mixture by condensing the unreacted NO_2 at -78° and transferring out the volatile product. Heating the reaction mixture at 80° increased the conversion rate.

Attack on the glass vessel became noticeable above 80° and lower yields of the product were obtained. ONF has been stored in the glass reaction vessel over CsF for at least a week without noticeable decomposition occurring. No SiF_4 has been observed in any of the preparations of the product, presumably due to the reaction or adsorption of any SiF_4 present by the excess CsF.

The reactivity of CsF and KF has been found to be greatly enhanced by first forming the hexafluoroacetone adduct of the metal fluoride in acetonitrile solution. The compound $MF \cdot OC_3F_6$ can then be decomposed by removing the solvent and hexafluoroacetone at 100° under dynamic vacuum. Heating of the salt at higher temperatures tends to decrease its reactivity.

When mmole samples of NO_2 were condensed into the bulb at -78° and were warmed to room temperature, FNO was the only volatile product. An average conversion of 48.6% was obtained on 12 runs. The reaction time was found to increase if the metal fluoride was not present in excess, and attempts to react CsF and NO_2 in stoichiometric amount, by this method gave a mixture of NO_2 and ONF. Reactions with the two metal fluorides were found to be similar in all cases.

If excess hexafluoroacetone is added to CsF or KF in acetonitrile to give a clear solution and the solvent is removed under vacuum at room temperature, the salt $MF \cdot OC_3F_6$ 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. This compound is a light yellow gas that freezes to a yellow solid and has been synthesized previously from ONF and $(CF_3)_2CO$[8].

Dinitrogen oxide and nitric oxide were not affected by CsF under analogous conditions. Dinitrogen trioxide was found to react with the alkali metal fluoride to give a mixture of ONF, NO, and unreacted N_2O_3 as gaseous products.

A gravimetric determination was carried out on the reaction of KF with NO_2 to help verify the stoichiometry. 0.4245 g. (9.230 mmoles) of NO_2 was reacted with 2 g. of KF in 100 ml. nickel weighing vessel and 4.615 mmoles of ONF were removed. For quantitative conversion of 4.615 mmoles of KF to KNO_3, a weight increase of 0.1985 g. is required. A 0.2025 g. increase was observed experimentally.

More conclusive evidence for the alkali nitrate as the solid product was obtained when the x-ray powder patterns of the solid residue from a reaction of KF with NO_2 and from reagent grade KNO_3 were found to be identical.

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

$$2NO_2 + MF = ONF + MNO_3$$

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

Bibliography

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

(2) G. W. Fraser and J. M. Shreeve, Chem. Comm., 532 (1966)

(3) E. A. Lawton and J. Q. Weber, J. Am. Chem. Soc., 81, 4755 (1959)

(4) D. P. Babb and J. M. Shreeve, Inorg. Chem., in press.

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

(6) C. T. Ratcliffe and J. M. Shreeve, Chem. Comm., 674 (1966).

(7) P. J. H. Woltz, E. A. Jones, and A. H. Nielsen, J. Chem. Phys., 20, 378 (1952).

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

Security Classification

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 1965 - 30 September 1966

5. AUTHOR(S) (First name, middle initial, last name)

Jean'ne M. Shreeve

6. REPORT DATE: October 1, 1966

7a. TOTAL NO OF PAGES: 16

7b. NO OF REFS: 8

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): Third Annual Report - October 1, 1966

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

Difluoroaminocarbonyl fluoride, which is easily prepared by the ultraviolet irradiation of N_2F_4 and CO, is readily absorbed by anhydrous KF to form compounds of the nature $KOCF_2NF_2$, $KOCF(NF_2)_2$, and $KOC(NF_2)_3$. If 1.5 equivalents of NF_2CFO is allowed to react with a single equivalent of KF to form what is likely a mixture of $KOCF_2NF_2$ and $KOCF(NF_2)_2$, this mixture may be thermally decomposed without explosion to yield perfluorourea. It has not been possible to prepare the hypofluorite, NF_2CF_2OF When $KOCF(NF_2)_2$ is reacted with $SiCl_4$, a new volatile compound, $NF_2C(Cl)O$ is obtained. $NF_2C(F)O$ gives $NF_2C(Cl)O$ with $AlCl_3$. [U]

N,N-bis (trifluoromethyl)hydroxylamine forms a solid adduct with either CsF or KF. The adduct will react at room temperature with perfluoroacyl and carbonyl halides to give the corresponding bis(trifluoromethyl)nitroxo-compounds. These compounds are stable, volatile liquids with characteristic nmr and ms spectra. The solid adduct seems to be $2(CF_3)_2NOH \cdot CsF$ which when reacted is converted to the residue, $CsF \cdot 2HX$. [U]

Bis(trifluoromethyl)ketene is highly reactive with compounds that ordinarily add across olefinic double bonds, e.g., $S_2O_6F_2$, N_2F_4, and NF_2OSO_2F. With the latter two, two isomers are obtained. Only fair separation of these has been realized. Treatmen with fluorine at -20° in the presence of CsF yields hypofluorites as indicated by the nmr. The ketene isomer, $(CF_3)C(=CF_2)C(O)F$, also will react with the above compounds and hypofluorites should arise. [U]

SEE ATTACHED SHEET

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6801

Security Classification

13. Abstract continued --

A simple preparation of FNO has been found which involves the reaction of nitrogen dioxide with KF or CsF. The conversion based on NO_2 consumed is about 48+%. This reaction may be carried out in metal or Pyrex glass vessels and the conversion rate is increased by heating. It has been found that if the KF is pretreated with hexafluoroacetone the much greater surface area remaining apparently causes reaction even at room temperature to be essentially instantaneous. The solid remaining is KNO_3 as determined by x-ray powder patterns. [U]

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
perfluorourea						
bis(trifluoromethyl)nitroxo compounds						
addition across $\rangle C = C \langle$ in bis (trifluoromethyl)ketene						
preparation of nitrosyl fluoride						