U.S. Army Contract No. DA-19-129-AMC-69(X)O.I. 9044

QMC Project No. 7X93-15-004

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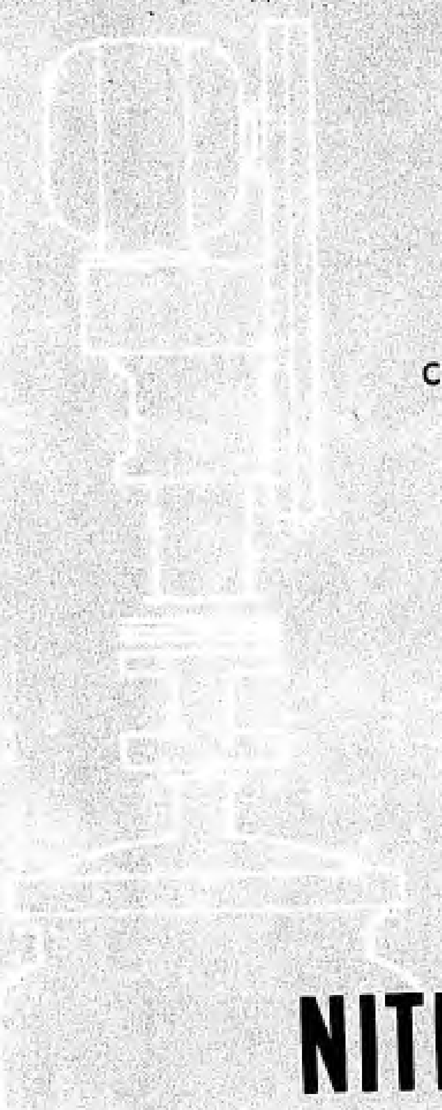

Report:

Reaction Motors Division RMD 8652-F

Chemical Operations Division RD 343-F

Report Period:

27 February 1963 to28 February 1965

NITROSO RUBBER

RESEARCH DEVELOPMENT And PRODUCTION

28538

Thiokol CHEMICAL CORPORATION
REACTION MOTORS DIVISION, DENVILLE, NEW JERSEY

Thiokol

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NITROSO RUBBER RESEARCH, DEVELOPMENT AND PRODUCTION,

(14)
Reaction Motors Division ~~Report~~ RMD-8652-F,
Chemical Operations Division ~~Report~~ RD 343-F

(15)
U.S. Army Contract No. DA-19-129-AMC-69(X) [redacted]
QMC Project No. 7X93-15-004
(16) QMC

Report Period: 27 February 1963 to 28 February 1965

(9) Rept. for 27 Feb 63-28 Feb 65,

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(11) 28 Feb 65,

(12) 129p.

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FOREWORD

This report was prepared by Thiokol Chemical Corporation under Army Contract No. DA-19-129-AMC-69(X)O.I. 9044, QMC Project No. 7X93-15-004, with Mr. Frank Babers as project engineer. This report covers work conducted from 27 February 1963 to 28 February 1965. This work was conducted at both the Reaction Motors and the Chemical Operations Divisions of Thiokol. Dr. Murray S. Cohen coordinated interdivisional operations as program manager. The project leader was Mr. Joseph Green of Reaction Motors with Mr. Warren Helmer supervising work at the Chemical Operations Division. Other contributors to all or part of the program are as follows:

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ABSTRACT

Processes for the production of ~~trifluoronitrosomethane~~ (CF_3NO) and of the CF_3NO/C_2F_4 copolymer were developed. These processes were utilized for the production of 200 lbs ~~pounds~~ of copolymer and 191 lbs ~~pounds~~ of CF_3NO in a pilot plant facility ~~designed and constructed for this program~~. The preparation and properties of the CF_3NO precursor, ~~trifluoroacetyl nitrite~~ (CF_3COONO), were studied. ~~In addition, the~~ development of preparative routes for nitroso termonomers containing reactive functionalities was pursued intensively. Both aliphatic and aromatic termonomers were prepared of which ONC_6F_4COOH and $ON(CF_2)_3COOH$ were of greatest interest. Experimental copolymers and terpolymers were prepared and evaluated. A CF_3NO/C_2F_4 copolymer of molecular weight greater than 3,500,000 was prepared by modified bulk polymerization techniques. A solution polymerization method was developed for the preparation of $CF_3NO/ON(CF_2)_3COOH/C_2F_4$ terpolymer gums. A curing and filler study was conducted in attempts to obtain vulcanizates of improved physical properties. Tensile strengths greater than 1600 psi with elongations greater than 350% were obtained with $CF_3NO/ON(CF_2)_3COOH/C_2F_4$ terpolymer vulcanizates.

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I. SUMMARY

The major goals of this program were the development of processes for the production of the trifluoronitrosomethane (CF_3NO)/tetrafluoroethylene (C_2F_4) copolymer at the rate of 10 to 50 pounds per day; and, utilizing these processes, the production of a quantity of the copolymer sufficient for end-use evaluation. These goals were met; 200 pounds of copolymer and 191 pounds of CF_3NO were produced in a pilot plant facility designed and constructed for this program. As a secondary goal, the preparation and utilization of nitroso monomers other than CF_3NO for elastomers of improved physical properties were investigated.

Because of the lack of an applicable preparative process for CF_3NO, an intensive developmental effort was initiated. This effort was successful; a continuous process was developed which was utilized at production rates of approximately 25 pounds per day.

Production of CF_3NO was effected by the preparation, then the pyrolytic decarboxylation of trifluoroacetyl nitrite (CF_3COONO). Conditions for the pilot plant production of CF_3COONO through the interaction of trifluoroacetic anhydride and dinitrogen trioxide were established and production successfully effected. Safety testing indicated that CF_3COONO was detonable with sufficient initiation but that its critical diameter was large enough to preclude propagation of a detonation through process piping. Ignition limits for CF_3COONO were also established.

It was found possible to continuously produce CF_3NO of at least 99% purity by metering CF_3COONO into a reactor containing an inert diluent at reflux. Decarboxylation is effected in the vapor phase and the CF_3NO swept continuously from the reaction zone through a purification train into traps at liquid nitrogen temperature where it is condensed. The inert diluent (triperfluorobutylamine, FC-43) is returned to the reactor by a partial condenser. CF_3NO purification is effected by a 5% caustic scrubber (to remove CO_2 and NO_2), a drying tower, and finally a molecular sieve column at $-100^\circ C$ to remove non-acidic nitrogen oxides and CF_3NO_2.

This process was successfully used in the pilot plant to produce purified CF_3NO at rates of approximately one pound per hour. CF_3NO yields were up to 43% of theory based on the starting trifluoroacetic anhydride.

The development of preparative routes for nitroso termonomers containing reactive functionalities (e.g., carboxyl) was pursued intensively. The synthesis of nitrosoperfluoroaliphatic acids, including 3-nitrosoperfluoropropanoic acid, 4-nitrosoperfluorobutanoic acid, 5-nitrosoperfluoropentanoic acid, and 4-nitrosoperfluorobutanoyl fluoride was investigated using several different synthetic approaches. Most of these approaches were unsuccessful, but it was found that 4-nitrosobutanoyl fluoride could be prepared by the addition of FNO to perfluoroglutaric anhydride followed by photolysis of the intermediate, nitrosylperfluoroglutaryl fluoride.

The synthesis of pentafluoronitrosobenzene and 4-bromotetrafluoronitrosobenzene was found to be facile and laboratory-scale quantities were prepared for polymerization studies. The synthesis of 4-nitrosotetrafluorobenzoic acid was attempted by several routes; the performic acid oxidation of 4-aminotetrafluorobenzoic acid was found to be successful with yields averaging 31% of theory.

Laboratory-scale CF_3NO/C_2F_4 copolymerizations were conducted both in suspension and in bulk. It was found that the most important parameter was the purity of CF_3NO; the presence of CF_3NO_2 was especially deleterious. It was also found that: incremental monomer addition may be effective in increasing molecular weights, large $MgCO_3$ (suspending agent) levels are not required, the presence of FC-43 does not interfere with the copolymerization and selected phosphines and phosphine oxides were ineffective in increasing copolymer molecular weights. Conditions were selected which resulted in suspension copolymers of 800,000 to 1,300,000 molecular weights. Modifications of the bulk copolymerization process resulted in copolymer fractions of molecular weights up to 3,500,000.

The heat of polymerization of the CF_3NO/C_2F_4 copolymer was determined experimentally. The value found was 74.8±0.5 kcal/mole.

Laboratory-scale terpolymerizations were also conducted. The monomers (in addition to CF_3NO and C_2F_4) included C_6F_5NO, BrC_6F_4NO, $HOOCC_6F_4NO$, $CH_2{=}CF_2$, $CF_2{=}CHF$, and $CH_2{=}CHCOOH$. A titration procedure was developed to determine the $CF_2{=}CH_2$ and $CF_2{=}CFH$ content of the polymers. These terpolymers were prepared for curing studies with the object being the development of nitroso vulcanizates of improved physical properties.

Initial CF_3NO/C_2F_4 copolymer batches were cured with the formulation (triethylenetetramine and hexamethylenediamine carbamate) developed at 3M (Minnesota Mining and Manufacturing Co.). The cured stocks possessed low tensile strength and attempts to increase the tensile strength by formulation studies were not successful. The use of different fillers, attempts to graft various compounds to the polymer chain resulting in new functional cure sites, treatment with sodium/liquid ammonia, and the use of gamma radiation all failed to increase copolymer tensile strength.

Nitroso terpolymers containing C_6F_5NO, BrC_6F_4NO, $CF_2{=}CH_2$, or $CF_2{=}CFH$ were cured with applicable curing agents; in no case, however, were vulcanizates of improved tensile strengths obtained. Good mechanical properties were obtained with $Cr(OOCCF_3)_3$-cured $CF_3NO/ON(CF_2)_3COOH/C_2F_4$ terpolymers using Silstone 120 as the filler. Tensile strengths greater than 1600 psi and elongation greater than 350% were obtained. These values, coupled with the demonstrated solvent and oxidation resistance, indicate the suitability of vulcanizates of this type for application such as gaskets, O-rings, tank linings and expulsion bladders.

II. INTRODUCTION

Army-sponsored research oriented toward the development of a chemical and fuel resistant arctic rubber resulted in the preparation of a 1:1 copolymer of trifluoronitrosomethane and tetrafluoroethylene, generally referred to as nitroso rubber (Ref 1, 2). The nitroso rubber gum stock exhibits excellent solvent and ozone resistance, is nonflammable, and is resistant to most solvents except those which are highly fluorinated. The glass transition temperature (Tg) is -51°C; this low Tg value is attributed to flexibility of the N-O bond.

Vulcanizates of nitroso rubber had been prepared; however, even the best of the gum vulcanizates possessed low tensile strengths. Reinforcement of the vulcanizate with silica filler resulted in improved, although still unsatisfactory, physical properties. Extensive research and development studies were conducted to investigate the effects of varying the nitroso and olefinic monomers (Ref 3, 4). This did not result in improved mechanical properties or low temperature serviceability. Terpolymers were prepared and cured through pendent carboxyl groups; the resulting vulcanizates possessed much greater tensile strength. The cured products continued to exhibit excellent solvent and ozone resistance, nonflammability and low temperature flexibility. Furthermore, field evaluation studies had been severely hampered by a shortage of nitroso rubber.

This program had as its ultimate goal the production of a quantity of nitroso rubber sufficient for more intensive end-use evaluation. To achieve this result, pilot plant operations were carried out and 200 pounds of polymer were produced during the course of the program. This pilot production required the development of monomer and polymer production processes as well as the design and construction of the plant.

Another goal was the development of a nitroso rubber with improved mechanical and low temperature properties. Such a polymer could be obtained through proper selection of co- and termonomers. If one of the monomers contained a reactive functionality (e.g., carboxyl), various crosslinking agents could be used with potential improvement in the mechanical properties of the vulcanizates.

Conferences were held with Minnesota Mining and Manufacturing Co. and Professor J. D. Park, University of Colorado, to gather detailed technical and safety information not normally found in technical reports. The conferences were highly informative with a free exchange of information. Personnel at 3M made the following recommendations to Thiokol, based on their extensive experience with nitroso rubber:

- The preparation of trifluoronitrosomethane (CF_3NO) by the vapor phase pyrolysis, liquid phase pyrolysis or by photolysis of trifluoroacetyl nitrite was not recommended for large scale production.
- The preparation of an acid modified terpolymer appeared desirable because of its superior mechanical properties. However, only gram quantities of acid nitroso monomer had been prepared by a cumbersome, low yield reaction which is not amenable to scaleup. The only method currently available for preparing the terpolymer is by low temperature (-65°C) bulk polymerization.
- The polymer production required by Natick-QM should be accomplished by bulk polymerization (30 days at -65°C) in one pound batches.

This information and that obtained from the literature, coupled with the requirements of the program, resulted in the following decisions:

- The trifluoronitrosomethane/tetrafluoroethylene copolymer was scheduled for production.
- A scalable method would have to be developed for pyrolyzing trifluoroacetyl nitrite to yield trifluoronitrosomethane.
- Copolymer production would utilize the aqueous suspension method.
- Research leading to the synthesis of selected termonomers would be conducted.
- Research leading to the development of improved polymerization methods would be conducted.

To implement this work, a four-phase R and D program was initiated:

I - Monomer Synthesis and Scaleup
II - Polymer Synthesis and Scaleup
III - Polymer Production
IV - Compounding Studies

Tasks I, II, and IV were conducted by the Reaction Motors Division and Task III by the Chemical Operations Division, Trenton, New Jersey

III. TECHNICAL WORK

PHASE I - MONOMER SYNTHESIS

The nitroso rubber which had been designated for production was the copolymer of trifluoronitrosomethane (CF_3NO) and tetrafluoroethylene (C_2F_4). The problem of greatest immediacy and importance in this Phase then became the development of practical procedures for production of CF_3NO in the quantities required. Although not required for the copolymer, termonomers containing reactive functional groups would be required for nitroso vulcanizates of improved physical properties; laboratory studies were initiated for the synthesis of such materials. Tetrafluoroethylene, the other comonomer, became available from Thiokol's Moss Point facility for use on this program and its synthesis on this program was not required.

Task 1. Process Development for Trifluoronitrosomethane (CF_3NO)

The objective of this task was the development of processes capable of producing CF_3NO in quantities of 10 to 50 pounds per 24 hour period.

The preparation of CF_3NO had been effected by several synthetic routes, most of which could be excluded as production methods because of low yields, expensive starting materials, and/or difficult processing. The preferred route for CF_3NO production appeared to be through the formation of trifluoroacetyl nitrite(CF_3COONO)and subsequent decarboxylation. The development of these reactions into production processes was effected in studies on this Task. In addition, an analytical development program was conducted so that analytical methods for starting materials and products could be found and specifications established.

A. PREPARATION OF TRIFLUOROACETYL NITRITE (CF_3COONO)

Trifluoroacetyl nitrite had been prepared by the interaction of trifluoroacetic anhydride $[(CF_3CO)_2O]$ with either dinitrogen trioxide (N_2O_3) or nitrosyl chloride ($ClNO$), (Ref 5, 6).

$$(CF_3CO)_2O + N_2O_3 \longrightarrow 2CF_3COONO \qquad (1)$$

$$(CF_3CO)_2O + ClNO \longrightarrow CF_3COONO + \text{byproducts} \qquad (2)$$

Reaction one was preferred because of superior yields. It can be effected by mixing the two starting materials at temperatures between -10° and $25^\circ C$ using autogeneous pressure or a reflux condenser to maintain the N_2O_3 in the liquid state (Ref 6).

Although this reaction had been successfully replicated, production at the scale required for this program had not been attempted. Therefore, a developmental program was instituted to define the process variables, to determine the degree of hazard and to develop a process (including equipment design) which could be successfully operated at the required level.

1. Preparative Reactions

A series of laboratory-scale CF_3COONO preparations were conducted to define the reaction conditions, determine yields, and furnish products for CF_3NO preparations. The reaction was found to be facile and little development was required.

Both starting materials are volatile [bp of $N_2O_3 = 3.5^\circ C$; of $(CF_3CO)_2O = 39^\circ C$] so that precautions had to be taken to avoid losses by evaporation. In addition, N_2O_3 dissociates into NO and NO_2 except at very low temperatures. For these reasons, a vacuum rack was designed and constructed for these reactions. Through the use of this rack, it was possible to quantitatively transfer weighed charges of the starting materials, follow the course of the reaction by monitoring pressure changes, and then fractionate and transfer the product. These techniques also eliminated exposure of starting materials to atmospheric moisture and oxygen, both deleterious.

The $(CF_3CO)_2O$ used in these experiments was obtained from Peninsular ChemResearch, Incorporated. As a routine procedure, the anhydride was rectified using a column estimated at 15 theoretical plates; the fraction boiling between 39° and $39.5^\circ C$ was taken and stored under dry nitrogen. The vapor pressure of $(CF_3CO)_2O$ was determined and found to conform to the equation $\log P = \frac{-2096.8}{T} + 9.753$. The $(CF_3CO)_2O$ vapor pressure curve is reproduced as Figure 1.

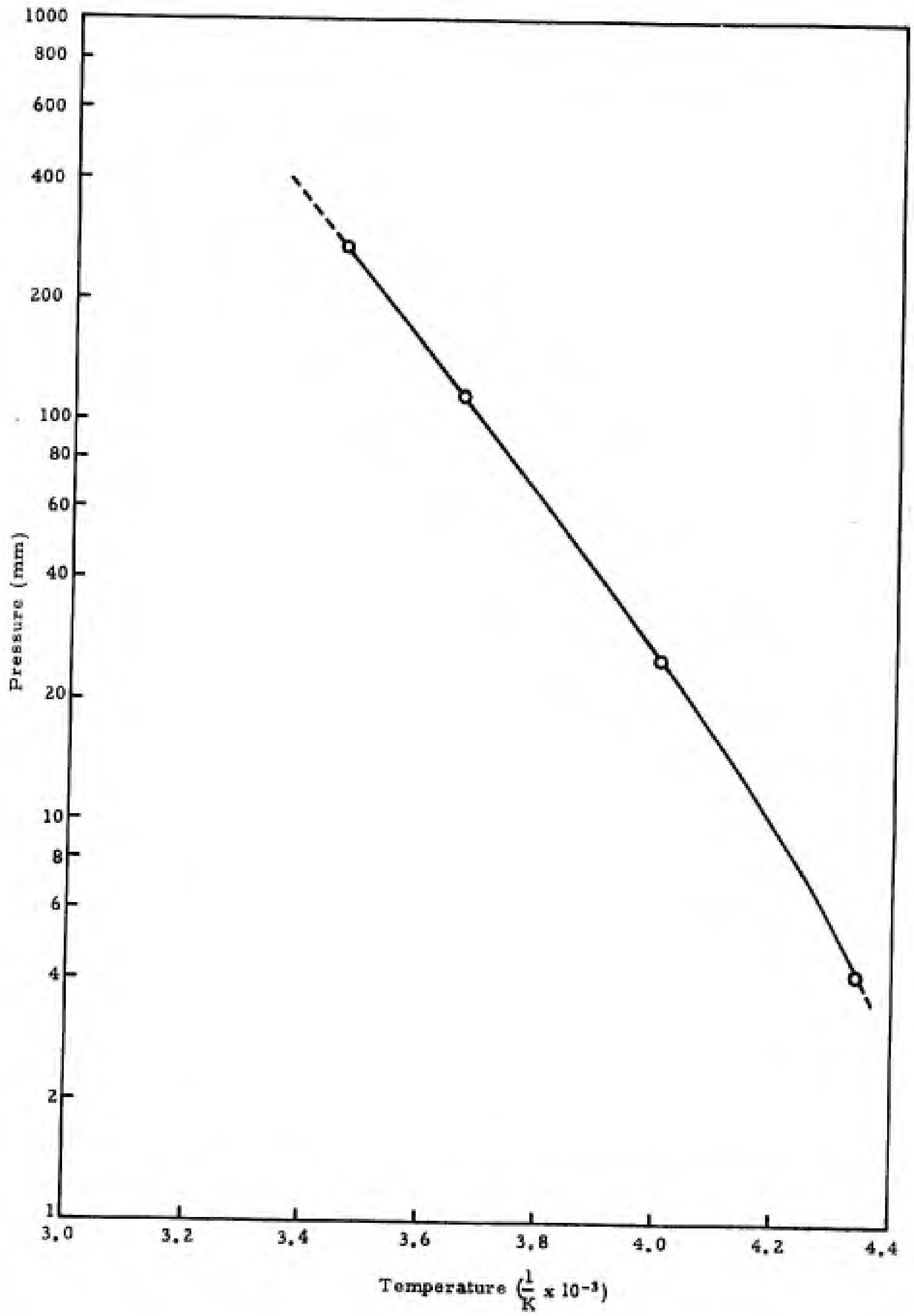

Figure 1 Vapor Pressure of CF_3COONO

The N_2O_3 was obtained from the Matheson Company, Incorporated and used as received. The purity was determined to be greater than 99%. Because of the facility with which N_2O_3 dissociates, it was removed from the storage cylinder as the liquid phase.

To reduce the possibility of CF_3COONO oxidation by NO_2, the anhydride was used in excess. In addition, NO from a separate cylinder was sparged through the reaction mixture to maintain N_2O_3 at a maximum. In a typical preparation (see also appendix), the anhydride (15% excess) and the N_2O_3 were condensed into a flask, warmed to 0°C and stirred until the color of the mixture changed from blue to amber (20 minutes). NO was then sparged through the mixture to convert any free NO_2 to N_2O_3; the color changed back to green. Sparging was continued until the mixture again became amber (20 minutes). At this point the reaction was complete and, after cooling to -20°C, evacuation to 1 mm/Hg removed the excess of anhydride and any dissolved oxides of nitrogen. The residue was identified as CF_3COONO by infrared analysis and could be used without further purification. Yields were virtually quantitative based upon the equivalent anhydride charge.

Ultimately, bench-scale reactions of up to 230 gm of product per batch were completed without incident. A total of 2100 gm was prepared for safety testing and laboratory conversion to CF_3NO.

2. Safety Evaluation

The literature indicated that under certain ill-defined conditions CF_3COONO would detonate. Before scaleup to multi-pound levels was considered, it was necessary to define the hazards relative to preparation, handling, storage, and utilization in the CF_3NO preparation. The explosive and rocket industries have developed many procedures for the evaluation of potentially hazardous materials. Two of these test procedures were utilized on this program.

The first of these, the Trauzl block test, is a small-scale version of an explosives test involving the initiation of a test sample in a lead cylinder (Ref 7). The RMD version of this test employs a 2.5 by 2 inch lead cylinder with a cavity 1 inch in diameter and 2 inches deep. The sample (1-3gm) is placed in this cavity along with a No. 8 blasting cap which is the initiator. An indication of detonability and a qualitative estimate of the explosive power is obtained from the amount of deformation found after firing the cap. This deformation is reported in terms of the increased volume of the cylinder in units of cc per gram of sample. An example of the results obtained with reference explosives is shown in Table I.

TABLE I

TRAUZL BLOCK RESULTS FOR REFERENCE EXPLOSIVES

Explosive	Expansion * (cc/gm)
RDX	30
TNT	5
Nitroglycerine	30
Nitromethane	5
Nitromethane/tetranitromethane	22

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* Expansion beyond that effected by the blasting cap alone.

The results of the CF_3COONO Trauzl tests are shown in Table II. These data indicate that the liquid does detonate although the detonation is not very brisant.

TABLE II

TRAUZL BLOCK RESULTS FOR CF_3COONO

Sample Size (gm)	No. of Tests	Expansion (cc/gm)
1	2	3.0
3	2	5.7

The other test was a modified card gap test which involved the determination of whether a sample contained in a tube of given diameter and composition would propagate a detonation wave from a 50 gm tetryl charge. CF_3COONO contained in stainless steel tubes 6 inches long and up to 11/16 inch in ID was tested in this manner; in no case did the CF_3COONO contribute to the detonation. Therefore, if piping between the reactor and the CF_3COONO storage vessel is stainless steel and less than 11/16 inch diameter, propagation of a reactor detonation back to the storage vessel should not occur. Plastic and glass containers normally result in critical diameters greater than those for steel, therefore the use of plastic or glass tubes should result in an even safer situation.

The ignition limits of CF_3COONO were determined over the range of 25°to 100°C as a function of concentration with nitrogen as the diluent. No determinations were made at temperatures greater than 100°C because of the appreciable decomposition at these temperatures. The tests were conducted at pressures between 50 and 760 mm/Hg; the ignition source was a high voltage spark between tungsten electrodes. The criterion for ignition was the observance of a sudden pressure increase since the ignitions were not always visible. No detonations were experienced. The data from these tests are given in Figure 2 and indicate that CF_3COONO will ignite on initiation, but only at concentrations greater than 50% up to about 65°C and at lower concentrations at higher temperatures. The low temperature limit for the ignition of CF_3COONO vapor appears to be about 40°C.

These conditions can be expected at some point in the reactor during the thermal decarboxylation, and it was decided to test the ignitibility (or detonability) of CF_3COONO under simulated reactor conditions.

For this test, the proposed reaction diluent (FC-43, see section B, below) was charged to a round-bottomed flask topped with a column which served as an air-cooled condenser. Electrodes were positioned immediately above the surface of the FC-43. The FC-43 was brought to a vigorous reflux and the CF_3COONO injected below the liquid level. The CF_3COONO vaporized immediately and a spark was induced by a Tesla coil. No effect of the spark was observed. The FC-43 reflux was maintained and gradual CF_3NO formation was observed (yellow→green→blue). During this time, the vapor phase was sparked at frequent intervals; at no time was an ignition or a detonation in evidence. It was therefore assumed that the dilution of the CF_3COONO vapors by FC-43 resulted in a significantly reduced detonation hazard.

B. PREPARATION OF TRIFLUORONITROSOMETHANE (CF_3NO)

The study of the preparation of trifluoronitrosomethane was conducted at a high level of effort. Although potential alternate methods were investigated, the bulk of this study was concerned with CF_3NO formation via the pyrolytic decarboxylation of CF_3COONO. All studies were conducted with the goals of maximum safety, product purity, and efficiency of operation. The preparation of CF_3NO from CF_3COONO had been effected by both photolysis and pyrolysis reactions, but both methods (at least in the then current state of the art) had serious shortcomings. Photolysis, in general, would have presented greater processing difficulties and the decision was made to concentrate on a pyrolysis method for the sake of expediency.

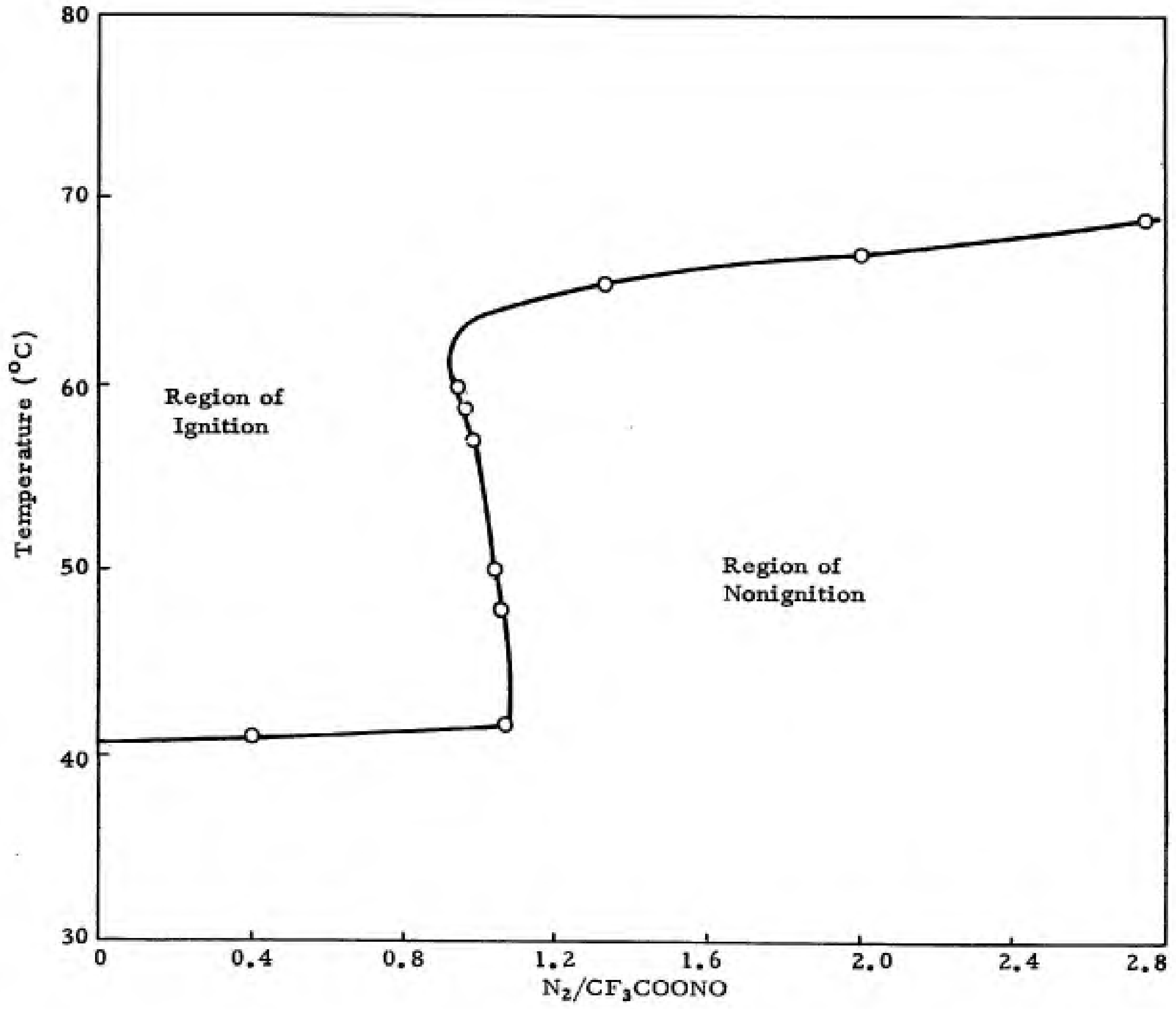

Figure 2. Ignition Limits of CF_3COONO in Nitrogen

1. Preparation from CF_3COONO

A vapor phase pyrolysis method had been developed at 3M* (Ref 6) but they found the pyrolysis tube length/diameter ratio to be optimum at 840/1. This ratio is very large, and the design of equipment for efficient and safe operation at a reasonable scale would have been very difficult. Over and above the problem of the 840/1 L/D ratio, the detonability of the nitrite was a matter of concern. It seemed probable that the tendency for CF_3COONO to detonate could be modified by dilution and that a solution pyrolysis could be operated with a minimum of equipment and control. Accordingly, a search was made for a high boiling (>150°C), inert reaction medium for CF_3COONO. FC-43, a 3M product consisting of isomers of $(C_4F_9)_3N$, was found to be a suitable material. It had the advantages of nonflammability and apparent nonreactivity toward CF_3COONO and CF_3NO, coupled with a convenient boiling point, 184°C. It was used exclusively in the CF_3NO pyrolyses.

Other potential solvents were scanned but not used because of one or more shortcomings, e.g., hydrocarbons (flammability, immiscibility with CF_3COONO, and capability of interfering with subsequent polymerizations) and trifluoromethyl-substituted aromatics (boiling points too low).

Several preliminary pyrolyses were completed using FC-43 solutions of CF_3COONO to determine the applicability of the general approach and to determine the temperature range required. The first technique used involved heating the solution at a constantly increasing temperature and observing the change in pressure as a function of temperature. This was accomplished by maintaining the reactor at atmospheric pressure and allowing any generated gases to bleed into a calibrated, previously evacuated volume. The pressure in this volume was measured and plotted as a function of the reactor temperature. A blank run with FC-43 alone served to establish the contribution of the solvent to the change in pressure. A heating rate of 2.8°C per minute was used and a reactor temperature of 80°C was chosen as the point at which the pressure change was zero. Volume limitation of the system dictated the use of small quantities of CF_3COONO. These data (Figure 3) indicated that a significant increase in the rate of reaction occurs at about 140°C; CF_3NO was first observed visually at about 145°C. The products of this reaction were collected and sampled for

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* Minnesota Mining and Manufacturing Company

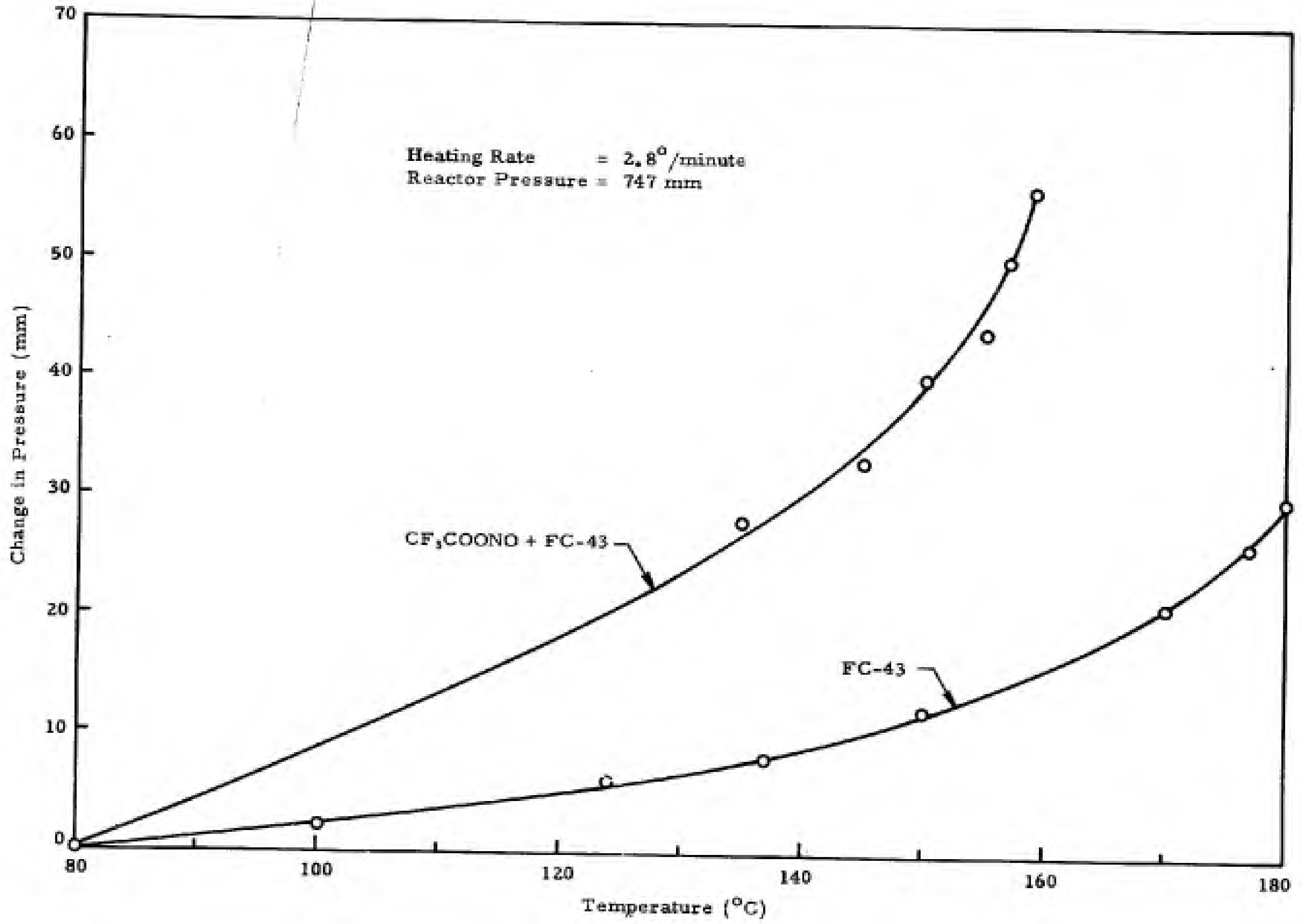


Figure 3. Pressure Change with Increasing Temperature, $CF_3COONO/FC-43$

mass spectroscopic analysis. Major constituents were identified as CF_3NO, CO_2, and NO_2. Small amounts of NO, CF_4, and COF_2 were also present as well as traces of unidentified materials.

In other experiments, the pressure change resulting from the decomposition of CF_3COONO was measured under isothermal conditions at temperatures up to the boiling point of FC-43. For these determinations, the nitrite was dropped into the FC-43 at temperature and the evolved gases allowed to expand into a closed, calibrated volume which was large with respect to the quantity of nitrite added. Thus, the system pressure did not rise appreciably over atmospheric. The pressure increase in the system was noted at intervals and plots of ΔP vs time prepared. These are reproduced as Figures 4 and 5. The time at which the rate of pressure increase approaches zero is the time required for complete nitrite decomposition. At 184°C, this period was about 5 to 7 minutes and at lower temperatures, the times were proportionally longer. Although higher temperatures could be obtained by operation under pressure, previous work had indicated that decreased CF_3NO yields and an increased hazard could be expected (Ref 6) at such temperatures. Therefore, it was decided to develop a process at 184°C, the boiling point of the solvent.

Since the nitrite residence time is relatively short at this temperature, attempts were made to make this process continuous. An apparatus was constructed for a reaction of this type which consisted of a nitrite addition funnel, a reaction flask containing the FC-43 surmounted by a water cooled condenser, and a purification system terminating in a vacuum line with liquid nitrogen-cooled traps for product collection. In operation, the FC-43 was heated to reflux and the nitrite added at a rate equal to, or less than, the rate of its disappearance by decomposition. A slow helium sweep was introduced for positive displacement of the products and to prevent any possibility of air diffusion into the collection traps. This apparatus was designed as a check of the method and the nitrite charges were normally quite small. These experiments were successful. Because of the lack of precise analytical data, the calculation of yields was not possible in most cases, but yields of up to 53% were indicated for certain runs. Other experiments were conducted at 165° and 175°C. Product weights were lower and the products appeared to be less pure.

The success of these experiments indicated feasibility of this approach and larger reactors were constructed and operated to obtain data from which the pilot plant could be designed.

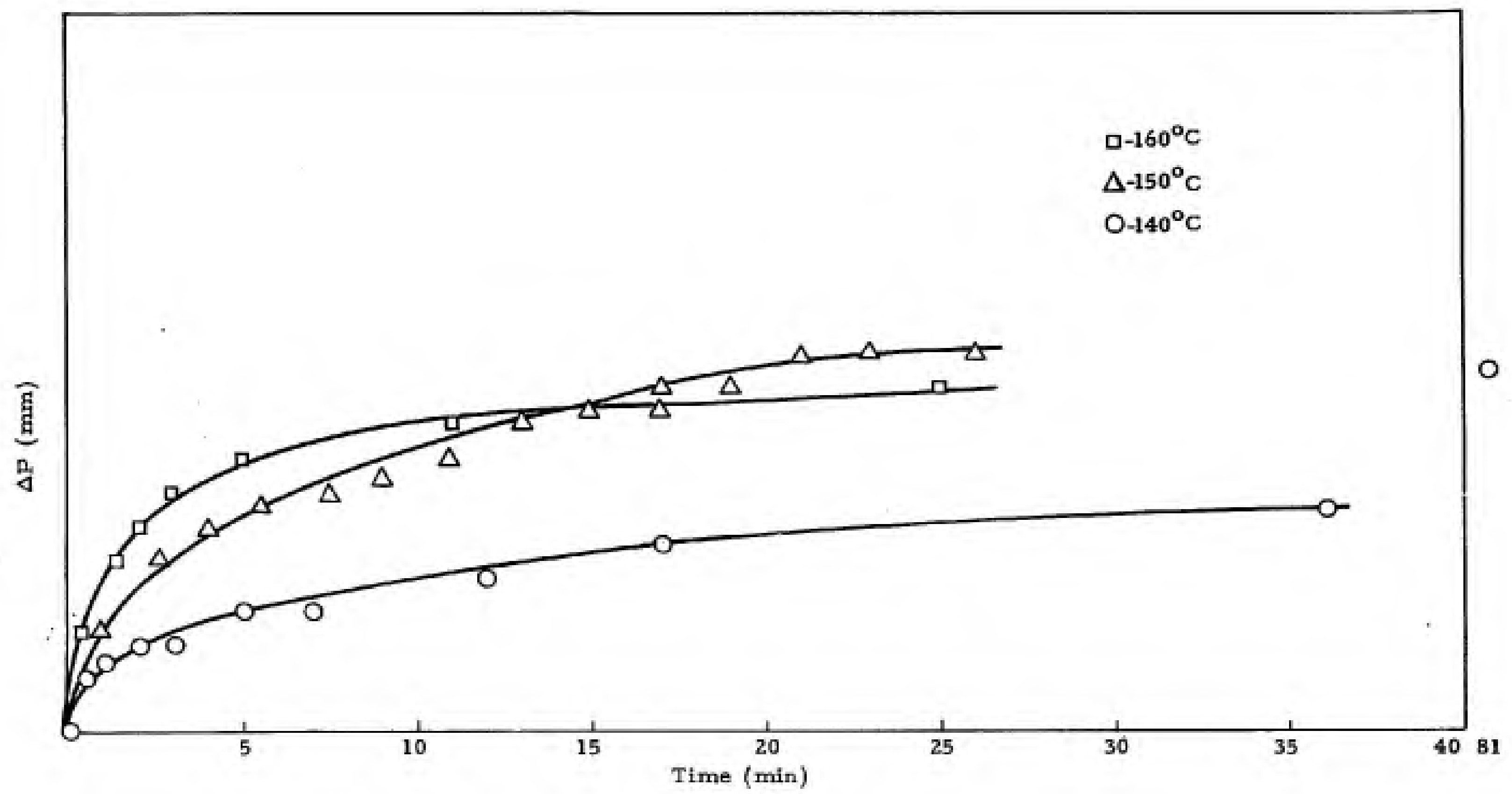


Figure 4. Rates of CF_3COONO Pyrolysis in FC-43

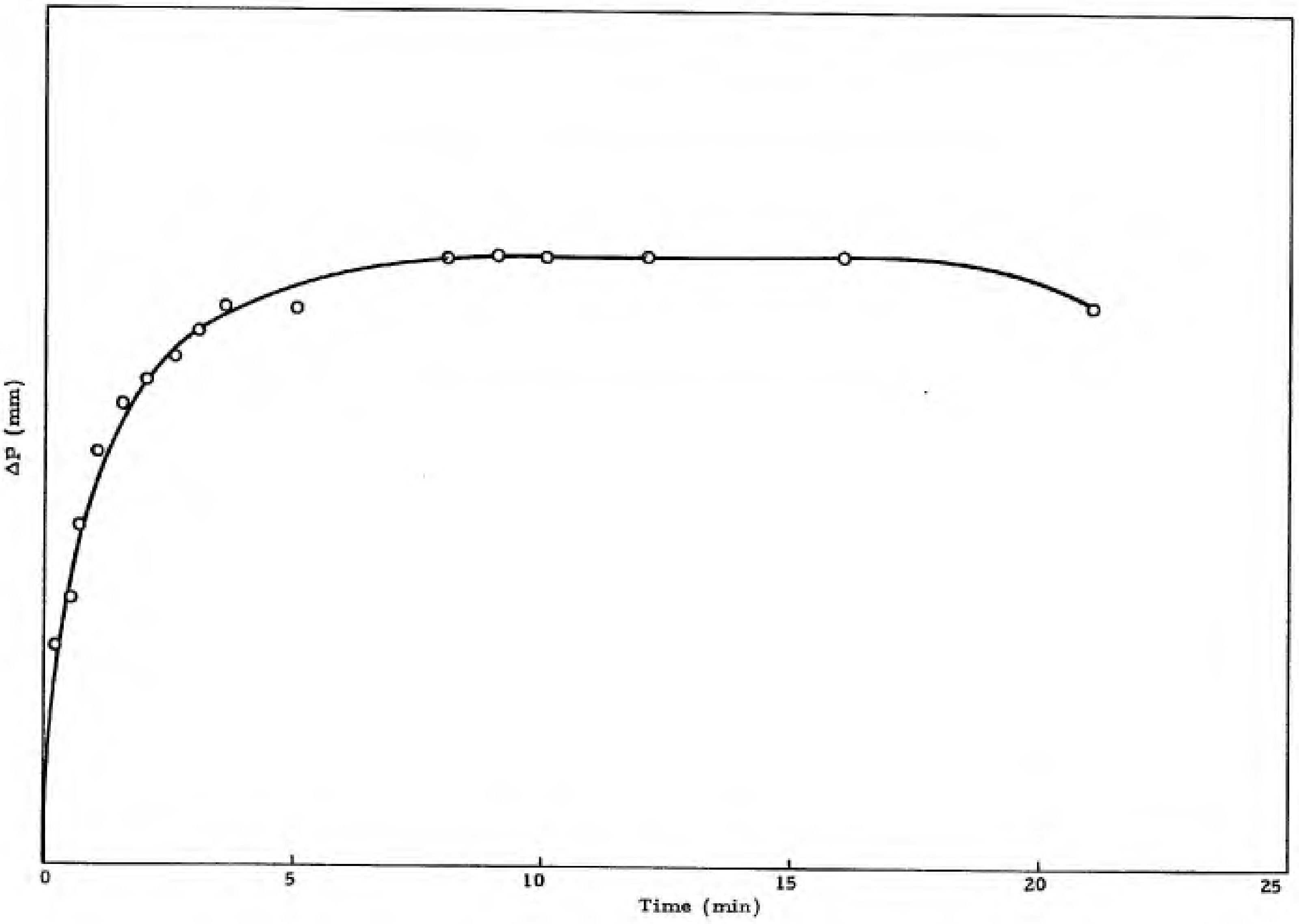


Figure 5. Rate of CF_3COONO Pyrolysis in FC-43 at 184°C

Since the preferred pyrolysis temperature (184°C) is significantly higher than the boiling point of the nitrite (99°C), the greatest part of the decarboxylation occurs in the vapor phase. Thus, to increase the capacity of the reactor, the vapor phase volume should be increased, not the liquid phase. Since the pyrolysis products are gas phase and since the FC-43 acts only as a heat transfer agent, only enough FC-43 is required to provide one atmosphere of vapor in the reactor and a refluxing liquid phase for the nitrite addition. No increase in the liquid phase volume during the reaction will occur. Because the hot FC-43 vapors serve as a diluent for the nitrite vapors, the possibility of the initiation and propagation of a detonation is minimized.

The largest laboratory reactor used on this program had a vapor phase reaction zone of 600 cc; a schematic diagram of this apparatus is shown in Figure 6. The FC-43 volume was 80 cc. In operation, the CF_3COONO was charged at a controlled rate through the tube leading below the surface of the refluxing FC-43. The decarboxylation occurred in the vapor phase heated by ascending FC-43 vapors. The water-cooled condenser returned the FC-43 and any unreacted nitrite to the boiler. The helium sweep at the top of the condenser carried the CF_3NO and other pyrolysis products through the purification train and into the collection traps where the purified product was condensed at liquid nitrogen temperatures (see also the appendix.) This apparatus was successfully used in the preparation of CF_3NO in purities greater than 99% and in yields of greater than 50%. Production of purified CF_3NO in this apparatus was approximately 370 gm in replicate runs; this material was utilized in the development of polymer processes.

The average rate of CF_3COONO charged to this reactor was 26 gm per hour, although rates up to twice that were successfully used. The average rate corresponds to a CF_3NO production of about 8-9 gm per hour. Thus, a reactor of only 10 gallons volume was expected to be capable of producing CF_3NO at a rate of two pounds per hour.

With the establishment of the pyrolysis conditions and the construction of the pilot plant, subsequent work was limited to studies of problems unique to the pilot plant operation.

One sample of CF_3COONO was stored in the dark at 40°C for a period of two weeks as an accelerated aging study to determine the effect of nitrite storage on CF_3NO yield. A pyrolysis was effected with the fresh nitrite followed by pyrolysis under equivalent conditions at weekly intervals. Yields of CF_3NO were 51% with fresh nitrite and 41% and 28% after one and two week's storage. No apparent yield reduction has been experienced with nitrite stored for an equivalent length of time at 0°C. Therefore, refrigerated storage is mandatory, and it is suggested that the nitrite be used as soon after preparation as possible.

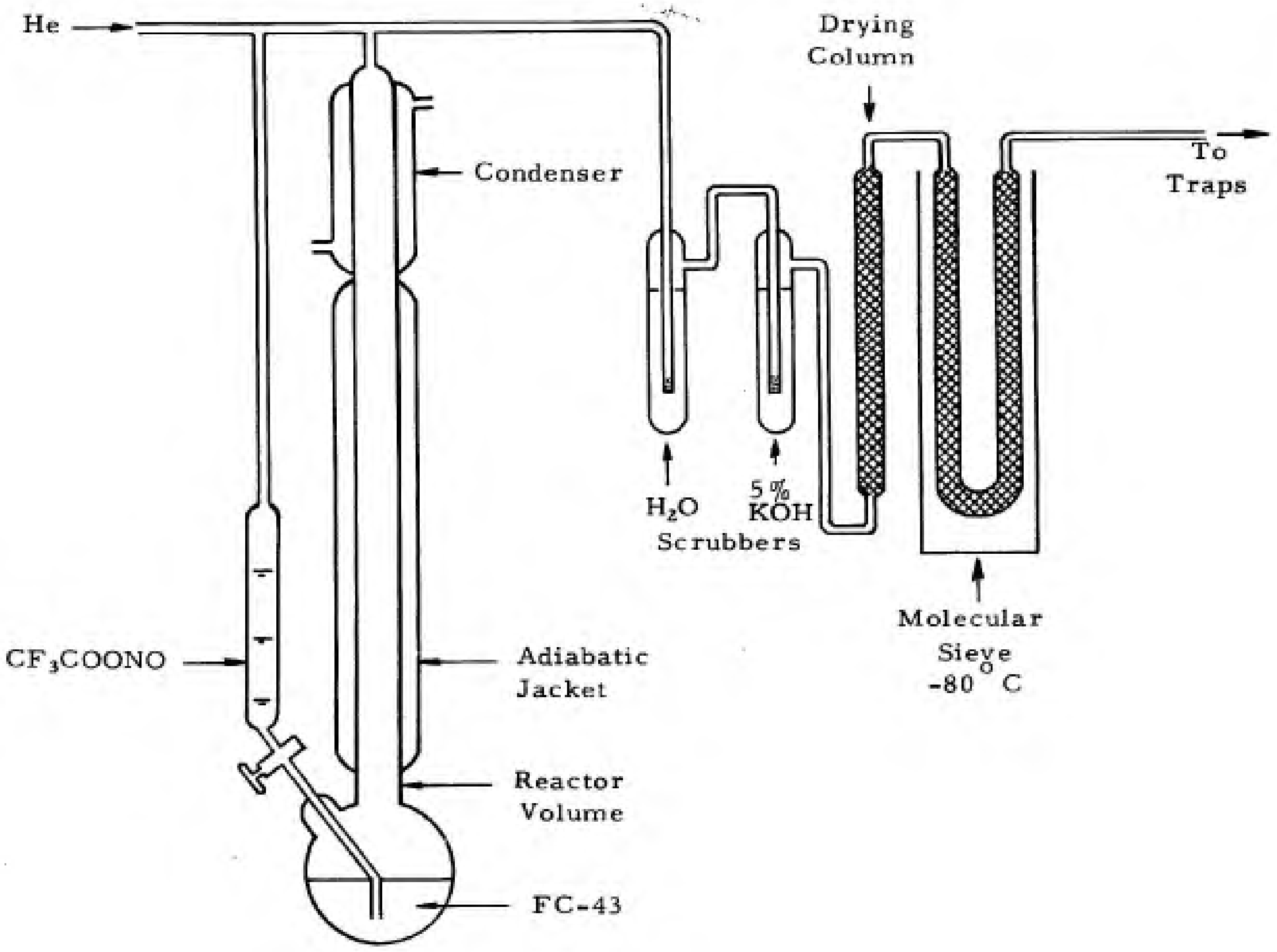


Figure 6. Laboratory Apparatus for CF_3NO Production

During operation of the pilot plant reactor, a gradual formation of a solid material in the FC-43 was observed. Since this material had not been observed in the laboratory operations, characterization of this material and the determination of its effect on the pyrolysis were desired. A sample was obtained from the production facility and submitted for infrared and elemental analyses. Exact identification was not obtained but it was established that the material was inorganic ($C<1.5\%$, H and $N<1\%$). Fluorine was present and the material was assumed to be a silicofluoride. The solid was not impact sensitive.

2. Purification

The formation of CF_3NO in the CF_3COONO decarboxylation is accompanied by a large number of other compounds. In addition to the formation of the nitroso compound, CO_2, N_2O, NO, NO_2, CF_4, C_2F_6, C_3F_8, C_4F_{10}, COF_2, CF_3NO_2 and $(CF_3NO)_2$ are among the other products identified. The products considered to be most deleterious to the copolymerization with C_2F_4 are the oxides of nitrogen (with the possible exception of N_2O), CF_3NO_2 and $(CF_3NO)_2$. Methods for removing these materials were studied intensively.

Data received from 3M (Ref 3) indicated that the use of a water scrubber was sufficient to remove all but the CO_2, and that the CO_2 could be removed by a 4X molecular sieve. The recommendation of fractional distillation (60 plates) for the purest possible CF_3NO was also made by 3M. The use of low temperature fractional distillation was not considered for this program because of the cost of the equipment, the difficulty of obtaining 60 plates on a production scale, and the need for a continuous unit. Therefore, other methods of purification of the process stream were investigated.

The original attempts at purification employed the units recommended by 3M. It was found, however, that two water scrubbers in series did not remove the oxides of nitrogen and that they were ultimately eluted from the molecular sieve column. Thus, contamination of the product occurred. The addition of a weak base (magnesium carbonate) either as a column of solid material or as a suspension in water was not found to reduce NO_2 contamination (Table III). Although the use of strong bases had not been recommended because of CF_3NO degradation (3M data), the use of 5% aqueous potassium hydroxide in the scrubbers did not degrade the CF_3NO. The KOH scrubbers effected a significant reduction in the NO_2 level as is shown by the data in Table III.

The use of more concentrated caustic was also investigated. In one experiment, 50% NaOH was used to determine the effect of much stronger solutions.

TABLE III

PYROLYSIS OF CF_3COONO IN FC-43

Experiment No.	CF_3COONO (gm)	Addition Time (min)	Purification System	Product Wt (gm)	Crude Yield (%)	Assay (%) [1]			
						CF_3NO	COF_2	NO_2	N_2O
866	13.0	150	Dry Ice trap + 5% $FeSO_4$ + 5% KOH	---	---	94.5	---	0.5	5.0
872	13.9	52	5% KOH	4.96	51.6	91.5	0.3	5.4	2.8
876	18.4	75	5% KOH + 15% $FeSO_4$ + 50% KOH	5.7	44.8	80.0	---	3.8	2.3
879	22.0	97	50% KOH + 15% $FeSO_4$ + Dry Ice	---	---	84.5	0.6	11.3	3.6
882	35.0[2]	---	5% NaOH + 15% $FeSO_4$ (acidified + -100°C Trap)	7.0	---	99+	---	---	---
884	42.8	275	5% NaOH + 15% $FeSO_4$ (acidified + -100°C Trap)	13.0	44.0	98	---	1.0	1.0
887	22.3	70	5% NaOH + 15% $FeSO_4$ (acidified)	---	---	96.8	0.1	2.0	0.8
888	43.5	126	5% NaOH + Mol. Sieve at -78°C	17.7	58.8	75.2	6.1	1.0	23.7
890	32.1	---	Counter-Current H_2O Scrubber +5% NaOH + Mol. Sieve at -78°C	---	---	75.0	contains air		
891	28.4	50	5% NaOH + H_2O + Mol. Sieve at -78°C	3.8	19.3	98	---	---	---
892	36.7	88	5% NaOH + H_2O + Mol. Sieve at -78°C	11.8	46.5	99	trace	trace	---
894	45.0	112	5% NaOH + H_2O + Mol. Sieve at -78°C	13.5	43.3	99.5	trace	---	---
895	55.0	150	5% NaOH + H_2O + Mol. Sieve at -78°C	17.0	44.7	99	trace	trace	---
896	57.4	163	5% NaOH + H_2O + Mol. Sieve at -78°C	19.8	50.0	98.6	0.4	0.7	---

---

(1) CF Materials make up the remainder.
(2) Reaction not completed.

Although absorption of neat NO_2 was found to be complete, analysis of CF_3NO process streams passed through this solution indicated significant NO_2 concentrations. In addition, recoveries were very low. Thus, significant breakdown of the CF_3NO apparently occurred and subsequent work was conducted with 5% caustic.

Since NO forms complexes with many transition metals of low valence state (e.g., ferrous, chromous), the use of these materials in scrubbers was investigated. It was thought that NO_2 would be reduced to NO, followed by NO removal as the complex. Ferrous sulfate (in both neutral and acid solution) was found to be somewhat effective, but not enough of the oxides were removed to recommend its use in the purification train. The use of chromous chloride (prepared in solution from chromium chloride in a Jones reductor) was found to remove CF_3NO as well, thereby reducing the yield of product. It may be possible to complex CF_3NO in this manner, and then regenerate it at will. This possibility was not investigated on this program, however.

During these experiments, the pH of the water scrubber was checked before and after pyrolysis. The pH was found to be unchanged and this scrubber was therefore removed from the purification system.

It was finally determined that CF_3NO of greater than 99% purity could be obtained through the use of 5% caustic scrubbers to remove the bulk of the nitrogen oxides and CO_2 followed by a cold (-78°to -100°C) molecular sieve column to remove the last trace of impurities. Material purified in this manner was contaminated only with traces of fluorocarbons. It was found essential to cool the molecular sieve, because at higher temperatures the nitrogen oxides would eventually elute from the column.

This study was continued to indicate the quantity of molecular sieve required for a unit CF_3COONO charge. The column studied was 1/2 inch ID and 2 feet long and carrier gas (He) flowrates averaged 95 standard cc/min. The sieves were activated by heating to 350°C overnight with a helium purge. The gases chosen for the study were NO_2 and NO; these are among the impurities considered to be most deleterious to the polymerization. NO has a very low boiling point (-151°C) and should be one of the more difficult to retain on the sieve. It was found that at -76°C, NO_2 was retained for at least 7.5 hours (the duration of the experiment), but that NO elution occurred in one hour.

With column operation at -95°C, no NO elution was observed during a seven-hour period. The weights of sieve and sample indicated that one pound of molecular sieve would be able to purify CF_3NO from at least one pound of CF_3COONO.

C. ANALYSIS OF TRIFLUORONITROSOMETHANE

The adverse effect on the copolymerization of certain CF_3NO impurities, such as CF_3NO_2, was well known. Others, as COF_2, were less well known. For this reason, methods for the qualitative identification of all CF_3NO contaminants and the quantitive determination of the levels of each were required so that a correlation of polymer properties with monomer feed could be established.

A method development study was undertaken to develop a simple, rapid and quantitative gas chromatographic (gc) procedure. During the initial phases of the study which involved screening of promising gc columns and optimization of conditions for the column selected, a combined gas chromatographic-mass spectrometric technique was employed. The gc was employed to separate the various components in a given sample and the effluent passed directly into the mass spectrometer(ms) for immediate identification. After identification, the various components could be collected and used as standards for gc and ms calibrations. A Bendix Time-of-Flight Mass Spectrometer Model 12-101, equipped with a Model-4-107 Ion Source and a Tektronix Oscilloscope, Type 545-86 was employed along with a Burrell Kromo-Tog Model K-2 gas chromatograph for these studies.

The first gc column packing used was 13X molecular sieve. The conditions used were as follows:

Column length	2 meter, glass
Carrier gas	Helium
Flowrate	100 cc/min
Column Temperature	90°C
Sample Temperature	50°C
Detector Temperature	50°C
Cell Current	120 ma

Retention times on this column were found to be:

O_2	10 sec
N_2	15 sec
NO_2	30 sec
CF_4	45 sec

C_2F_6-------------------------------- 4 min 45 sec
CF_3NO---------------------------- 6 min 10 sec
N_2O--------------------------------- 8 min 30 sec

This column could not be used for complete quantitative measurements of CF_3NO samples which contained NO_2, as the NO_2 peak was deformed and not generally reproducible. The column was, however, generally useful for CF_3NO analysis and in addition enabled pure CF_3NO and C_2F_6 to be collected and used as mass spectrometer standards. Other components necessary for calibration were commercially available and were purified as required for standardization.

Table IV gives the mass spectral data obtained for chromatographically pure CF_3NO and for a CF_3NO sample as received from the laboratory.

TABLE IV

MASS SPECTRAL DATA FOR CF_3NO

		Relative Intensities	
m/e	Ionic Species	GC Purified Sample	As Received
26	$C\text{-}N^+$	1.3	1.3
30	$N\text{-}O^+$	100.0	100.0
31	$C\text{-}F^+$	12.5	10.5
44	N_2O^+	--	1.8
45	FCN^+	2.1	2.1
46	NO_2^+	--	0.7
47	COF^+	--	0.2
50	F_2C^+	16.8	14.4
64	F_2CN^+	3.3	2.2
69	F_3C^+	42.0	40.5
99	F_3CNO^+	3.2	2.7
119	$F_3CCF_2^+$	--	1.9
131	$C_3F_5^+$	--	0.06

An additional problem encountered was the fact that CF_3NO_2, a possible impurity in the samples being analyzed, had the same retention time as CF_3NO on the 13X molecular sieve column and the Time-of-Flight mass spectrometer could not detect its presence if NO_2 were also present in the sample.

A column of 33% Kel-F oil (grade 8126) on Celite (20-30 mesh) was found to be effective in the separation. Using a 9-1/2 ft coiled copper column at $0^{\circ}C$, a helium flowrate of 100 cc/minute, a cell current of 120 ma and a gas phase sample, the following retention times were observed::

O_2, N_2	1 min 39 sec
CF_3NO	1 min 48 sec
N_2O	2 min 6 sec
CF_3NO_2	3 min 18 sec

CF_3NO_2 could be determined in the presence of CF_3NO with this column. In general, most analyses on CF_3NO were carried out by employing mass spectrometry and gas chromatography using both the 13X molecular sieve and Kel-F on Celite columns. As the program progressed and synthetic techniques improved, resulting in higher purity CF_3NO, experience showed that gas chromatography alone provided acceptable analytical data if both the above mentioned gc columns were employed.

Task 2. Preparation of Tetrafluoroethylene (C_2F_4)

The objective of this task was to prepare or procure sufficient quantities of tetrafluoroethylene for both the initial research studies and for production of the required amount of nitroso rubber.

Tetrafluoroethylene for the production phase of this program was manufactured in the Thiokol TFE facilities at Moss Point, Mississippi. The amounts required for the initial polymer development tasks were prepared in the laboratory by the debromination of tetrafluorodibromoethane.

$$CF_2BrCF_2Br + Zn \xrightarrow{CH_3OH} CF_2{=}CF_2 + ZnBr_2 \qquad (3)$$

An apparatus for this process was assembled and put into operation (Figure 7). Tetrafluoroethylene was generated by the controlled addition of the tetrafluorodibromoethane to a refluxing suspension of activated zinc in methanol. The effluent vapors were precooled by a cold water condenser and then passed through a condenser at $-35^{\circ}C$ to remove any dimethyl ether which might have been produced by a side reaction of zinc and methanol. The product was then condensed at liquid nitrogen temperatures under a slight helium pressure to preclude contamination by atmospheric oxygen. After the reaction was complete, the condensate was warmed to $-76^{\circ}C$ and transferred in vacuo to a stainless

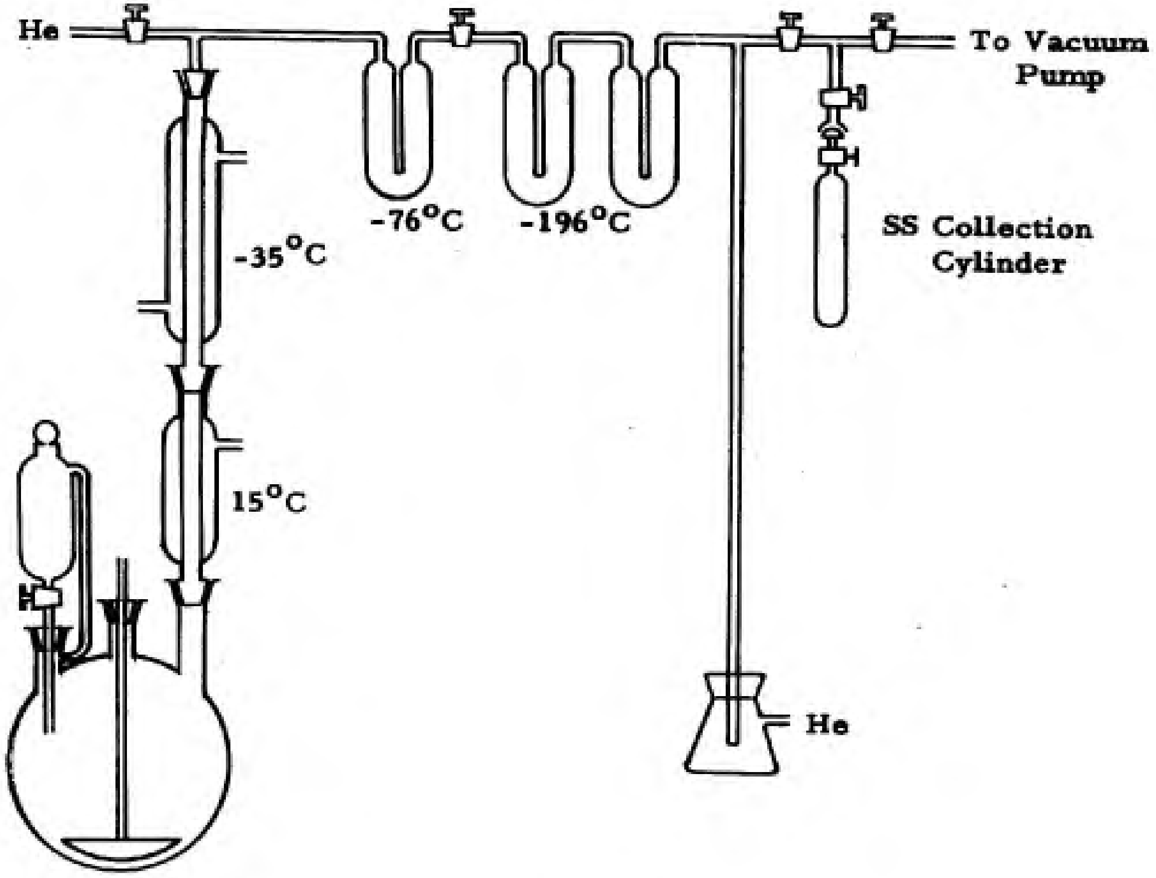


Figure 7. Apparatus for Preparation of C_2F_4

steel storage cylinder containing an inhibitor (Terpene B). Residual material in the -76°C trap was found to be a mixture of fluorocarbons (including tetrafluoroethylene) and dimethyl ether. This fraction was discarded. These preparations were completed at the scale and frequency required for the supply of product for polymerization studies without the necessity for long term storage. Fourteen preparations were completed with a combined yield of 431 gm. These products were shown to be about 98.5% C_2F_4, 1.0% C_3F_8 and 0.5% C_2F_6 by mass spectral and chromatographic analyses.

Task 3. Nitroso Monomer Research

The objective of the research carried out on this task of the program was the preparation of new polyfluoronitroso monomers that would be expected to improve the low temperature properties of nitroso rubber and/or to provide functionalities which could become crosslinking sites for improved mechanical properties. Further work to develop a more suitable synthetic procedure for CF_3NO was also conducted.

Earlier reports (Ref 3, 4) had described the preparation of terpolymers which were cured through pendent carboxyl groups. The cured product had a higher tensile strength than the copolymer and the vulcanizate also exhibited excellent solvent resistance, nonflammability, low temperature flexibility and ozone resistance. Accordingly, much of the Task 3 effort was directed toward the synthesis of perfluoronitroso compounds containing carboxyl groups as cure sites. The preparation of both aliphatic and aromatic compounds was attempted in order to determine the effect of structure variation on the properties of the terpolymers. In addition, studies of the preparation of nitrosyl fluoride (FNO) and new CF_3NO preparative methods were conducted.

The experimental conditions utilized for this work are summarized in the appendix.

A. NEW TRIFLUORONITROSOMETHANE PREPARATIVE METHODS

Although the preparation of CF_3NO via pyrolysis of CF_3COONO was facile, one of the starting materials $[(CF_3CO)_2O]$ is expensive and the handling and pyrolysis of CF_3COONO represents a potential hazard. Therefore, other methods of preparation were investigated. Although no new preparative method would have been considered for initial production, increased operating economy and safety could have been realized for subsequent operations.

One potential method was the interaction of nitrosyl fluoride and sodium chlorodifluoroacetate:

$$\mathrm{ClCF_2COONa} \xrightarrow{\qquad\qquad} \mathrm{:CF_2 + CO_2 + NaCl} \qquad (4)$$

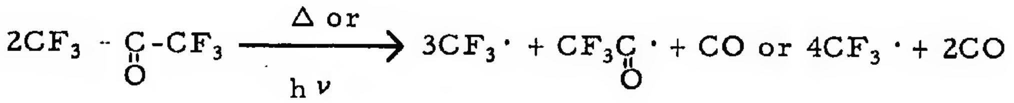
$$\mathrm{:CF_2 + FNO} \xrightarrow{\qquad\qquad} \mathrm{CF_3NO} \qquad (5)$$

Reaction 4 is known and it was considered that if the difluorocarbene could be generated in the presence of FNO, reaction 5 would take place. FNO was not available at the time of this experiment but as a check of the feasibility of the reaction, nitrosyl chloride (ClNO) was used. The product in this case would be chlorodifluoronitrosomethane (Reaction 6).

$$\mathrm{:CF_2 + ClNO} \xrightarrow{\qquad\qquad} \mathrm{ClF_2NO} \qquad (6)$$

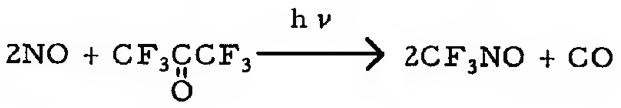
The $\mathrm{ClCF_2COONa}$ was prepared by neutralization of the free acid with NaOH and dried at low temperature to prevent decomposition. This material was dissolved in diethyleneglycol dimethyl ether and heated while sparging ClNO through the solution. At temperatures between 95°and 130°C, a blue color was observed in the effluent gas stream, indicating that $\mathrm{ClCF_2NO}$ had been prepared. A white solid, presumably NaCl, was precipitated. The gases were passed through a trap at -76°C to remove excess ClNO, then condensed at -196°C. Mass spectral and infrared analyses of this material indicated the presence of $\mathrm{ClCF_2NO}$.

The interaction of hexafluoroacetone and nitric oxide was also studied. Hexafluoroacetone is known to decompose pyrolytically and photolytically to give products which are best explained by assuming decomposition as follows:



$$\mathrm{2CF_3 - \underset{\underset{O}{\|}}{C} - CF_3} \xrightarrow[h\nu]{\Delta\ \text{or}} \mathrm{3CF_3\cdot + CF_3\underset{\underset{O}{\|}}{C}\cdot + CO\ or\ 4CF_3\cdot + 2CO} \qquad (7)$$

The synthesis of $\mathrm{CF_3NO}$ by photolysis of hexafluoroacetone in the presence of NO has been reported (Ref 8). The only products are $\mathrm{CF_3NO}$ and CO.



$$\mathrm{2NO + CF_3\underset{\underset{O}{\|}}{C}CF_3} \xrightarrow{h\nu} \mathrm{2CF_3NO + CO} \qquad (8)$$

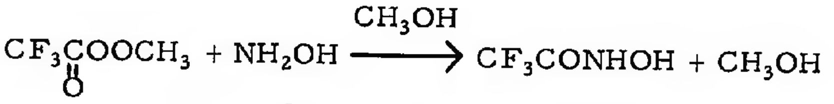
Attempts were made to prepare CF_3NO by a thermal route. One experiment involved the passage of a stoichiometric mixture of the ketone and NO through a 1/4 inch diameter stainless steel tube and allowing a portion of the exit gases to pass into the mass spectrometer. The tube was heated at temperatures to 650°C, but only ketone decomposition products (at $>$ 585°C) were observed.

B. PREPARATION OF ALIPHATIC NITROSO COMPOUNDS

This portion of the monomer synthesis program was concerned with the preparation of known and new perfluoronitroso compounds including those containing carboxyl or olefin groups. The major objective of the study with the known compounds was to develop improved techniques for the synthesis of these compounds in order to produce them in higher yields and at lower cost.

1. Trifluoronitrosomethane

Because of the difficulties encountered in the synthesis of CF_3NO <u>via</u> acyl nitrite, an alternate route to this compound was sought. The pyrolysis of trifluoroacethydroxamic acid, prepared by the reaction of methyl trifluoroacetate and hydroxylamine, has been reported (Ref 9) to give CF_3NO in 68% yield. Treatment of methyltrifluoroacetate with hydroxylamine gave a white solid, mp 72-75°C.



$$CF_3\underset{\overset{\|}{O}}{C}OOCH_3 + NH_2OH \xrightarrow{CH_3OH} CF_3CONHOH + CH_3OH \qquad (9)$$

$$CF_3CNHOH \xrightarrow{80\text{-}85^{\circ}} CF_3NO + (CH_2O)_n \qquad (10)$$

The elemental analysis of this material, however, indicated that it was not the desired hydroxamic acid. Attempts to prepare this compound by reaction of trifluoroacetic anhydride with hydroxylamine or its hydrochloride were also unsuccessful.

2. 3-Nitrosoperfluoropropanoic Acid

The need for carboxyl-substituted nitroso compounds as termonomers was emphasized above and an early attempt to prepare nitrosoperfluoropropanoic acid by ultraviolet irradiation of a mixture of methyl perfluorosuccinate and nitrosyl chloride was made but only starting materials were recovered.

The reaction of FNO with perfluoroolefins has been used successfully to prepare perfluoronitroso compounds (Ref 10) and the synthesis of the propanoic acid derivative <u>via</u> this route appeared feasible. The reported preparation of trifluoroacrylic acid through the Grignard reaction was attempted (Reaction 11) but none of the desired product was obtained.

$$CF_2{=}CFI + Mg \longrightarrow CF_2{=}CFMgI \xrightarrow{CO_2} \xrightarrow{FNO} \begin{array}{c} ON(CF_2)_2COOH \\ \text{or} \\ CF_3CF(NO)COOH \end{array} \qquad (11)$$

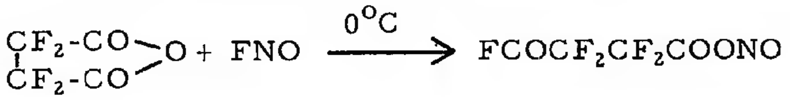
The synthesis of the nitroso acid in low yield has been described previously (Ref 4) by the photolysis of dinitrosyl perfluorosuccinate. It was obtained in high yield by the reaction of perfluorosuccinic anhydride and N_2O_3. To substantiate this procedure and to obtain the product for reference purposes, these reactions were explored briefly. The dinitrosyl compound was obtained in

$$\overline{OC(CF_2)_2COO} + N_2O_3 \longrightarrow ONOOC(CF_2)_2COONO \qquad (12)$$

$$ONOOC(CF_2)_2COONO \xrightarrow[-CO_2]{h\nu} ON(CF_2)_2COONO \xrightarrow{H_2O} ON(CF_2)_2COOH \qquad (13)$$

high yield (>90%), consistent with the reported procedure (Equation 12); however, the subsequent photolysis of the derivative (Equation 13) did not yield the desired product. Photolysis for 2 hours in a Pyrex flask with ultraviolet light of wavelength 2537 Å gave brown decomposition products and N_2O_3 and perfluorosuccinic anhydride were the only products obtained. The reaction shown by Equation 12 is apparently reversible, the driving force being the formation of a five membered ring.

To avoid this problem, an effort was made to prepare a mononitrosyl derivative of perfluorosuccinic anhydride. The reaction of the anhydride with FNO (Equation 14) yielded nitrosyl perfluorosuccinyl fluoride in 87% yield. The product, a yellow, moisture-reactive liquid, was characterized by elemental analysis, equivalent weight, infrared spectrum and mass spectral



$$\begin{array}{l} CF_2\text{-}CO \\ CF_2\text{-}CO \end{array}\!\!>O + FNO \xrightarrow{0^{\circ}C} FCOCF_2CF_2COONO \qquad (14)$$

analysis (Table V). When $FCO(CF_2)_2COONO$ was irradiated with ultraviolet light for 6 hours under reduced pressure, perfluorosuccinic anhydride, N_2O_4, HF and $(CF_2COONO)_2$ were obtained but none of the desired nitroso acid fluoride was isolated. The formation of a 62.5% yield of $(CF_2COONO)_2$ indicates that the major reaction which takes place is disproportionation. The other products arise as a result of the photolysis of $(CF_2COONO)_2$ (Equation 15) and hydrolysis of perfluorosuccinyl fluoride (Equation 16) which was produced along with $(CF_2COONO)_2$. No further attempts were made to prepare the desired compounds.

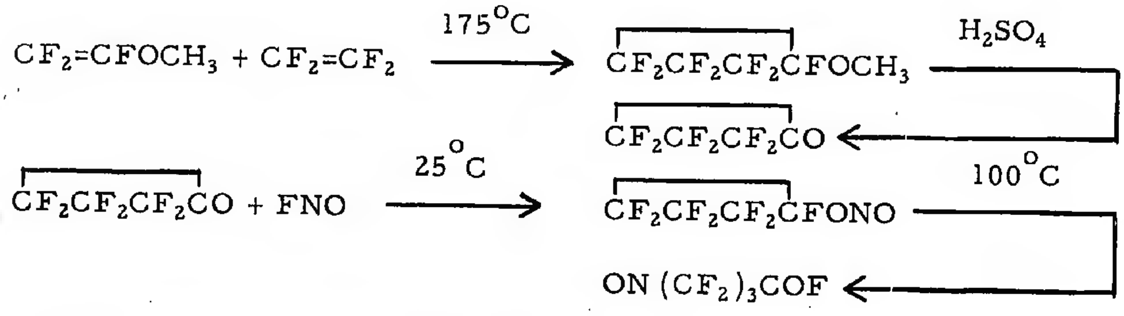
$$2\begin{array}{l}CF_2COONO\\|\\CF_2COF\end{array} \xrightarrow{h\nu} (CF_2COONO)_2 + (CF_2COF)_2 \qquad (15)$$

$$\begin{array}{l}CF_2COF\\|\\CF_2COF\end{array} \xrightarrow{H_2O} (CF_2CO_2H)_2 + HF \qquad (16)$$

3. 4-Nitrosoperfluorobutanoic Acid

A considerable amount of work has been done in an effort to prepare 4-nitrosoperfluorobutanoic acid $\left[ON(CF_2)_3COOH\right]$. Early efforts to react perfluoroglutaric acid with nitrosyl chloride under irradiation with ultraviolet light resulted only in the recovery of unchanged starting materials. More recently, a series of reactions which have been reported in the literature (Ref 11, 12) suggested another route to the acid (Equations 17, 18, 19). Repeated attempts to prepare

$$CF_2{=}CF_2 + NaOCH_3 \xrightarrow{100^\circ C} CF_2{=}CFOCH_3 + NaF \qquad (17)$$



$$CF_2{=}CFOCH_3 + CF_2{=}CF_2 \xrightarrow{175^\circ C} \overline{CF_2CF_2CF_2CFOCH_3} \xrightarrow{H_2SO_4} \overline{CF_2CF_2CF_2CO} \qquad (18)$$

$$\overline{CF_2CF_2CF_2CO} + FNO \xrightarrow{25^\circ C} \overline{CF_2CF_2CF_2CFONO} \xrightarrow{100^\circ C} ON(CF_2)_3COF \qquad (19)$$

methyltrifluorovinyl ether via the reaction shown by Equation 17 have given either trace amounts of product or no product at all. As a result of these difficulties, this route was abandoned in favor of a more direct one.

TABLE V

PARTIAL MASS SPECTRUM OF $FCOCF_2CF_2COONO$

m/e	Relative Intensity	Probable Ion Fragment
30	97.5	NO^+
31	87.3	CF^+
43	6.4	C_2F^+
44	4.8	COO^+
46	9.3	ONO^+
47	100.0	COF^+
50	31.0	CF_2^+
62	5.5	CCF_2^+
78	24.8	$CFCOF^+$
81	4.8	$C_2F_3^+$
93	0.9	$C_3F_3^+$
97	25.4	CF_2COF^+
100	47.5	$CF_2CF_2^+$
109	7.8	$CFCFCOF^+$
119	64.2	$C_2F_5^+$
128	1.1	$CF_2CF_2CO^+$
131	1.8	$CF_2CF_2CF^+$
147	12.4	$CF_2CF_2COF^+$
202	0.2	$ONOOCCF_2CF_2CO^+$
221	Molecular Ion Is Not Observed	

The photolysis of dinitrosyl perfluoroglutarate $\left[ONOOC(CF_2)_3COONO\right]$ has been reported (Ref 4) to give very low yields of impure $ON(CF_2)_3COOH$. The procedure described above for the synthesis of $(CF_2COONO)_2$ was used to prepare a 90% yield of $ONOOC(CF_2)_3COONO$ by the reaction of perfluoroglutaric anhydride and N_2O_3. Photolysis of this compound for periods of 12 to 16 hours produced, after hydrolysis, 12 to 38% yields of the desired nitroso acid, (Equation 20).

$$ONOOC(CF_2)_3COONO \xrightarrow{h\nu} ONOOC(CF_2)_3NO \xrightarrow{H_2O} ON(CF_2)_3COOH \qquad (20)$$

The product was characterized by its infrared spectrum, elemental analysis and equivalent weight.

The success obtained above prompted an examination of the photolysis of nitrosyl perfluoroglutaryl fluoride $\left[ONOOC(CF_2)_3COF\right]$. Its preparation was carried out in 72.5% yield by the reaction of perfluoroglutaric anhydride with FNO in a Monel cylinder at room temperature. An 86.6% yield of the compound was obtained by passing FNO through the anhydride at $0^{o}C$. The product, which was characterized by its infrared spectrum, elemental analysis and mass spectrum, was a yellow liquid which reacted readily with moist air.

$$\overline{OOC(CF_2)_3CO} + FNO \longrightarrow ONOOC(CF_2)_3COF \qquad (21)$$

The pyrolysis of $ONOOC(CF_2)_3COF$ was briefly explored but none of the desired product formed. A summary of these experiments is included in Table VI. In addition, one experiment was conducted in which $ONOOC(CF_2)_3COF$ was photolyzed with ultraviolet light for 2 hours. After hydrolysis, the resulting blue liquid was found to have ultraviolet and visible spectra identical to those of $ON(CF_2)_3COOH$; a further investigation of this reaction is required.

Attempts to react perfluoroglutaric anhydride with nitrosyl chloride resulted in the recovery of unchanged starting materials.

4. 5-Nitrosoperfluoropentanoic Acid

The reaction of terminally unsaturated acids with nitrosylhalides offers another attractive route to nitrosoperfluoroaliphatic acids. This phase of the investigation has therefore been concerned with the synthesis of perfluoro-4-pentenoic acid $\left[CF_2{=}CF(CF_2)_2COOH\right]$. The oxidation of 2,2,3,3,4,4,5,5-octafluoropentanol was carried out with potassium permanganate to give a 25% yield of the intermediate carboxylic acid, (Equation 22). The dehydrofluorination of the intermediate, however, was unsuccessful.

TABLE VI

PYROLYSIS EXPERIMENTS WITH $FCOCF_2CF_2CF_2COONO$

$FCO(CF_2)_3COONO$ (gm)	Method	Temperature ($^\circ$C)	Results
0.1	Capillary Tube	125	Material turned green then yellow; liberation of gas was noted.
4.1	(1)	150	A yellow liquid, 1.4 gm, was obtained after hydrolysis of the green distillate.
17.1	(1)	150	Trace amounts of yellow liquid were obtained after hydrolysis of the small quantity of distillate.
4.0	(2)	125-350	No volatile blue or green products were collected.
5.6	(3)	135-180	No volatile blue or green products were collected.

Methods: (1) - Added dropwise to a flask immersed in an oil bath at the desired temperature under reduced pressure. The product was collected in a -78°C trap.

(2) - Vaporized and passed through a glass tube held at the desired temperature.

(3) - A solution in FC-43 was heated from 135°C to reflux.

$$HCF_2(CF_2)_3CH_2OH \xrightarrow{[O]} HCF_2(CF_2)_3COOH \xrightarrow{-HF} CF_2{=}CF(CF_2)_2COOH \qquad (22)$$

Attempts to effect this conversion with refluxing ethyldiisopropylamine, a reagent which is known to give dehydrohalogenation exclusively (Ref 13), resulted in the formation of tars. Amberlite IR-45, a weak base ion-exchange resin which has been used successfully to dehydrofluorinate sensitive compounds (Ref 14), gave no reaction and the starting materials were recovered unchanged. Additional attempts to effect this conversion with potassium tert- butoxide or with ethyl diisopropylamine in refluxing ether or benzene were also unsuccessful.

5. Nitrosotrifluoroethylene

Several attempts to prepare nitrosotrifluoroethylene by a published procedure (Equation 23),(Ref 15) were made but none of the desired compound was obtained.

$$CF_2{=}CFI + NO \xrightarrow[Hg]{h\nu} CF_2{=}CFNO + 1/2\ I_2 \qquad (23)$$

C. PREPARATION OF AROMATIC NITROSO COMPOUNDS

Perfluoroaromatic nitroso compounds were of interest as termonomers because of the apparent relative ease of synthesis of derivatives with groups which might act as cure sites. In addition, the effect of the aromatic rings on the mechanical properties of the resultant polymers was to be determined. The research described here was directed primarily toward the preparation of para-substituted halo- and carboxylperfluoronitrosobenzenes.

1. Pentafluoronitrosobenzene

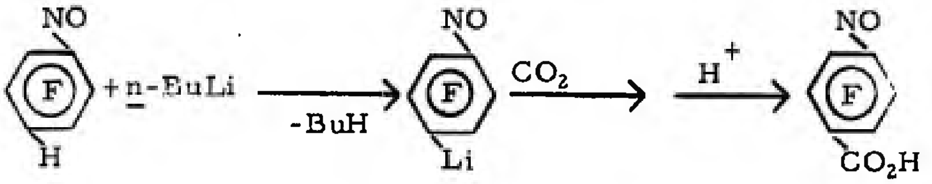
The previously reported procedure (Ref 16), which involved the oxidation of pentafluoroaniline with performic acid, was used to prepare pentafluoronitrosobenzene in 46.6% yield. The product was obtained as the monomer in the crystalline state (blue crystals, mp 44.5°C) and was characterized by comparison of its infrared spectrum and melting point with those reported in the literature. A total of 75 grams of the compound was prepared for polymerization studies.

2. 4-Nitrosotetrafluorobromobenzene

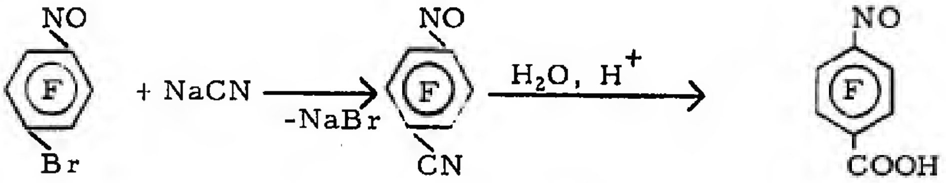
The potentially greater reactivity of the para-bromine atom in 4-nitrosotetrafluorobromobenzene toward nucleophilic reagents makes this compound an interesting termonomer candidate. Its synthesis was effected in two steps by the bromination of 2,3,5,6-tetrafluoroaniline (70%) followed by the performic acid oxidation of the resultant 4-bromotetrafluoroaniline (64%). Both compounds were characterized by infrared spectra and elemental analyses. 4-Nitrosotetrafluorobromobenzene was obtained as the colorless dimer which would be converted to the monomer by heating (mp 39-40°C to a blue-green liquid) or by dissolving the compound in a suitable solvent (i.e., methylene chloride). Ten grams of the nitroso monomer was prepared for polymerization studies.

3. 4-Nitrosotetrafluorobenzoic Acid

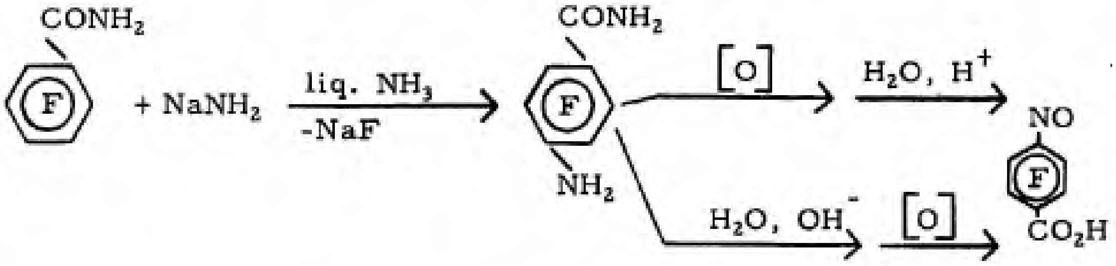
The relative ease of crosslinking through a carboxyl group (Ref 3,4) makes 4-nitrosotetrafluorobenzoic acid a most important aromatic nitroso termonomer and a considerable amount of work was directed toward its synthesis. Three separate routes were investigated and the reaction sequences are illustrated by Equations 24, 25 and 26.



(24)



(25)



(26a)

(26b)

The preparation of 2,3,5,6-tetrafluoronitrosobenzene was carried out in 9.2% yield by the performic acid oxidation of 2,3,5,6-tetrafluoroaniline. The product, which was isolated as the colorless dimer, mp 67-8°C, was treated with a solution of n-butyllithium in hexane. The reaction mixture was carbonated by the usual procedure but none of the desired product was obtained. Direct addition across the N=O group, a reaction which has been reported (Ref 17) to occur with Grignard reagents and zinc alkyls, is probably the major process which takes place.

Since the nitroso group has a very strong activating influence on an aromatic ring for nucleophilic substitution at the para position, the reaction of 4-bromotetrafluoronitrosobenzene with cyanide ion was attempted (Equation 25). Treatment with ethanolic sodium cyanide, however, resulted in the formation of a red-brown polymer. A similar reaction occurred between pentafluoronitrosobenzene or 4-bromotetrafluoronitrosobenzene and sodium hydroxide in water/alcohol. Failure to detect any of the nitroso compounds in the products of these reactions indicates that initial attack of the nucleophile is probably on the nitroso group.

The preparation of 4-nitrosotetrafluorobenzoic acid by the sequence of reactions shown in Equation 26 was extensively explored. Pentafluorobenzamide was prepared by a previously reported procedure (Ref 18) from pentafluorobenzoyl chloride. Treatment of the amide with ammonia and methanol at 100°C and 130 psi resulted in the formation of a 20% yield of 4-aminotetrafluorobenzamide. Many other attempts to prepare this compound by the reaction of pentafluorobenzamide with sodium in liquid ammonia were unsuccessful. The product was identified by its infrared spectrum, elemental analysis and comparison of its melting point with that reported in the literature (Ref 19). When the oxidation of 4-aminotetrafluorobenzamide with performic acid was conducted (Equation 26a) no evidence for the formation of the desired compound was observed and a 31% yield of 4-nitrosotetrafluorobenzamide was obtained instead.

The reaction sequence shown by Equation 26b was successfully used to prepare 4-nitrosotetrafluorobenzoic acid in 28-47% yields. Hydrolysis of the benzamide for ten hours with 20% aqueous sodium hydroxide produced 4-aminotetrafluorobenzoic acid in 64-70% yields. Conversion of this compound to 4-nitrosotetrafluorobenzoic acid was successfully effected by performic acid oxidation in methylene chloride. The product and unreacted starting material were separated by utilizing the difference in their distribution coefficients in methylene chloride and water. Yields of 28 to 34% were obtained by this method with higher yields (38-47%) obtained by extraction of the aqueous solution with ether and isolation of the product by silica-gel column chromatography (Table VII). A total of 9.0 grams of the product was produced by the former method of isolation for polymerization studies.

TABLE VII

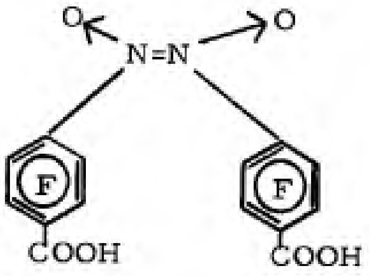
PERFORMIC ACID OXIDATION OF $NH_2C_6F_4COOH$ TO ONC_6F_4COOH

Starting Materials				Product			
$NH_2C_6F_4COOH$ (gm)	CH_2Cl_2 (ml)	98% HCOOH (ml)	90% H_2O_2 (ml)	Product (gm)	(%)	Method of Purification	Notes
2.0	100	20^{a}	5	1.0	47	Chromatograph	
2.0	100	20	5	0.8	38	Chromatograph	(1)
2.0	100	20	5	1.0	47	Chromatograph	(2)
5.0	250	40	10	1.8	34	Solvent Separation	
5.0	250	40	10	1.5	28	Solvent Separation	
10.0	600	80	20	3.0	28	Solvent Separation	
10.0	600	80	20	3.0	28	Solvent Separation	(3.)

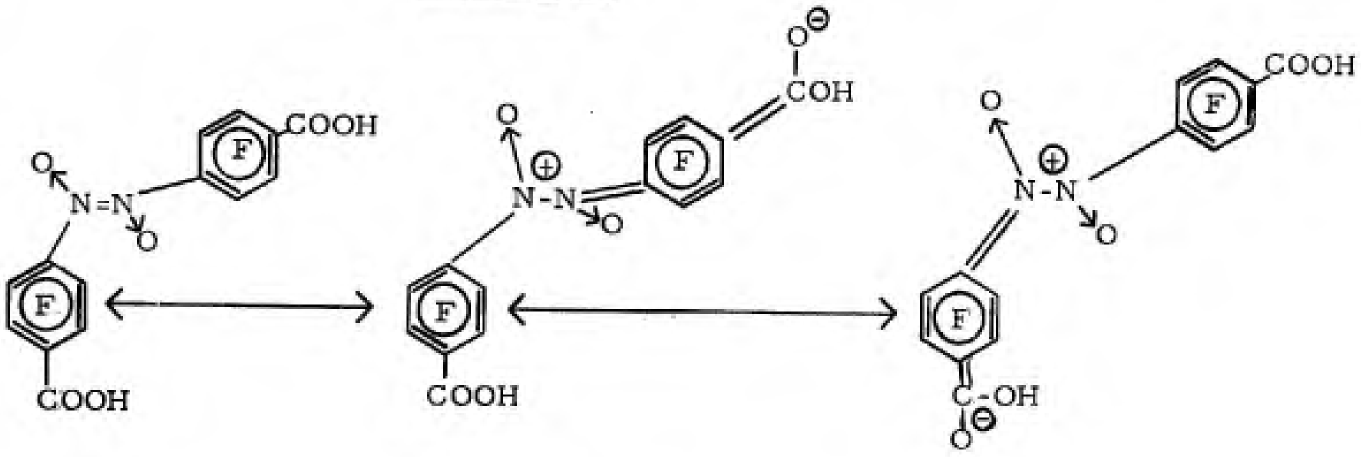
---

(1) The material decomposed on attempts to chromatograph on acid-washed alumina.
(2) The material decomposed on attempts to recrystallize from $CHCl_3$ and CCl_4.
(3) A 3.0 gm yield of white solid, mp > 360°C, was also obtained.

The nitroso-acid was isolated in two dimeric forms: (A), a pale yellow, crystalline solid which was converted to the monomeric form on dissolution in alcohols, ether, or acetone; and (B), a colorless, crystalline solid recovered from the aqueous phase which did not become monomeric in solution. When (A) was heated slowly, a change from yellow to brown occurred between 100° and 200°C; at 226-7°C, the material decomposed sharply with the evolution of gas. However, when the material was heated very rapidly, it melted at 150-151°C to a green liquid which then decomposed. The dimer (B), however, darkened above 200°C but did not melt below 360°C. Despite these differences in behavior, the infrared spectra of (A) and (B) were virtually identical. This suggests that (A) and (B) are cis-trans isomers. Since (A) is readily converted to the monomeric form, it is probably the cis isomer. The trans isomer (B) would be stabilized by virtue of the coplanarity of the aromatic rings with concomitant electron delocalization. A study of non-fluorinated nitroso dimers (Ref 20), in which the structure of these compounds is shown to have the azoxy-type linkage, appears to support this hypothesis. The proposed structures of these isomers are:



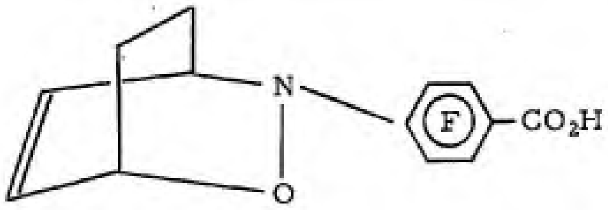
Isomer (A)

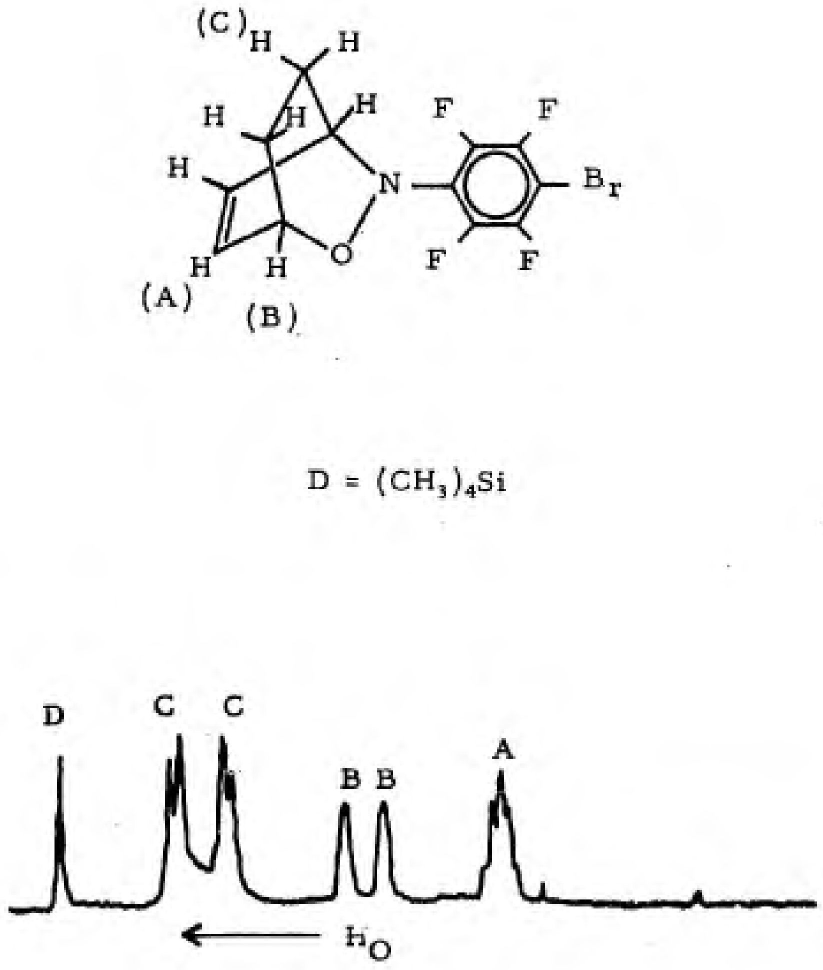


Isomer (B)

Dimer (A) decomposed on attempted recrystallization from chloroform or carbon tetrachloride and on prolonged exposure to the atmosphere at ambient room temperature. It appeared that the material could be stored indefinitely under refrigeration.

Characterization of 4-nitrosotetrafluorobenzoic acid was complete and included elemental analysis, infrared spectrum, equivalent weight and formation of a bicycloxazine derivative. These derivatives are prepared by the reaction of the nitroso compounds with 1,3-cyclohexadiene (Ref 21). The structures of the analogous derivatives of pentafluoronitrosobenzene and bromotetrafluoronitrosobenzene were elucidated with nuclear magnetic resonance (Figure 8), thus indicating the nature and generality of the reaction. The NMR spectrum of the 4-nitrosotetrafluorobenzoic acid derivative was not obtained (a suitable solvent could not be found), but the elemental analysis and infrared spectra were consistent with the assigned structure.





D = $(CH_3)_4Si$

Figure 8. Proton NMR Spectrum of $BrC_6F_4C_6H_8ON$

PHASE II - POLYMER SYNTHESIS

The objectives of this phase were: (1) development of a capability for the production of CF_3NO/C_2F_4 copolymer in quantities of 10 to 50 pounds per 24 hour period, and (2) preparation of nitroso polymers with functional curing sites and improved vulcanizate properties. The first objective was attained through a program of investigation of polymerization procedures and the reaction variables that would be encountered in pilot plant production. This program culminated with the successful operation of the pilot plant. Toward the attainment of the second objective, the polymerization process for obtaining CF_3NO/C_2F_4 copolymer of significantly higher molecular weight on a large scale was developed. In the research effort to obtain new polymers, a number of terpolymers containing functional groups were prepared.

A. NITROSO COPOLYMER PROCESS DEVELOPMENT AND POLYMER IMPROVEMENT

This phase of the work was essentially a process development study so that the preparation of nitroso rubber could be scaled from laboratory size batches of 40 gm or less to pilot plant batches of 10 to 50 pounds. The study began with attempts to repeat the results obtained in the original laboratory preparations (Ref 3,4) for the purpose of gaining first hand knowledge of the system and continued with the investigation of the reaction variables that would be encountered in pilot plant production.

CF_3NO/C_2F_4 copolymer may be prepared by solution, suspension, emulsion or bulk polymerization. The choice of the system for use in pilot plant production was virtually dictated by the findings of the 3M research team (Ref 3,4). They found that emulsion polymerization led to low molecular weight products and that solution and bulk polymerizations had the disadvantage of poor heat transfer which in large scale polymerizations could lead to low molecular weight polymer or uncontrolled reactions. Low temperature bulk polymerization could be scaled to meet the production requirements; however, the long reaction times necessary (2 weeks for 50% conversion at -65°C) make this method undesirable. Suspension polymerization was investigated and it was found that the copolymer could be prepared at low temperatures in an aqueous suspension employing an insoluble inorganic material as a suspending agent and a soluble inorganic salt to lower the freezing point of the aqueous phase. Using magnesium carbonate and lithium bromide, respectively, for these purposes, polymer was obtained in the form of very small particles which could be separated by filtration. The salts could be removed by washing with mineral acid and water. The polymer molecular weights thus obtained were comparable with those obtained by low temperature bulk polymerization and higher than those obtained in solution.

These findings were confirmed by the preliminary work completed on this program and the decision was made to utilize suspension polymerization as the process for production of the polymer in the pilot plant. Although most of the work on this task was devoted to the suspension process, studies of bulk and solution processes were conducted in attempts to obtain copolymer of improved physical properties. In addition, bulk polymerization techniques were employed in the evaluation of some reaction variables, particularly monomer purity.

In the experiments conducted to evaluate reaction variables the aqueous suspension polymerizations were conducted in sealed Pyrex ampoules with total monomer charges of 2 to 4 gm. Experimental details for these polymerizations are summarized in the appendix.

1. Evaluation of Reaction Variables

a. Monomer Purity

The purity of the CF_3NO was obviously critical as shown by the first attempts to prepare copolymer. The CF_3NO for the very early experiments was obtained both from Peninsular ChemResearch, Incorporated and from laboratory preparations at Thiokol. These products were impure with significant concentrations of nitrogen oxides in most batches. The polymers prepared from these batches were consisently low in molecular weight. In conjunction with efforts to purify the CF_3NO discussed elsewhere in this report, a study was undertaken to determine the effects of some specific contaminants on the type of polymer obtained. Polymerizations were conducted using CF_3NO containing known amounts of N_2O, NO_2, CF_3NO_2 and COF_2 and the effects of these contaminants were evaluated by visual observation and/or intrinsic viscosity values of the products (Table VIII). These products ranged from viscous liquids to rubbery gums to elastomers depending on the molecular weight. The low molecular weight liquids resulted from relatively high levels of N_2O and NO_2. It was apparent that as the level of contamination decreased, the product molecular weight increased.

The effect of contamination by CF_3NO_2 and COF_2 was less obvious because of the small number of experiments completed; however, the COF_2 apparently had no effect on the polymerization and it was assumed to be inert. On the other hand, CF_3NO_2 apparently caused low molecular weights as shown in Table VIII.

TABLE VIII

EFFECT OF CF_3NO PURITY ON COPOLYMERIZATION OF CF_3NO/C_2F_4

Exp. No.	Polymerization Method	NO_2 (%)	N_2O(%)	COF_2(%)	CF_3NO_2(%)	Polymer
088-7	Bulk	2.0	--	--	-	$[\eta] = 0.4$
088-8	Bulk	2.0	--	--	-	$[\eta] = 0.23$ $[\eta] = 0.5$ (1)
091-13	Bulk	4.3	2.2	--	-	Soft rubber
091-16	Bulk	9.3	--	--	-	Viscous liquid
091-17	Bulk	15.0	--	--	-	Viscous liquid
091-15	Bulk	(2)	--	--	-	Rubber
091-16	Bulk	(2)	--	--	-	Rubber
092-2	Suspension	2.8	--	--	-	Rubber
092-4	Suspension	9.3	--	--	-	Viscous liquid
092-1	Suspension	(2)	--	--	-	Rubber
092-5	Suspension	(2)	--	--	-	Rubber
092-8	Suspension	1.1	2.7	0.3	-	Rubber $[\eta] = 0.57$ (1)
092-11	Suspension	3.8	2.3	0	-	Soft rubber
092-12	Suspension	4.3	2.2	0	-	Soft rubber
212082B	Suspension	0	0	0	0	Rubber, $[\eta] = 1.00$ $[\eta] = 1.22$ (1)
212083A	Suspension	0	0	(3)	(3)	Rubber, $[\eta] = 0.50$ $[\eta] = 0.64$ (1)

---

(1) High molecular weight fraction.
(2) Most of the NO_2 was removed by trap to trap distillation.
(3) CF_3NO_2 and COF_2 combined was 0.7%, CO_2 was 1.8%.

Another aspect investigated was the effect of storage time on CF_3NO purity and its subsequent polymerization. The experiments showed, as reported in Table IX, that CF_3NO may be kept at least 10 days in stainless steel cylinders at -20°C without detriment to its subsequent polymerization. Later experience has shown that CF_3NO may be stored in this manner for several months without apparent harmful effects.

b. Solution Polymerization

It was previously shown that solvents containing hydrogen or chlorine could act as chain transfer agents for the CF_3NO/C_2F_4 polymerization (Ref 22). One other solvent, carbon disulfide, was investigated at Thiokol. Solution polymerization in carbon disulfide yielded a viscous liquid polymer and indicated that carbon disulfide is also a chain transfer agent in the polymerization.

c. Catalysts

Three organophosphorous compounds, $C_6H_5POCl_2$, $C_6H_5PCl_2$, and $(C_6H_5)_2PCl$, were investigated as catalysts for the CF_3NO/C_2F_4 polymerization. Polymerizations were conducted in bulk to minimize masking side effects and to permit use of lower temperatures. Experiments were conducted at -25°, -65° and -80°C and the results evaluated in terms of the conversions and visual observation of the products (Table X). The only effects noted were some increase in conversion at -25°C in the presence of the phosphines, $C_6H_5PCl_2$ and $(C_6H_5)_2PCl$; however, the products were obviously of lower molecular weight and inferior in physical properties to the control.

d. Polymerization Time

A series of suspension polymerizations utilizing otherwise equivalent conditions was maintained over the range of 2 to 120 hours at -25°C to determine the optimum polymerization time (Table XI). A common lot of CF_3NO of 95% purity was used for these reactions. The major impurity was C_2F_6; trace amounts of CF_4 were also present. In experiments 065, 056-1, 056-2, and 056-5 the reactant stoichiometry was not adjusted for this impurity. This adjustment was made for experiments 056-3 and 056-4 and higher molecular weight polymers were obtained. It was apparent that there was no significant increase in molecular weight after a 24 hour reaction period. In addition, these experiments indicated the sensitivity of the polymerization to the monomer ratio.

TABLE IX

EFFECT OF CF_3NO STORAGE TIME ON POLYMERIZATION

Exp. No.	Storage Time/Temp (hr/°C)	Reaction Vessel	Conversion (%)	High Mol. Wt. Fraction (%)	Inherent Viscosity.[1] $\langle\eta\rangle$ Unfractionated	Inherent Viscosity.[1] $\langle\eta\rangle$ Fractionated
212082A	0/-20	Pyrex glass	68	78	0.72	1.22
212082B	48/-20	Pyrex glass	91	77	1.00	1.22
212082C	240/-20	Pyrex glass	86	91	1.08	1.32

---

[1] 0.5 gm polymer/100 gm solvent.

TABLE X

EFFECT OF ORGANOPHOSPHOROUS COMPOUNDS ON CF_3NO/C_2F_4 POLYMERIZATION

Exp.No.	Compound	Reaction Temp (°C)	Reaction Time (days)	Conversion (%)	Observation
081-4	None	-25	3	67	Rubber
081-1	$C_6H_5POCl_2$	-25	3	67	Rubber
081-2	$C_6H_5PCl_2$	-25	3	89	Soft rubber
081-3	$(C_6H_5)_2PCl$	-25	3	79	Soft rubber
081-8	None	-65	21	67	Soft rubber
081-5	$C_6H_5POCl_2$	-65	21	66	Soft rubber
081-6	$C_6H_5PCl_2$	-65	21	68	Soft rubber
081-7	$(C_6H_5)_2PCl$	-65	21	68	Soft rubber
081-12	None	-80	21	17	Paste
081-9	$C_6H_5POCl_2$	-80	21	17	Paste
081-10	$C_6H_5PCl_2$	-80	21	14	Paste
081-11	$(C_6H_5)_2PCl$	-80	21	19	Paste

TABLE XI

EFFECT OF REACTION TIME ON MOLECULAR WEIGHT OF CF_3NO/C_2F_4 COPOLYMERS

Exp. No.	Time (hr)	Conversion (%)	Intrinsic Viscosity $[\eta]$
065	2	15	0.24
056-1	24	72	0.37
056-2	48	69	0.38
056-3(1)	72	73	0.52
056-4(1)	96	74	0.51
056-5	120	64	0.36

---

(1) Monomer ratios adjusted to account for impurities.

e. Corrosion by Lithium Bromide

As a check of the possible corrosion of a steel reactor by the lithium bromide solution, samples of 316 stainless steel were contacted with the solution for a period of three weeks at room temperature. Neither staining nor a weight change occurred during this period, even at the interface of a partially immersed metal sample.

f. Purity of Lithium Bromide

A reagent grade of lithium bromide had been used in laboratory polymerizations; however, use of a technical grade in production would result in significant savings. Experiments, shown in Table XII, indicated that use of technical grade lithium bromide was not detrimental to conversion or molecular weight and that it could be used in the production process.

g. Purity of Water

Distilled water had been used in laboratory polymerizations; however, the use of deionized water at the production plant was desirable. A polymerization conducted using deionized water (Table XII) yielded high quality polymer and showed conclusively that deionized water may be used in production.

h. Contamination by FC-43

Hydrocarbons will adversely affect the polymerization, therefore hydrocarbon oils could not be used as seals in the stirrer of the production reactor. FC-43 was found to be acceptable as a stirrer seal and an experimental polymerization was completed to determine the effect of FC-43 contamination on the polymerization and the copolymer molecular weight. Although the copolymer resultant from this experiment was of somewhat lower molecular weight than the control (Table XII), the difference was within experimental error and it was concluded that the presence of small amounts of FC-43 would not be deleterious.

i. Magnesium Carbonate Concentration

Although the use of $MgCO_3$ (suspending agent) at a level of 1gm:8gm of monomers had been successful, it was possible that increased levels might result in better suspensions and a superior product. Therefore, two reactions,

TABLE XII

EFFECT OF VARIABLES ON CF_3NO/C_2F_4 POLYMERIZATION

Exp.No.	Variable	Conversion (%)	High Mol.Wt. Fraction (%)	Inherent Viscosity (1) <η>	
				Unfractionated	Fractionated
4329-941-1	Technical Grade LiBr	75	83	1.01	---
212084-A1	Technical Grade LiBr	--	79	0.80	1.15
212084-A2	Technical Grade LiBr	--	--	0.82	---
212084-C	FC-43 Contamination	--	75	0.81	---
212084-B	Deionized Water	--	74	1.02	1.23

---

(1) 0.5 gm polymer/100 gm solvent

one a standard, the other utilizing a fourfold $MgCO_3$ increase, were conducted. The resultant polymers were equivalent and it was assumed that an increase in the $MgCO_3$ level was not required.

2. Heat of Polymerization

The heat of the CF_3NO/C_2F_4 polymerization was experimentally determined. This polymerization can be effected in 30 minutes or less in bulk at 80 atmospheres in the temperature range of -20°C (Ref 23). This technique was utilized for this determination.

The monomers were charged to a Parr calorimeter (at an initial temperature of 25°C) to approximately 52 atmospheres. The rate of temperature rise in the first experiment indicated that the polymerization was essentially complete in 1.5 hours; therefore, subsequent reactions were run for two-hour periods. Corrections for unconverted monomers and external heat sources (such as solenoid valves) were made. Analysis of the unconverted monomers after reactions showed that CF_3NO and C_2F_4 were still in a 1:1 molar ratio and were basically unchanged.

The heat of polymerization was found to be 74.8 ± 0.5 kcal/mole (average of three determinations).

3. Bench Scale Polymerizations

The above experiments were on a small scale in sealed glass tubes. To more closely approximate the reaction conditions to be employed in the production reactor, a 300 cc autoclave of 403 stainless steel was used for intermediate-scale polymerizations. This autoclave was fitted with a glass insert, thus agitation was effected magnetically with a stirring bar. It was expected that polymerization of up to 50 gm total monomer charges would be facile.

For operation, the volumes of the tubing connecting each monomer to the reactor were made equal and the magnitude determined. Allowing each monomer to expand into these volumes (previously evacuated) to equivalent pressures would then effect the transfer of equivalent monomer quantities (pressures were kept below criticality). At this point, the valves to the monomer storage cylinders were closed and the monomers in the calibrated volumes were allowed to expand into the reactor (evacuated) containing brine at -25°C.

It was hoped that this apparatus could be used to determine the optimum charging conditions (incremental, bulk, or alternate addition), as well as the optimum working pressure and time of reaction. However, the agitation proved to be insufficient, at least after polymer formation began, and only low molecular weight polymers were obtained.

Of significance, however, was an experiment in which 20 gm of each monomer was added simultaneously and in one charge. No temperature rise was noted which indicated that Carius tube fracture in some small scale experiments was due to poor seals and not to an uncontrollable exothermic polymerization. The rather high heat of polymerization value does indicate, however, the possibility that the polymerization can become uncontrollable and that adequate provisions for temperature control and heat transfer are essential.

4. Modified Bulk Polymerization

Experiments were conducted for the purpose of relating reaction time to polymer molecular weight in bulk CF_3NO/C_2F_4 copolymerizations. The initial experiments were conducted in sealed Pyrex glass Y-tubes and it was noted that although monomers had been charged to only one leg of the tube, polymer formed in both legs. Moreover, the polymer in the originally charged leg amounted to only about 30% of the total and was of low molecular weight, about 400,000. The other leg contained the majority of the polymer and this portion was of about 3.5 million molecular weight. Up to this point, the highest molecular weight CF_3NO/C_2F_4 copolymer obtained was about 2.0 million obtained by solvent fractionation of selected gum stocks. The usual molecular weight of unfractionated bulk copolymer is 1.0 million or less.

These experiments, summarized in Table XIII, indicated that an initial partial polymerization occurred in one leg which consumed impurities and allowed pure monomers to distill into the other leg where they polymerized to high molecular weight. Some additional experiments were conducted to test this hypothesis.

The experiments were done using specially prepared reaction vessels consisting of two heavy-walled Pyrex tubes separated by a break seal. The monomers were introduced into one tube, allowed to react for a given time and then transferred to the other tube through the breakseal where they were allowed to react to completion. Using this procedure, two variables, time and temperature of the initial polymerization, were studied and their effect on the

TABLE XIII

CF_3NO/C_2F_4 MODIFIED BULK COPOLYMERIZATIONS AT -65°C

Reaction No. 212091-	2H	3H	4H	5H
Reaction time (days)	6	9	12	16
Conversion (%)	72.6	88.3	88.3	91.0
High mol.wt.fraction (% of total polymer)	69.5	63.2	63.2	86.3
Inherent viscosity (1) of high mol.wt. fraction	2.06	2.88	2.70	1.39
Molecular weight (2) ($x10^6$)	2.5 (3)	3.5 (4)	3.3 (3)	1.5 (3)

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(1) 0.5 gm polymer/100 ml Freon 113.

(2) Molecular weight was calculated from the previously determined intrinsic viscosity - molecular weight relationship (Ref 3).

(3) By extrapolation from inherent viscosity datum point.

(4) From intrinsic viscosity.

molecular weight of the secondary polymerization product was determined. The data, which have been summarized in Table XIV, confirmed the observation that the two-step bulk polymerization yielded higher polymer than a similar one-step process.

The polymer molecular weight was not substantially affected by change in initial reaction time. This is shown in both series of experiments (Table XIV) where, within each series, no consistent molecular weight deviation occurred. Initial reaction of as little as 5% of the monomers in 18 hours leads to high molecular weight product in the secondary reaction.

The data relating initial reaction temperature to molecular weight of secondary product seemed to indicate higher molecular weight from the lower temperature reactions; however, there is a variable in the reaction conditions that makes this uncertain. In series 098 where initial reactions were at -85°C, the secondary reactions at -65°C were complete within 14 days; however, in series 16302 where initial reactions were at -65°C, the secondary reactions at -65°C were not complete after 21 days. In order to complete the latter reactions, they were allowed to warm up to -25°C; these polymers possessed lower molecular weights. The longer reaction time for series 16302 was apparently due to a lower rate of initiation of polymerization (unreacted monomer was present after 21 days) and is possibly due to the absence of a catalytic impurity consumed in the initial reaction.

Another experiment was conducted to determine the effect of prepolymerization of monomers on a subsequent suspension polymerization. Here, CF_3NO and C_2F_4, in equimolar ratio, were allowed to react 12 and 24 hours at -65°C (two reactions) and the remaining monomers were transferred to suspension polymerization systems where they were allowed to polymerize at -25°C. The resultant products were of 0.5 and 0.6 inherent viscosity, respectively. These values are about the same as are obtained without pretreatment and indicate no improvement by the pretreatment.

B. EXPERIMENTAL POLYMERS

Although CF_3NO/C_2F_4 copolymers can be cured (only with polyfunctional amines), the physical properties of the cured stocks are poor. For this reason, an intensive study was directed toward the preparation of nitroso terpolymers containing functional groups capable of more facile reaction with curing agents and thus resulting in vulcanizates of improved physical properties.

TABLE XIV

MODIFIED BULK COPOLYMERIZATION OF CF_3NO and C_2F_4

INITIAL POLYMERIZATION									
Exp. No.	098 (1)	098-1	098-2	098-3	098-4	16302-1	16302-2	16302-3	16302-4
Time (days)	18	0.75	1	2	3	0.75	1	2	5
Temperature (°C)	-65	-85 to -80	-85 to -80	-85 to -75	-85 to -65	-65	-65	-65	-65
FINAL POLYMERIZATION (5)									
Time (days)	-	14	14	14	14	21 (2)	21 (2)	21 (2)	21 (2)
Temperature (°C)	-	-65	-65	-65	-65	-65	-65	-65	-65
Yield (%) (3)	-	95	93	89	77	56	51	48	38
Inherent Viscosity $<\eta>$ (4)	0.7	1.59	1.67	1.56	1.48	0.97	1.09	0.92	0.90

---

(1) Control polymerization.
(2) Monomer remained after 21 days, polymerization was completed in one additional day at -25°C.
(3) Yield from final polymerization is based on total initial charge.
(4) 0.5 gm polymer in 100 ml FC-43.
(5) Monomer transferred to the other leg of a Y-reaction tube.

Nitroso compounds investigated as termonomers included pentafluoronitrosobenzene (C_6F_5NO), p-bromotetrafluoronitrosobenzene (BrC_6F_4NO), and 4-nitrosoperfluorobutanoic acid. Polymers containing C_6F_5NO were expected to be curable through labile p-fluorine atom. Similarly, the polymers containing p-bromine atoms and p-carboxyl groups should be curable through these sites. Olefinic functional termonomers investigated were acrylic acid and acrylyl chloride.

Another approach investigated was terpolymerization with small quantities of partially fluorinated olefins, such as vinylidene fluoride and trifluoroethylene. Such polymers might be cured through labile hydrogen atoms or they might lend themselves to dehydrofluorination and curing through the resultant unsaturation.

1. Polymers Containing C_6F_5NO

A suspension (water, $MgCO_3$ and LiBr) polymerization of CF_3NO, C_6F_5NO and C_2F_4 in a 0.5/0.5/1.0 molar ratio at -25°C gave a 35% conversion to a heterogeneous solid polymer. Subsequent preparations of this terpolymer were conducted in methylene chloride solution and yielded homogeneous polymers with conversions up to 88%. The terpolymers were rubbers at low C_6F_5NO levels (Table XV); at higher levels the terpolymer was resinous. Several batches (15-25 gm) of terpolymer with 5 and 10 mole percent C_6F_5NO (in monomer feed) were prepared to obtain a total of 145 gm for use in curing studies.

2. Polymers Containing BrC_6F_4NO

Copolymer and terpolymers containing BrC_6F_4NO were prepared by allowing this material to react with C_2F_4 and C_2F_4/CF_3NO mixtures (Table XVI). The copolymer of BrC_6F_4NO and C_2F_4 was prepared from an equimolar mixture of the reactants in methylene chloride solvent at -25°C. The product, a hard resin, was rubbery in the temperature range of 55-130°C and soluble in the usual solvents for nitroso rubber. The polymer was analyzed for bromine and was shown to be essentially a 1:1 copolymer of the starting materials.

Terpolymers of $BrC_6F_4NO/CF_3NO/C_2F_4$ were prepared from monomer mixtures containing various proportions of BrC_6F_4NO. The proportion of BrC_6F_4NO in the polymer increased directly as the concentration of this component in the monomer feed increased. This observation was supported by the bromine analyses which indicated that the BrC_6F_4NO entered the polymer to approximately the same extent that it was present in the monomer feed. The physical properties of the polymers varied from resin to rubber being more

TABLE XV

$CF_3NO/C_6F_5NO/C_2F_4$ TERPOLYMERIZATIONS
(CH_2Cl_2 Solutions)

Exp.No.	Mole Ratio Charged CF_3NO	C_6F_5NO	C_2F_4	Conversion (%)	Product
055-2	0.9	0.1	1.0	76	Rubber, $[\eta] = 0.38$
055-3	0.8	0.2	1.0	78	Rubber
061	0.8	0.2	1.0	80	Similar to 055-3
055-4	0.5	0.5	1.0	86	High modulus rubber
055-5	0.2	0.8	1.0	58	Resin
055-6	0.0	1.0	1.0	50	White powder

TABLE XVI

POLYMERS (1) CONTAINING BrC_6F_4NO

Exp.No.	Monomer Molar Feed Ratio BrC_6F_4NO	CF_3NO	C_2F_4	Conversion(2) (%)	Bromine Content (%) (Found)	(Theoretical)	Product
E-16304-1	1.0	---	1.0	42	24.4	22.3	Brittle resin, rubber >55°C
E-16304-2	1.0	trace	1.0	40	----	----	Brittle resin, rubber >55°C
E-16305-4	0.7	0.3	1.0	43	----	----	Brittle resin, rubber >55°C
E-16305-3	0.5	0.5	1.0	40	-----	----	Rubber
E-16305-2	0.3	0.7	1.0	85	6.7	9.7	Rubber
E-16305-1	0.1	0.9	1.0	79	2.8	3.2	Rubber
E-16311	0.1	0.9	1.0	82	2.6	3.2	Rubber

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(1) Prepared in CH_2Cl_2 solution 24 hours at -25°C.
(2) Based upon total charge.

resinous with increasing concentration of BrC_6F_4NO. Such behavior parallels that of the analogous C_6F_5NO terpolymer. The terpolymer prepared from a monomer feed containing 5% BrC_6F_4NO was obtained in 80% yield as a resilient rubber of relatively good physical properties. An additional quantity (21 gm) of this polymer was prepared for curing studies.

3. Polymers Containing ONC_6F_4COOH

The preparation of 4-nitrosotetrafluorobenzoic acid (ONC_6F_4COOH) terpolymer was preceded by an investigation of the copolymerization of CF_3NO and ONC_6F_4COOH. The copolymerization was accomplished using a mixed solvent system of methylene chloride and ether. Data for these experiments are given in Table XVII. The mixed solvent was necessary to effect solution of both monomers. The copolymerization, conducted at -25°C, yielded a resin which was soluble in mixed solvent.

Terpolymerizations were conducted in both bulk and mixed solvent solution. A bulk terpolymerization yielded a brown pasty solid containing 60% CF_3NO/C_2F_4 copolymer and 40% terpolymer.

The mixed solvent systems were methylene chloride/ether and methylene chloride/acetone. After conducting several small scale (1 gm) solution polymerizations, the methylene chloride/acetone system was chosen for continued study and the preparation of larger (11-20 gm) polymer batches.

The terpolymer structure was confirmed by infrared analysis which showed absorption bands for -COOH and the aromatic ring. The terpolymer acid content was determined by titration with standard base. Conversions were 75-81%. The polymer products were rubbery gums of varying degrees of tackiness probably dependent on the molecular weight. The products of low acid content (5 mole percent or less) were insoluble in the polymerization solvent and were isolated as a separate phase. Products higher in acid content remained in solution and, after isolation, were found to be soluble in acetone. The amount of acid in the polymer (hence its solubility) was dependent on the ratio of monomers in the feed, i.e., the use of 10 mole percent 4-nitrosotetrafluorobenzoic acid resulted in 50% conversion to acetone-insoluble polymer of 5 mole percent acid and 30% conversion to acetone-soluble polymer of 7 mole percent acid. With less than 10% acid in the feed, correspondingly lower quantities of the acetone-soluble fraction were obtained.

TABLE XVII

POLYMERS CONTAINING ONC_6F_4COOH

Reaction No.	Solvent System	Mole Ratio			Total Charge (gm)	Reaction Time and Temperature (hr/°C)		Product
		CF_3NO	ONC_6F_4COOH	C_2F_4		Initial	Subsequent	
16328-3	CH_2Cl_2/Et_2O	----	1.0	1.0	1.0	24/-25	----	Resin
16327	None	0.9	0.1	1.0	1.0	24/-25	3/50	Soft rubber
16329-1	None	0.9	0.1	1.0	1.0	24/-25	4/50	60% of product was CF_3NO/C_2F_4 copolymer, 40% was a pasty terpolymer
16328-1	CH_2Cl_2/Et_2O	0.9	0.1	1.0	1.0	24/-25	----	Liquid
16328-2	CH_2Cl_2/Et_2O	0.5	0.5	1.0	1.0	24/-25	----	Soft rubber
16329-2	$CH_2Cl_2/(CH_3)_2CO$	0.9	0.1	1.0	1.0	24/-25	72/25	Soft rubber terpolymer; soluble in FC-43/Freon 113 mixture
16342	$CH_2Cl_2/(CH_3)_2CO$	0.97	0.03	1.0	20.0	24/-25	----	75% Conversion to a soft rubber
16344	$CH_2Cl_2/(CH_3)_2CO$	0.8	0.2	1.0	11.0	24/-25	24/25	50% Conversion to acetone-insoluble rubber containing 5 mole % acid; 30% conversion to acetone-soluble rubber containing 7 mole % acid
16348-1	$CH_2Cl_2/(CH_3)_2CO$	0.94	0.06	1.0	20.0	24/-25	24/25	75% Conversion to a soft rubber
16348-2	$CH_2Cl_2/(CH_3)_2CO$	0.94	0.06	1.0	20.0	144/-25	----	79% Conversion to a soft rubber containing 1.6 mole % acid
16348-3	$CH_2Cl_2/(CH_3)_2CO$	0.94	0.06	1.0	20.0	72/-25	----	81% Conversion to soft rubber containing 1.5 mole % acid

4. Polymers Containing 4-Nitrosoperfluorobutanoic Acid

The preparation of the $CF_3NO/C_2F_4/ON(CF_2)_3COOH$ terpolymer has been reported (Ref 6). Since $ON(CF_2)_3COOH$ is water soluble, suspension polymerization techniques could not be used and the terpolymer was prepared in bulk at -60°C. Bulk polymerizations are not considered to be practical for operation at a large scale because of long reaction times and poor heat transfer with difficulty in controlling the reaction rates. For this reason, the preparation of this terpolymer in solution was investigated.

It was found that terpolymerization occurred readily in methylene chloride solution yielding rubbery gums containing free carboxyl groups as determined by infrared analysis and titration with standard base. It was observed that the reaction temperature was a critical factor in determining polymer molecular weight and polymer composition. At temperatures greater than -25°C low molecular weight liquid products resulted. At temperatures below -35°C molecular weights were high; however, lesser amounts of 4-nitrosoperfluorobutanoic acid entered the terpolymer. Within the range of -25°C to -35°C polymers were produced as rubbery gums of approximately the same composition as the monomer feed.

5. Polymers Containing Vinylidine Fluoride

The incorporation of vinylidine fluoride ($C_2F_2H_2$) into a nitroso rubber molecule would be expected to result in a polymer curable by dehydrofluorination and subsequent crosslinking. The copolymerization of $C_2F_2H_2$ and CF_3NO was attempted as a preliminary step. Copolymerization at -15° to +20°C in bulk has been reported as being successful (Ref 3), but attempts at suspension copolymerization at -25°C in these laboratories did not yield polymer. Terpolymerizations in suspension and bulk systems, however, were successfully effected.

The presence of $C_2H_2F_2$ in the terpolymer was detected indirectly by thermal degradation of the polymer which yielded, in addition to the products normally obtained from pyrolysis of the copolymer (COF_2 and CF_3-N=CF_2), a solid ash which exhibited an absorption for CH at 3.4 μ in the infrared spectrum. A direct and quantitative determination of $C_2H_2F_2$ in the polymer was accomplished by a titration based on the reaction of acidic hydrogens in the polymer with base. In this case, a Freon 113 solution of the polymer is treated with an excess of a standard solution of dibutylamine in Freon 113. An immediate reaction occurs, probably dehydrofluorination, and the amount of hydrogen originally present in the polymer may be determined by back titration with a standard solution of trifluoracetic acid in Freon 113.

Terpolymers prepared in suspension (water, $MgCO_3$ and LiBr) systems at -25°C or in bulk systems at -65°C and -25°C (see below) were rubbers containing a maximum of 0.6 mole percent of $C_2F_2H_2$ (Table XVIII). The low level of $C_2F_2H_2$ in the terpolymers is a reflection of the low reactivity of CF_3NO toward $C_2F_2H_2$ as was also indicated by the failure of the $CF_3NO/C_2F_2H_2$ copolymerization in a suspension system. The bulk terpolymerizations were conducted at two temperatures to shorten the polymerization time. Bulk nitroso polymerizations are usually conducted at low temperatures (-65°C) to prevent violent reaction; however, under such conditions reaction is slow and 2 to 3 weeks are necessary to obtain high molecular weight polymer in high yield. It was found that good conversion to polymer without mishap can be accomplished by a 24 hour treatment at -65°C followed by 24 hours at -25°C. The $CF_3NO/C_2F_4/C_2F_2H_2$ terpolymerizations are summarized in Table XVIII.

6. Polymers Containing Trifluoroethylene

Before the synthesis of terpolymers containing trifluoroethylene monomer was attempted, its ability to copolymerize with CF_3NO, previously reported (Ref 4), was investigated. A CF_3NO/C_2F_3H copolymer was obtained on reaction of these monomers, in bulk, 20 hours at -65°C followed by 120 hours at -25°C. The polymer obtained was a stiff rubber which was soluble in acetone, but not soluble in fluorocarbon solvents.

TABLE XVIII

$CF_3NO/C_2F_4/C_2F_2H_2$ TERPOLYMERIZATIONS

Exp.No.	Type	Reaction Conditions Time and Temperature (hr/°C) Initial	Reaction Conditions Time and Temperature (hr/°C) Subsequent	$C_2F_2H_2$ Charged (mole %)	$C_2F_2H_2$ in polymer (mole %)(1)	Inherent Viscosity, $\langle\eta\rangle$ (2)	Conversion(3) (%)	Product
E16321-3	Bulk	24/-65	24/-25	5.0	0.6	----	80	Rubber
E16321-4	Bulk	24/-65	24/-25	2.0	0.5	----	84	Rubber
212099	Suspension	24/-25	-----	0.5	---	----	40	Rubber
E16303	Suspension	24/-25	-----	2.0	---	0.64	70	Rubber
E16306-1	Suspension	24/-25	-----	50.0	---	----	--	No reaction
E16306-2	Suspension	24/-25	-----	25.0	---	----	45	Rubber
E16306-3	Suspension	24/-25	-----	12.5	---	0.54	63	Rubber
E16306-4	Suspension	24/-25	-----	6.25	---	0.63	71	Rubber

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(1) Values obtained by titration.
(2) 0.5% FC-43 solution.
(3) Based on total charge.

The two-temperature bulk polymerization procedure was similarly used to prepare C_2F_3H terpolymers. A series of such polymerizations was made in which the proportion of C_2F_3H in the monomer charge was varied between 2 and 25 mole percent (Table XIX). The C_2F_3H content of the resulting polymers was directly proportional to the concentration of C_2F_3H in the monomer charge. Thus, polymers of C_2F_3H content varying between 0.8 and 27 mole percent were obtained. In a number of instances, the ratio of monomers found in the polymer closely approximated the ratio of monomers in the charge. This was true in every case in which the total polymerization time was four days. It was also true for some two-day polymerization products, but other two-day polymerization products contained smaller proportions of $C_2F_2H_2$ than were in the monomer charges. Because of the irregularity in the two-day reaction products, no definite correlation could be made between reaction time and $C_2F_3H_2$ content; however, there is some indication that the amount of C_2F_3H in the polymer is dependent on reaction time, as well as concentration of C_2F_2H in the monomer charge.

The C_2F_3H terpolymerization was also investigated using suspension polymerization at -25°C (suspension medium was an aqueous solution of $MgCO_3$ and LiBr). Two polymerizations in which the monomer charges contained 25 and 2 mole percent C_2F_3H yielded, respectively, a soft and a relatively tough rubber. Under the conditions of these experiments (Table XIX), the high proportion of C_2F_3H in the monomer charge led to low conversion and low molecular weight product. The $C_2F_3H_2$ content of this product is not known, but is apparently low since no CH absorptions could be seen in the infrared spectrum. The low proportion of $C_2F_3H_2$ in the monomer charge led to higher conversion and high molecular weight product (a tough rubber containing 1.4 mole percent C_2F_3H).

The polymers containing C_2F_3H reacted with dibutylamine as did the $C_2F_2H_2$ terpolymers and thus they could be analyzed quantitatively for C_2F_3H by titration. The reaction with dibutylamine suggested that dehydrofluorination occurred and that the residual polymer contained unsaturation. An attempt was made to dehydrofluorinate a C_2F_3H terperpolymer in FC-43/Freon 113 solution using dibutylamine. A solid precipitate was obtained which was approximately the theoretical quantity of amine hydrofluoride salt expected. It was water soluble, gave a positive test for fluoride, and its infrared spectrum showed absorption for CH at 3.4μ and for amine hydrofluoride at 6.5μ. The latter assignment is tentative and is based on a similar absorption found in the spectrum of ammonium fluoride. Dehydrofluorination apparently occurred as was evidenced by the formation of dibutylamine hydrofluoride; however, the

TABLE XIX

$CF_3NO/C_2F_4/C_2F_3H$ TERPOLYMERIZATIONS (1)

Reaction Number	Reaction Conditions: Type	Time and Temperature (hr/°C): Initial	Time and Temperature (hr/°C): Subsequent	C_2F_3H Charged (Mole %)	C_2F_3H in Polymer (2) (Mole %)	Total Charge (3) (Grams)	Conversion (%)	Remarks
E16315-A	Suspension	24/-25	--	25	--	11.4	47	Soft rubber, IR shows no C-H
E16315-B	Suspension	24/-25	--	2	1.4	11.9	68	High modulus rubber
E16316-A	Bulk	20/-65	120/-25	50	--	1.79	78	Tough rubber
E16316-B	Bulk	20/-65	120/-25	20	--	1.91	94	Tough rubber
E16320-1	Bulk	24/-65	24/-25	5	4.7	11.2	73	Rubber
E16321-1	Bulk	24/-65	24/-25	5	2.6	11.6	75	Rubber
E16330-A	Bulk	24/-65	24/-25	5	2.1	93.6	80	Rubber
E16320-2	Bulk	24/-65	24/-25	2	2.1	11.3	78	Rubber
E16321-2	Bulk	24/-65	24/-25	2	1.6	11.3	82	Rubber
E16326	Bulk	24/-65	24/-25	2	0.8	192.0	87	Rubber
E16330-B	Bulk	24/-65	72/-25	5	4.9	117.0	81	Rubber
E16331	Bulk	24/-65	72/-25	25	27	22.9	82	Tough rubber

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(1) CF_3NO/C_2F_3H copolymer is included for reference.

(2) Values obtained by titration.

(3) Largest single reaction approximately 12 grams. Larger total charges are several combined reactions.

residual polymer appeared to have decomposed from a rubber to a viscous liquid and an iodine number determination indicated no unsaturation. The infrared spectrum showed absorptions at 5.45, 5.85, 5.93, and 6.03μ which may indicate unsaturation. There was still an absorption at 3.38μ, however, which indicated remaining CH.

7. Polymers Containing Acrylic Acid

A liquid terpolymer containing acrylic acid (CH_2=CHCOOH) has been prepared and cured to rubbery products using a trisimine (MAPO) curative (Ref 24). The preparation of a high molecular weight polymer of this composition and the determination of its curability and properties were desired. Preparation of the liquid terpolymer had been accomplished in solution polymerization using a chain transfer solvent, such as Freon 113. In efforts to obtain high molecular weight products, the polymerization was investigated using another solvent, methylene chloride, and bulk polymerization.

The solution polymerizations (Table XX) yielded only low molecular weight products as indicated by their soft gum-like or liquid consistency. Several glass tubes ruptured during polymerization attempts at room temperature due to overpressurization. The bulk polymerizations (Table XXI), when conducted at low temperature (-65°C), yielded only CF_3NO/C_2F_4 copolymer. When the bulk polymerizations were done at higher temperatures (0°C or above) liquid terpolymers were obtained.

Because acrylyl chloride (CH_2=CHCOCl) has a freezing point lower than that of acrylic acid, its reactions with CF_3NO were investigated (post-polymerization hydrolysis would then yield the acid derivative). Several bulk terpolymerizations attempted at -25°C for 72 hours yielded only liquid products. An attempt to copolymerize CF_3NO and CH_2=CHCOCl under the same conditions was unsuccessful.

PHASE III - PRODUCTION OF NITROSO COPOLYMER

The objective of this phase was the production of 200 pounds of C_2F_2/CF_3NO copolymer. To meet this goal, a pilot plant facility was constructed and successfully operated. A total of 208 pounds of the copolymer was prepared in replicate batches; CF_3NO production totaled 191 pounds. The C_2F_4 was available to the program from the new Thiokol-C_2F_4 production facility.

TABLE XX

POLYMERS CONTAINING CH_2=CHCOOH - SOLUTION POLYMERIZATIONS

Reaction Number	Mole Ratio CH_2=CHCOOH	C_2F_4	CF_3NO	Reaction Time and Temperature (hr/°C) Initial	Subsequent	Solvent	Results
16317-4	1.0	--	1.0	-/25	--	CH_2Cl_2	Tube ruptured
16317-5	0.5	0.5	1.0	-/25	--	CH_2Cl_2	Tube ruptured
16317-6	0.1	0.9	1.0	-/25	--	CH_2Cl_2	Tube ruptured
16314	0.1	0.9	1.0	23/-25	--	CH_2Cl_2	Soft rubber, no COOH
16318	0.5	0.5	1.0	20/25	--	CH_2Cl_2	Liquid polymer
16317-7	1.0	--	1.0	24/-65	120/-25	Freon 113	No reaction
16317-8	0.5	0.5	1.0	24/-65	120/-25	Freon 113	Liquid polymer
16317-9	0.1	0.9	1.0	24/-65	120/-25	Freon 113	Liquid polymer

TABLE XXI

POLYMERS CONTAINING CH_2=CHCOOH - BULK POLYMERIZATIONS

Reaction No.	Mole Ratio			Reaction Time and Temperature (hr/°C)		Results
	CH_2 = CHCOOH	C_2F_4	CF_3NO	Initial	Subsequent	
16317-1	1.0	--	1.0	24/-65	120/-25	No reaction
16317-2	0.5	0.5	1.0	24/-65	120/-25	Gum, no COOH
16317-3	0.1	0.9	1.0	24/-65	120/-25	Gum, no COOH
16319	Excess	0.9	1.0	20/10-20	--	Liquid and gum products, liquid terpolymer
16322-1	0.1	0.9	1.0	20/0	--	Liquid terpolymer
16322-2	0.1	0.9	1.0	20/0	3/50	Liquid terpolymer

A. EQUIPMENT AND FACILITIES

The apparatus and unit operations in the production of CF_3COONO, CF_3NO, C_2F_4 and the nitroso copolymer are shown in the material and apparatus flow charts reproduced as Figures 9 through 16. Except for the polymerization unit, the synthesis equipment was assembled from standard Pyrex kettles and piping, modified as required for the particular task. The polymerization kettle was stainless steel.

A circulating brine system cooled by direct injection of liquid CO_2 furnished the refrigeration requirements for the polymerization kettle; lower temperatures required for the purification system and product collection traps were obtained with liquid nitrogen. The pyrolysis unit was heated by a circulating oil system.

B. PRODUCTION OF TRIFLUORONITROSOMETHANE

A total of 191 pounds of CF_3NO was produced in eleven batches. Experimental details for these runs are summarized in Table XXII. The CF_3COONO was prepared as required for these runs; details are also given in Table XXII.

Although most of the runs were completed without incident, a sudden pressure increase in the purification section caused significant product loss in one run. Two minor detonations were experienced in the nitrite feed section of the pyrolysis column. In neither case did the shockwave propagate back to the CF_3COONO reservoir, an effect predicted by the safety testing completed early in the program. The first incident occurred after a change in the feed rate of the CF_3COONO to the reactor and resulted in destruction of the column feed section. It was hypothesized that the neat CF_3COONO superheated in the tubing section adjacent to the pyrolysis unit. Therefore, provisions for dilution of the nitrite with helium were incorporated into the system. Despite this, another detonation was experienced during a subsequent run. This occurred at the same place but with less force and less equipment damage.

It was noted that the total utilization time of the FC-43 before explosion was the same in both cases, 88 hours and 89 hours. Thus, there may be a concentration of some relatively non-volatile impurity in the FC-43 over a prolonged period which sensitizes the CF_3COONO or is itself sensitive.

Other reasons may be the buildup of solid residues in the FC-43 which might cause blockage in the nitrite feed tube. Stagnation of the nitrite for this or other reasons might cause superheating of the undiluted nitrite and rapid decomposition.

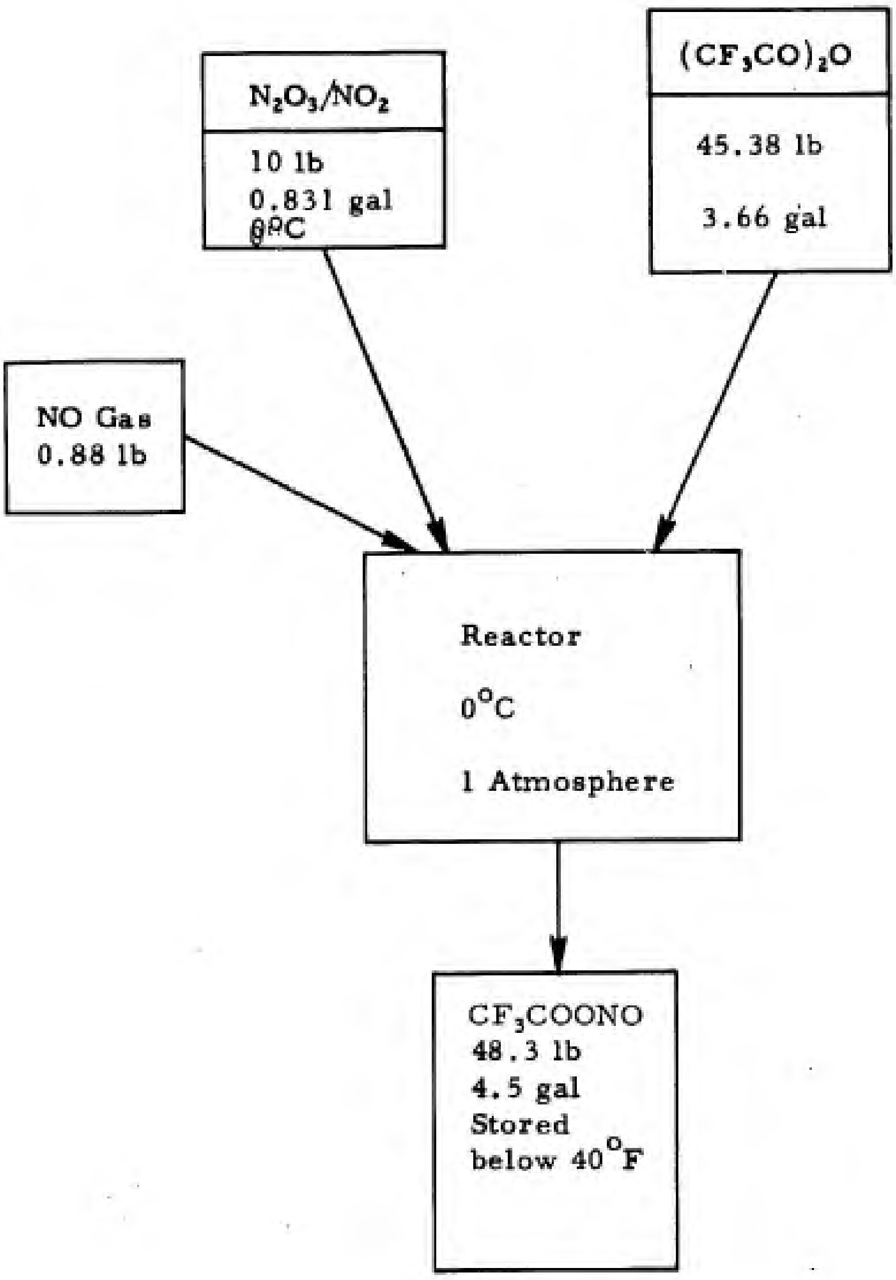

Figure 9. Material Flow Chart - CF_3COONO Production

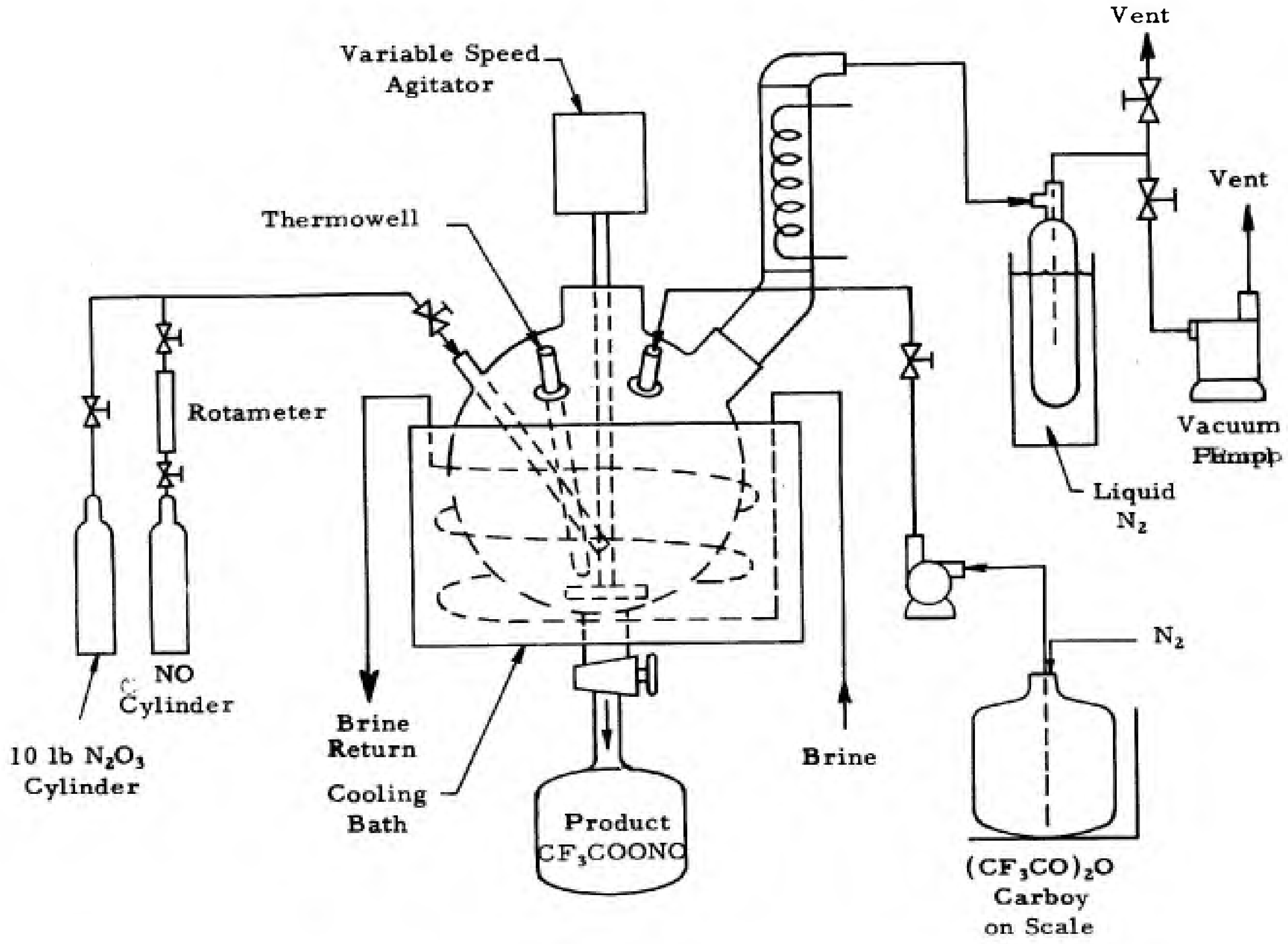

Figure 10. Equipment Flow Chart - CF_3COONO Production

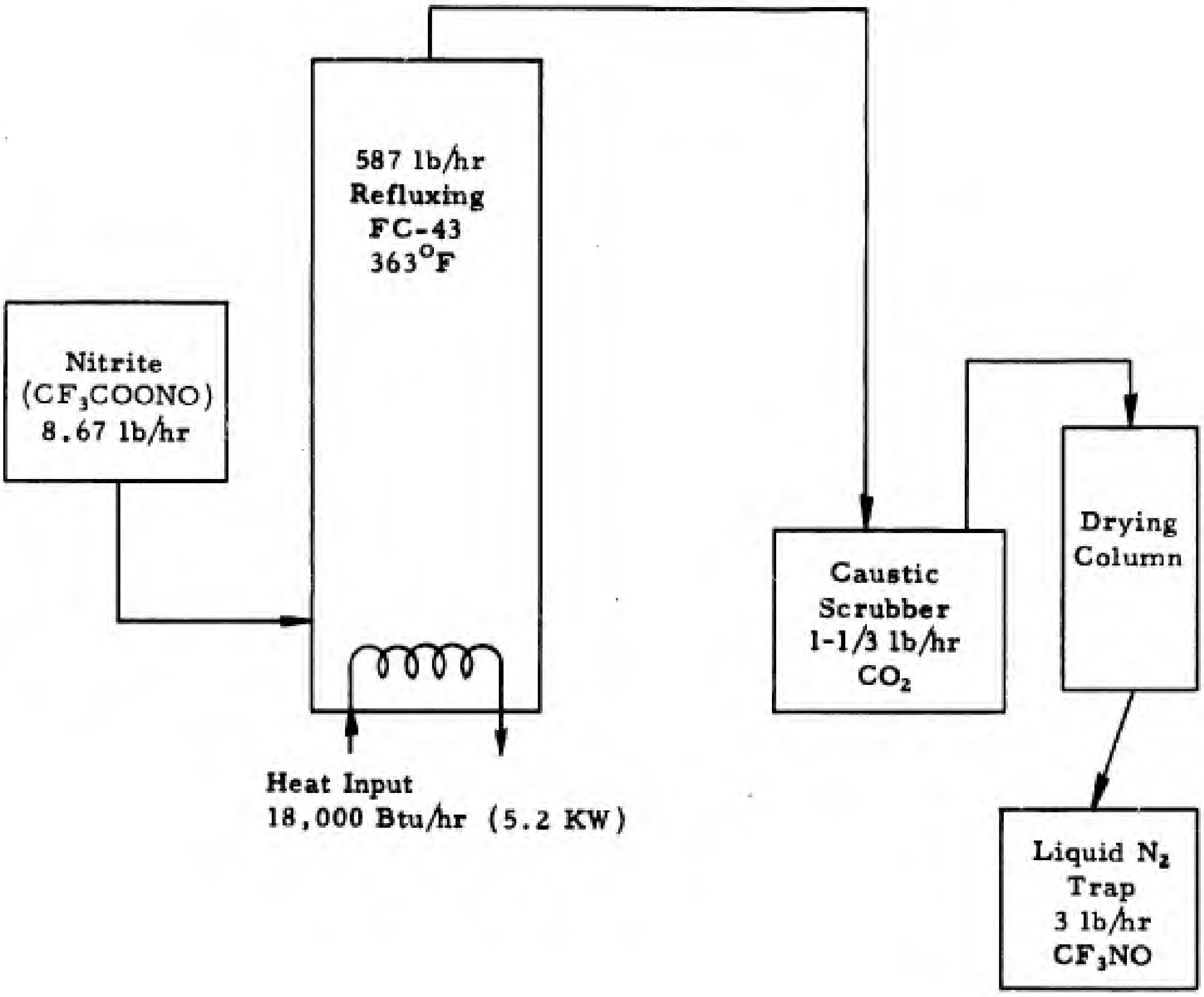

Figure 11. Material Flow Chart - CF_3NO Production

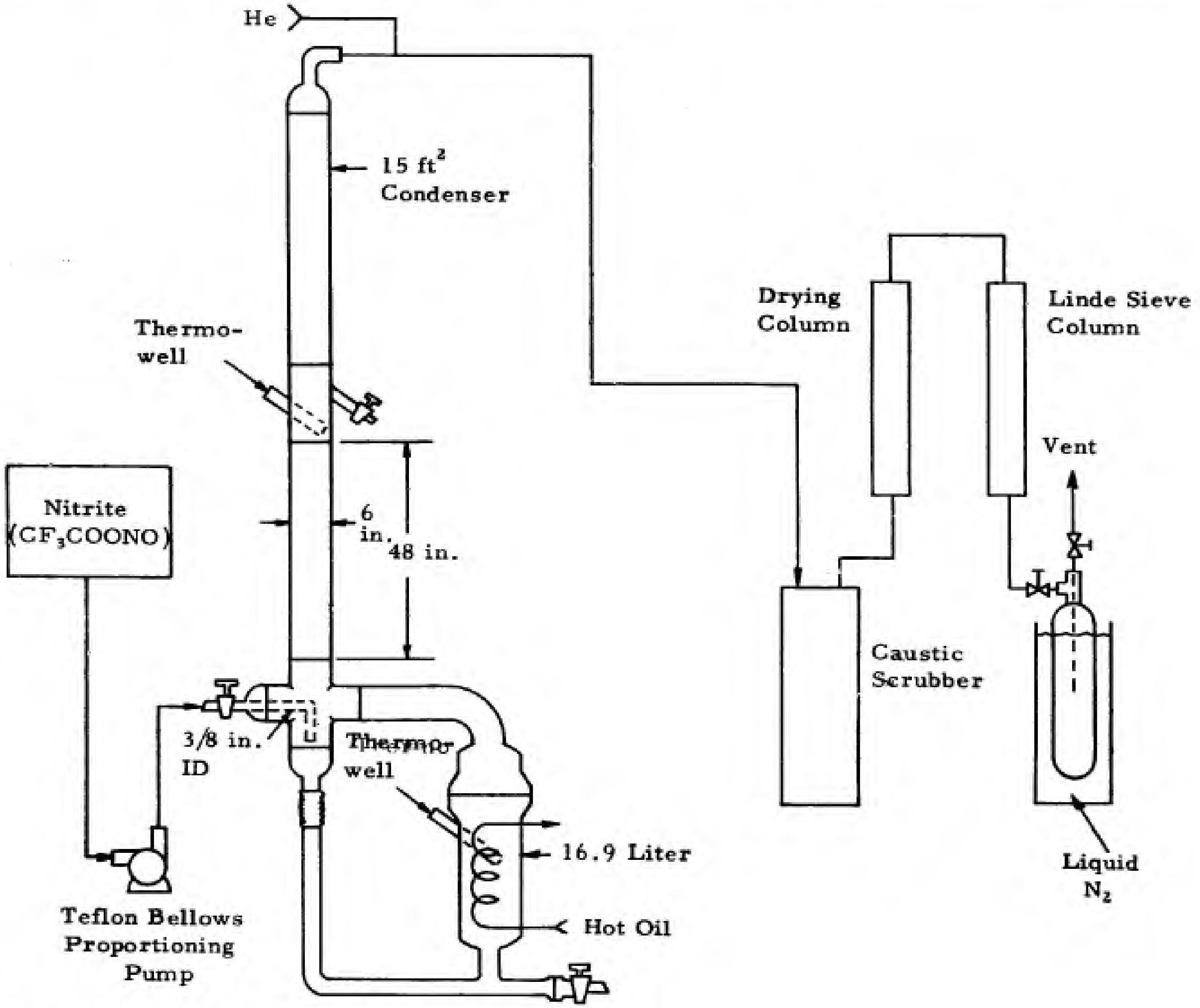

Figure 12. Equipment Flow Chart - CF$_3$NO Production

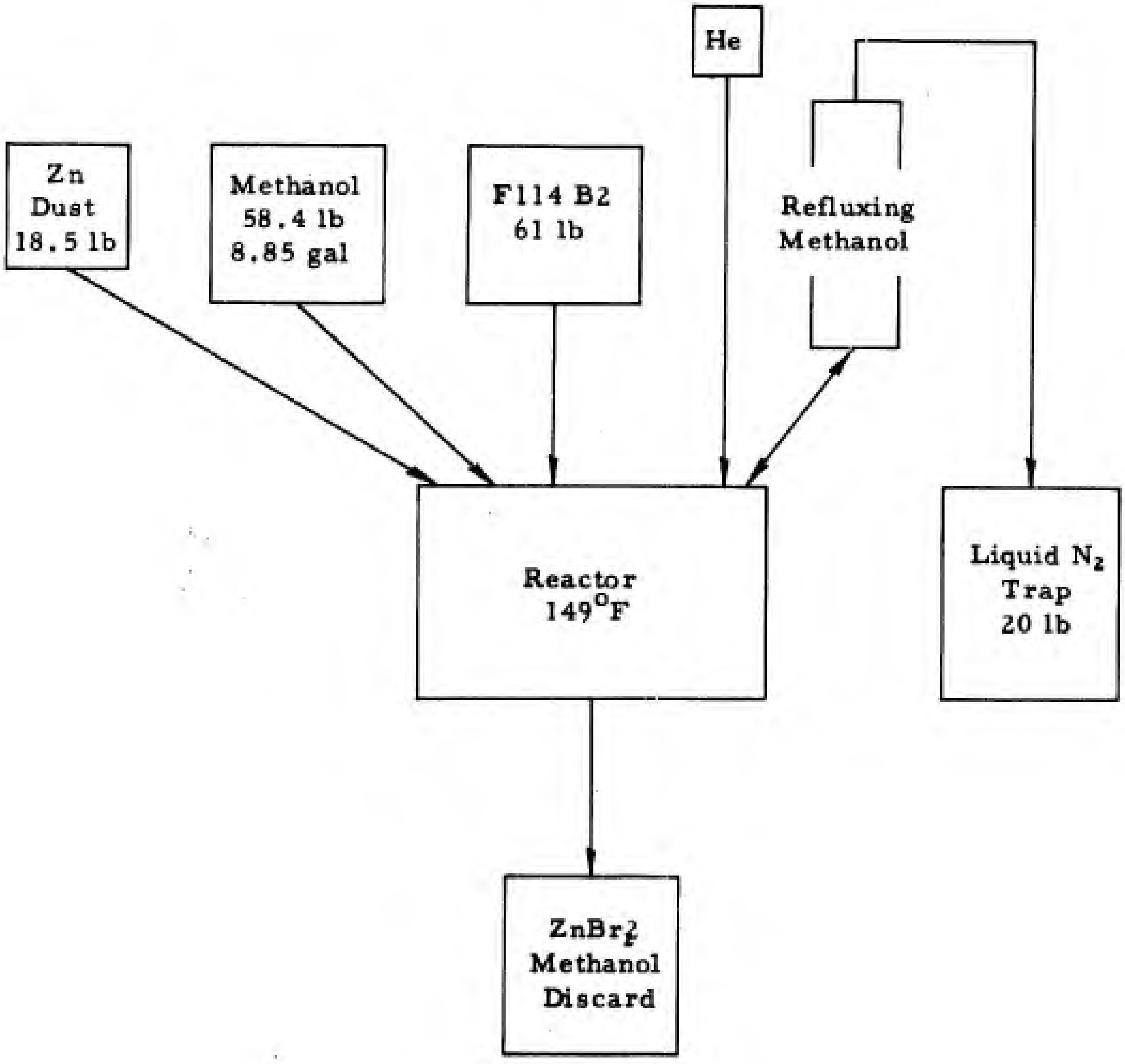

Figure 13. Material Flow Chart - C_2F_4 Production

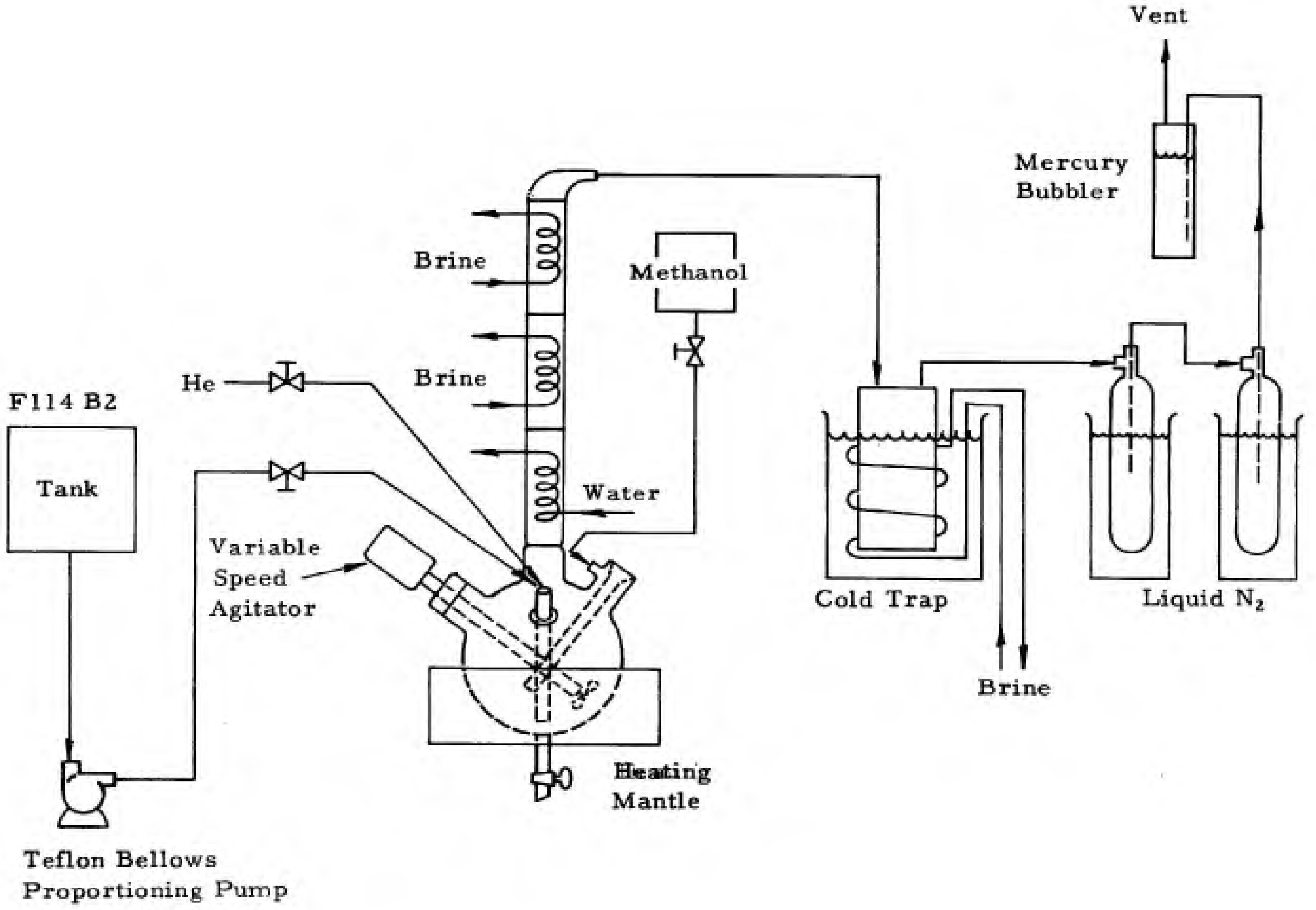

Figure 14. Equipment Flow Chart-C_2F_4 Production

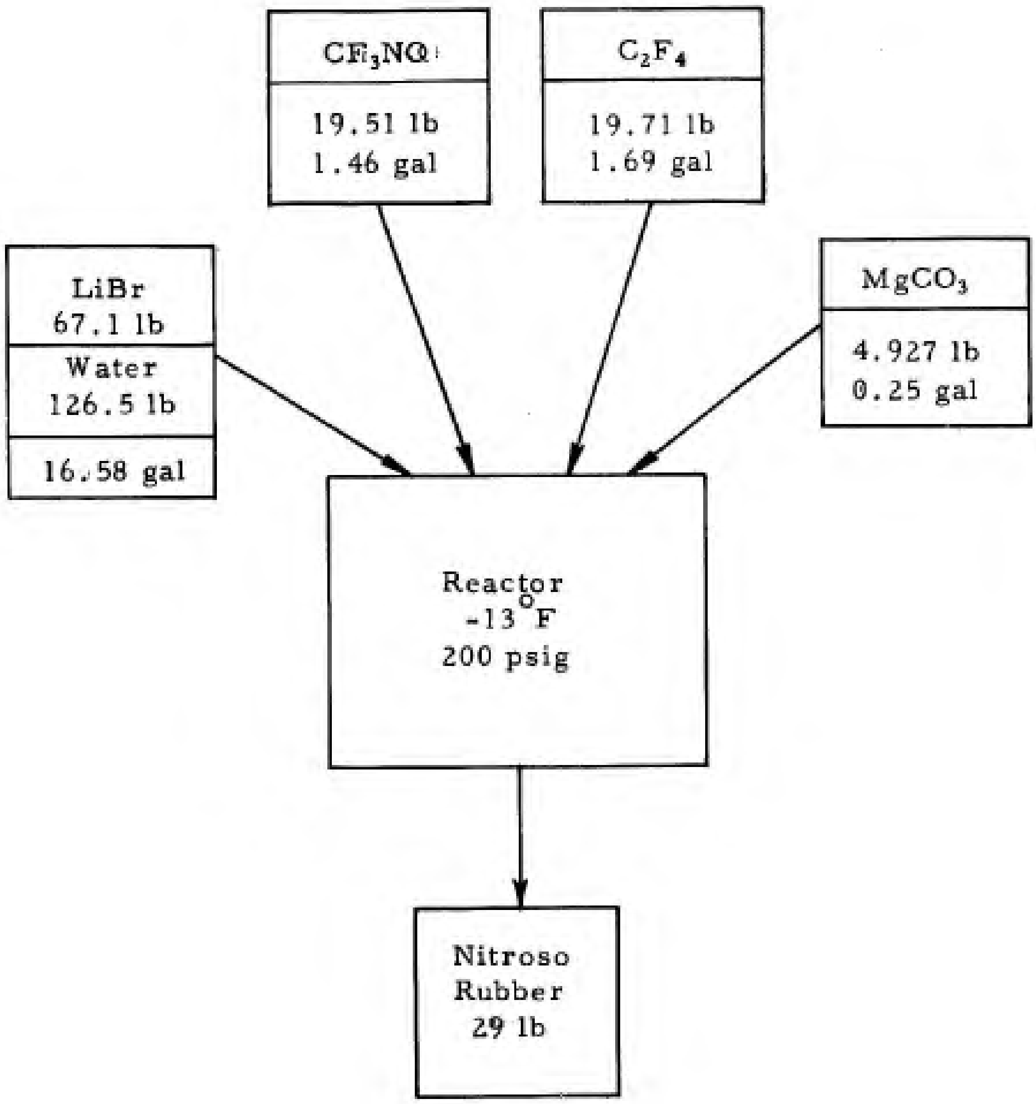

Figure 15. Material Flow Chart - Nitroso Copolymer Production

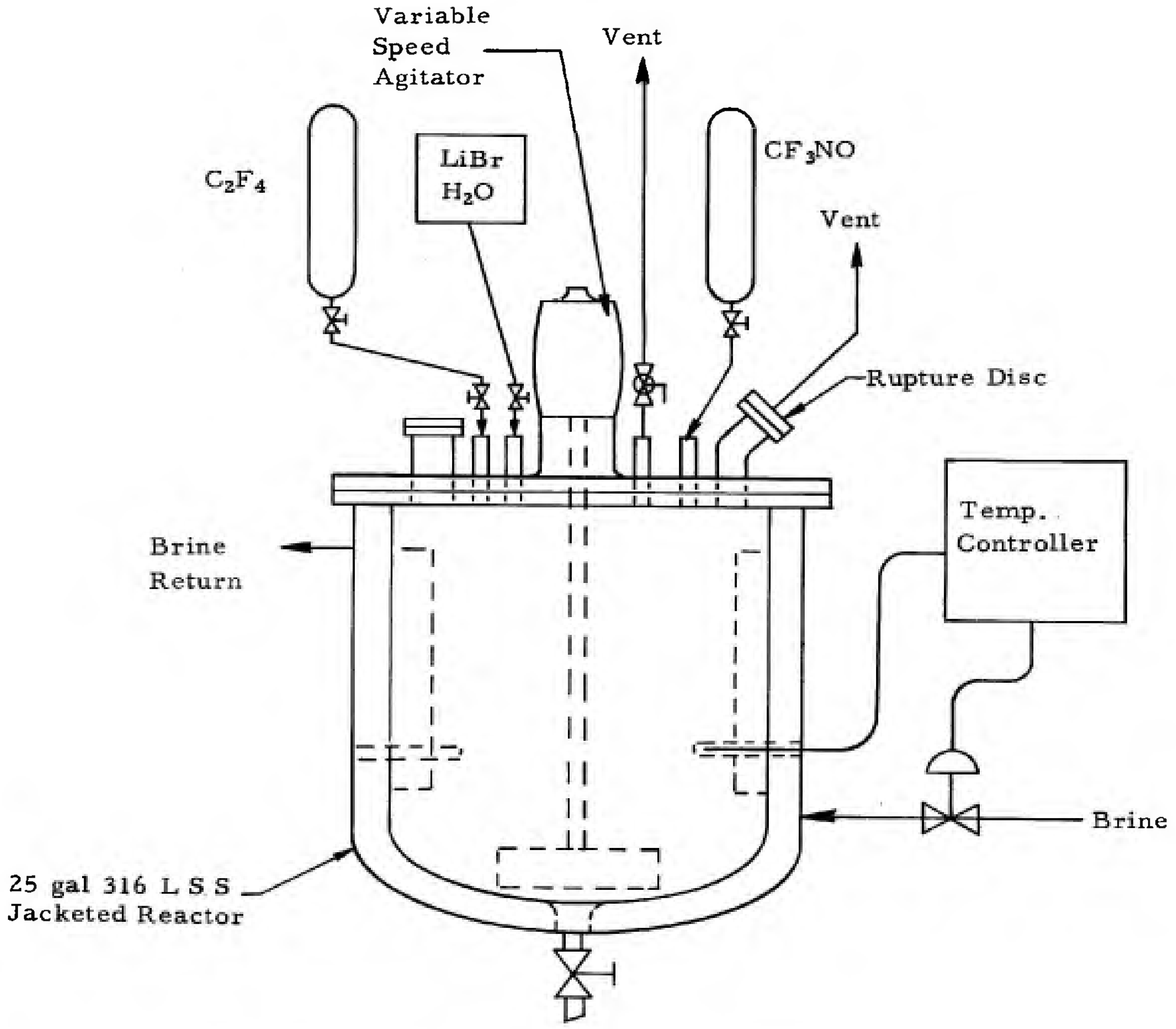

Figure 16. Equipment Flow Chart - Nitroso Copolymer Production

TABLE XXII

PRODUCTION OF CF_3COONO AND CF_3NO

Batch No.	CF_3COONO Production $(CF_3CO)_2O$ Charge (lb)	 $N_2O_3/(CF_3CO)_2O$ Mole Ratio	Reactor Temp(°F)	CF_3NO Production Reaction Time(hr)	 CF_3NO Yield (1) (%)	 (wt, lb)
5592	18.1	0.66	345-360	4	30.4	6.5
5600	41.6	0.66	350-360	7	37.4	15.0
5658	41.6	0.66	340-373	18	----	6.0
5674	35.5	0.70	360	12	29.1	10.0
5678	35.3	0.73	360	30	35.9	12.5
5703	70.6	0.73	353-360	15	28.3	20.5
5705 (2)	70.6	0.73	360-365	1.6	----	3.8
5706	70.6	0.73	360-370	25	36.7	25
5707	70.6	0.73	355-363	21	14.7	10
5808	70.6	0.73	296-340	13.5	29.9	20.4
5809 (2)	70.6	0.73	358-362	30	42.9	30.2
5813	70.6	0.73	360-367	26	34.5	25.8
5860	70.6	0.73	360-365	30	39.2	26.8

---

(1) Yields are based upon $(CF_3CO)_2O$ charged with no allowance for excess. Corrections based upon the CF_3NO content of the products have been applied.

(2) Detonation in CF_3COONO feed line.

The data in Table XXII indicate that with normal operation, yields in the range of 30 to 40% were obtained. These yields were calculated on the basis of the $(CF_3CO)_2O$ originally charged; however, if allowance is made for the excess anhydride used, these yields become 40 to 55%, equivalent to the yields obtained in the laboratory.

Assays of the products of typical CF_3NO production runs are listed in Table XXIII. These data indicate CF_3NO contents of 95-97% on the average (neglecting air). These materials were considered to be too impure for utilization in polymerizations and they were given an additional pass through the low temperature molecular sieve column to yield products with purities of 99% or greater.

C. NITROSO COPOLYMER PRODUCTION

A total of 208 pounds of nitroso copolymer was prepared in the pilot plant in replicate batches. The polymerizations were effected in aqueous suspensions under conditions developed under Phase II of this program. The kettle was maintained at -25°C during polymerization. Magnesium carbonate was the suspending agent used and lithium bromide was added to prevent freezing of the aqueous phase.

The CF_3NO was charged to the kettle gas phase by its own vapor pressure. Reactor pressures were about 190 psig at completion of the feed. The C_2F_4 was initially condensed into a separate container at -85°C, then allowed to vaporize and flow into the reactor under its own vapor pressure. An H_2SO_4 scrubber (to remove last traces of inhibitor) was installed in the feed line. At equilibrium, the system pressure was 200 psi. All transfer lines and the kettle were purged with nitrogen; monomer feeds were not started until an oxygen contact of 20 ppm or less had been reached.

Eight copolymer batches were prepared; data for the individual batches are given in Table XXIV. Of these, five were considered to have acceptably high molecular weights.

In one batch (5814), both conversion and molecular weight were low. Since the CF_3NO charged to this batch was equivalent to that used in more successful batches, it was suspected that the C_2F_4 inhibitor (Terpene B) was carried into the kettle during C_2F_4 transfer. The Terpene could act as a chain terminator as well as an inhibitor, thus both effects could be produced. In the other two batches, conversions were more normal and the presence of

TABLE XXIII

ANALYSES OF PILOT PLANT CF_3NO

Lot No	CF_3NO (%)	CF_3NO_2 (%)	C_2F_6 (%)	Higher Sat CF (%)	Air (1) (%)	CO_2 (%)	COF_2 (%)
5674	94	1 (2)	-	-	-	4	1
5678	90.5	-	4.5	-	5	-	-
5703	80	2	3	1	10	4	-
5706	97.5	1.5	-	-	1	-	-
5707	96	1	-	1.0	2	-	-
5808	97.5	1.7	-	0.5	0.3	-	-
5707/5809	94.5	3.6	-	0.6	1.3	-	-
5810	99	0.4	-	0.4	0.2	-	-
5811	99	0.8	-	0.1	0.1	-	-
5816	99.3	0.4	-	0.3	-	-	-
5861	99.2	0.3	-	0.5	-	-	-
5862	99.3	0.4	-	0.3	-	-	-

---

(1) Air apparently introduced during sampling and not actually present in the batch.

(2) May be NO_2.

TABLE XXIV

PILOT PLANT NITROSO COPOLYMER PRODUCTION

Exp.No.	Exp.No. of CF_3NO	Wt.Charged		C_2F_4 Addition Time (hr)	Reaction Time (hr)	Wt. Polymer (lb)	Yield (%)	MW x 10^6 (1)
		CF_3NO (lb)	C_2F_4 (lb)					
5675	5674	10.1	10.1	1-1/4	18	13.5	66.8	1.65
5702	5678	21	20.9	4	25	28	66.8	1.4
5704	5703	19	19	1	22	25	66	0.7
5807	5706	25	24.4	1	27	34	68	0.7
5812	5810	23	22.7	1	24	39.5	87	0.9
5814	5862	22	21.8	1	29	11.3	31	0.22
5887	5861	19	18.9	1-1/2	26	35.6	94.5	(2)
5891	5816	13	12.9	1	28	21.2	83.4	0.92

---

(1) Molecular weight (MW) was determined at RMD by the extrapolation of inherent viscosity of a dilute polymer solution (0.5 gm/100 ml FC-43).

(2) This batch of polymer has the appearance of high molecular weight, i.e., no cold flow and is rubbery. In addition, not all of the rubber dissolved in the solvent used to measure molecular weight.

appreciable quantities of CF_3NO_2(1.5-2%) in the CF_3NO is presumed to be the reason for the somewhat low molecular weights. These three batches were fractionated to effect products of improved physical properties (Table XXV). The fractionation was effected by dissolving the rubber in Freon 113 in a closed reactor at elevated temperatures, then filtering while still hot. On cooling, the high molecular weight fraction precipitated, and was separated, washed and dried under vacuum. The lower molecular weight fractions recovered from the Freon solutions were combined and dried. This material was a viscous liquid. Of a total of 64.3 pounds charged to this process, 34.1 pounds of high molecular weight rubber and 20.6 pounds of low molecular weight liquid were recovered.

PHASE IV - COMPOUNDING AND CURING STUDIES

The objective of this phase was to establish by formulation studies, the best methods of realizing the unusual properties of nitroso rubber.

A. NITROSO RUBBER COPOLYMER (CF_3NO/C_2F_4)

Initially, the nitroso copolymer vulcanizates prepared from pilot plant batches were porous and of low tensile strength. They were compounded using the formulation previously developed (Ref 4) consisting of Diak No 1 (hexamethylenediamine carbamate), 2.5 phr; TETA (Triethylenetetramine), 1.25 phr; and Hi-Sil 303, 15 phr. Elimination of Diak No. 1 from the formulation, lowering the pressure temperature, or hot milling ($>200^{\circ}F$) all resulted in nonporous vulcanizates. The best physical properties could be obtained with a compound containing 2.5 phr TETA and 15 phr Hi-Sil 303 (tensile strength 380-480 psi obtained with micro-dumbbells). The volatiles responsible for the porosity in the initial vulcanizates were identified by their infrared spectra as COF_2, $CF_3N{=}CF_2$ and CF_3NCO, the same compounds reported by Shultz from the thermal and ultraviolet degradation of CF_3NO/C_2F_4 copolymer (Ref 25). Since evolution of these materials ceased after a period of time at constant temperature, it can be concluded that only the lower molecular weight polymers were being degraded. Schultz had shown an intrinsic viscosity increase with temperature treatment.

A filler study was conducted in an attempt to improve the physical properties of the vulcanizate. The fillers included a complete spectrum of carbon blacks (thermal, furnace, channel and acetylene), as well as nonblack fillers of various chemical compositions, particle size and surface activity. Only Quso H-40 and Silstone 120 yielded elastomers with properties equal to Hi-Sil 303 and none significantly improved the vulcanizate's properties (Table XXVI).

TABLE XXV

FRACTIONATION OF NITROSO COPOLYMER

Batch No. (Fract.)	Batch No. (Charge)	Wt. Charged (lb)	Inherent Viscosity of Charge(1)	Wt. Recovered Hi. Mol. Wt. Fract. (lb)	Inherent Viscosity Hi. Mol. Wt. Fract. (lb)
5928	5807	29	0.73	14.1	0.75
5939	5814	11.3	0.29	5.5	0.40
5953	5704	24.0	0.73	14.5	1.10

---

(1) 0.5 gm polymer in 100 ml FC-43.

TABLE XXVI

NITROSO COPOLYMER FILLER STUDY

Formula:

CF_3NO/C_2F_4 - 100; TETA - 2.5; Filler - 15

Filler	Description	Dia(mμ)	pH	Vulcanizate Properties
Statex R	HAF-high structure	25	8	Poor
Neotex 130	HAF-low structure	20	8	Poor
Thermax	MT	300	7-8	Poor
Micromex W-6	EPC	25	4.8	Poor
Shawinigan	CF-Acetylene black	42	---	Poor to fair
Magnesium carbonate	Reagent	--	---	Fair
Hydrite 10S	Hydrated aluminum silicate	--	---	Poor
Ultrasil 4580	Ppt silica acid	15	5.5	Poor
Baymal	Aluminum	--	4	Poor
Silane EF	Hydrated ppt calcium silicate	200	10	Poor to fair
Barytes No. 91	Barium sulfate	--	---	Poor
Hi-Sil 233	Ppt hydrated silica	22	7	Poor
Hi-Sil 303	Ppt silica	--	4.5	Good;tensile-405 psi; elong-525%;200% modulus-200 psi
Hi-Sil 404	Ppt silica	80-130	9.4	Poor to fair
Quso H-40	Ppt silica	16	4	Good; tensile-410 psi; elong-650%; 200% modulus-115 psi
Silstone 120	Silicone oil coated silica	--	---	Good; tensile-480 psi; elong-375%;200% modulus-400 psi

Additional nitroso copolymer cure studies performed on an Air Force program (Ref 26) to develop rocket propellant resistant elastomers showed that TETA-containing copolymers can be cured to a tensile strength of 450 psi at temperatures as low as 120°F. Further efforts on the Air Force program were conducted by attempting to graft diallylamine and aminoacetic acid (glycine) to the polymer chain (similar to the crosslinking reaction with diamines) and subsequently crosslinking the polymer through the resultant double bonds or carboxyl groups. This work was not successful.

In another attempt to produce crosslinking sites,the copolymer gum was treated with anhydrous liquid ammonia which contained freshly cut metallic sodium, a process used to prepare Teflon for bonding. Some reaction, as evidenced by a slight clouding of the gum and surface stiffening was obtained. Compounding of this gum with several curatives did not show any potential for further study (Ref 25).

Ionizing gamma radiation in the presence of polyunsaturated compounds was evaluated as a means of inducing crosslinking of the copolymer (Ref 25). No crosslinking was obtained and, at high radiation intensities, the sample appeared softer, indicating chain scission similar to that reported by Shultz for the neat copolymer (Ref 24).

B. NITROSO RUBBER TERPOLYMERS

Terpolymers containing functional groups as crosslinking sites have been prepared as described in the above section. A compounding study was conducted in an attempt to develop a nitroso rubber with improved mechanical properties.

1. $CF_3NO/C_6F_5NO/C_2F_4$ TERPOLYMERS

Cure systems investigated for this terpolymer include: magnesium oxide, disodioresorcinol,dipotassium perfluoroglutarate and dipotassium hydroquinone. Because of the limited amount of terpolymer available, the above curatives were mixed separately with the terpolymer in Freon 113 without reinforcing filler. The solvent was then evaporated under vacuum and the dry compounds refined on a two-roll mill. None of these compounds yielded suitable vulcanizates. An attempt to cure this terpolymer (mixed using conventional milling techniques) with TETA, Diak No. 1, and Hi-Sil 303 was also unsuccessful and the terpolymer seemed to degrade. All the above cures were attempted using a minimum cure cycle of one hour at 250°F. Another series of compounds in which the cure temperature was 150°F did result in cured products; however, the tensile strengths were low (150 psi). Varying concentrations of TETA were used as the curative (2.5 phr was best) with 15 phr Hi-Sil 303 as the filler.

2. $CF_3NO/C_6F_4BrNO/C_2F_4$ Terpolymers

Pentafluoronitrosobenzene terpolymer was difficult to cure through the para-fluorine; however, a para-bromine would be expected to be more labile. 2-Mercaptoimidazoline (NA-22), zinc oxide, zinc oxide/benzothiazyl disulfide (Altax) and zinc/2-mercaptobenzothiazole (Captax) were evaluated as curatives for this terpolymer. The products were soft and appeared uncured (Ref 25).

3. $CF_3NO/C_2H_2F_2/C_2F_4$ Terpolymers

Two vinylidene fluoride ($C_2H_2F_2$) containing terpolymers were investigaged, one containing 0.5% and the other 2.0% $C_2H_2F_2$ in the monomer feed. Attempts were made to cure these with a typical Viton formulation (Diak No. 1, 1 phr; MgO, 15 phr; and Thermax MT, 20 phr) and with a typical nitroso rubber copolymer formulation (TETA, 1.25 phr; Diak No. 1, 2.5 phr; and Hi-Sil 303, 15 phr). The physical properties of these vulcanizates are given in Table XXVII. The nitroso copolymer could not be cured with Diak No. 1 alone, but such a cure was obtained with the terpolymer (Table XXVII). Tensile strengths were low, however, possibly due to the low $C_2H_2F_2$ content in the polymer.

4. $CF_3NO/C_2F_3H/C_2F_4$ Terpolymers

The same formulation which resulted in the best cure for the vinylidene fluoride terpolymer (Diak No. 1, 2.5 phr; MgO, 10 phr; and Hi-Sil 303, 15 phr) was evaluated with two batches of C_2F_3H terpolymer containing 2 and 5 mole percent C_2F_3H. These were cured for one hour at 250°F and post-cured for 20 hours at 212°F. The 2 mole percent sample exhibited a 420 psi tensile strength and 200% elongation while the 5 mole percent sample appeared degraded. Crosslinking studies were also conducted on the Air Force program with terpolymers containing 1.0, 1.5 and 25 mole percent C_2F_3H termonomer. Many additional curing systems were evaluated; however, acceptable cures were not obtained (Ref 26).

Samples of the terpolymer containing 1 mole percent C_2F_3H have been exposed to ionizing radiation from a Co^{60} source with no evidence of crosslinking (Ref 25).

TABLE XXVII

$CF_3NO/C_2H_2F_2/C_2F_4$ TERPOLYMER CURE STUDIES

Ingredients	Amount (phr)							
$CF_3NO/C_2H_2F_2/C_2F_4$								
0.5% $C_2H_2F_2$	100	100	100	100	----	----	---	---
2.0% $C_2H_2F_2$	---	---	---	---	100	100	100(2)	100
Hi-Sil 303	---	---	15	15	----	15	15	15
Thermax MT	20	20	---	---	20	----	---	---
Diak No. 1	1	1	2.5	2.5	1	2.5	2.5	2.5
TETA	---	---	1.25	1.25	----	1.25	---	---
Magnesium oxide	15	15	---	---	15	----	10	10
Postcure(hr/°F)(1)	---	18/212	---	18/212	18/212	18/212	18/212	---
Tensile strength (psi)	105	140	270	240	290	265	285	210
Elongation (%)	700	725	375	250	1125	525	315	300
200% Modulus (psi)	35	45	195	205	70	140	265	210
Porosity	No	No	Yes	Yes	No	Yes	No	No

---

(1) Initial cure, one hour at 250°F for all formulations.

(2) A new batch of polymer containing 2% $C_2H_2F_2$ with this formulation yielded a vulcanizate with a tensile strength of 400 psi.

5. $CF_3NO/ON(CF_2)_3COOH/C_2F_4$

Two carboxyl-containing terpolymers consisting of 1.5 and 3.0 mole percent of perfluoronitrosobutyric acid were cured through the pendent carboxyl groups. Chromium trifluoroacetate in amounts of 3 and 8 phr, respectively, was used as the curative and Silstone 120 (a silicone coated silica) was used as the filler. Both vulcanizates exhibited tensile strengths greater than 1600 psi and elongations greater than 350%. As part of an Air Force program (Ref 25), these vulcanizates were shown to possess excellent resistance to nitrogen tetroxide, a very strong oxidizer.

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V. APPENDIX

EXPERIMENTAL

V. APPENDIX

EXPERIMENTAL

Details of the syntheses of monomers and monomer precursors are given in this section. The reactions were run in standard laboratory glassware except as noted. The infrared spectra were obtained on Perkin Elmer Model 521 and Infracord spectrophotometers; the NMR spectra were obtained on a Varian Associates A-60 spectrometer. Melting points were taken with an A. H. Thomas melting point apparatus and are uncorrected unless otherwise noted.

A. NITROSO MONOMERS

1. Trifluoronitrosomethane

The design of the laboratory reactor is shown in Figure 6. The oil heated flask containing the FC-43 is fitted with an eductor tube for nitrite addition. The pyrolysis section is a silvered, vacuum jacketed column 53 cm long having a volume of approximately 900 cc. This column was surmounted by a water-cooled condenser which returned FC-43 and undecomposed nitrite to the reactor. Gas phase products passed through the condenser and were led through the purification train (helium sweep) into the liquid nitrogen-cooled product collection cylinder. The helium flowrate was 100 cc/min.

The purification train consisted of two 500 cc, 5% aqueous caustic scrubbers, a $CaSO_4$ drying tower, and a 4 ft by 1 in. diameter 4X molecular sieve column maintained at -90°C.

In a typical operation, FC-43 (130 gm) was charged to the reactor and heated to reflux (184°C). Trifluoroacetyl nitrite (55 gm) was then added dropwise over a 2.5 hour period. The FC-43 boilup and the helium sweep were maintained for one additional hour to insure complete reaction. The CF_3NO yield was 17 gm (44.7% of theory based upon nitrite charged). Mass spectral and gas chromatographic analyses indicated a purity of greater than 99%.

The trifluoroacetyl nitrite used in these preparations was prepared as follows: a one-liter, three-necked round bottomed flask was charged with 617 gm (2.93 moles) of trifluoroacetic anhydride and cooled to 0°C. Dinitrogen trioxide

(164 gm, 2.16 moles) was added over a 30 minute period with stirring. Nitric oxide was then bubbled through the reaction mixture at a rate of 160 cc/min for a total of 1.5 hours. The mixture was cooled to -20° to -25°C and excess anhydride stripped under vacuum. The yield was 746 gm, 89% of theory based on the excess anhydride charge. The product was stored in the dark at 0°C until used.

2. Tetrafluoroethylene

The apparatus utilized is shown in Figure 7. Helium was used as the sweep gas. In a typical preparation, 1,2-dibromotetrafluoroethylene (130 gm, 0.5 mole) was added over a period of 1.3 hours to a refluxing dispersion of zinc dust (38 gm, 1.58 moles) in 250 ml of tetrahydrofuran. The helium sweep was continued for one-half hour after addition was complete. The condenser was maintained at -45°C during the reaction and sweep. The products were collected at -196°C, then allowed to warm and pass through a trap at -78°C into a steel storage cylinder containing Terpene B. The yield was 46 gm (92%). Mass spectral analyses indicated 100% purity.

3. Methyl Perfluorosuccinate

A 100 ml flask containing 34.4 gm (0.2 mole) of perfluorosuccinic anhydride (Pierce Chemical Co.) was cooled in an ice bath while 6.4 gm (0.2 mole) of methanol was added slowly with stirring below 50°C. The mixture was stirred at room temperature for four days and distilled under reduced pressure to yield 27.9 gm of crude product, bp 90-115°C/3 mm. Distillation of this material with a Podbelniak micro-spinning band column gave 24.8 gm (61%) of methyl perfluorosuccinate, bp 76-77°C/0.9 mm.

Anal. Calcd. for $C_5H_4F_4O_4$: C, 29.43; H, 1.98
Found: C, 30.60; H, 2.52.

4. Methyl Perfluorosuccinate/Nitrosyl Chloride

A 100 ml quartz flask was charged with 10.0 gm (0.05 mole) of methyl perfluorosuccinate and nitrosyl chloride diluted with nitrogen was bubbled through the liquid. The flask was irradiated with a 140 watt Hanovia ultraviolet lamp for 2.5 hours. A small amount of blue liquid was collected in the -78°C trap but when the material warmed to room temperature it vaporized to a mixture of NO and NO_2. (This is characteristic of N_2O_3.) In addition NOCl, SiF_4, NO_2F and 7.8 grams of unreacted starting material were obtained.

5. Nitrosyl Perfluorosuccinyl Fluoride

A 50 ml Kel-F reactor was charged with 10.0 gm (0.058 mole) of perfluorosuccinic anhydride in an inert atmosphere. The reactor was cooled to -5°C with an ice-ethanol bath and nitrosyl fluoride (Ozark-Mahoning Chemical Co.) was bubbled through the liquid at a moderate rate for 40 minutes. Completion of the addition could be observed by the appearance of large bubbles of unreacted FNO. The resulting yellow liquid was flushed with dry nitrogen for ten minutes and was held under reduced pressure (0.1 mm) for 1 hour to remove any volatile material. The product, 11.2 gm (0.0506 mole, 87%), was identified as nitrosyl perfluorosuccinyl fluoride by mass spectral analysis (Table V), elemental analysis,

Anal. Calcd. for $C_4F_5NO_4$: C, 20.98; N, 6.34
Found: C, 21.73; N, 6.68.

infrared spectrum (Figure A-1) and equivalent weight (Calcd.: 55; Found: 56). The liquid reacted rapidly with moisture in the air to give perfluorosuccinic acid, mp 86-8°C[Lit. (Ref 27) mp 86.4-7.4°C].

6. Photolysis of Nitrosyl Perfluorosuccinyl Fluoride

A 100 ml Pyrex flask containing 20.0 gm (0.09 mole) of nitrosyl perfluorosuccinyl fluoride was connected to a series of traps immersed in cooling baths held at -78°C and -196°C. The system was evacuated to 18-20 mm Hg and the flask was irradiated with a 200 watt Hanovia ultraviolet (2537 Å) lamp for six hours. During this time the flask was cooled with ice-water in order to maintain a temperature of 15-30°C in the reaction vessel. At the end of the reaction period, the flask was closed off from the system and water was added to each of the traps. The first trap, which had been cooled at -78°C, contained a small amount of blue liquid which formed NO_2 upon treatment with water. The second Dry Ice trap contained a considerable quantity of deep blue liquid. When water was added to this trap, however, almost all of the liquid was converted into NO_2 and only a pale blue aqueous solution remained. Etching of the glass trap indicated the presence of HF in this solution. The aqueous solution was then extracted with ether and the ether solution dried over anhydrous sodium sulfate and evaporated to dryness to yield 1.6 gm of perfluorosuccinic acid. The residue in the flask consisted of perfluorosuccinic anhydride (mass spectral analysis) and a yellow solid. After removal of the volatile anhydride under vacuum, 7.0 gm (62.5%) of yellow dinitrosyl perfluorosuccinate, mp 44-46°C [Lit. (Ref 4) mp 44-48°C] remained which reacted with water to give NO_2 and a quantitative yield of perfluorosuccinic acid.

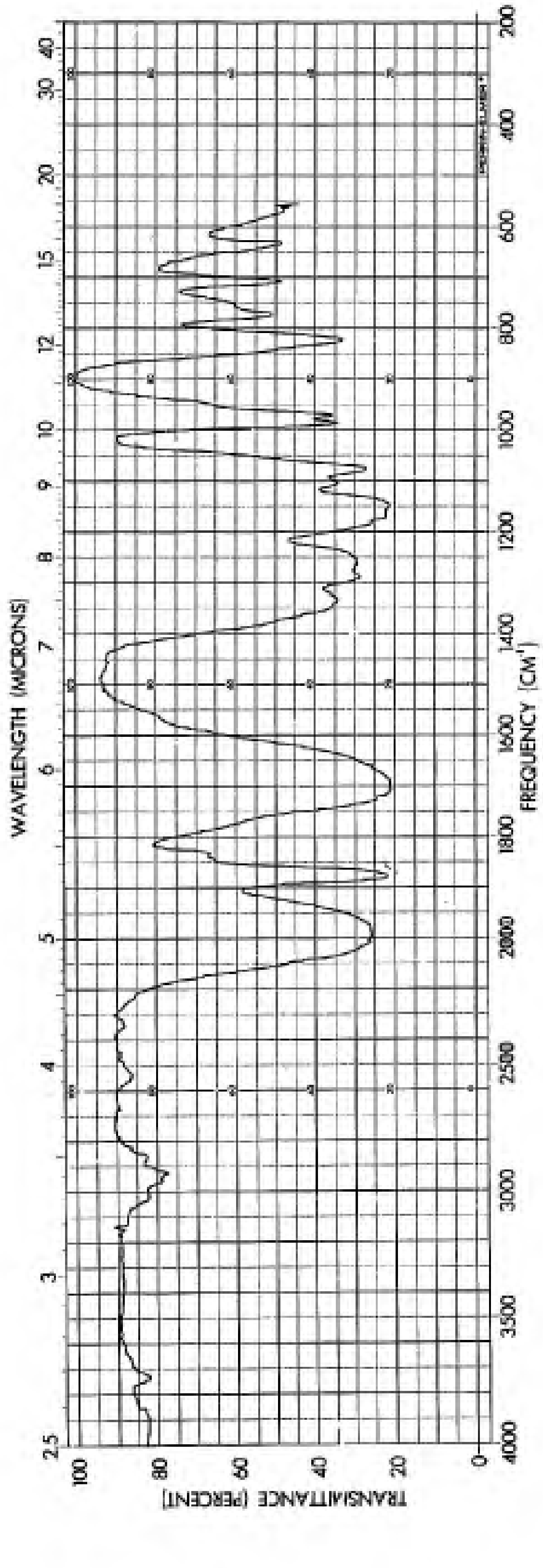


Figure A-1. Infrared Spectrum of $FCO(CF_2)_2COONO$

7. Nitrosyl Perfluoroglutaryl Fluoride

(A) The procedure described above for the preparation of nitrosyl perfluorosuccinyl fluoride was used to prepare nitrosyl perfluoroglutaryl fluoride in 86.6% yield. The infrared spectrum (Figure A-2), mass spectrum and elemental analysis of the yellow, moisture reactive liquid were consistent with

<u>Anal</u>. Calcd. for $C_5F_7NO_4$: C, 22.16; N, 5.17
Found: C, 22.03; N, 5.68.

the assigned structure.

(B) A 30 ml Monel cylinder was charged with 15.0 gm (0.068 mole) of perfluoroglutaric anhydride and 3.0 gm (0.061 mole) of FNO was condensed at -196°C. The bomb was allowed to warm to room temperature overnight. At the end of this time, only a few millimeters of pressure could be observed. The volatile materials, which included unreacted anhydride, were removed in vacuo to yield 12.0 gm (0.0443 mole, 72.5%) of product. The infrared spectrum of this material was identical to that prepared in (A) above.

8. Photolysis of Nitrosyl Perfluoroglutaryl Fluoride

A 50 ml Pyrex flask containing 4.0 gm (0.015 mole) of nitrosyl perfluoroglutaryl fluoride was irradiated for two hours with a 200 watt Hanovia ultraviolet lamp. The system was evacuated to 10 mm Hg and the products collected in a series of traps as described above. The -78°C trap contained 0.4 gm of deep blue liquid. After hydrolysis of this material, the resulting blue aqueous solution was extracted with ether and the ether solution dried over anhydrous sodium sulfate. A small amount (<1 gm) of blue liquid was obtained after evaporation of the ether. The ultraviolet-visible spectrum of this material was identical to that obtained from 4-nitrosoperfluorobutanoic acid, which was secured by a previously reported procedure (Ref 4) as part of another program (Ref 28).

9. Pyrolysis of Nitrosyl Perfluoroglutaryl Fluoride

A number of unsuccessful attempts to produce 4-nitrosoperfluorobutanoic acid by pyrolysis of nitrosyl perfluoroglutaryl fluoride were made and the results are summarized in Table VI.

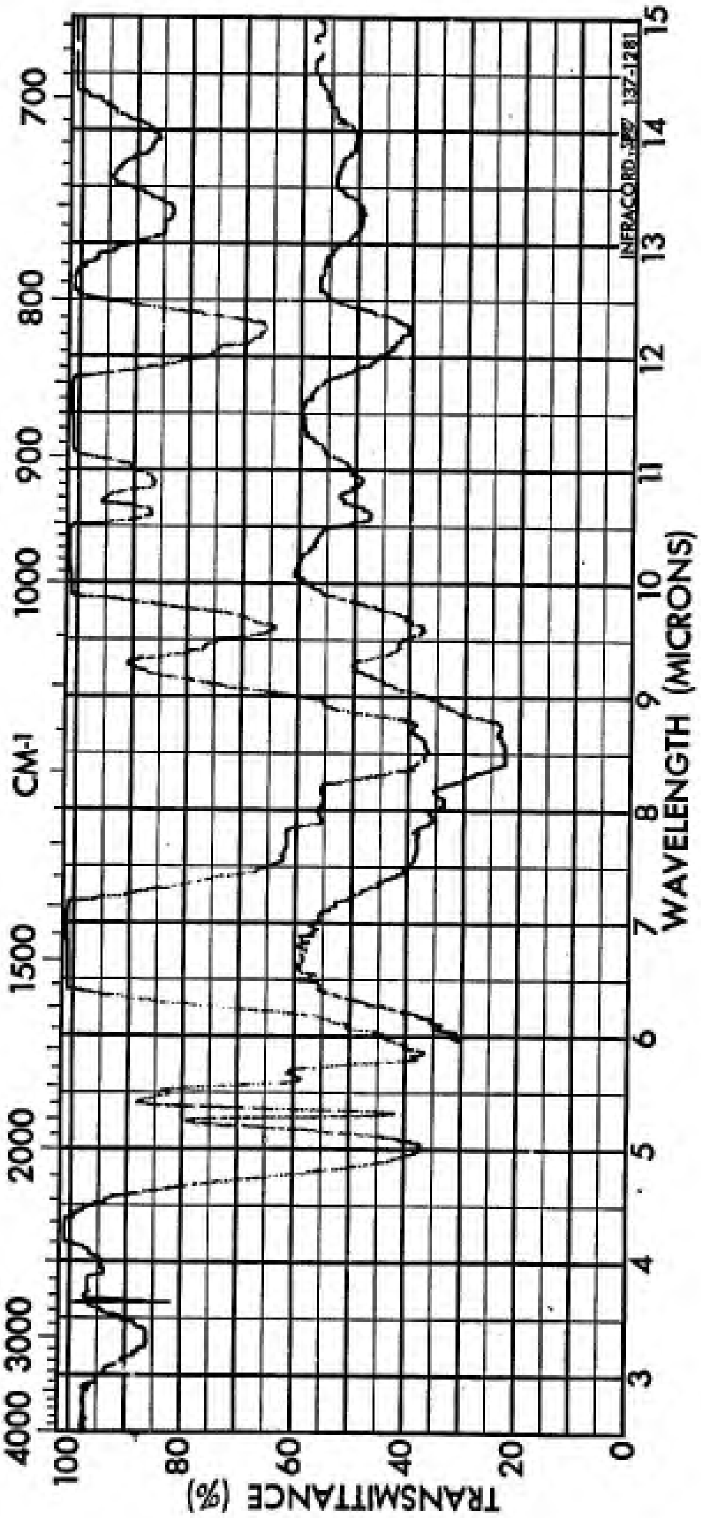


Figure A-2. Infrared Spectrum of $FCO(CF_2)_3COONO$

10. 2, 2, 3, 3, 4, 4, 5, 5-Octafluoropentanoic Acid

A solution of 16 gm (0.101 mole) of potassium permanganate, 2.0 gm of sodium carbonate and 250 ml of of water in a 500 ml flask was treated with a mixture of 10.0 gm (0.043 mole) of 2, 2, 3, 3, 4, 4, 5, 5-octafluoropentanol (Du Pont, bp 104-141°C) and 15 ml of water at room temperature with stirring. The temperature rose gradually to 40°C and, after stirring for two hours at 35-40°C, the mixture was refluxed overnight. The mixture was filtered to remmove manganese dioxide and the filtrate was made acid with 9N sulfuric acid. After the solution was decolorized by the dropwise addition of 3% aqueous hydrogen peroxide solution, it was extracted four times with 200 ml portions of ether. The ether solution was dried over anhydrous sodium sulfate and evaporated to dryness. Distillation of the residue yielded 2.7 gm (25.5%) of colorless liquid, bp 164-166°C. The infrared spectrum (Figure A-3) indicated that the material was the carboxylic acid hydrate.

Anal. Calcd. for $C_5HF_8O_2 \cdot 1.5H_2O$: C, 21.99; H, 1.85
Found: C, 22.05; H, 1.75.

11. Pentafluoronitrosobenzene

The method described previously (Ref 16) was modified and used to prepare pentafluoronitrosobenzene. A mixture of 200 ml of 98% formic acid, 50 ml of 90% hydrogen peroxide and 600 ml of methylene chloride was stirred while a solution of 50 gm(0.27 mole) of pentafluoroaniline (Pierce Chemical Co., mp 34-35°C) in 200 ml of methylene chloride was added slowly over a 45 minute period at room temperature. The mixture was refluxed for 5 hours. After the addition of 500 ml of water, the dark green mixture was refluxed for 2 hours. The organic solution was separated, washed three times with water and dried over anhydrous sodium sulfate. Evaporation of the solvent yielded 47.6 gm of crude green liquid which was distilled to yield 28.0 gm of blue liquid, bp 50-60°C (20 mm). Sublimation of the product afforded 25.1 gm (0.128 mole, 46.6%) of blue-green pentafluoronitroso benzene, mp 42-44°C [Lit. (Ref 16) mp 45°C]. Recrystallization of this material gave a product with mp 44.5-45°C. The infrared spectrum (Figure A-4) produced a strong absorption at 1550 cm^{-1} which has been assigned to the NO stretching frequency.

12. 4-Bromotetrafluoroaniline

A solution of 20.0 gm (0.121 mole) of 2, 3, 5, 6-tetrafluoroaniline (Pierce Chemical Co., mp 30-32°C) in 100 ml of glacial acetic acid was treated with a solution of 8.00 ml (23.4 gm, 0.146 mole) of bromine in 20 ml of glacial

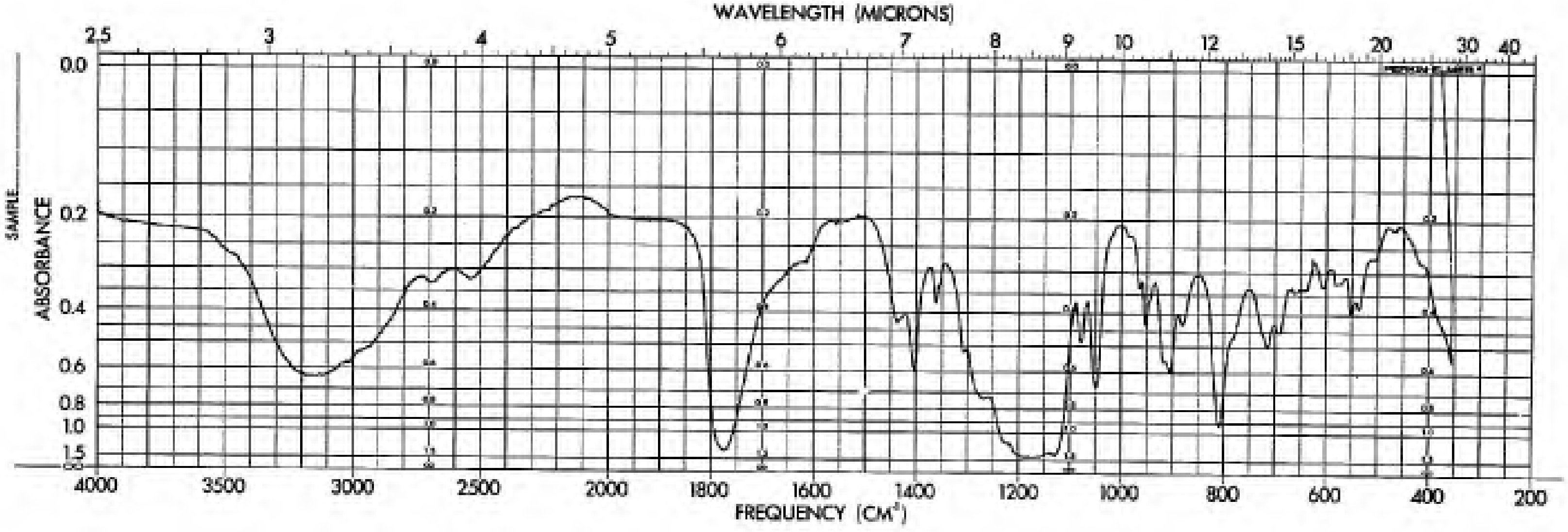


Figure A-3. Infrared Spectrum of $HCF_2(CF_2)_3COOH \cdot 1.5\ H_2O$

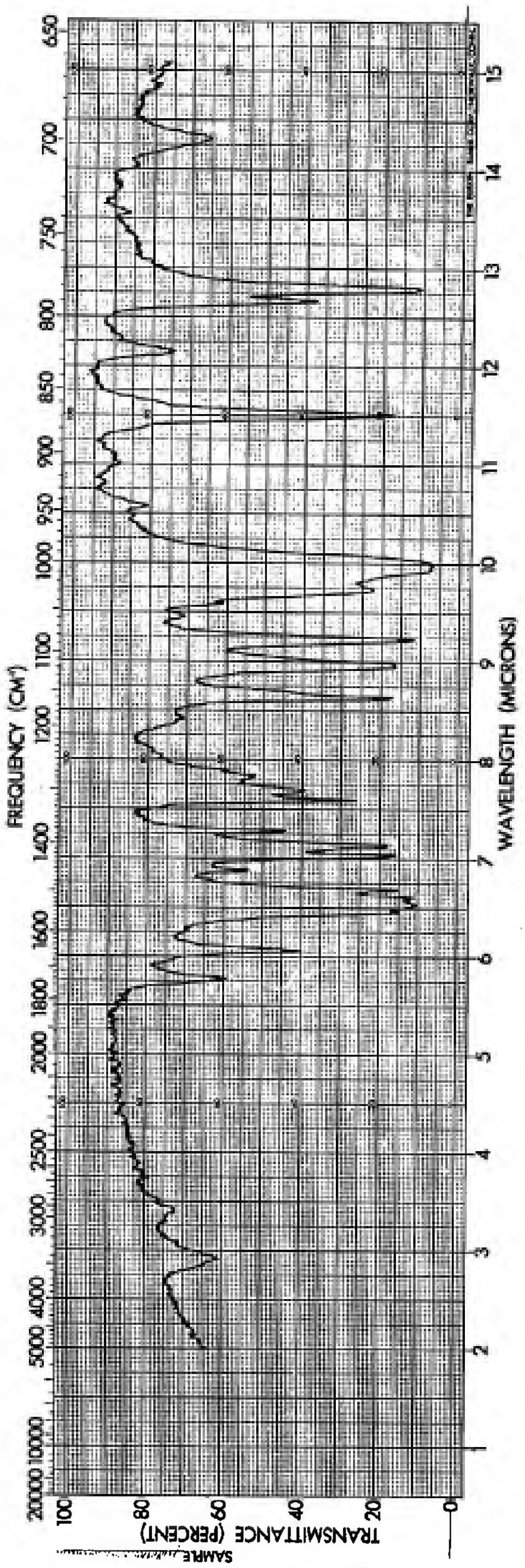
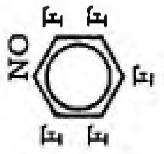


Figure A-4. Infrared Spectrum of



acetic acid at room temperature in a 500 ml flask. The bromine solution was added at a moderate rate and the resultant mixture was stirred at room temperature for two hours. After the mixture was poured into 500 ml of cracked ice, the precipitate was collected by filtration. The yellow solid was washed with water, dried by suction and recrystallized from pentane to yield 20.8 gm (0.0853 mole, 70.5%) of colorless crystals, mp 54-55°C. After a second recrystallization from pentane the melting point was 57-58°C (corr.). The infrared spectrum is shown in Figure A-5.

Anal. Calcd. for $C_6F_4H_2NBr$: C, 29.53; H, 0.83; N, 5.74; Br, 32.75
Found: C, 29.57; H, 0.82; N, 5.97; Br, 32.80.

This material was found to be insoluble in concentrated HCl solution and attempts to prepare the acetamide and benzamide derivatives by the usual method (Ref 29) resulted in recovery of unchanged starting materials.

13. 4-Nitrosotetrafluorobromobenzene

A mixture of 120 ml of 98% formic acid and 30 ml of 90% hydrogen peroxide was stirred for fifteen minutes at room temperature and added to a solution of 15.0 gm (0.062 mole) of 4-bromotetrafluoroaniline and 400 ml of methylene chloride in a one liter flask. The resulting solution was refluxed for five hours. After the mixture was treated with 250 ml of water and refluxed for thirty minutes, the deep green organic phase was separated, washed with water and dried over anhydrous sodium sulfate. The solvent was removed in vacuo, the residue taken up in pentane and the solution chromatographed on a 2 by 50 cm column of acid-washed alumina (Merck, suitable for chromatographic analysis). After the column was eluted with pentane, the blue-green solution was collected and evaporated to dryness to yield 10.2 gm (0.0396 mole, 64.2%) of pale yellow solid, melting at 36-37°C to a blue-green liquid. Recrystallization of the material from ethanol produced colorless crystals, mp 39-40°C (corr.), of 4-nitrosotetrafluorobromobenzene.

Anal. Calcd. for C_6F_4BrNO: C, 27.93; Br, 30.98; N, 5.43
Found: C, 28.15; Br, 31.00; N, 5.29.

The infrared spectrum of the blue-green liquid (Figure A-6) exhibited strong, sharp absorptions at 1530, 1510, 1480 and 1360 cm^{-1}. The absorption at 1530 cm^{-1}, which has been assigned to the N=O stretching frequency, however, is much weaker in intensity in the spectrum of the solid dimer (Figure A-7). In addition, the 1360 cm^{-1} absorption is completely absent in the spectrum of the solid.

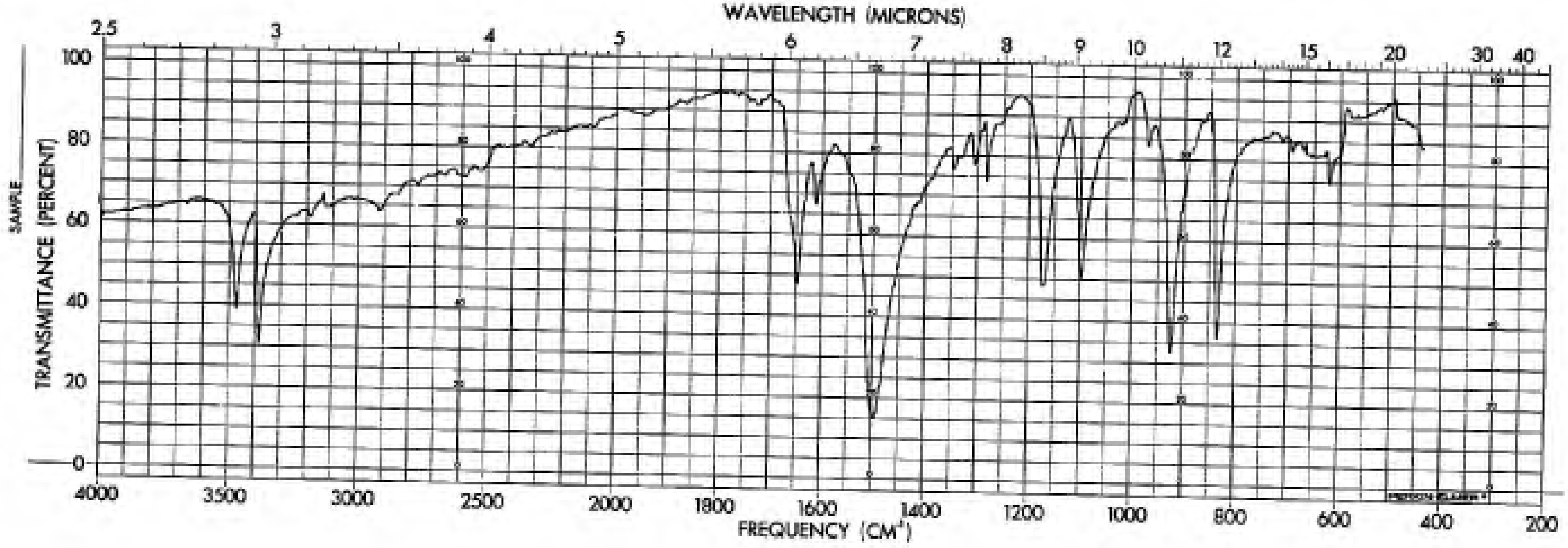
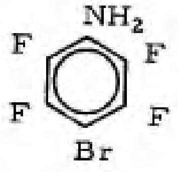


Figure A-5. Infrared Spectrum of



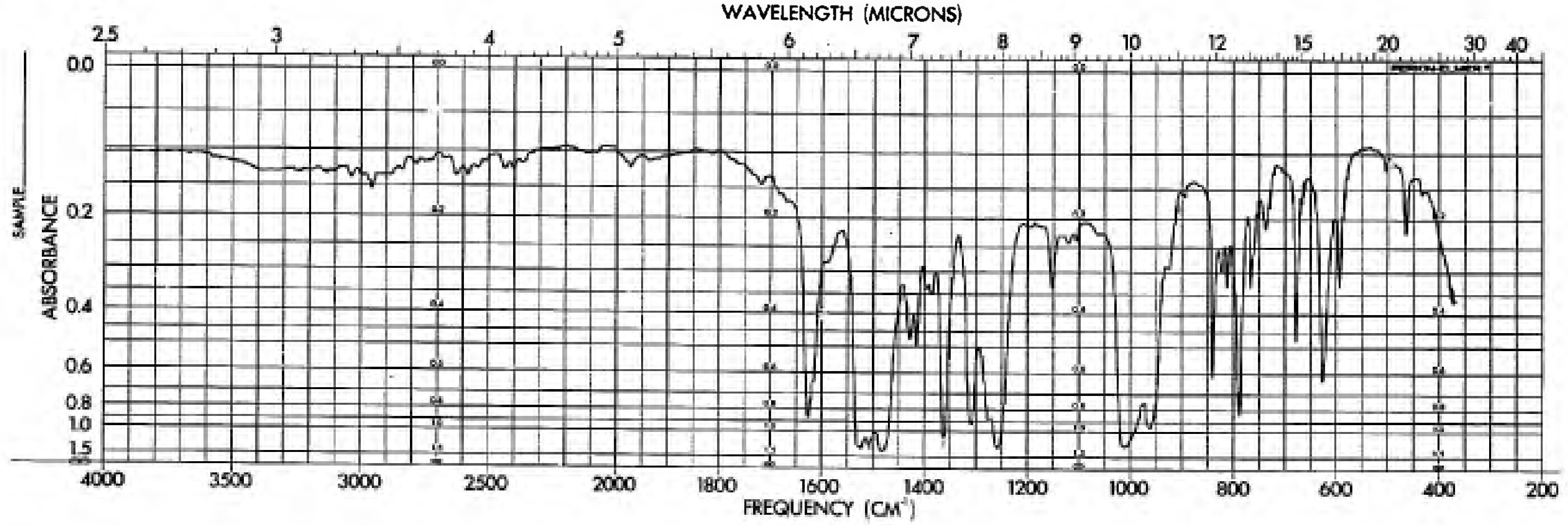
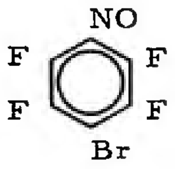


Figure A-6. Infrared Spectum of Liquid 

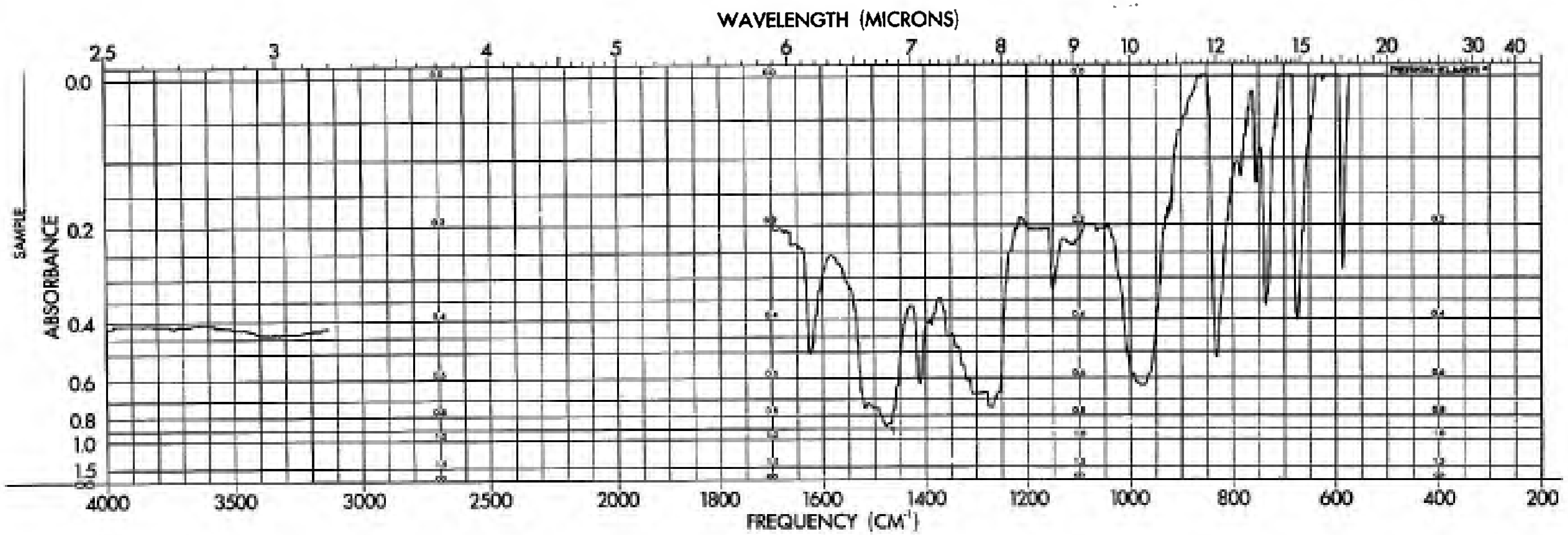
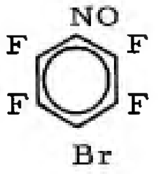


Figure A-7. Infrared Spectrum of Solid



14. Tetrafluoronitrosobenzene

A mixture of 40 ml of 90% formic acid, 10 ml of 90% hydrogen peroxide and 120 ml of methylene chloride in a 500 ml flask was treated with 10.0 gm (0.0605 mole) of 2, 3, 5, 6-tetrafluoroaniline and the mixture refluxed for 6.5 hours. After the addition of 170 ml of water, the mixture was stirred overnight at room temperature. The green methylene chloride solution was separated, dried over anhydrous sodium sulfate and evaporated to dryness to yield 7.3 gm of tan solid. Sublimation of this material at 50-55°C (20 mm) gave 2 gm of off-white solid which was taken up in ethanol (blue solution) and precipitated with water to yield 1.0 gm (0.0056 mole, 9.2%) of 2, 3, 5, 6-tetrafluoronitrosobenzene, mp 67-68°C. The infrared spectrum (Figure A-8) indicated it to be the desired compound.

15. Ethyl Pentafluorobenzoate

A mixture of 30 gm (0.14 mole) of pentafluorobenzoic acid (Pierce Chemical Co., mp 98-100°C), 150 ml (118 gm, 2.56 moles) of absolute ethanol and 5 ml of concentrated sulfuric acid in a 500 ml flask was refluxed for 6 hours. The ethanol was removed by evaporation and the residue poured into 250 ml of water. After the organic layer was separated, washed with 0.5N sodium hydroxide solution and water, it was dried over anhydrous sodium carbonate and evaporated to dryness. Distillation of the residue yielded 8.0 gm (0.033 mole, 24%) of colorless liquid, bp 61-61.5°C (0.5 mm); n_D^{20} 1.4275.

Anal. Calcd. for $C_9H_5F_5O_2$: C, 45.02; H, 2.09
Found: C, 45.15; H, 2.14.

The infrared spectrum (Figure A-9) exhibited a carbonyl absorption at 1745 cm^{-1}.

16. Pentafluorobenzamide

The previously described procedure (Ref 18) was used to prepare pentafluorobenzamide, mp 148-150°C (corr.) [Lit. (Ref 18) mp 150°C], in 60% yield by the reaction of ammonia with pentafluorobenzoyl chloride (prepared from pentafluorobenzoic acid and phosphorous pentachloride).

17. 4-Aminotetrafluorobenzamide

Attempts to prepare 4-aminotetrafluorobenzoic acid and 4-aminotetrafluorobenzamide by the reaction of the acid or amide, respectively, with sodium amide in liquid ammonia by the previously described procedure (Ref 19) were unsuccessful. An alternate method of amination was modified and used successfully.

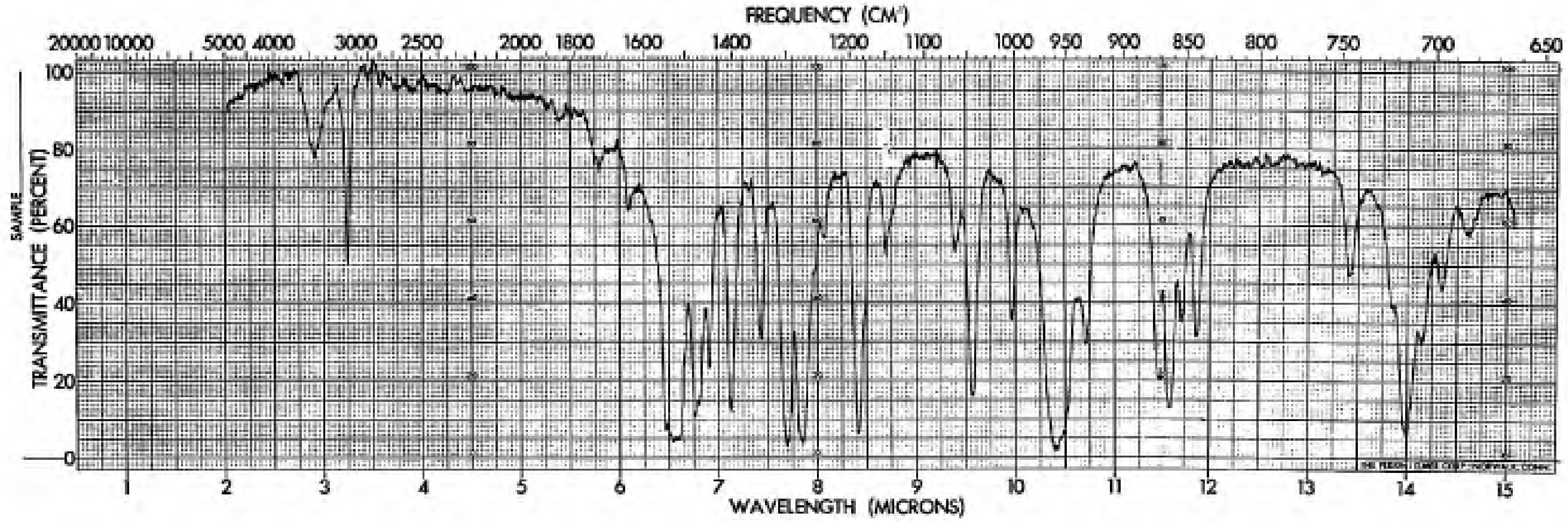


Figure A-8. Infrared Spectrum of

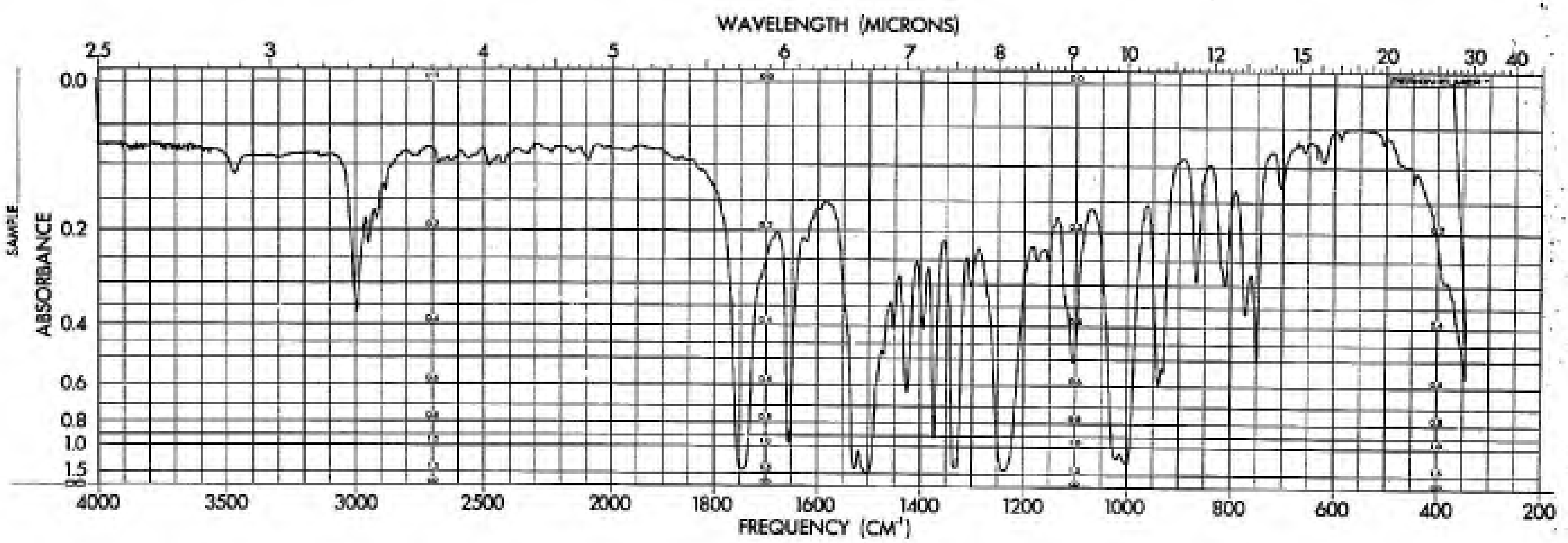
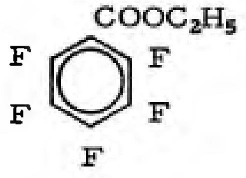


Figure A-9. Infrared Spectrum of



Fifty ml of methanol saturated with ammonia was treated with 5.0 gm (0.024 mole) of pentafluorobenzamide and the mixture transferred to a Fischer-Porter pressure reactor. The reactor was placed into a steam bath and heated for 8 hours. The pressure was observed to be 120 lb/sq in. The mixture was cooled, evaporated to dryness and recrystallized from toluene-methanol to yield 1.05 gm (0.0051 mole, 23%) of pink needles, mp 180-182°C [Lit. (Ref 19) mp 171-171.5°C]· solution in ethyl acetate. The infrared spectrum (Figure A-10) was consistent with the assigned structure.

Anal. Calcd. for $C_7H_4F_4N_2O$: C, 40.39; H, 1.94; N, 13.46
Found: C, 39.96; H, 1.92; N, 13.23.

18. 4-Aminotetrafluorobenzoic Acid

The previously described procedure (Ref 19) was modified and used to prepare 4-aminotetrafluorobenzoic acid. A mixture of 50.0 gm (0.24 mole) of 4-aminotetrafluorobenzamide and 250 ml of 20% aqueous sodium hydroxide was refluxed for 10 hours. The resulting solution was acidified with concentrated hydrochloric acid and the precipitated acid collected by filtration. The solid was recrystallized from acetone to yield 32 gm (0.15 mole, 64%) of colorless crystals, mp 170-172°C. A second recrystallization from CCl_4 gave crystals melting at 176-177°C [Lit. (Ref 19) mp 181-181.5°C]; equivalent weight 2-8 (calcd. 209); pKa 3.65. Elemental analysis and the infrared spectrum (Figure A-11) confirmed the identification.

Anal. Calcd. for $C_7F_4H_3NO_2$: C, 40.21; H, 1.45; N, 6.70
Found: C, 39.66; H, 1.77; N, 6.73.

19. 4-Nitrotetrafluorobenzamide

A mixture of 7 ml of 98% formic acid, 3 ml of 90% hydrogen peroxide, 1.0 gm (0.0048 mole) of 4-aminotetrafluorobenzamide and 50 ml of ethyl acetate in a 100 ml flask was stirred for one hour at room temperature. The color of the solution changed from amber to yellow. Failure to detect a green color indicated that oxidation to the nitro compound had taken place. The mixture was then refluxed for 2.5 hours (temp 80°C) and allowed to cool overnight. After the addition of 1.5 ml of 90% hydrogen peroxide, the mixture was refluxed for an additional 2.5 hours. The yellow mixture was poured into 100 ml of 10% sodium carbonate solution and the organic solution separated, washed with water and dried over anhydrous sodium sulfate. The solution

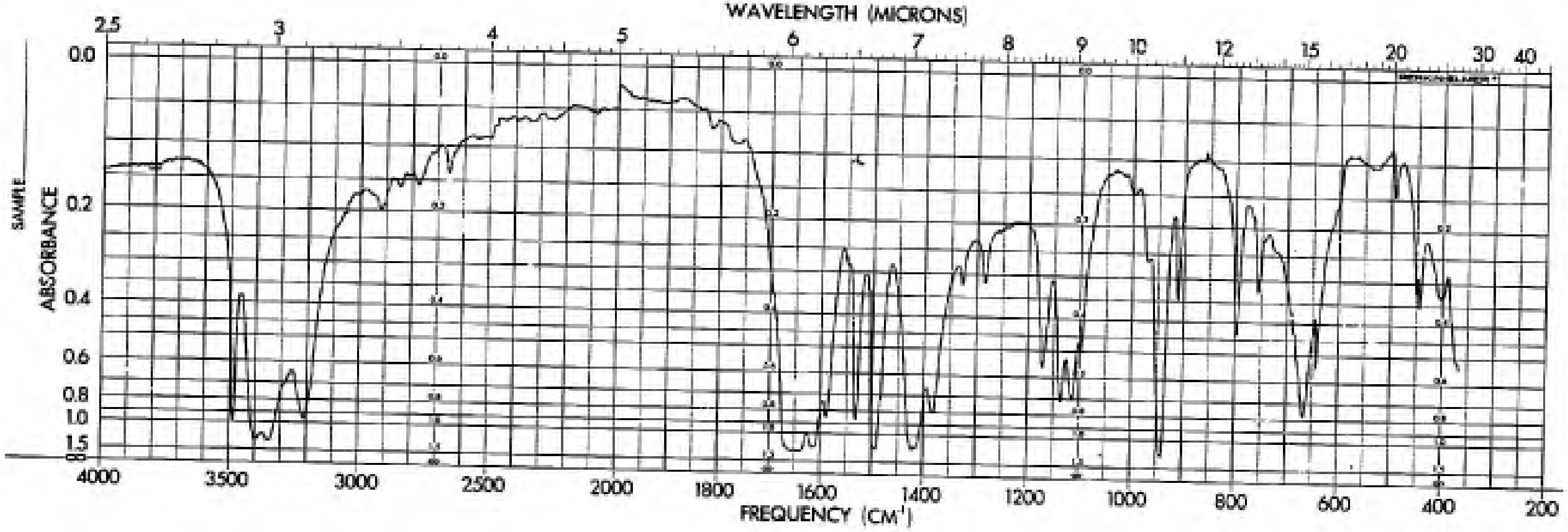


Figure A-10. Infrared Spectrum of

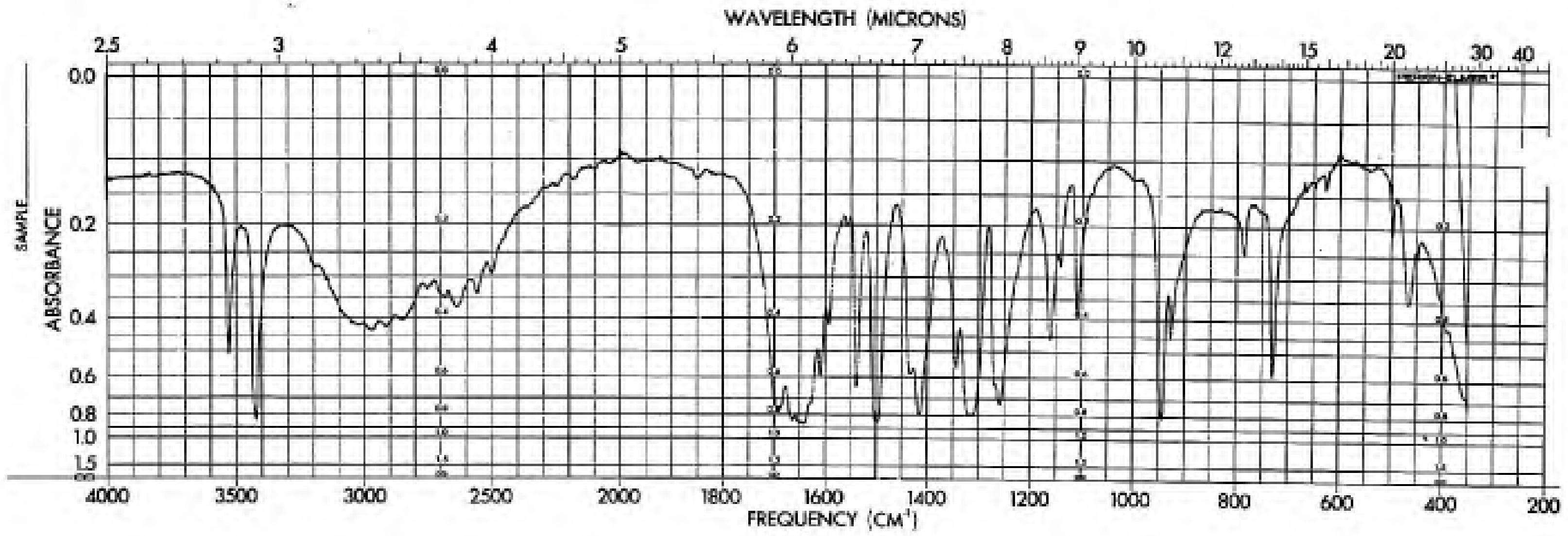
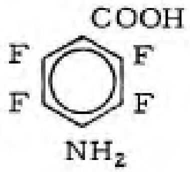


Figure A-11. Infrared Spectrum of



was evaporated to dryness to yield 0.9 gm (79% crude yield) of yellow solid, mp 101-106°C. This solid was recrystallized twice from carbon tetrachloride to yield 0.35 gm (0.0013 mole, 31%) of colorless plates, mp 110-112°C.

Anal. Calcd. for $C_7H_2F_4N_2O_3$: C, 35.31; H, 0.85; N, 11.76
Found: C, 35.39; H, 1.03; N, 11.55.

The compound was characterized by elemental analysis and infrared spectrum (Figure A-12).

20. 4-Nitrosotetrafluorobenzoic Acid

(A) A mixture of 5.0 gm (0.024 mole) of 4-aminotetrafluorobenzoic acid and 250 ml of methylene chloride in a 500 ml flask was treated with a previously prepared solution of 40 ml of 98% formic acid and 10 ml of 90% hydrogen peroxide and refluxed for five to six hours. After the addition of 200 ml of water, the mixture was refluxed for one hour. The blue-green organic phase was separated, dried over anhydrous sodium sulfate and evaporated to dryness to yield 1.8 gm (0.008 mole, 34%) of pale yellow solid, mp 150-151°C, 226-227°C (dec.); equivalent weight 225 (calcd. 223).

Anal. Calcd. for $C_7HF_4NO_3$: C, 37.69; H, 0.45; N, 6.28
Found: C, 37.89; H, 0.63; N, 5.91.

The melting characteristics of this compound are worthy of note. Slow heating from room temperature causes a gradual darkening in the color of the solid above 100°C. At 226°C the material is black and decomposes sharply (one degree range) with the evolution of gas. When a capillary tube containing the product was plunged into an oil bath at 145°C and the temperature then slowly raised, the compound melted at 150-151°C to a green liquid which immediately liberated gas. The latter value is probably the correct melting point while the former represents the melting point of another compound apparently formed during the heating process.

The infrared spectrum (Figure A-13) of 4-nitrosotetrafluorobenzoic acid exhibited a CO absorption at 1715 cm^{-1} and an NO absorption at 1555 cm^{-1}.

(B) A solution of performic acid was prepared by stirring 20 ml of 98% formic acid with 5 ml of 90% hydrogen peroxide for fifteen minutes at room temperature. This solution was added to a stirred suspension of 2.0 gm (0.010 mole) of 4-aminotetrafluorobenzoic acid in 100 ml of methylene chloride. The mixture was refluxed for 4 hours. After the addition of 50 ml of water, the

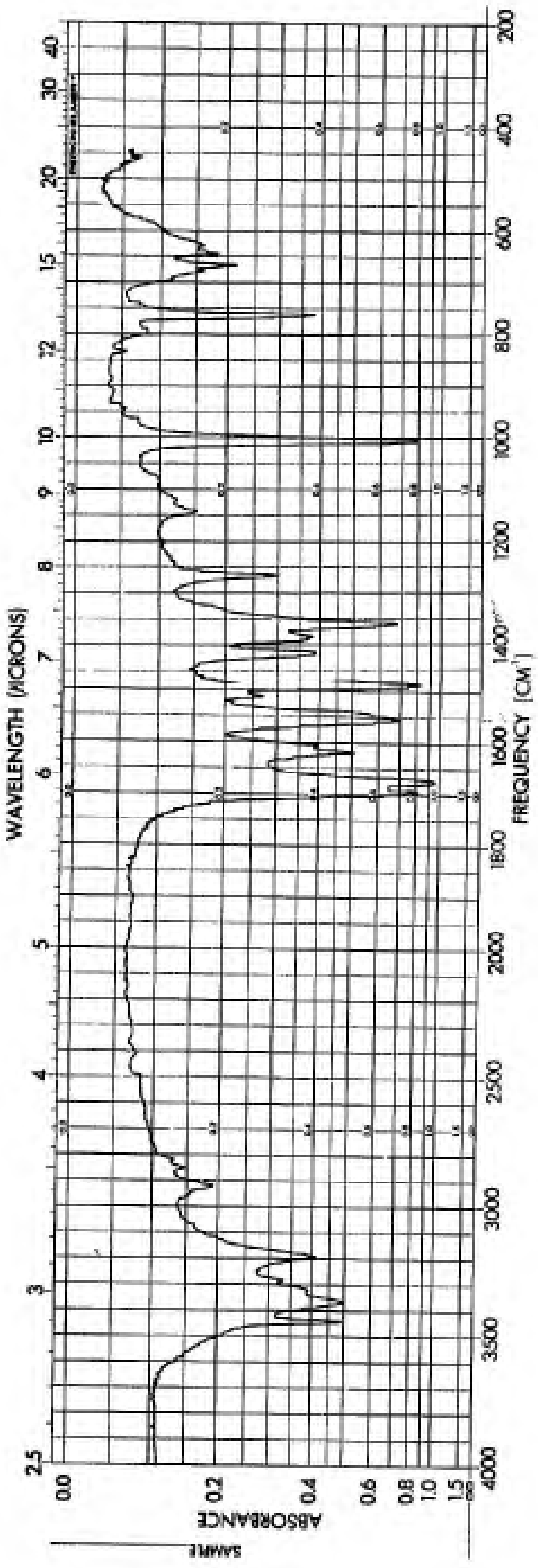
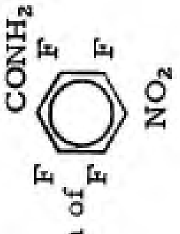


Figure A-12. Infrared Spectrum of



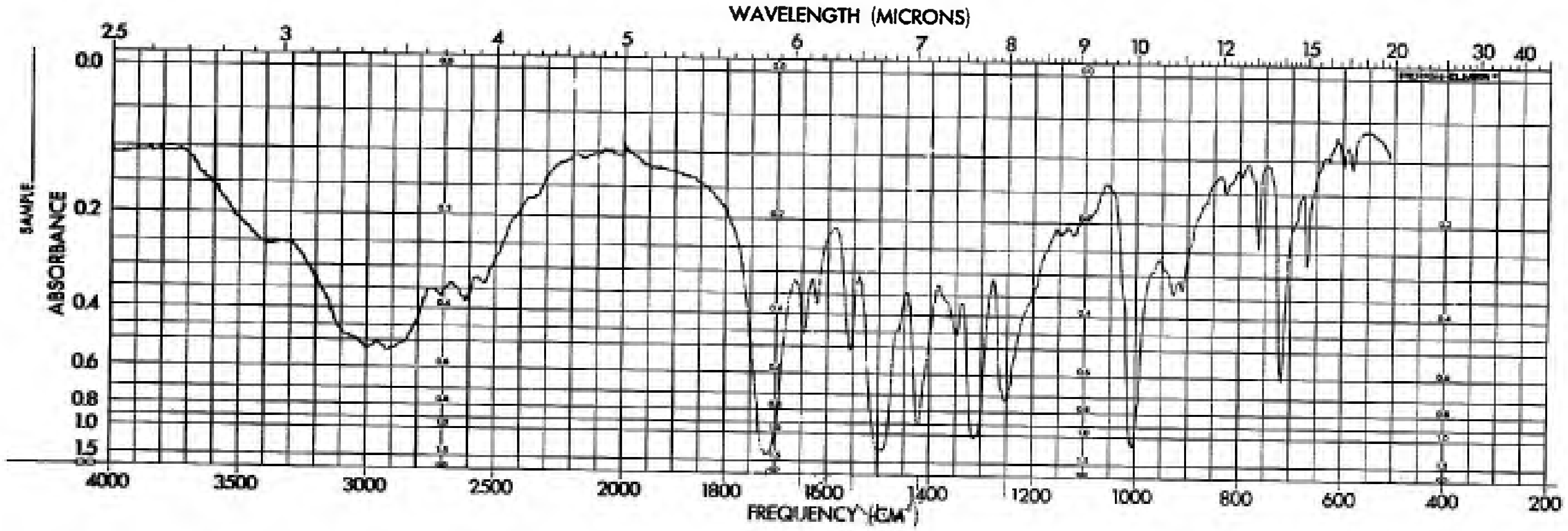
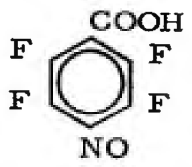


Figure A-13. Infrared Spectrum of



green mixture was refluxed for 1 hour. The organic phase was separated and the aqueous solution extracted with ether. All of the green color was transferred from the aqueous phase to the organic layer. The organic solutions were combined and dried over anhydrous sodium sulfate. After removal of the solvent in vacuo, the residue was taken up in ether and the solution chromatographed on a carefully packed column of silica gel (Baker) which was kept at 15°C by a water cooled jacket. The deep blue-green solution was evaporated to dryness to yield 1.0 gm (0.0044 mole, 47%) of pale yellow dimer, mp 223-225°C (dec.).

The results of a number of experiments utilizing both procedures are summarized in Table VII. In one experiment the former method (A) was used and the aqueous solution produced during workup of the reaction mixture was extracted with ether. After the ether extract was dried over anhydrous sodium sulfate, the solvent was removed in vacuo and the resulting yellow paste treated with water. The concentrated aqueous solution was then extracted with methylene chloride containing a small amount of ether and the organic solution dried over anhydrous sodium sulfate. Removal of the solvent in vacuo gave a yellow solid, mp > 360°C, which had an infrared spectrum (Figure A-14) almost identical to that of the nitroso acid. Refer to analyses and discussion section of the possible structure (page 40).

21. 3-(4'-Bromo-2',3',5',6'-tetrafluorophenyl)-2-oxa-3-azabicyclo [2.2.2]-5-octene

A solution of 1.0 gm (0.0039 mole) of 4-nitrosotetrafluorobromobenzene in 50 ml of methylene chloride was treated with 3.0 ml (2.5 gm, 0.032 mole) of 1,3-cyclohexadiene (Aldrich Chemical Company). The solution turned from deep blue-green to colorless immediately. The solvent was evaporated under vacuum to yield 1.20 gm (0.0036 mole, 92%) of the adduct, mp 101-103°C.

Anal. Calcd. for $C_{12}H_8F_4BrNO$: C, 42.63; H, 2.39; N, 4.14; Br, 23.64
Found: C, 42.65; H, 2.30; N, 4.32; Br, 24.07.

The infrared spectrum illustrated by Figure A-15 and the H' nuclear magnetic resonance spectrum by Figure 8 confirm the structural assignment. The latter illustration shows a multiplet centered at 3.38 τ which is due to the protons on the double bond, while the broad peaks at 5.25 τ and 5.70 τ are assigned to the bridgehead protons. An A_2B_2 multiplet with the appearance of an AB quartet gives peaks at 8.60 τ, 8.43 τ, 7.78 τ and 7.63 τ due to protons on the saturated carbon atoms.

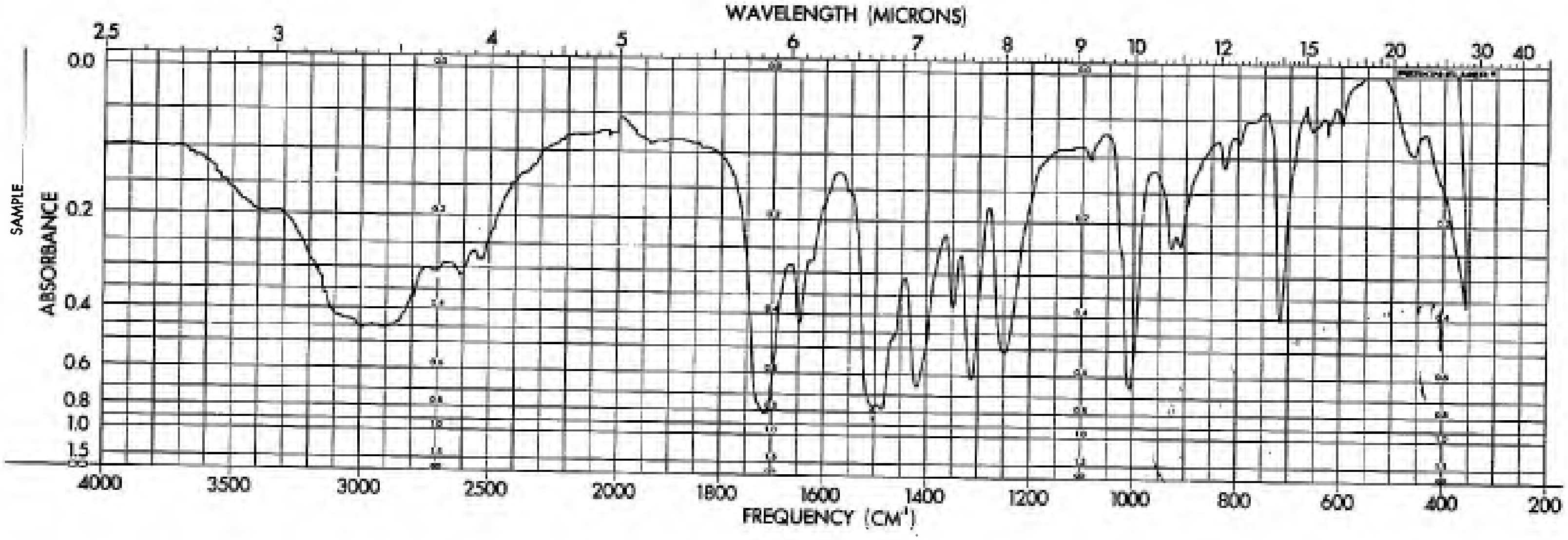
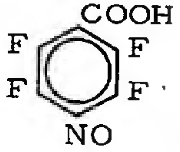


Figure A-14. Infrared Spectrum of Unknown Compound Produced During Synthesis of



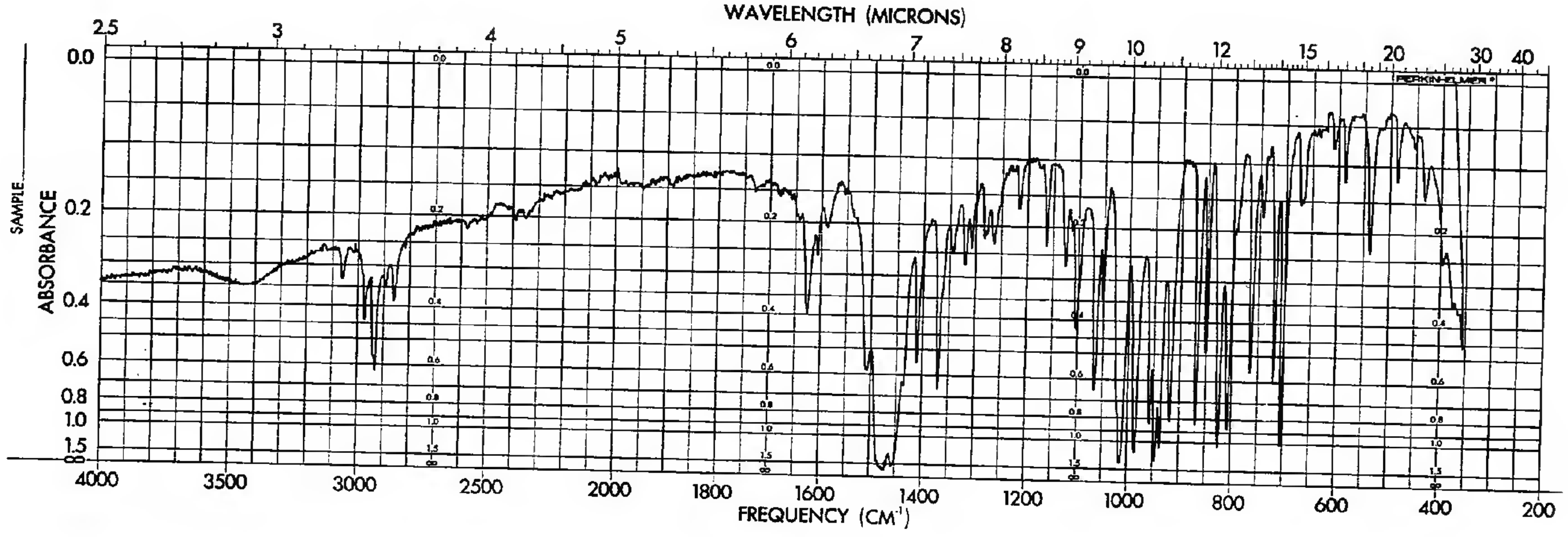
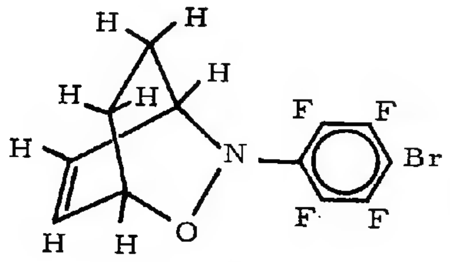


Figure A-15. Infrared Spectrum of



22. 3-Pentafluorophenyl-2-oxa-3-azabicyclo [2.2.2.] -5-octene

Pentafluoronitrosobenzene was allowed to react with 1,3-cyclohexadiene as above to give a 90.5% yield of the Diels-Alder adduct, mp 67.5-69°C.

<u>Anal</u>. Calcd. for $C_{12}H_8F_5NO$: C, 52.00; H, 2.91; N, 5.05
Found: C, 52.30; H, 2.99; N, 4.93.

The H' NMR spectrum of this compound is identical to that of the analogous bromo-compound and the infrared spectrum (Figure A-16) is also quite similar.

23. 3-(4-Carboxy-2',3',5',6'-tetrafluorophenyl)-2-oxa-3-azabicyclo [2.2.2.] -5-octene

4-Nitrosotetrafluorobenzoic acid was allowed to react with 1,3-cyclohexadiene as above to give an 86% yield of the Diels-Alder adduct, mp 174-176°C (dec.).

<u>Anal</u>. Calcd. for $C_{13}H_9F_4NO_3$: C, 51.49; H, 2.99; N, 4.62
Found: C, 50.89; H, 3.07; N, 4.53.

The infrared spectrum (Figure A-17) was very similar to those of the analogous bromo- and fluorine compounds. The NMR spectrum was not obtained because of the lack of a suitable solvent.

B. NITROSO POLYMERS

1. Suspension Polymerization

These polymerizations were conducted in 30 ml glass ampoules to which were charged 15 ml of saturated lithium bromide solution (53 gm LiBr/100 gm H_2O) and 0.5 gm of magnesium carbonate. The ampoule contents were then degassed by the freeze-thaw method and equimolar quantities of CF_3NO and C_2F_4 were charged into the ampoules by means of a volume-calibrated vacuum manifold. The total monomer charge ranged from two to four grams for most experiments. In some instances where as much as 16 gm of monomers were charged, the ampoule size and the amounts of other ingredients were proportionately increased. The ampoules were sealed under vacuum at liquid nitrogen temperature (-196°C) and placed in a shaker assembly contained in a freezer chest maintained at -25°C. After agitating for 20 hours, the ampoules were opened and the polymeric products separated by centrifugation. The polymers were then washed three times with distilled water to remove lithium bromide,

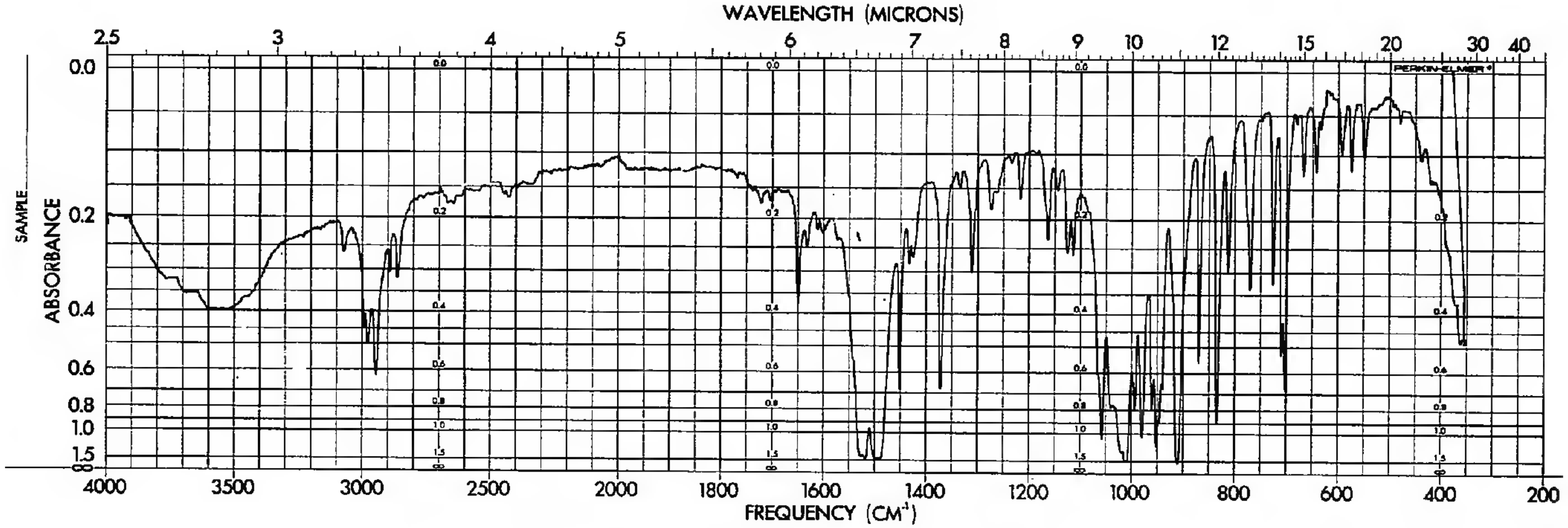
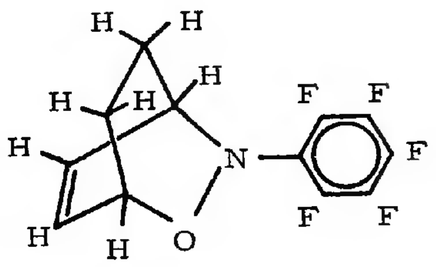


Figure A-16. Infrared Spectrum of



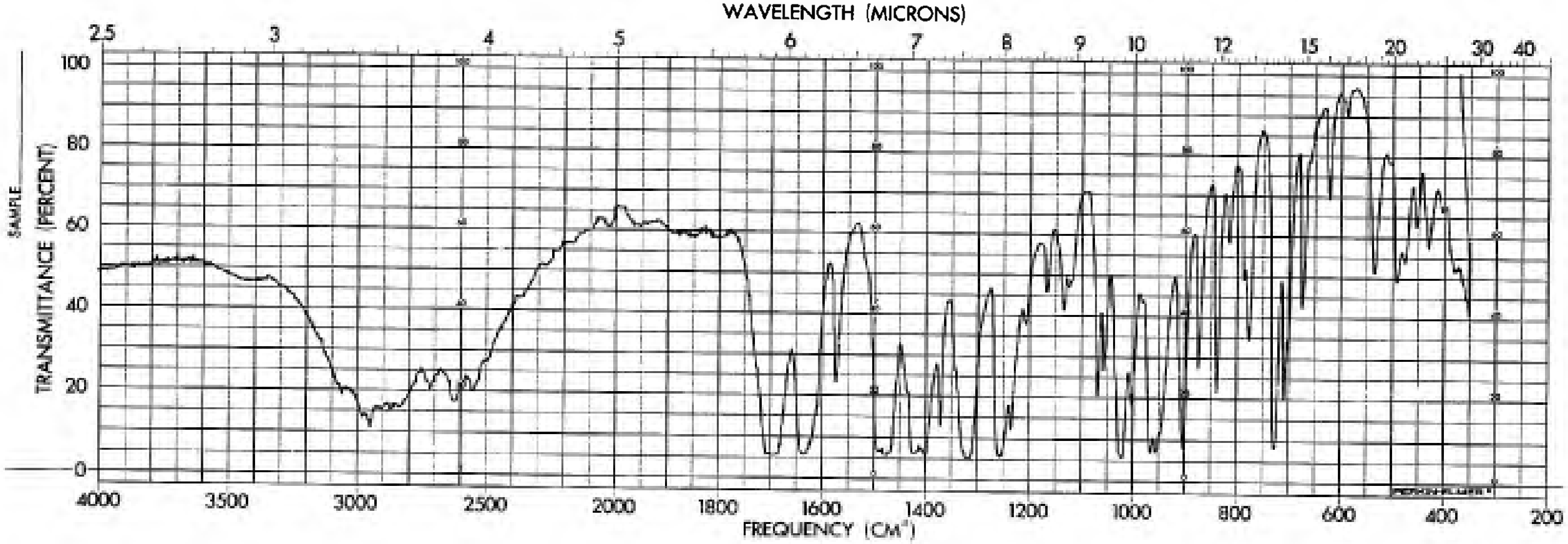
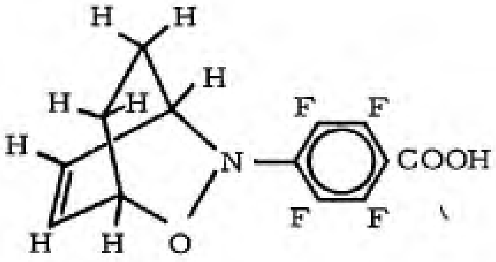


Figure A-17. Infrared Spectrum of



treated with concentrated hydrochloric acid until cessation of gassing indicated all magnesium carbonates had reacted and finally washed with water to remove the acid and water soluble salts. In addition to the CF_3NO/C_2F_4 copolymer, the $CF_3NO/C_2F_4/C_2F_3H$ terpolymer was prepared by this technique. The infrared spectrum of this terpolymer is reproduced as Figure A-18.

2. Bulk Polymerizations

Bulk polymerizations were also conducted in sealed Pyrex ampoules. The monomers were charged in equimolar ratios to the evacuated ampoule by means of the volume calibrated vacuum manifold. The ampoule was sealed under vacuum at -196°C and placed in a freezer chest at -65°C for 30 days. Unreacted monomers and low molecular weight by-products were removed by vacuum treatment for several hours.

3. Solution Polymerizations

These polymerizations were also conducted in sealed Pyrex ampoules. For terpolymerizations the termonomer was generally a non-volatile compound which was added to the solvent first and both were degassed by the freeze-thaw method. The gaseous monomers, CF_3NO and C_2F_4, were then charged to the ampoule by means of the volume calibrated manifold and the ampoule was sealed under vacuum at -196°C. The ampoule was placed in a shaking or rotating device and allowed to warm up to room temperature or other polymerization temperature while the ampoule contents were being agitated. Without agitation during the warm-up period, overpressures and ampoule ruptures occurred. Solution polymerizations were conducted at -25°C to 25°C and at these temperatures were usually precipitated from solution which was freed of traces of solvent by treatment under vacuum at 75°C. In addition to the CF_3NO/C_2F_4 copolymer, $CF_3NO/ONC_6F_4COOH/C_2F_4$, $CF_3NO/ON(CF_2)_3COOH/C_2F_4$ and $CF_3NO/C_2F_4/CH_2{=}CHCOOH$ terpolymers were prepared by this technique. The infrared spectra of these terpolymers are reproduced as Figures A-19, A-20, and A-21, respectively.

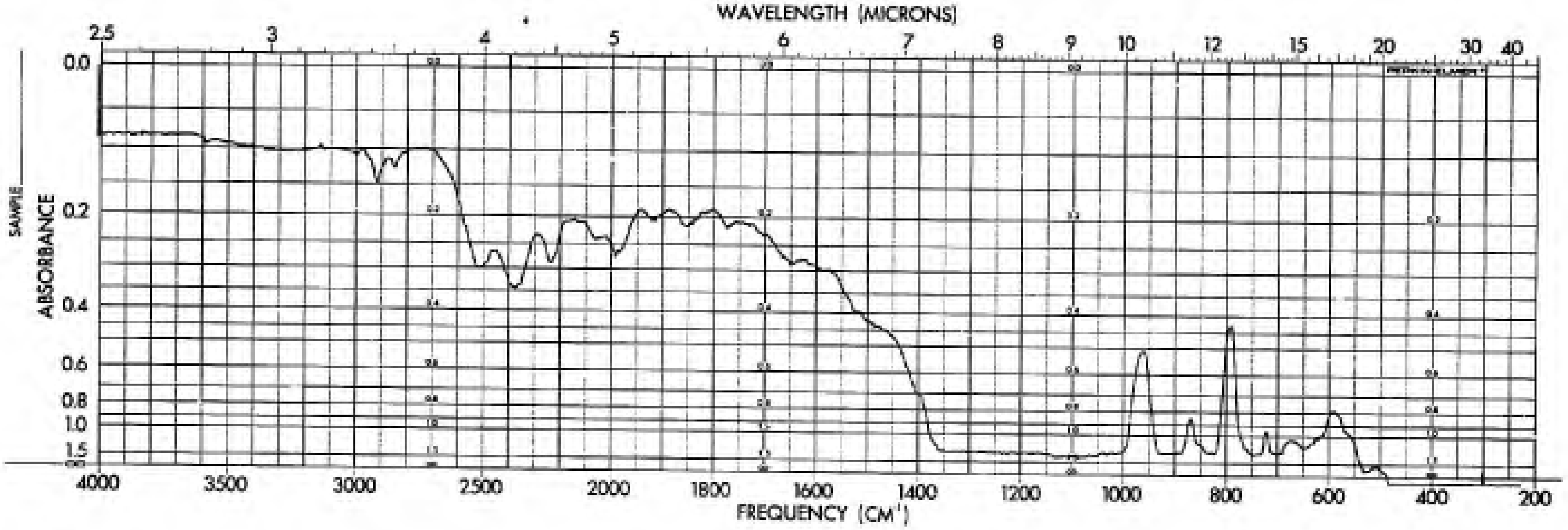


Figure A-18. Infrared Spectrum of $CF_3NO/C_2F_4/C_2F_3H$ Terpolymer

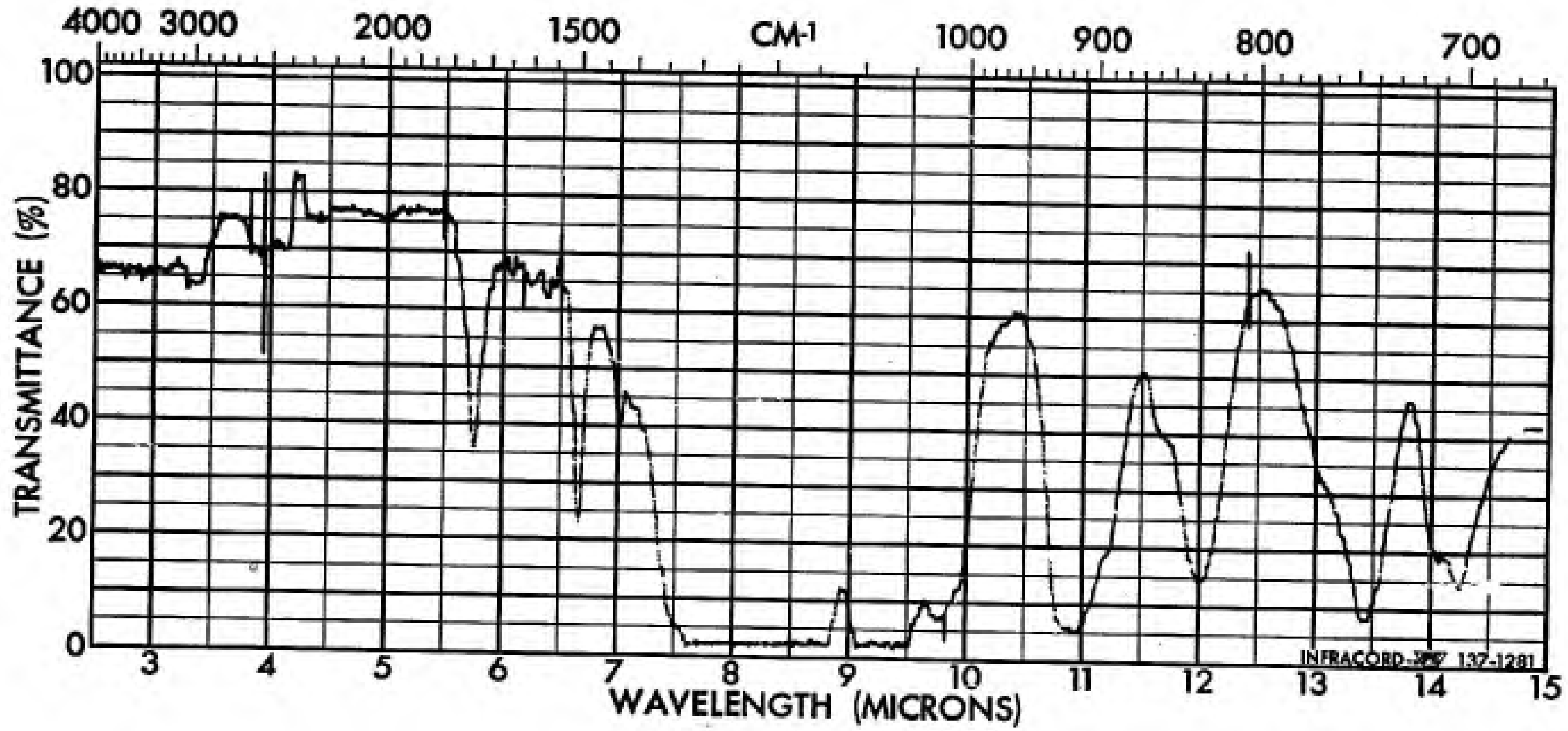


Figure A-19. Infrared Spectrum of $CF_3NO/C_2F_4/ONC_6F_4COOH$ Terpolymer

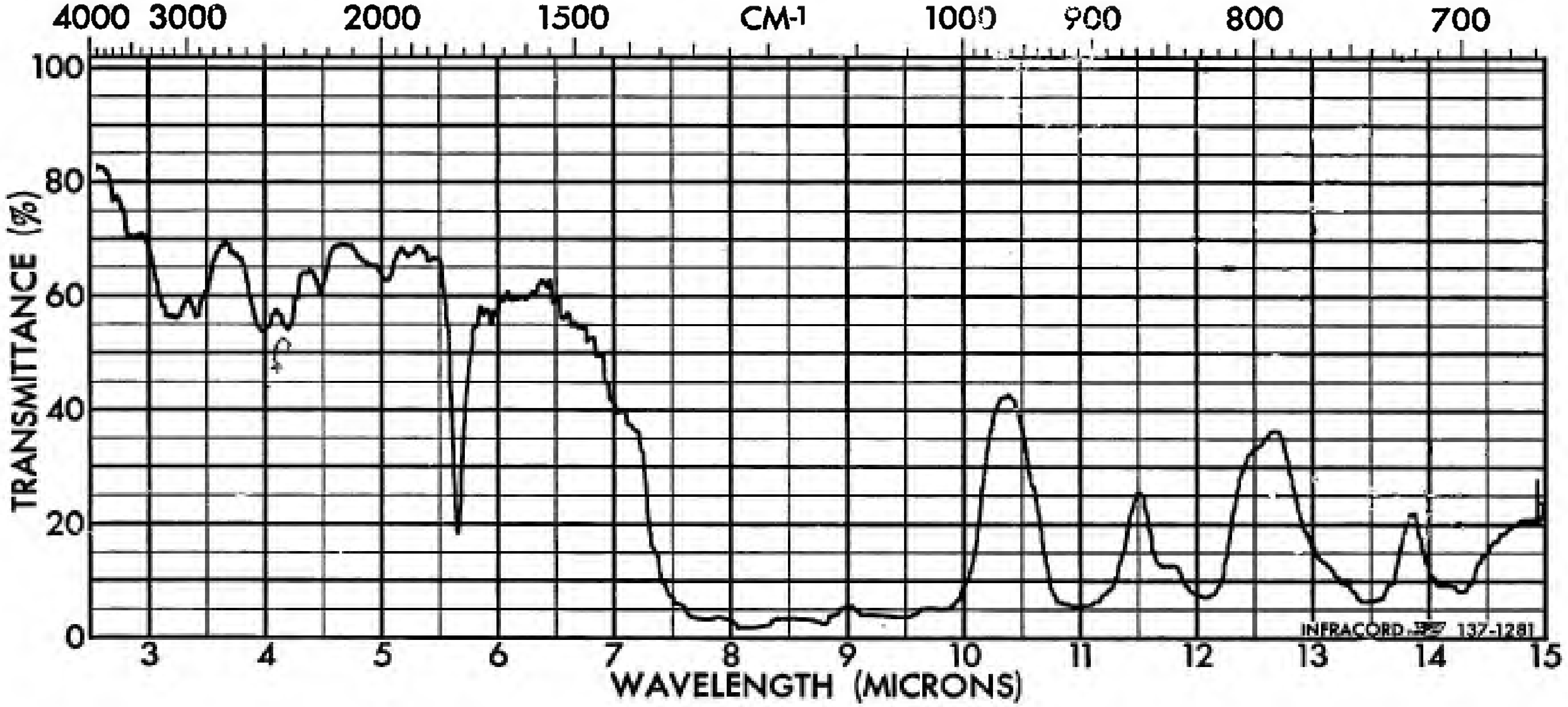


Figure A-20. Infrared Spectrum of $CF_3NO/ON(CF_2)_3COOH/C_2F_4$ Terpolymer

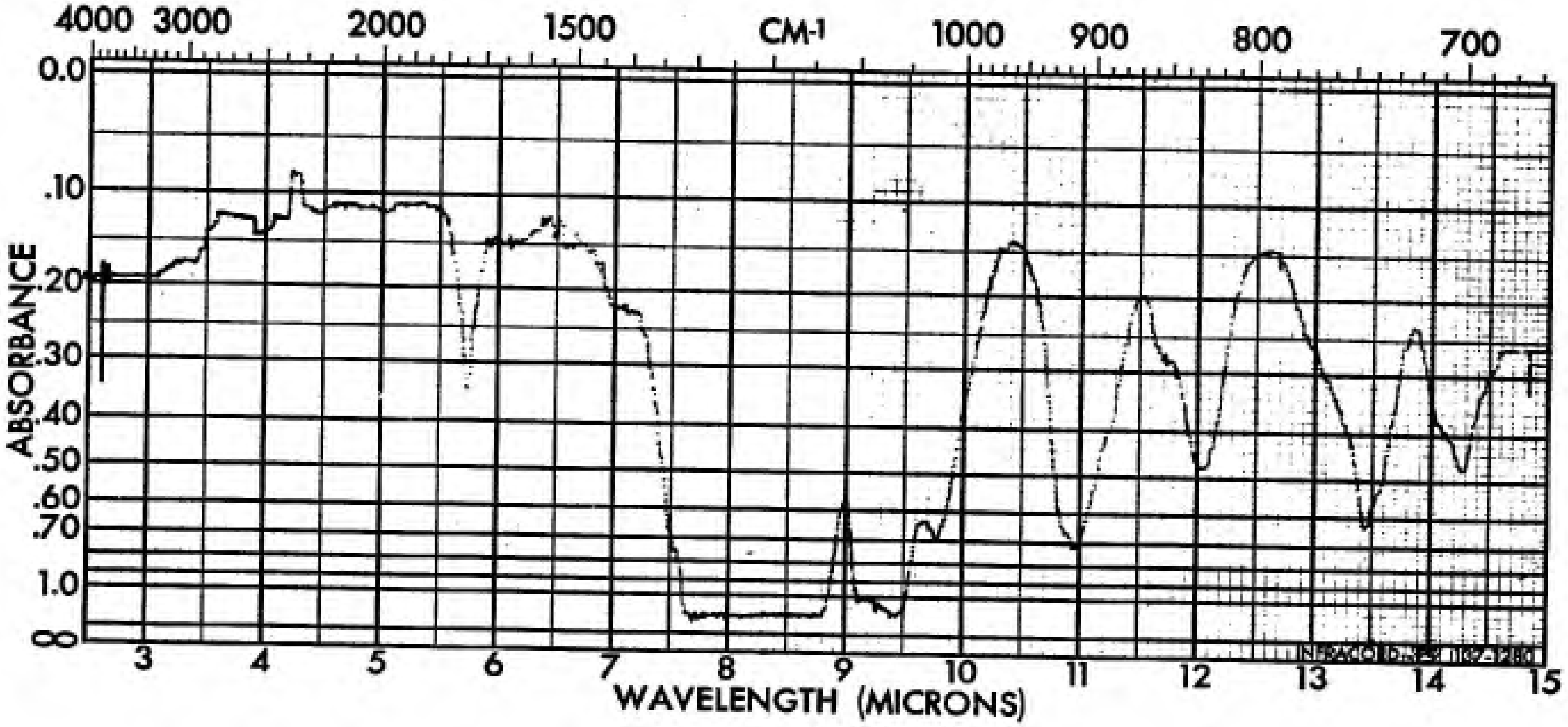


Figure A-21. Infrared Spectrum of $CF_3NO/C_2F_4/CH_2{=}CHCOOH$ Terpolymer

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