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FINAL REPORT

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National Aeronautics and Space Administration
Contract NSR-10-005-047

SYNTHESIS OF ELASTOMERS FOR USE WITH LIQUID FLUORINE

Henry C. Brown
A. R. Mukherjee

Submitted by
Department of Chemical Engineering
Florida Engineering and Industrial Experiment Station
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FOREWORD

This report has been prepared according to the provisions of Contract NSR-10-005-047, National Aeronautics and Space Administration, with the University of Florida.

Personnel engaged in this work were Dr. Henry C. Brown, Principal Investigator, and Dr. A.R. Mukherjee.

I. INTRODUCTION

The objective of this research is the synthesis of elastomeric polymers that will be resistant to the strong oxidizing effect of fluorine, oxygen difluoride, nitrogen tetroxide and similar agents. In addition, it is desirable that the material be flexible at cryogenic temperatures.

During the present report period, attempts have been made to use some trialkyl or triaryl phosphines as initiators for ionic polymerization of hexafluorobutyne-2 and its copolymerization with some suitable comonomers. Being ionic in nature, the rate of homopolymerization was extremely fast even at very low temperature in some cases; in regard to copolymerization, little success has been achieved.

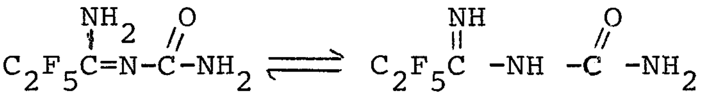
Efforts have been made to copolymerize hexafluorobutyne-2 and tetrafluoroethylene in the presence of dichlorohexafluorobutyne-2 and ultraviolet light as initiator with the monomers in different proportions. Solubility and melting behavior of the end-products were studied. Homopolymer from tetrafluoroethylene, prepared under similar conditions, was found to be a soluble easily fusible material but the homopolymer from hexafluorobutyne-2, prepared under identical conditions, was an insoluble and infusible product. While homopolymerization of hexafluorobutyne-2 could be carried out in presence of air, oxygen not being an inhibitor in this system, hexafluoroactone imine acted as a total inhibitor.

Attempts to homopolymerize hexafluorobutyne-2, using a) K-tert-butoxide and b) sulfonyl chloride + azobis isobytyronitrile as initiators, did not work. But when sodium cyanide was used as initiator in presence of polar solvents, some type of reaction did take place leading to dark solvent-soluble product; no polymerization, however, did take place.

Reaction of perfluorobutadiene and sulfur tetrafluoride in the presence of cesium fluoride in a sealed glass tube or pressure tube at high temperature for long time results in some high boiling liquid product, not yet characterized. Some glass reacts probably with SF_4, resulting in some insoluble, infusible product. Other reaction conditions, such as use of diglyme as solvent, were also tried. The results were not quite reproducible. The higher boiling liquid product was found to contain C, F and S by elemental analysis, but analysis result was not conclusive.

Attempts have been made to synthesize trifluoromethyl hydroxamic acid and the corresponding isocyanate. This hydroxamic acid being rather unstable, attempts were made to stabilize it in the form of its copper salt. The reaction between trifluoromethyl isocyanate and ammonia was also studied further.

Reaction of perfluorobutyroisocyanate and ammonia has been studied under various conditions. While the reaction product is a mixture of products in most of the areas, one procedure has resulted in reaction of four moles of ammonia with one mole of isocyanate, product being



$$C_2F_5\overset{NH_2}{\overset{|}{C}}=N-\overset{O}{\overset{//}{C}}-NH_2 \rightleftharpoons C_2F_5\overset{NH}{\overset{\|}{C}}-NH-\overset{O}{\overset{//}{C}}-NH_2$$

(65-70%) and NH_4F (by-product, 25%, approximately).

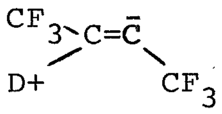
It was found that while synthesis of hydroxamic acids from the ethyl esters of perfluorosuccinic, perfluoroglutaric, perfluoroadipic and perfluorosebacic acid was rather smooth, their conversion to the corresponding diisocyanates was quite difficult. All the hydroxamic acids were produced in good yield and they are stable, high melting solids. Little or no isocyanate resulted on heating perfluoroglutaro hydroxamic acid with phosphorous pentoxide or polyphosphoric acid. In the case of perfluoroadipo- and perfluorosebaco hydroxamic acid, the yield was a mixture of isocyanate and acid or anhydride which could not be completely separated. The analysis of crude perfluorosebacodiisocyanate (obtained as distillate during distillation of the liquid product) by glc showed three ingredients. The major one on isolation turned to a white solid, perhaps by reaction with moisture and had the same C:N ratio as that of $(CF_2)_8(NCO)_2$.

Reaction of perfluorosebacodiacid chloride with silver cyanide above 170°C resulted in some dark resinous product, which was perhaps a mixture and did not show any absorption for the -CN group in the infrared spectra.

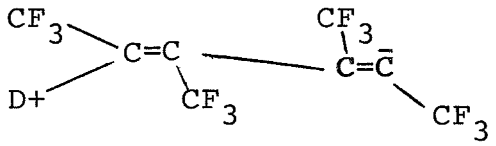
II. DISCUSSION

A. Use of Phosphines as Initiators of Polymerization of Hexafluorobutyne-2

While studying some reactions of hexafluorobutyne-2 with phosphines and amines, Cullen and Dawson noticed that triphenylphosphine causes the butyne to polymerize at -78°. A similar but slower reaction takes place with triethylamine Ref: W.R. Cullen and D.S. Dawson, Canad. J. Chem., 45, 2887 (1967). They also noticed that in a toluene solution of triphenyl phosphine, the polymerization reaction was smooth at temperatures as low as -78°C, and resulted in a white, solid, high melting polymer, but in absence of solvent the reaction can be violent at or above room temperature. The obvious mechanism is the formation of a 1,3-dipolar intermediate such as



in the initiation step and then propagation via addition of butyne-2 molecules as



, etc., D being the nucleophile such as triphenylphosphine.

To date, attempts have been to homo- or copolymerize hexafluorobutyne-2 in the presence of three phosphines:

Triphenyl phosphine, $(C_6H_5)_3P$	Yellowish solid, m.p. 75-77°C
Tri-n-butyl phosphine $(C_4H_9)_3P$	High boiling colorless liquid

Trioctyl phosphine	$(C_8H_{17})_3P$	High boiling colorless liquid

Phosphines have been used both in the presence and the absence of solvents; solvents used in these experiments were toluene and tetrahydrofuran.

When toluene was used as a solvent, it was recovered almost in full after the experiment (Expt. M-1,3); thus the solvent did not take any part in the reaction.

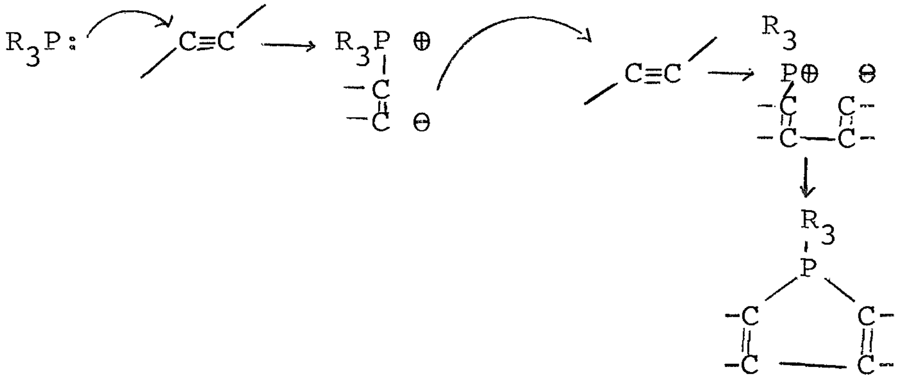
1. Homopolymerization of Hexafluorobutyne-2

Homopolymerization of hexafluorobutyne-2 in the presence of triphenyl phosphine is almost instantaneous and the yield is over 90% if sufficient initiator is present in the system (Expt. M-4). In the presence of toluene, the reaction takes place at a low temperature (-50°C to -60°C) with darkening of the whole mass and though the reaction is almost instantaneous, not much heat is generated in the process. Polymer is formed in flakes, film and powder and it is very difficult to remove all thephosphine even after repeated extraction with ether or chloroform. Toluene (solvent) perhaps becomes incorporated in films or flakes and comes out under vacuum and heat.

In one particular experiment (Expt. M-13), an effort has been made to find the limiting concentration of initiator (triphenyl phosphine), using toluene as a solvent. I was noticed that little or no reaction took place when the initiator: monomer molar ratio was 1:120; (approx); on increasing the ratio to 1:30 (approx), about 75% of the monomer could be polymerized. Polymer in the final form was a yellowish white powder or flakes having an infrared spectrum the same as that of typical polyhexafluorobutyne-2 (prepared by $\mathrm{Co}^{60}\gamma$ - radiation or under ultraviolet radiation) with an extra strong peak at 3.4μ, probably due to phosphine in some form incorporated in the polymer. The portion extracted with ether or chloroform is dark solid with a melting range and might be a mixture of products of the phosphine. The polymer is insoluble and infusible and gives a brittle mold at 300° and 4200 lbs./sq. inch pressure. Molding under similar conditions in the presence of 10% sulfur, also gave a brittle mold.

In an attempt to use methyl alcohol as chain transferring agent (Expt. M-14), HFB-2, alcohol, toluene (solvent) and triphenyl phosphine were kept together in the temperature range of -70°C to room temperature; no reaction took place. Probably the alcohol destroyed the initiating capacity of phosphine.

Attempted homopolymerization of hexafluorobutyne-2 in the presence of tri-n-butyl phosphine in toluene as a solvent resulted in a mixture of products (Expt. M-1) and some reaction took place even when the tube was cooled in liquid air (as indicated by darkening of mass). The reaction is almost instantaneous at about -70° to -80°C and the product is a very dark liquid and some yellowish solid (polymer). Almost all the toluene could be pumped out and the dark, viscous liquid product was taken out by repeated extraction with ether. About 90% of the monomer was consumed but yield of polymer was about 45%. Perhaps the viscous dark mass was the addition product of phosphine and perfluorobutyne-2, or very low molecular weight polymer. Its infrared spectra showed a very strong peak at 3.4μ (C-H) and other peaks at 5.75μ (C=C), 6.8μ (CH_3), 7.2μ, 7.7-9μ (C-F, strong), etc. Cyclization is a possibility under such conditions, according to following scheme:



Attempted homopolymerization of hexafluorobutyne-2 in the presence of either trioctyl phosphine or tributyl antimony resulted in blackening of the initiator (temperature of reaction -70 to 100°C); but very little monomer was consumed in the process and no polymer was formed, (Expts. M-11, 12).

2. Attempted Copolymerization of Hexafluorobutyne-2

Co-polymerization of hexafluorobutyne-2 with comonomers such as trifluoronitroso methane (CF_3NO), hexafluoroacetone (CF_3COCF_3), tetrafluoroethylene (C_2F_4), hexafluorobutadiene ($CF_2=CF=CF=CF_2$) and perfluorobutyl isocyanate (C_3F_7NCO) in the presence of either triphenyl phosphine or tri-n-butyl phosphine was tried without success (Expts. M-2,3,8,9, 10, 15 and 16).

In presence of CF_3NO as a comonomer and toluene solution of $(C_6H_5)_3P$, no reaction (Expt. M-2) took place at -70° to room temperature (overnight). An attempt was made to pump out CF_3NO under vaccum at low temperature, but both the monomers volatilized. However, during the process, some polyhexafluorobutyne-2 was formed (about 20% of the respective monomer), and no other type of polymer product. The remainder of the reaction product was soluble in ether (products from phosphine).

Attempted copolymerization with CF_3COCF_3 using either $(C_6H_5)_3P$ or $(C_4H_9)_3P$ as initiators in the presence or absence of toluene (solvent) over a wide range of temperature, resulted only in darkening of the mass, but no polymer was formed (Expt. M-3, 10 and 15). The reaction product was almost completely soluble in ether, chloroform, etc. Thus hexafluoroacetone rather inhibited the polymerization of hexafluorobutyne-2 in this process. In one experiment (M-3), some colorless liquid product volatilized under vacuum (immiscible with and heavier than toluene) and showed infrared absorption at 5.4μ, $5.7-6.3\mu$ (broad), 7.5-

9μ (C-F), 10.2μ, 10.5μ, etc.

In presence of the C_2F_4 as the comonomer and $(C_4H_9)_3P$ as initiator, almost 50% of the butyne-2 monomer could be polymerized as in Expt. M-1 (Expt. M-8) and some dark viscous material was also formed. In the presence of $CF_2=CF-CF=CF_2$ as comonomer, and $(C_6H_5)_3P$ as initiator, there was no reaction below room temperature. With time some polyhexafluorobutyne-2 (about 25-30% of the monomer was formed; no further reaction took place even when the mixture was heated to 100°C. In the presence of $(C_4H_9)_3P$ as initiator, only some dark colored, viscous material was formed. Perfluorobutadiene was almost fully recovered and thus there was probably no copolymerization (Expt. M-9).

Attempted copolymerization of HFB-2 and C_3F_7NCO in the presence of triphenyl phosphine and toluene (solvent) resulted in no polymerization over a temperature range of -60°C to room temperature. Isocyanate perhaps acted as inhibitor to this system, (M-16).

Perfluorobutadiene alone did not react with $(C_6H_5)_3P$. Hexafluoroacetone or perfluorobutyronitrile also did not react with $(C_6H_5)_3P$ either in absence of solvent or in the presence of toluene or tetrahydrofuran as solvent, (Expt. M-5, 6 and 15).

B. Copolymerization of Hexafluorobutyne-2 and Tetrafluoroethylene in larger scale

Larger scale copolymerizations of hexafluorobutyne-2 (HFB-2) and tetrafluoroethylene (TFE) were carried out in a 5ℓ threenecked flask with a quartz immersion well for introducing the ultraviolet light source. Monomers were taken in different proportions and hexafluoro 2:3 dichlorobutene-2 was used as initiator. Though conversion at any one run was rather low, considerable yield was obtained by repeating the process for the same monomer feed with fresh initiator injection each time.

Products in these polymerization reactions ranged from loose powder to sticky solid, mainly depending on ratio of monomers used. The products were tested for their solubility in tetrahydrofuran and hexafluorobenzene respectively and melting behavior of each fraction was also tested. The tetrahydrofuran soluble part was a fluid or semisolid and other fractions had definite melting range. It might be mentioned that a homopolymer of HFB-2 made under similar conditions is infusible up to about 400°C and insoluble in any of the solvents; but a homopolymer of TFE, made under similar conditions, melts rather easily with fuming on a hot plate and is partly soluble too, in hexafluorobenzene. Both of these homopolymers are loose white powders in appearance.

C. Polymerization of Hexafluorobutyne-2 in presence of a) Air and b) Hexafluoroacetone imine

Polymerization of hexafluorobutyne-2 was attempted in a Vycor vessel in the presence of air, using dichlorohexafluorobutene-2 and ultraviolet light as initiator. Polymerization proceeded with some initial inhibition and the yield was quite high. Thus, air, usually an inhibitor in free radical initiated system, was not an inhibitor in this system.

Attempted copolymerization of HFB-2 and hexafluoroacetone imine, using dichloro compound and ultraviolet as initiator, resulted in total inhibition; no polymer was formed. Probably the imine destroyed the initiator. (Please see Experimental, Table III)

D. Attempted Polymerization of Hexafluorobutyne-2 using a) K-tert-butoxide and b) Sulfuryl chloride and azo--bio-isobutyronitrite as initiator

K-tert-butoxide is an ionic initiator and SO_2Cl_2 + AIBN system generates chlorine radicals by the reaction:

$$\text{AIBN} \xrightarrow{\text{heat}} 2R^{\circ} + N_2 \quad [R^{\circ} \approx (CH_3)_2\overset{\circ}{C}(CN)]$$

$$R^{\circ} + SO_2Cl_2 \longrightarrow RCl + \overset{\circ}{Cl} + SO_2\uparrow$$

None of the above mentioned initiation systems initiated polymerization of hexafluorobutyne-2.

E. Attempted Polymerization of Hexafluorobutyne-2 using Sodium Cyanide as Initiator

Sodium cyanide, when kept in contact with HFB-2 in presence of a solvent such as dimethyl sulfoxide (DMSO), acetonitrile (CH_3CN) or a mixture of dimethyl formamide (DMF) and dimethyl acetamide (DMAc), a slow reaction takes place even at low temperature leading to formation of dark product soluble in the solvent; no polymerization, however, takes place.

F. Reaction of Hexafluorobutadiene (HFBD) and Sulfur Tetrafluoride in presence of Cesium Fluoride

Hexafluorobutadiene and sulfur tetrafluoride, when kept in presence of cesium fluoride in a sealed glass tube or pressure tube for a long time at high temperature (150-250°C) react to produce some higher boiling, fairly volatile, colorless liquid. The yield might be as high as 50% (based on HFBD and SF_4 used). Under the conditions of the experiment, the glass reactor was highly corroded, and some dark colored insoluble, infusible solid was left as residue after taking off residual gas and higher boiling liquid product. In one experiment, the higher boiling liquid product was found to have approximate boiling range of 145-147°C, as determined by microcapillary method, though it might contain some lower boiling material also.

The crude liquid product could be easily transferred in a vacuum system, developed pressure of about 2 - 0.5 cm at room temperature with corresponding molecular weights (vapor density) from 330-500; actual mol. wts. might be higher as the sample might contain some HFBD as indicated by the infrared spectra of the gas showing very weak absorption at 5.6μ (for HFBD) and 5.8-6.2μ (for C=C?). The samples on being passed through a column of fluorosilicone in an 'Autoprep' gas chromatograph showed at least five peaks of variable intensities. For one sample, the first two components and last three components (major fraction) were collected as fraction 1 and 2, respectively. The infrared spectra of fraction 1, 2 and the stored sample itself looked almost alike. The spectra showed almost no absorption below 7.0μ, strong C-F absorption at 7.5-9.0μ and other absorption peaks thereafter. From gas chromatographic analysis and the infrared spectra, it seems that the liquid might even be a mixture of telomers as suggested in the proposed reaction:

$$CF_2 = CF{-}CF = CF_2 + SF_4 \longrightarrow \{\, CF_2CF_2 - CF_2 - CF_2 - SF_2 \,\}_n$$

terminated probably by F^- ions. The liquid product being immiscible in 'diglyme', the reaction was conducted in 'diglyme' meduim for better yield. The residual gas in this reaction was found to corrode the glass traps, the thick walled glass reactor was highly corroded leaving appreciable amount of insoluble infusible dark solid residue, yield of higher boiling liquid product was very low and only small amount of diglyme could be recovered even under high temperature and vacuum. It is advisable to conduct the reaction in metal reactor, to avoid the reaction with glass. (Please see Experimental, Table V.)

G. 1. Trifluoromethyl hydroxamic acid, its preparation and purification

Trifluoromethyl hydroxamic acid is formed in good yield (80-90%) from the corresponding methyl ester and hydroxylamine, following the standard procedure. But among all the perfluoromonohydroxamic acids, it is the most hygroscopic (transforms to a liquid on standing in air). It can almost completely be sublimed under vacuum at or above 50°, giving shining white crystals as sublimate. The crystals melt at 82-84° with some softening from 70°. The difference from the other monohydroxamic acids is pronounced in elemental analysis and infrared spectra; the elemental analysis of CF_3 hydroxamic acid shows a lower carbon and fluorine content and a higher hydrogen and nitrogen content, which can only be explained in terms of the presence of some free hydroxylamine in the system (elemental analysis of other hydroxamic acids are quite close to theory). Preparation of the hydroxamic acid from freshly distilled ester or reaction of the sublimed hydroxamic acid with excess of freshly distilled ester and subsequent purification by sublimation, etc., did not improve the analysis result. On addition of hydrochloric acid to the hydroxamic acid, some hydroxylamine hydrochloride separated (m.p. 151-153°C) as white crystals. The infrared spectra of the trifluoromethyl hydroxamic acid showed some differences from the other hydroxamic acids, peaks being found at 3-4μ (somewhat broad), 5.8μ, 6.0μ, 6.2μ, 6.45μ, 6.7μ, etc. Thus it might be concluded that trifluoromethyl hydroxamic acid is rather unstable in nature.

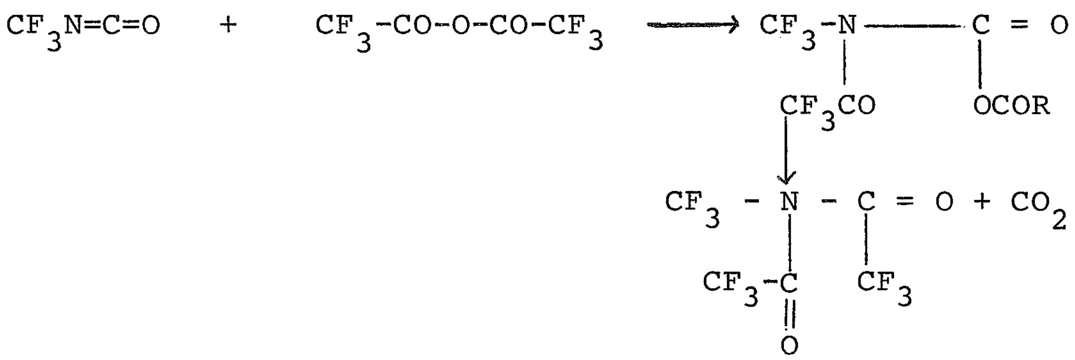
2. Stabilization of trifluoromethyl hydroxamic acid by Cu salt formation

On addition of an aqueous solution of copper acetate to an aqueous solution of trifluoromethyl hydroxamic acid, a dark green gelatinous copper salt separates and slowly settles overnight. On filtration, washing and drying, it gives dark green solid which is insoluble in organic solvents but quickly decomposes in acetic acid or ammonium hydroxide. It most probably decomposes at about 245°, as indicated by blowing out of the material from the melting point tube. It is very stable and nonhydroscopic; further purification is difficult as it is insoluble and cannot be sublimed. The infrared spectra shows peaks at 2.6-3.5μ (weak, broad - OH?) (small hump, C=O)?) 5.9μ, 6.3μ (Strong, C=N), 6.95μ (strong CF_3), 8-9μ (broad, C-F), 10.45μ, 10.8μ, 13.2μ, etc.

The elemental analysis is quite close to theory, but does show a high value for carbon, low nitrogen and a trace of hydrogen. Most probably the sample contains a little copper acetate [$Cu(CH_3COO)_2 \cdot H_2O$] , entrapped by co-precipitation, which cannot be removed by washing. This has been further confirmed by tracing the infrared spectra of a mixture of $Cu(Ac)_2 \cdot H_2O$ and the sample; the pattern of the spectra remained unchanged.

3. Preparation of trifluoromethyl isocyanate from the corresponding hydroxamic acid

Preparations of monoisocyanates from corresponding perfluoroalkyl hydroxamic acids, by heating them with P_2O_5, have one problem in common - i.e. this reaction has a tendency to become violent and go out of control. In the cases of C_2F_5 and C_3F_7 hydroxamic acids, the problem could be avoided by increasing the reaction temperature very slowly, thereby preventing any excessive heat generation. In case of CF_3 hydroxamic acid, however, this did not work; and, once the reaction starts, it proceeds with excessive heat generation and much of the product escapes. The problem was solved by mixing an inert material such as sand with the reaction mixture, which could take up most of the heat generated in the system and thus the reaction proceeded smoothly. The reaction products condensed in the trap and, coming out under vacuum at room temperature, were identified as CO_2, CF_3NCO and $(CF_3CO)_2$, respectively. Complete separation of CO_2 from CF_3NCO posed a problem due to close boiling points and some of CF_3NCO was lost in the process. The anhydride was most probably formed from the acid, generated by decomposition of hydroxamic acid. The formation of CO_2 can best be explained by reaction between the anhydride and the isocyanate, as reported by Wurtz as early as 1854 [Ref: A. Wurtz, Ann. Chem. Phys., <u>42</u>(3), 54(1854)]



Incidentally it may be mentioned that CO_2 was one of the reaction products in the preparation of C_2F_5 and C_3F_7 isocyanates also. The other reaction product must be higher boiling and might be in the residue left after distilling the isocyanates.

H. Attempted Characterization of Isocyanate-ammonia Reaction Products

It was reported earlier that reaction between isocyanates such as CF_3NCO, C_2F_5NCO or C_3F_7NCO and ammonia always result in a number of products; the expected product $R_FNHCONH_2$ (R_F being CF_3, C_2F or C_3F_7), a substituted urea, was probably not present in any of the mixtures. However, some ammonium salt, evidently NH_4F, was detected in all the product mixtures, indicating liberation of HF in the process; this was also indicated by etching of the glass vessel during reaction.

1. Reaction of trifluoromethyl isocyanate with ammonia

The reaction product of pure CF_3NCO and excess NH_3 in ether is a white solid, almost insoluble in ether, acetone, tetrahydrofuran, etc., but partially soluble in water or methanol and completely soluble in caustic soda solution. The reaction takes place with almost 50% increase in weight, thereby indicating addition of at least 3 moles of NH_3 to 1 mole of isocyanate. Part of this NH_3 is fixed as NH_4F, as indicated by presence of free F^- in the system. The F^- can, however, be removed from the system by addition of $Pb(NO_3)_2$ to the water-soluble portion of the product, when PbF_2 separates (dil. acetic acid medium). Further separation of ingredients has not yet been possible.

The reaction product of CF_3NCO and NH_3 was different from other two mixtures, as regards solubility, fusibility, infrared spectra, etc. It did not show any fusibility up to 300°C except some sublimation and was almost completely soluble only in caustic soda solution, and partially soluble in alcohol and water. It could only be sublimed partially under vacuum at high temperature (∿130°C) resulting in a poor separation. Infrared spectra of the overall mixture or of separate parts (obtained through sublimation or solubility difference) were not sharp enough to characterize any part, but there were absorptions at 3-3.5μ (broad, $\overset{+}{NH_4}$), 4.0μ, 4.5μ, 5.8-6.4μ, 6.8-7.0μ, etc.

2. Reaction of C_2F_5NCO and C_3F_7NCO with ammonia

The reaction products of C_2F_5NCO and C_3F_7NCO were a mixture consisting of viscous semisolid to white solid and the best way of separating NH_4F from the mixture was extraction with tetrahydrofuran. The tetrahydrofuran insoluble part was not completely NH_4F (as indicated by some C-F absorption and partial melting), though it was almost completely soluble in water. In the case of the C_3F_7NCO and NH_3product, this part showed infrared absorption at 2.95μ, 3.05μ, 3.1-3.5μ (NH_4) 4.5μ, 5.0μ, 6.0μ, 6.25μ, 6.7μ and some broad C-F absorption. The tetrahydrofuran soluble part of the C_2F_5NCO and NH_3 reaction product was a sticky white solid, soluble in ether also and was evidently a mixture (range of melting point and infrared pattern). It could be completely sublimed under vacuum and showed strong infrared absorption at 2.95μ, 3.0μ, 3.1μ , 5.8μ, 6.0μ, 6.2μ, 7.1μ, (7.5μ, 8.3μ, 8.5μ, 9μ- all due to C-F), 10.5μ, etc.

In the case of the C_3F_7NCO and NH_3 reaction product, the mixture was first extracted with ether; the ether solution (Fraction I) on being dried under vacuum overnight, gave a very viscous liquid which was soluble in water also. Some crystals separated out of this viscous mass on standing. The viscous mass on being heated at about 70-80°C for a long time gave a viscous semisolid having infrared absorption peaks at 2.9-3.5μ (broad), 5.8-6.3μ (broad), 6.6-7.1μ (broad), 7.5μ (C-F), 8-8.7μ, (C-F) and some other strong peaks at higher wave lengths. It could be sublimed, but further purification was not possible by that method. Perhaps the viscous mass had some other things solubilized in it. The crystals separating out were dried; their melting range and infrared pattern indicated it to be a mixture. It had very low solubility in ether and portions after repeated washing with ether showed infrared absorption at 2.9μ, 3.0μ, 5.9μ, 6.1-6.3μ, 6.8μ, etc. The residual mass was then extracted with tetrahydrofuran to give some white crystalline nonhygroscopic mass, soluble in other solvents such as CF_3COOH, acetone, alcohol, ethyl acetate, etc. but insoluble in water and sparingly soluble in ether (Fraction II). It remained unchanged on being treated with either CF_3COOH or NH_3. It was recrystallized from tetrahydrofuran and showed the following characteristics:

Sample A-252 M.P. 191-193°C

a. % C = 23.26
% H = 1.16
% N = 13.50
% F = 50.56

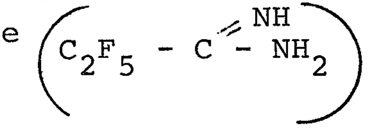
Infrared absorption:
2.9μ, 3.0μ, 3.1μ, 5.8μ, 6.2μ, 6.65μ, 7.2μ, (7.5μ, 7.8μ, 8.1μ, 8.25μ, 8.4μ, 8.6μ, 9.0μ- all due to C-F), 9.6μ, 10.5μ, 11.5μ, 12.5μ, 13.5μ, 14.1μ, etc.

b. Mol. Wt. (by V.P.O.) 200 ± 5 (using tetrahydrofuran as solvent and $C_2F_5\,C\overset{O}{\leqq}NH_2$ as standard).

c. It could be sublimed completely under vacuum at about 90-100°C.

d. Ultraviolet absorption maxima at 213-215 mμ. $\log\varepsilon_{max}$ = 3.43 (approx) in methanol solution.

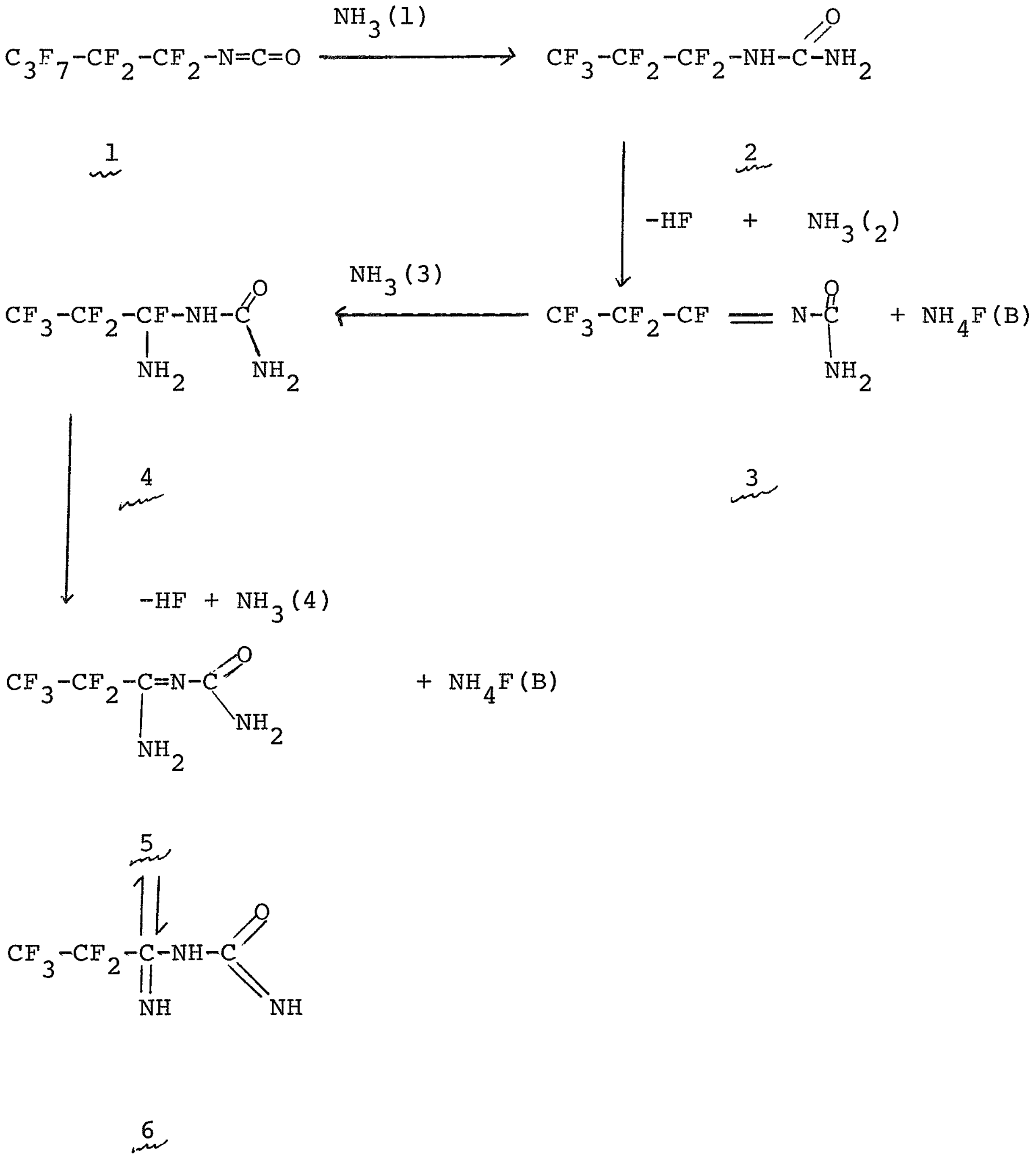
e. NMR spectra (in THF) showed only the presence of CF_3 and CF_2 groupings.

The sample (5g) was heated with P_2O_5 and some gaseous product (A252G) was collected (1.5 g) having mol. wt. of 142 (approx). It was found to be pure by gas chromatographic analysis (only one peak except air) and infrared spectra did show peaks at 4.45μ (C≡N), (7.45μ, 8μ, 8.3-8.4μ, 9.5μ- for C-F), a triplet at 12.3-12.5μ and no other peaks. 1 g of the gas was reacted with NH_3 (excess) in 10 ml ether and a white, crystalline hygroscopic solid (A276) was obtained having m.p.: 49-50°C and infrared peaks at 3.0μ, 3.2μ, 3.5μ (hump), 5.9μ, (7.5μ, 8-9μ broad for C-F), 9.6μ, 9.7μ, 12.5μ, etc. NMR spectra of the gas (A252G) showed the presence of only CF_3 and CF_2 groupings. A276 has been identified as perfluoropropamidine  $\left(C_2F_5 - C\begin{smallmatrix}\nearrow NH \\ - NH_2\end{smallmatrix}\right)$ and the gas (A252G) as $CF_3CF_2C{\equiv}N$.

3. Reaction of perfluorobutyroisocyanate with excess of ammonia in ether medium

It has been reported previously that the reaction of C_3F_7NCO with one to two moles of ammonia per mole of isocyanate, always resulted in a mixture of products (solid + semi-solid mass), with overall yield ranging from 60-100%, based on 1:1 addition, and with ammonium fluoride being one of the by-products. Some isocyanate always was left unreacted suggesting an insufficient ammonia supply. Therefore it might be concluded that one mole of C_3F_7NCO could react with more than two moles of NH_3.

An experiment carried out by keeping the isocyanate in ether at dry-ice temperature and by slowly condensing in ammonia until it was in excess, resulted mainly in two reaction products. The material balance indicated addition of approximately three to four moles of ammonia per mole of C_3F_7 - NCO. The most probable scheme of addition might be presented as:


C3F7-CF2-CF2-N=C=O
NH3(1)
CF3-CF2-CF2-NH-C(=O)-NH2
1
2
-HF + NH3(2)
NH3(3)
CF3-CF2-CF(NH2)-NH-C(=O)NH2
CF3-CF2-CF=N-C(=O)-NH2 + NH4F(B)
4
3
-HF + NH3(4)
CF3-CF2-C(NH2)=N-C(=O)NH2 + NH4F(B)
5
CF3-CF2-C(=NH)-NH-C(=O)=NH
6

According to this scheme, the overall yield is 132% of isocyanate used; yield of 5 or 6 $\approx$ 73.5% and NH_4F $\approx$ 26.5% of overall yield. In actual experiment, the product was a white solid showing a weight increase of about 25-30% over the weight of isocyanate used. Yield of NH_4F (identified by using pure NH_4F as reference) was about 24% of overall yield. Other main product (65-70% of total yield) has been identified as either 5 or 6 by elemental analysis and infrared spectra. The remainder was a little semi-solid mass.

I. Perfluorodihydroxamic Acids

Altogether four dihydroxamic acids have so far been prepared from the corresponding ethyl esters, succinic $\left((CF_2CONHOH)_2\right)$, glutaric $\left(CF_2(CF_2CONHOH)_2\right)$, adipic $\left((CF_2CF_2CONHOH)_2\right)$ and sebacic $\left((CF_2)_8(CONHOH)_2\right)$. Crude yield is always above 100% as it contains some sodium chloride. All these dihydroxamic acids, unlike monohydroxamic acids, are nonhygroscopic, amorphous solids which cannot be sublimed under vacuum. The best way of purification seems to be the removal of the impurities by solution in suitable solvents and heating under vacuum. Acetone seems to be the best solvent for this purpose, in which all the dihydroxamic acids have good solubility, while sodium chloride is almost insoluble in acetone. On heating the acetone soluble part under vacuum, some viscous sublimate was always obtained; this sublimate might contain some unconverted ester as it showed an infrared absorption peak at 5.6μ. The dihydroxamic acids undergo a vigorous decomposition reaction at certain temperatures under vacuum and as such heating under vacuum must be carried out below that decomposition temperature. When no further liquid sublimate is obtained, the residue might be considered to be fairly pure dihydroxamic acid. Overall yield of purified dihydroxamic acid ranges from 65-80%.

The infrared abosrption spectra for all the four dihydroxamic acids are similar except for relative intensities of each peak. For example, perfluorosuccinodihydroxamic acid absorbs at 3.1μ, 3.3μ, 3.45μ, 5.9μ, 6.5μ, 6.75μ, 7.1μ, 7.6μ, 8.3μ, 8.65μ, 8.8μ, 9.4μ, 10.2μ, 11.6μ, 11.9μ, etc. As the CF_2 chain length increases from succinic to sebasic, absorption in 8.9 for $C-F_2$ becomes stronger while other absorptions become weaker.

J. Attempted synthesis of Perfluoroalkyl Diisocyanates

Attempted synthesis of perfluoroglutaro diisocyanate by heating the hydroxamic acid with P_2O_5 resulted in some high boiling liquid collected under partial vacuum. The liquid product might contain some isocyanate as indicated by infrared spectra. The yield was low and cyclization was expected at higher temperature. Better result can be expected, if the experiment is carried out under high vacuum with a lower reaction temperature. Another attempt was made with polyphosphoric acid as the dehydrating agent, but only some liquid product came out at high temperature under vacuum, which became solid and semi-solid at room temperature; this was apparently unreacted hydroxamic acid and probably some phosphoric acid. More favorable reaction conditions for this synthesis has not yet been found.

For synthesizing $(CF_2)_8(NCO)_2$ from the corresponding hydroxamic acid, the hydroxamic acid was heated in the presence of P_2O_5 under vacuum and some liquid product was collected in the trap; the final product was mostly colorless liquid and some solid at room temperature. The liquid was decanted and distilled quite a number of times under N_2 atmosphere with different types of distillation arrangements; however, the boiling point gradually increased (145-195°) with collection of distillate. The distillate showed infrared peaks at 4.4μ (strong -NCO) - two peaks of variable intensity at 5.3μ and 5.55μ (acid or anhydride), 6.8μ (strong -NCO), 8-9μ (C-F), etc. Even distillation in a spinning band column gave the same result. The distillate (Sample A 280) was colorless hygroscopic liquid; elemental analysis showed carbon and hydrogen content close to theory but a high nitrogen content. The fraction collected at 190-195° or at 38-39°/1-1.5mm did not show any I.R. peak at 5.3, but the distillate was cloudy and some white solid separated out. Perhaps the solid sublimed under those conditions. The distillate (Sample A 280) was passed through a fluorosilicone column in an Autoprep gas chromatograph under helium flow and was found to contain mainly three ingredients. The one coming out last was the major component and was collected; however, it soon turned to white solid, probably by reacting with moisture. The solid was extracted with ether, dried and analyzed (m.p.:230-233°C). It might be either $(CF_2)_8(NHCOOH)_2$ or $(CF_2)_6(CF{=}NCOOH)_2$ as per theory with C:N ratio at 10:2 in both of them. The analysis result (Sample A 285) did show C:N ratio 10.2, but the infrared spectra of this sample resembled that of a perfluoroacid amide.

A portion of distilled isocyanate mixture (Sample A 280) was treated with water overnight, resulting in formation of some white solid having a melting point range. This solid, on being heated under vacuum at about 100-120°C for a long time, gave some white sublimate mostly melting at 100-105°C. The residue could be sublimed at or above 170°C under vacuum (Sample No. A 287) and had a melting point and infrared spectra similar to that of Sample A285. The lower melting sublimate had an infrared spectra almost the same as that of A 287, but had an extra peak at 4.4μ.

A small portion of perfluoroadipodihydroxamic acid, on being heated with excess of P_2O_5 at high temperature, gave some product which condensed as a liquid at dry-ice-acetone temperature. A portion of it was a low boiling, low molecular weight (42 approx) gas having infrared absorption at 5.5μ-5.6μ. The residual liquid was a mixture containing some isocyanate as indicated by infrared spectra and could be transferred in vacuum system at room temperature.

K. Reaction of Perfluorosebacodiacid Chloride with Silver Cyanide

Like perfluoroglutarodiacid chloride, perfluorosebacodiacid chloride also produced some dark resinous mass when heated in the presence of AgCN (170-230°C) for several hours in a pressure tube. Any unreacted acid chloride must have been converted to acid in atmosphere, as it was difficult to separate. The Ag salt turned dark colored during reaction. A portion extracted with tetrahydrofuran and then with ether was a dark colored mass, probably a mixture containing some acid, showing no infrared absorption for the CN group.

III. EXPERIMENTAL

A. Use of Trisubstituted Phosphines as Initiators

Reactions using trisubstituted phosphines or tributyl antimony as initiators were carried out in pressure tubes made of glass (100 ml capacity) and having metal cap and valve fitted through rubber 'O' ring. The initiators were handled in a nitrogen atmosphere and bath temperature was varied by adding dry-ice to acetone.

Tabular Summary of Results

Abbreviations: Hexafluorobutyne-2, HFB-2; Hexafluoroacetone, HFA; Perfluorobutadiene, PFBD; Perfluorobutyronitrile, PFBN; Tetrahydrofuran, THF; Tetrafluoroethylene, TFE.

TABLE I

Attempted Homo- or Copolymerization of HFB-2 in the Presence of Trisubstituted Phosphines or Tributylantimony as Initiators.

No. of Expt.	Initiator, gms. or ml.	HFB-2 gms.	Other Co-monomer gms.	Conditions of Expt.	Results
M-1	$(C_4H_9)_3P$ 2 ml	4.79	-	Toluene-10ml; -70 to -80°C bath - then room temp. overnight.	Residual gas: 10% Poly HFB-2:45% (yellowish powder) -2.15 gm Ether soluble dark viscous mass (Instantaneous reaction at low temp.)
M-4	$(C_6H_5)_3P$ 0.58 gms	2.7	-	Toluene-10ml; Tube kept at -70°C and slowly warmed	Residual gas: 5% Poly-HFB-2 (yellowish powder & flakes): 2.53g. Reaction instantaneous at about -50°C; probably not exothermic. Ether soluble part: 0.5 g.
M-13 a.	$(C_6H_5)_3P$ 0.052 gm.	4	-	Toluene-10ml; -70 to room temp.	No reaction
b.	0.2 gm.	Monomer (a) recovered & used	-	Toluene-5ml Bath Temp slowly raised from -70°C	Reaction instantaneous at -30 to Residual monomer: 23% Poly-HFB-2: 3.08 g, yellowish powder and flakes gave brittle mold at 300°C & 4200 lbs/sq.in. press. Ether soluble part: 0.5 g.
M-12	$(C_8H_{17})_3P$ 0.4 ml. (approx)	2.7	-	No solvent; Temp. of bath raised from -70°C to 100°C.	Phosphine became dark colored and viscous. Residual gas: 85%; Very little reaction and no polymerization. Product soluble in ether.

Table I (cont'd)

No. of Expt.		Initiator, gms. or ml.	HFB-2 gms.	Other Co-monomer gms.	Conditions of Expt.	Results
M-14		$(C_6H_5)_3P$ 0.48 g	2.3 g	-	Toluene-5 ml CH_3OH (as chain transferring agent); 5 ml; temp:-70°to room temp.	No reaction or polymerization after 3 hours
M-11		$(C_4H_9)_3Sb$ 0.5 ml (approx)	2.07	-	No solvent; Temp of bath -70° to room temp. overnight	Liquid turned dark; Monomer recovered: Almost 100%; little or no reaction
M-5		$(C_6H_5)_3P$	-	PFBN 2.84	No solvent	No reaction up to room temp.
					THF (10 ml)	No reaction up to room temp; kept overnight - rubber 'O' ring disintegrated
M-2		$(C_6H_5)_3P$ 1.32 gm	2.50	CF_3NO 1.25	Toluene: 10ml Temp of bath: -80°C to 30°C overnight	Apparently no reaction
					Monomers slowly pumped out at low temp.	Some reaction takes place; Poly-HFB-2 formed: 0.53 g; No reaction with CF_3NO
M-3		$(C_6H_5)_3P$ 1.85 gm	2.82	HFA 1.25	Toluene- 10 ml Bath temp: -80°C to 30°C overnight	No poly-HFB-2 formed. Product: dark mass soluble in ether (2.93 g) Res. gas: Mixture of both the monomers (2.65 g) Some colorless liquid (immiscible with toluene) also came out under vacuum and did show C-F absorption.
M-10	a.	$(C_6H_5)_3P$ 0.6 g	2.40	HFA 2.25	No solvent: Temp: 30-100° C (few Hours)	Very little poly-HFB-2 formed; about 90% monomer recovered. Residual black mass mostly soluble in ether.
	b.	$(C_4H_9)_3P$ 1 ml	Residual gas above expt.		Tube warmed up to 30°C	Liquid in tube turned dark; no poly-HFB-2 formed. Residual gas: 75%

Table I (Cont'd)

No. of Expt.		Initiator, gms. or ml.	HFB-2 gms.	Other Co-monomer gms.	Conditions of Expt.	Results
M-15	a.	$(C_6H_5)_3P$ 0.55 g	-	HFA 2.7 g	Toluene: 5 ml overnight at room temp.	No polymerization. Residual gas coming out under vacuum- 75-80% of original. Rest perhaps remained dissolved in solvent.
	b.	$(C_6H_5)_3P$	2.1 g	Res. gas from Expt.15a	Toluene: 5 ml overnight at room temp.	HFB-2 was condensed in the reaction tube. No reaction or polymerization.
M-9	a.	$(C_6H_5)_3P$ 0.5 gm	2.13	PFBD 2.1	Tube warmed up to 100°C. Some reaction at or above room temp., and no further reaction.	Product: Solid product (probably poly-HFB-2) -0.57 gm. and some ether soluble dark material. Residual gas: about 70% of monomer.
	b.	$(C_4H_9)_3P$	Residual gas from 9(a)		room temp.	Product: Dark colored viscous liquid soluble in ether. Residual gas: mostly PFBD and little HFB-2 (About 45% of Starting monomer, 9(a)).
M-8		$(C_4H_9)_3P$	2.08	C_2F_4 1.13	Tube kept at -70 to -80°C. and them slowly heated after primary reaction	Instantaneous reaction and then no further reaction on heating. Product: slightly colored solid (probably HFB-2): 0.94 g Residual gas: 1.47 gm. (Mol.wt.: 108, mostly C_2F_4). Ether soluble dark mass: 0.8 gm.
M-16		$(C_6H_5)_3P$ 0.51 g	1.5 g	C_3F_7NCO 1.0	Toluene: 10 ml. All condensed in thick glass vessel, kept at -60°C to room temp.	No polymerization even at room temp. No reaction. Perhaps isocyanate acted as inhibitor.

B. Reaction between Perfluorobutadiene and Sulfur Tetrafluoride in Presence of Cesium Fluoride

Cesium fluoride was finely powdered and introduced in the reaction tube under a dry nitrogen atmosphere. The reaction tube was then attached to vacuum system and heated in a tubular heater. For reaction in a diglyme medium, diglyme was also introduced under nitrogen. SF_4 and PFBD were then condensed in the tube, the tube was either sealed or the valve was closed and the tube was then heated as described.

The higher boiling liquid product was found to contain sulfur by sodium fusion test. The infrared spectra and other physical tests have been reported in the discussion section. The elemental analysis of one sample (Expt. # 286), though inconclusive, is reported below:

% C = 21.25
% H = 0
% N = 0 } (from Penn. Chem. Res.)
% S = 7.81
% F = 41.93 } (from Galbraith)

TABLE II Reaction between Perfluorobutadiene and Sulfur Tetrafluoride in the Presence of Cesium Fluoride

Powdered CsF (gms)	PFBD gms.	SF_4 gms.	Condition of expt.	Remarks
a. 0.32 (Heated, 200°C, Vac., 3 hours)	9.5	6.9	Pressure tube, 30-35 atm., room temp. 90 hours	No reaction; monomers recovered in full. Probably HF in SF_4 etched glass.
2.5 (Heated 200-260°C Vac. overnight)	Recovered gas mixture from above expt.		Tube heated up to 150°C and kept there for 65 hours.	Some high boiling liquid product was formed. 75% of reactants recovered.
10 (new stock, heated, 250-300°C Vac. Overnight	Recovered gas mixture from above expt.		Tube kept at 100-150°C for few hrs. and at room temp. for a few days.	Very little reaction; no liquid product visible.
5 (old stock heated 300-350°C vac. 2hrs.	Recovered gas mixture from above expt.		Tube kept at about 150°C overnight	Some liquid product formed. Residual CsF on dissolving in water gave some water insoluble grey solid. Residual gas: only about 15% of the starting material. It seems that a portion of the reactants was lost during one of the operations. (Product: Liquid: 2.5-3 g; solid: 2 g (approx.)
b. 13.5 g (Heated, 200-275°C Vac., 2 days)	6.8	5.0	Sealed in thick walled glass tube heated up to 250°C over a few days. The mass gradually turned dark. Tube opened after 2 weeks and attached to the vacuum system.	Residual gas coming out under vacuum, 6.4 g, Mol.wt. 100-180, contained unreached SF_4 and PFBD. Residual higher boiling liquid developed only 2.5-0.5 cm pressure at room temperature, 4-4.2 g. Rest of input, 1.2-1.4 g, unaccounted for. Part of residual dark solid, insoluble and infusible, 3g approx.

Table II (Cont'd)

Powdered CsF (gms)	PFBD gms.	SF_4 gms.	Condition of expt.	Remarks
c. 12 g (Heated, 210°C, Vac. 2 days	9.3	8.3	10 ml diglyme was taken in CsF containing thick glass tube, gases were condensed in and tube was sealed. Tube slowly heated up to 200°C in a rocker over 2 days. The mass turned very dark and inside surface of the tube was highly corroded. Tube opened and attached to vacuum system.	Residual gas, M.W. less than 80 (70-80), 10-11 g, reacted with glass in the trap even at very low temperature leaving white stains. Either SF_4 or PFBD did not make such stains. Then even on heating the tube at 140-160°C under vacuum, little diglyme and some liquid, immiscible with diglyme came out. Appreciable amount of dark solid material was left in the tube.

C. 1. Preparation of trifluoromethyl hydroxamic acid

Method of preparation and purification was same as that described in Annual Interim Report, 1968, p 35-36.

Yield: 80-90%

Analysis

Theory		Found	
		A-53	A-53(R)
18.6	%C	17.75	15.98
1.5	%H	2.59	2.14
10.9	%N	13.9	14.30
44.2	%F	39.9	-

* A-53 Sample prepared with long stored ester.
A-53(R) Sample prepared with freshly distilled ester.

Five grams of doubly sublimed $CF_3CONHOH$ (A-53R) was dissolved in 10 ml CH_3OH and about 2-3 ml of freshly distilled CF_3COOCH_3 was added to it dropwise with stirring. The product left after vacuum drying was highly hygroscopic and showed the same type of infrared absorption spectra and other physical properties as the original product.

2. Preparation of the copper salt of trifluoromethyl hydroxamic acid

About 5 g of $CF_3CONHOH$ (sublimed) was dissolved in 20 ml water. About 2 g of $Cu(CH_3COO)_2$, H_2O was dissolved in 50 ml of hot water and the solution was slowly added to the hydroxamic acid. An almost gelatinous dark green precipitate slowly settled overnight. It was filtered in a Gooch crucible and washed repeatedly with water, acetone, methyl alcohol and ether, then dried under vacuum at 100°. The sample was a dark, nonhygroscopic solid, with decomposition point at about 245°C. It is insoluble in any common solvent (sample a 279). A part of this sample was finely powdered and repeatedly washed with boiling water and dried under vacuum at 120°C (sample A 279R).

Analysis Result

Theory		Found	
		A-279	A-279R
12.60	%C	12.94	12.8
0	%H	0.36	0.37
7.35	%N	6.45	6.56

3. Preparation of trifluoromethyl isocyanate

Sublimed $CF_3CONHOH$ (50 g), P_2O_5 (fresh, about 250 g) and sand (dried at about 220° and cooled under N_2 flow, about 1 kilogm.) were intimately mixed in a 2ℓ flask. The flask was attached to two dry-ice acetone-cooled traps and guard tubes for moisture and CO_2 and heated slowly. No product came out until the pot temperature reached about 200°C; and the product then slowly evolved over 48 hours as pot temperature was slowly increased. Product consisted of some CO_2, about 20 gms. of CF_3NCO and about 10 gms. of residual liquid having some $(CF_3CO)_2O$ in it.

D. Preparation of Perfluorobutyroisocyanate and its reaction with excess ammonia in Ether

1. Preparation and purification of isocyanate

Perfluorobutyrhydroxamic acid, sublimed sample, 61 g, was intimately mixed with about 200 g of fresh P_2O_5 and heated in a flask with two dry-ice-cooled traps and guard tubes for CO_2 and moisture. At about 96-98°C (m.p. of hydroxamic acid), suddenly the whole mass melted and fumed (gas evolution); the vigorous reaction started with a rise of temperature. The heating mantle was removed to cool the flask. No isocyanate was formed or collected in the trap during this reaction. The flask was again heated without any further reaction until 200°C when isocyanate began to collect in the trap. The flask was slowly heated up to 320°C over 2 days and heating was stopped when no further isocyanate was collected:

Product: Some CO_2 (which is probably highly soluble in isocyanate, C_3F_7NCO and some anhydride, 40 g approx. Isocyanate was separated from anhydride by keeping the trap in dry-ice-acetone and collecting the isocyanate in another trap cooled in liquid air in vacuum system. Total isocyanate collected: 34 g, M.W. : 200-217 (by vapor density), purity checked by infrared spectra.

2. Reaction with Excess Ammonia:

100 ml ether was taken in a 1ℓ flask fitted with a cold finger. About 24-25 g of C_3F_7NCO was condensed in the flask, cooled in dry-ice-acetone and dry-ice was kept in the

cold finger which was fitted with guard tubes for moisture and CO_2. NH_3 gas was slowly passed in the flask through a side tube and flask was shaken from time to time. In this way reaction proceeded slowly and no explosive situation developed. Product settled as white solid in ether. When excess NH_3 began to condense from cold finger, flow of NH_3 was stopped, and flask was kept under reduced pressure and then under vacuum to remove excess NH_3 and ether. The product was a white, dry solid, fairly hygroscopic; it partially melted over a range of temperature (a mixture).

Yield: 31.5-32 g. One mole of C_3F_7NCO reacted, apparently, with 3-4 moles of NH_3.

10.2 g of white solid product was treated with 50 ml acetone in which major portion was soluble. Residue left, 2.4 g white solid, which was highly hygroscopic in nature, mostly melted at 170-175°C, was completely soluble in water; an aqueous solution liberated NH_3 on addition of caustic soda. This is characteristic of pure NH_4F, prepared by addition of liquid NH_4OH and HF (49%) and crystallization of the solid out of aqueous solution. The infrared spectra of the two solids were also similar, e.g. peaks at 2.8-3.7μ, (broad), 4.4μ, 5.0μ, 5.8-6.2μ (weak), 6.7μ, 7.1μ, etc. Further extraction of the solid with acetone gave no product.

On repeated evaporation and cooling of an acetone solution, a white crystalline solid separated, total 6.8 g, nonhygroscopic, very low solubility in ether and insoluble in water; this product could be totally sublimed at 80-85°C, vacuum, m.p. 153-155°C. (Sample A-283). The remainder was a little semisolid mass (about 1 g).

Analysis Results (Sample A-283)

Theory for $C_4F_5N_3H_4O$		Reported
23.41	%C	23.58
20.49	%N	20.23
1.95	%H	1.92
46.34	%F	46.22, 46.44

E. Preparation of Perfluorodihydroxamic Acids

1. Preparation of perfluoroadipodihydroxamic acid

a. Oxidation of decafluorocyclohexene to perfluoroadipic acid:

Decafluorocyclohexene (C_6F_{10})	--197 g (0.75 m)
Acetone	--1.6 litre
Water	--170 ml
$KMnO_4$	--158 g (1m)

Finely powdered $KMnO_4$, acetone and water were placed in a 3ℓ 3-necked flask having a stirring bar, reflux condenser and dropping funnel. Contents of the flask were cooled by ice water and C_6F_{10} was slowly added from a dropping funnel with stirring over a period of 3 hours, keeping the contents fairly cold (near room temperature) all the time. After completion of addition, stirring was continued for one more hour, then contents allowed to stand overnight, and filtered twice to remove MnO_2 completely. Acetone was removed from the filtrate under reduced pressure, then about 100 ml H_2SO_4 was added slowly. In this stage, the mass turns dark colored if it is not sufficiently cooled before acid addition. Perfluoroadipic acid forms a separate layer from the remaining mass at this stage and it can be further separated by addition of some ether in which it is highly soluble. The ether solution was then put under reduced pressure and then under vacuum to remove the last trace of ether; crude perfluoroadipic acid was obtained as dark or whitish solid; Yield: 75-85%; color of the acid can be removed by bleaching with SO_2 in ether solution, which was not tried.

b. Preparation diethylperfluoroadipate:

$(CF_2)_4\ (COOH)_2$	-----145 g (0.5 m)
Benzene	-----600 ml
Ethyl alcohol (Abs)	-----130 ml
H_2SO_4 (conc)	-----2 ml

Contents were taken in a 2ℓ flask with a stirring bar and a distillation head attached to a water separator and allowed to reflux till no more water was collected in the receiver. Benzene and alcohol was removed under reduced pressure. The dark viscous residual liquid in the flask was washed repeatedly with cold water, extracted with ether and ether was removed under reduced pressure to leave the crude ester. It was dried overnight over Drierite and distilled either under atmospheric pressure (b.p. 221-224°C) or under reduced pressure (b.p. 122-124°C/50-55 mm pressure). The distillate was a clear colorless liquid; Yield: 70-75%

c. Preparation of dihydroxamic acid from ethyl ester:

$(CF_2)_4\ (COOC_2H_5)_2$ ----69.2 g (0.2 m)

$NH_2OH \cdot HCl$ ----28 g (0.4 m)

CH_3ONa ----21.6 g (0.4 m)

CH_3OH ----550 ml (approx)

Method of preparation has been described previously. NaCl separated: 20 g (Theor. 23.2 g), crude yield: almost white solid, 68 g (Theor. 64 g), approx. 100% yield. Crude product can be dissolved in either tetrahydrofuran or acetone to remove the last trace of NaCl present, which is insoluble in both the solvents. The solution on being dried and heated under vacuum at 80-100°C, gives some sticky white sublimate and residual solid which is considered to be fairly pure hydroxamic acid. The sample on heating under vacuum at about 115-120°C decomposes, the reaction being rather vigorous and probably exothermic. $(CF_2)_4(CONHOH)_2$ prepared: m.p.: 195-196°C.

Analysis results (sample A-281)

Theory		Reported
22.50	%C	22.54
8.75	%N	8.45
1.25	%H	1.25

2. Preparation of perfluorosuccinodihydroxamic acid

$(CF_2COOC_2H_5)_2$	:	Distilled Sample, b.p. 101-103°C/ 50-55 mm pressure 18.4 g (0.075 m)
CH_3ONa	:	8.1 g (0.15 m)
$NH_2OH \cdot HCl$	:	10.5 g (0.15 m)
CH_3OH	:	200 ml approx.

The method of preparation has been reported previously. NaCl separated: 6 g (Theor.: 8.7 g). Crude Yield: 18.5 g of white solid (Theor.: 16.5), almost 100%. Crude sample was dissolved in tetrahydrofuran or acetone to remove last trace of NaCl, then heated under vacuum at 80°C for a few hours. Residual solid, whitish solid, appears moist.; m.p. : 176-178°C.

Analysis results: (Sample A-282)

Theory		Reported
21.82	%C	22.46
12.73	%N	12.27
1.82	%H	2.00

3. a. <u>Preparation of ethyl perfluorosebacate</u>

Eighty-two grams (0.2 m) of crude $(CF_2)_8(COOH)_2$ was mixed with 300 ml benzene, 80 ml absolute ethyl alcohol and 0.8 ml of conc. H_2SO_4 in a 2ℓ flask containing a stirring bar and reflux condenser with Drierite guard tube. The mixture was refluxed for 24 hours. The azeotrope (b.p. 65°C and up) was taken out by using a distillation head. After 230 ml of distillate was collected and no further water was being formed, an additional 250 ml benzene and 80 ml absolute alcohol was added. The same procedure was repeated, then the last portions of solvents were taken out under vacuum. The ester $(CF_2)_8(COOC_2H_5)_2$, distilled at 125-127°/2-3 mm, yield 79 gms. of colorless liquid (86%). Some tar-like black material was left in the pot.

b. <u>Preparation of $(CF_2)_8(CONHOH)_2$</u>

The method was the same as described in the Annual Interim Report, 1968 (p. 36).

Ingredients used:

$(CF_2)_8(COOC_2H_5)_2$	0.1 m	54.6 g
$NH_2OH \cdot HCl$	0.2 m	14 g
CH_3ONa	0.2 m	10.8 g
CH_3OH	500 ml (approx)	

NaCl separated ... 7.5 g (Theor. 11.6 g). The crude product, a white, nonhygroscopic solid, about 55 g, contains some sodium chloride. It is almost insoluble in water, ether and ethylacetate; it is moderately soluble in tetrahydrofuran and mostly soluble in acetone. Extraction with tetrahydrofuran seems to be the best method of purification, NaCl being completely insoluble in that solvent. The sample did neither sublime at high temperature under vacuum nor crystallize out form solvents (Sample A-278).
m.p. : 193-195°C

Result of analysis (Sample A-278)

Theory or Range		Found
23.0	%C	22.77
0.8	%H	0.97
5.4	%N	5.16

F. Attempted preparation of $(CF_2)_8(NCO)_2$

Thirty grame of $(CF_2)_8(CONHOH)_2$ was intimately mixed with about 150 g of P_2O_5 in a 500 ml flask; the flask was connected to two dry-ice-cooled traps and guard tubes and heated. No product was evolved up to about 220°. Vacuum was applied and liquid product began to collect in first trap kept at room temperature. As pot temperature was increased, some of the product coming out solidified at room temperature. Finally about 8-10 ml liquid collected in first trap, along with some solid. The liquid was taken out and distilled under nitrogen atmosphere.

Distillate: B.P. 146-185°C, clear colorless liquid

B.P. 185-195°C, cloudy liquid due to some suspended solid in it

Distillation under vacuum B.P. 38-40°C 1-1.5 mm, cloudy liquid distillate

I.R. spectra: shows presence of some acid or anhydride in the isocyanate.

Analysis Result (Sample A-280, clear distillate)

Theory		Found In Duplicate	
24.8	%C	23.86	23.59
0	%H	0.17	0.19
5.8	%N	9.16	9.40

Distillate ⟶ passed through gas chromatograph ⟶ major fraction collected turns to white solid, Sample A-285, m.p. 230-233°C. Infrared spectra peaks at 2.95μ, 3.15μ, 5.8μ, 6.15μ, 7.1μ, 8.3μ, 8.7μ, etc., looks like the spectra of an acid amide.

(Please see Discussion, Sec. B. for details.)

Analysis Result (Sample A-285)

Theory			Found
$(CF_2)_8(NHCOOH)_2$	$(CF_2)_6(CF{=}NCOOH)_2$		
23.08	25.0	%C	24.08
5.4	5.84	%N	5.97
0.77	0.83	%H	1.04

A white solid was obtained by treating distillate A-280 with water overnight. (Please see Discussion Sec. B for details, Sample A-287).