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SYNTHESIS OF ELASTOMERS FOR USE WITH LIQUID FLUORINE

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to

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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 and covers work performed during the period 1 April 1969 through 30 June 1969.

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

TABLE OF CONTENTS

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, the material should be flexible at cryogenic temperatures.

During the present quarter two more perfluorodihydroxamic acids, namely succinic and adipic, were prepared and purified. Like perfluorosebacic hydroxamic acid, the perfluoroadipo hydroxamic acid, on heating with phosphorous pentoxide, yielded a mixture of isocyanate and acid or anhydride. The analysis of crude perfluorosebacodiisocyanate (obtained as distillate during distillation of the liquid product) by gas chromatogram 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 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 $CF_3-CF_2-\overset{NH_2}{\overset{|}{C}}=NH-\overset{\nearrow O}{C}-NH_2 \rightleftharpoons CF_3-CF_2-\overset{NH}{\overset{\|}{C}}-\overset{\nearrow O}{C}-NH_2$ (65-70%) and NH_4F (by-product, 25%, approximately).

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 are being studied.

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. 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 absorption 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 8.9µ for $C-F_2$ becomes stronger while other absorptions become weaker.

B. Attempted synthesis of diisocyanates from dihydroxamic acids.

It was reported in Letter Report No. 8 that liquid product obtained by heating perfluorosebacodihydroxamic acid and P_2O_5 did contain some isocyanate, but it could not be separated from the mixture by distillation. The distillate (sample A280) thus obtained, 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.

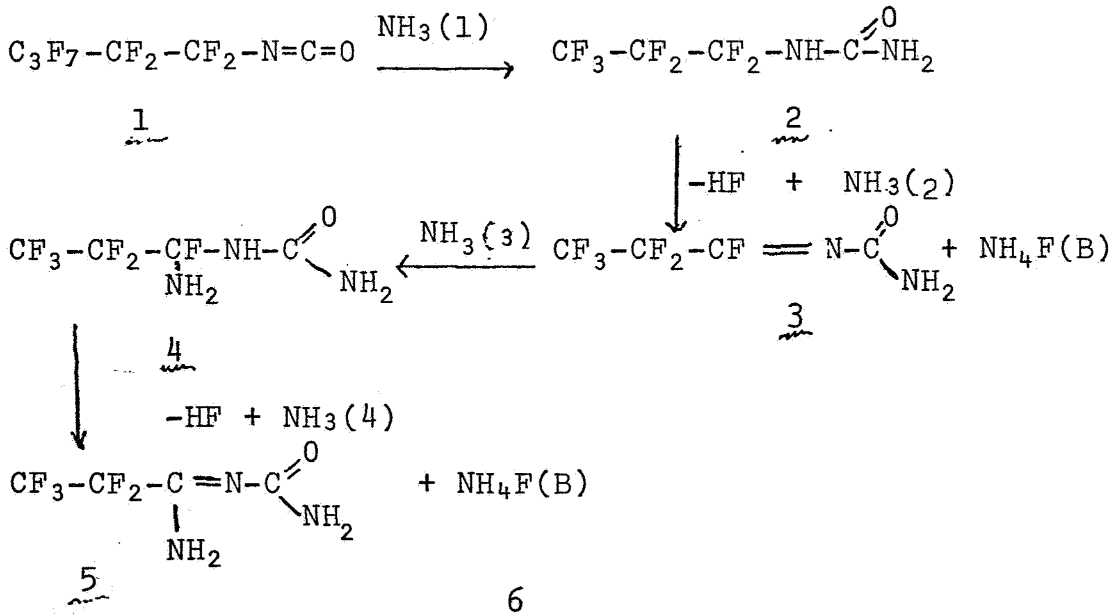
A portion of distilled isocyanate mixture (Sample A-280) was treated with water overnight, resulting in formation of some white solid having a melting point range. This solid, on being heated under vacuum at about 100-120°C for a long time, gave some white sublimate mostly melting at 100-105°C. The residue 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 A-285. The lower melting sublimate had an infrared spectra almost the same as that of A-287, but had an extra peak at 4.4μ.

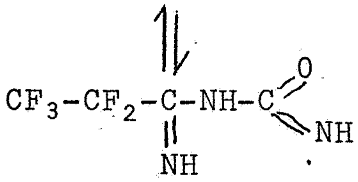
A small portion of perfluoroadipodihydroxamic acid, on being heated with excess of P_2O_5 at high temperature, gave some product which condensed as a liquid at dry-ice-acetone temperature. A portion of it was a low boiling, low molecular weight (42 approx) gas having infrared absorption at 5.5μ—5.6μ.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

C. Reaction of perfluorobutyroisocyanate with excess of ammonia.

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:





6

According to this scheme, the overall yield is 132% of isocyanate used; yield of **5** or **6** ≈ 73.5% and NH_4F ≈ 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. Products from reaction of CF_3NCO and C_2F_5NCO with excess of ammonia under similar conditions are being characterized.

D. 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,), reacts 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 is corroded, probably by reaction with hydrogen fluoride in the SF_4 and some dark colored insoluble, infusible solid is obtained.

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 little HFBD as indicated by 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 'Auto-prep' 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. But 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 chromatograph analysis and infrared spectra, it seems that the liquid might even be a mixture of telomers as suggested in the proposed reaction:

$$CF_2{=}CF{-}CF{=}CF_2 + SF_4 \longrightarrow \left[CF_2CF_2{-}CF_2{-}CF_2{-}SF_2\right]_n$$

terminated probably by F^- ions. The liquid product being immiscible in 'diglyme', the reaction will be conducted in 'diglyme' medium for better yield, etc. The elemental analysis is awaited.

E. 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. Preparation of perfluorodihydroxamic acids.

1. Preparation of perfluoroadipodihydroxamic acid.

a. Oxidation of decafluorocyclohexene to perfluoroadipic acid:

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

Finely powdered $KMnO_4$, acetone and water were placed in a 31 3-necked R.B. 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 in drops from 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, thencontents 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:

$(CF_2)_4$ $(COOH)_2$	- - - 145g (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:

$(CF_2)_4$ $(COOC_2H_5)_2$	- - - 69.2g (0.2 m)
$NH_2OH \cdot HCl$	- - - 28 g (0.4 m)
CH_3ONa	- - - 21.6g (0.4 m)
CH_3OH	- - - 550 ml (approx).

Method of preparation has been described previously. NaCl separated : 20 g (Theor. 23.2g), 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
: 18.4g (0.075 m)
CH_3ONa : 8.1g (0.15 m)
$NH_2OH \cdot HCl$: 10.5g (0.15 m)
CH_3OH : 200 ml approx.

The method of preparation has been reported previously. NaCl separated :6g (Theor.: 8.7g). Crude Yield: 18.5g 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

B. Attempted synthesis of diisocyanate from dihydroxamic acids.

$(CF_2)_8(CONHOH)_2$ heated with $P_2O_5 \longrightarrow$ Liquid product distilled $\longrightarrow$ Distillate collected over a range of temperature (145-190°C) $\longrightarrow$ A mixture containing some isocyanate as indicated by infrared spectra. (Sample A-280).

Distillate $\longrightarrow$ passed through gas chromatograph $\longrightarrow$ 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			Reported
$CF_2)_8(NH\ COOH)_2$	$(CF_2)_6(CF{=}NCOOH)_2$		
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).

C. Preparation of perfluorobutyroisocyanate and its reaction with excess of 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 40g 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: 34g, M.W. : 200-217 (by vapor density), purity checked by infrared spectra.

2. Reaction with ammonia: 100 ml ether was taken in a 1ℓ flask fitted with a cold finger. About 24-25g 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: 31.5-32g. One mole of C_3F_7NCO reacted,apparently, with 3-4 moles of NH_3.

10.2g of white solid product was treated with 50 ml acetone in which major portion was soluble. Residue left, 2.4g 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 happens to be the characteristics of pure NH_4F, prepared by addition of liq. 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 6.8g, 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 $C_4F_5N_3H_4O$ (Dissc. Sec.C.).		Reported
23.41	%C	23.58
20.49	%N	20.23
1.95	%H	1.92
46.34	%F	46.22, 46.44

D. Reaction of Hexafluorobutadiene (HFBD) and sulfur tetrafluoride in the presence of Cesium Fluoride.

Powdered C_sF, 13.5g, was taken in a thick-walled glass tube under nitrogen atmosphere, and heated under vacuum at 200-275°C for two days. Then 5.0g of SF_4 and 6.8g of HFBD were condensed in the tube, the tube was sealed and heated up to 250°C over a few days. The whole mass gradually turned very dark. The tube was opened after 2 weeks and attached to the vacuum system. Residual gas, coming out under vacuum, had molecular weight ranging from 100-180, contained unreacted SF_4 and HFBD and total weight of gas was 6.4g. Residual liquid, developing very little pressure (2.5-0.5 cm) at room teperature, contained some HFBD and weight 4-4.2g. Rest of input (1.2-1.4g) was unaccounted for. Residual dark solid in the tube was not completely soluble in water. A portion of it, 3g approx. was insoluble, infusible material.