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DIRECT FLUORINATION OF ORGANIC COMPOUNDS

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NOTICE

DIRECT FLUORINATION OF
ORGANIC COMPOUNDS

DR. JOHN L. MARGRAVE
Principal Investigator

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FOREWORD

This is the report of research on the direct fluorination of a variety of organic compounds and materials. This research was performed for the United States Air Force Systems Command under Wright-Patterson Air Force Base Contract No. F33615-71-C-1043 during the period October 1, 1970, through September 30, 1971, in the laboratories of Dr. John L. Margrave, Professor of Chemistry and Chairman of the Department of Chemistry, William Marsh Rice University, Houston, Texas. In addition to Professor Margrave, the Principal Investigator, the following members of his research group contributed significantly to the project:

Dr. R. B. Badachhape, Research Associate
Dr. A. P. Conroy, Research Associate
Dr. J. L. Wang, Research Associate
Mr. F. D. Catrett, Research Assistant

The Project Engineer was Dr. Christ Tamborski, (AFML/LNP) Polymer Branch, Nonmetallic Materials Division.

This research was supported by the Air Force Materials Laboratory - Laboratory Director's Funds.

This technical report has been reviewed and is approved.

R. L. Van Deusen

R. L. VAN DEUSEN
Chief, Polymer Branch
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ABSTRACT

The following report contains the results of the work performed on the direct fluorination of a variety of organic compounds and materials. The majority of the compounds studied were acids or acid derivatives such as esters or salts of acids. The compounds studied included: ortho-toluic acid, meta-toluic acid, para-toluic acid, sodium acetate, diglycolic acid, diphenyl ether, 2-ethoxyethylacetate, 3-oxoglutaric acid, 2-oxoglutaric acid, methoxyacetic acid, methoxyphenoxyacetic acid, diethyl carbonate, malonic acid, adipic acid. These materials have been fluorinated at low concentrations of fluorine and at a variety of temperatures varying from room temperature to -78°C. Invariably with extremely low fluorine concentrations, the resulting products contained very little fluorinated material as evidenced by their infrared spectra. Under longer reaction times and or higher fluorine concentrations, the materials tended to be degraded into low molecular weight volatiles such as CO_2 and CF_4. In some instances complete charring of starting material was observed. Polyethylene has been surface fluorinated and the kinetics of the process have been studied from 25 to 50°C. The rate was determined as indicated by weight gain as a function of time. The rate constants for each temperature and the activation energy of the process are reported. Natural rubber samples were surface treated with fluorine and appear to survive acceptably with a subsequent lowering of surface energy. Matrix isolation studies of organic molecules in fluorine matrices are also reported. The species studied were methane, ethane, ethylene, acetylene, and formic acid. It was found that fluorine molecules at 4-15 K behaved essentially like an inert substrate, but fluorine atoms, prepared *in situ* by photolysis, are very reactive and lead to various fluorinated derivatives.

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SECTION I

INTRODUCTION

It is well known that organic substances, especially hydrocarbons under extreme conditions are susceptible to unwanted reactions such as oxidative and thermal degradation. The replacement of hydrogen by fluorine in many of these compounds enhances the chemical resistance towards oxidation or thermal degradation (1-7). In the past, many techniques for the fluorination of organic compounds have been used (8). These include: a) reaction with elemental fluorine (9-12), b) fluorination by high valency oxidative metallic fluorides such as AgF_2, CoF_3, PbF_4, and MnF_3 (13-15), c) use of hydrogen fluoride as an addition, substitution or catalytic agent (16,17), d) electrochemical fluorinations (18,19) and e) gas phase jet fluorinations (20,21).

Previously, use of elemental fluorine as a fluorinating agent for the preparation of perfluoro-analogues of hydrocarbons has not been very successful and most previous attempts were accompanied by explosions or by charring. Almost all of the work reported has been carried out in the gaseous or liquid phase with yields in most cases being low. Recent experiments in this laboratory (22) have indicated that solid organic substances can be fluorinated to give high yields of perfluoro materials by the use of solid reactants with very dilute concentrations of fluorine as well as a suitable heat sink for removing excess heat of reaction, the La-Mar Process. This process has shown promising results. For example, such compounds as anthracene, tetracene, pentacene, naphthalene, coronene, ovalene and decacyclene have been successfully converted into the perfluorinated derivatives (23).

Aliphatic hydrocarbons also have been converted to their perfluorinated analogues in high yields. Organic compounds containing functional groups have been successfully fluorinated with less decomposition than previously reported and solid polymeric materials can also be successfully fluorinated.

With this as a first step, the possibility of preparation of perfluoro compounds containing functional groups such as alcohols, acids, amides, aldehydes, esters, etc., from solid starting materials is apparent and a wide field of research using this fluorination technique needs to be explored.

The aim of this contract was to investigate the feasibility of preparing perfluoroorganic compounds from their hydrocarbon analogues. These materials after fluorination hopefully would contain the same functional groups as in the starting material. At the same time the replacement of hydrogen by fluorine should enhance the resistivity to oxidation and thermal degradation. The materials to be fluorinated were to include:

1. Pure organic compounds selected from aliphatic straight-chain and branched chain hydrocarbons, aromatic and polynuclear hydrocarbons, heterocyclic species, selected functional compounds, e.g., acids, alcohols, ethers, esters, ketones, aldehydes, amines, and acid anhydrides.

2. Selected species which could be useful as monomeric building blocks

for polymers or co-polymers. These species could serve as model compounds for establishing properties and providing basic data for the chemical design of new polymer systems. In particular, solid monomers selected from unsaturated hydrocarbons, unsaturated esters and ethers, solid dicarboxylic acids, diamines, dialcohols, and dinitriles were to be investigated.

3. Selected known polymers which would be more useful in the perfluorinated form with enhanced chemical, oxidative, and thermal stability were investigated. In particular, polymeric samples of various molecular weights and other unique chemical and physical forms were to be fluorinated as powders in an attempt to completely fluorinate the chemical system. In addition, known polymers in other physical form than powders, e.g., films, fibers and irregularly shaped elastomeric materials were to be partially surface fluorinated in order to obtain a fluorocarbon protective coating on bulk polymer substrates.

4. The selection of the above three classes of materials was the result of mutually agreed consultation between the principal investigator, Professor J. L. Margrave and the AFML project engineer.

5. The direct fluorination of polyethylene films was studied to try to find means of controlling the physical properties of the fluorinated film. Fluorinations were carried out at various temperatures from 25 to 50°C. The fluorine was introduced at atmospheric pressures and was undiluted. No scorching or burning was noted on any of the samples. The rate of fluorination varied from 4.13×10^{-4} mg/cm^2/min at 25° to 10.12×10^{-4} mg/cm^2 min at 50°. The activation energy was calculated to be 15.90 Kcal/mole.

Subsequent discussion with the project director during the course of the contract, indicated a need to stress the attempted synthesis of perfluoro poly-functional ether monomers. These would be used by the Air Force Materials Laboratory for the preparation of thermally and oxidatively stable materials ranging in properties from fluids to elastomers.

SECTION II

DIRECT FLUORINATION OF ORGANIC MOLECULES

1. Experimental

Reactions carried out under the contract included the following general types:

a. Solid materials $\xrightarrow{F_2}$ Solid products

b. Solid reactants $\xrightarrow{F_2}$ Volatile products

c. Liquid reactants $\xrightarrow{F_2}$ Liquid and volatile products

d. Bomb (solids) $\xrightarrow{F_2}$ Products

e. Kinetics of polyethylene fluorination.

f. Matrix isolation of small molecules in pure F_2-matrices.

2. Apparatus

a and b. The apparatus for the fluorination of solid starting materials was as follows. A 1" I.D. nickel tube was flanged at each end to facilitate placing and removal of samples. Fluorine, purchased from Allied Chemicals was passed through a NaF trap prior to use. Flow rates of fluorine were regulated by a monel Hastings Raydist Mass Flowmeter, Model LP-50. All gas carrying lines were of thick-walled copper tubing. All fluorine regulating valves were monel. Prior to entering the reactor a gas mixing chamber was in line to premix the appropriate diluent gas. All samples were placed in a nickel boat. The system was purged before and after passing fluorine. The reactor could be operated from $-78^{\circ}C$ to any higher temperatures as required. The outlet of the reactor was connected to traps which could be held at any desired temperature in order to trap possible volatiles. After the traps any excess fluorine was destroyed by passing through a charcoal trap.

c. The liquid reactor was designed as follows. A 1" O.D. stainless steel tube was closed at one end and flanged at the other end. The top flange contained the inlet tube which extended almost to the bottom of the reactor. The outlet tube was also connected to the top flange. The reactor was rotated by a chain drive mechanism to facilitate stirring. All other features of a and b were the same.

d. For sealed bomb reactions, a monel, Parr bomb Model 251A10D was used. The reactor was loaded and then evacuated. A pressure-vacuum gauge was attached to the bomb. The bomb was loaded with the desired amount of fluorine. The bomb could be attached directly to a vacuum system, a gas chromatograph, or mass spectrograph.

e. Measurement of a variety of parameters was utilized in order to obtain as much kinetic information as possible regarding the reaction. The methods of study included: (1) Measurement of the weight increase of a thin film of polyethylene as a function of time of fluorination. The film was of known surface area and thickness and was weighed prior to fluorination. The temperature of fluorination could also be varied. The reaction has been carried out to date at room temperature and 50°C on a number of samples. (2) The monitoring of a variety of infrared frequencies with respect to the intensity of the band and the time of fluorination. These fluorinations were carried out under similar conditions to the weight increase samples except the samples were removed after various lengths of time and were suspended in the reactor by a nickel wire. The Pyrex spring was not used in these runs. (3) Total chemical analyses were obtained for the fluorinated polyethylene sheets which were used for the infrared studies.

f. The matrix trapping apparatus and general procedure were very similar to those described elsewhere (24,25), and only the modifications new to this work are described. Fluorine was deposited on a Cu mirror simultaneously with a small amount of a reactive component (Figure 1). The reactive component was brought in through an independent stainless steel inlet line to avoid premature mixing and gas-phase reactions. Molecular beams of organic molecules, such as CH_4, C_2H_6, C_2H_4, C_2H_2, and HCOOH with pressures of 10^{-4} atm or less, were cocondensed, with an excess ($\sim 10^4$) of F_2 at temperatures of 5 to 20 K.

Infrared absorption spectra were recorded by reflection off the Cu mirror substrate utilizing a Beckmann IR-9 spectrometer. The spectral region scanned extended from 400-4000 cm^{-1}. The optical system for photolysis consisted of an air-cooled medium-pressure 110 watt mercury short arc lamp and a quartz focusing lens.

Most of the gases used for this work were of high purity and were used without further purification. Formic acid (Baker and Adamson), C. P. Grade, was 98-100% pure. The fluorine used was supplied by the Matheson Co. (98% purity, typical) and was passed through a sodium fluoride trap and a liquid nitrogen trap prior to use.

Most of the chemicals used were supplied by Eastman Kodak. Infrared spectra were recorded on a Beckmann IR-8. Mass spectral measurements were made on a Bendix T.O.F. Mass Spectrometer. A Hewlett Packard 700 gas chromatograph was used for gas and liquid sample separations. A Varian 5660 nmr was utilized.

3. Results

a. The Reaction of Fluorine with o-Toluic Acid.

1 g of o-toluic acid was placed in a nickel boat which was then placed in a 1" nickel reactor. The system was purged for 0.5 hours by passing dry nitrogen. Then fluorine was carefully introduced at 2 cc/min along with nitrogen at 50 cc/min. The flow of nitrogen gas was progressively decreased over about an hour and thereafter pure fluorine gas was passed for several hours. After this the flow of F_2 gas was cut off, the system was again purged with dry nitrogen for an hour and the product removed from the reaction chamber. The product was a white solid powder. This crude material showed

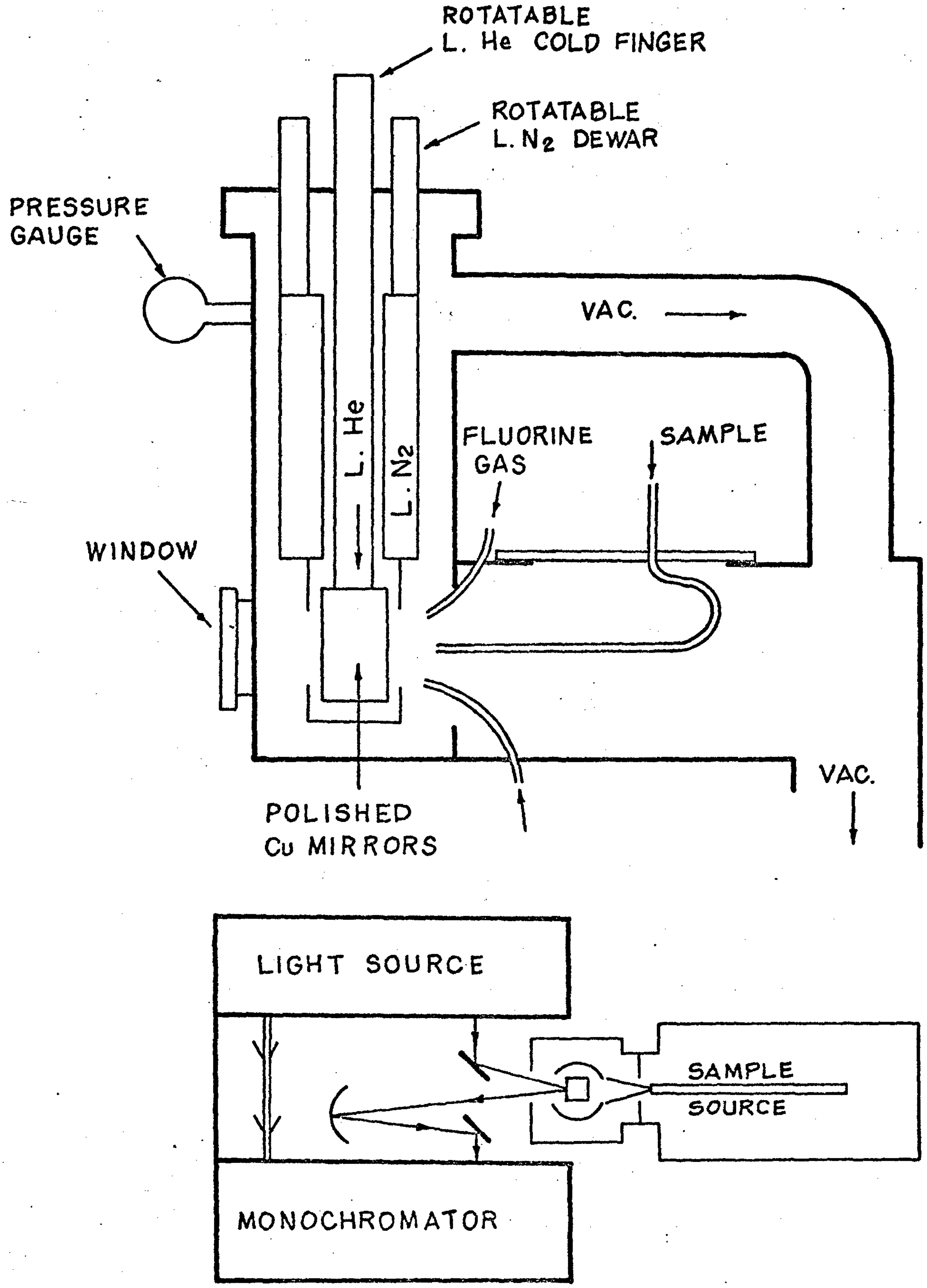


Figure 1.

Matrix Isolation Apparatus

very broad and intense peaks from 1500-900 cm^{-1} in the IR spectrum, indicating the presence of C-F stretching frequencies. There was no evidence of C-H stretching modes present in the material. A weak, broad peak was also observed in the region of 1650-1900 cm^{-1}. This is in the region of C=O stretching vibrations for fluorinated carbonyl groups.

Attempts to further purify the material by traditional crystallization from organic solvents were unsuccessful as evidenced by the lack of a parent peak in the mass spectrum, as well as by the presence of peaks at higher masses than the expected parent peak. The mass spectrometer indicated the existence of fragments that could be assigned to perfluorinated species. Some of the observed peaks also could be assigned to oxygen containing fragments. This material softened and melted over a range of temperatures from 105 to 140°C indicating that the product was not a pure compound. Attempts to separate this material by sublimation and gas chromatography into pure compounds have been unsuccessful.

b. The Reaction of Fluorine with m-Toluic Acid.

1 gram of m-toluic acid was placed in a nickel boat and then placed in a nickel reactor. The system was purged with dry nitrogen for 0.5 hours. Then, a mixture of F_2:N_2 of 2 cc/25 cc was passed over the sample for 48 hours. The F_2 was stopped and the system purged for 1 hour. The product was a white solid. This material, as in the fluorinated o-toluic acid, exhibited the broad intense C-F stretching frequencies in the 900-1500 cm^{-1}. The C-H stretching frequency was absent. The carbonyl region showed a weak and broad peak in the 1650-1900 cm^{-1} range. Attempts to purify the material by crystallization and sublimation were unsuccessful as evidenced by continued broad infrared spectra, long melting ranges and virtually identical mass spectra.

c. The Reaction of p-Toluic Acid and Fluorine.

(1) In a typical run, one gram of p-toluic acid was placed in a nickel boat in the 1" reactor and the system was flushed for one half hour with dry nitrogen. Then fluorine was carefully introduced at 3 cc/min along with nitrogen at 30 cc/min. The flow of N_2 was progressively decreased over a period of 2-3 hours, after which pure fluorine was passed for 72 hours. The fluorine was stopped and the reactor flushed for 0.5 hours. This crude material had a melting range of 95-125°C. The infrared spectrum showed a lack of C-H stretches, very broad and intense peaks in the 1500-1000 cm^{-1} range indicating the presence of C-F stretching frequencies. A very weak broad peak was observed in the 1650-1900 cm^{-1}. This corresponds to a carbonyl region but the broadness and weak intensity suggests multiple carbonyl containing species. This might be explained by a residual amount of C=O linkages remaining in a polymeric and highly crosslinked material. The broad range for the MP and higher m/e peaks than a theoretical fluorocarbon parent for such a molecule as $C_6F_{11}COF$, support the above assumption. Subsequent recrystallizations and sublimations failed to increase the purity of the material.

(2) From the above results it was concluded that a shorter reaction time might be necessary. Thus, the following runs were made in the same manner as in a:

(a) $3ccF_2/30ccN_2$ for 2 hours, then $3ccF_2$ for 46 hours.

(b) $3ccF_2/30ccN_2$ for 2 hours, then $3ccF_2$ for 22 hours.

(c) $3ccF_2/30ccN_2$ for 8 hours.

In all cases the carbonyl region became less intense and broader. It appeared that decarboxylation to some extent was occurring. The shorter time reactions, (8 hours and 22 hours) showed starting materials in the infrared and mass spectra as evidenced by C-H peaks. Work-up of the materials was unable to produce any pure fluorinated materials. All appeared to be mixtures of starting materials and crosslinked polymeric materials or just crosslinked highly fluorinated material. In many cases the acid function was lost, probably by decarboxylation.

d. The Reaction of Sodium Acetate and Fluorine.

(1) In a typical experiment, 1 gram of sodium acetate was placed in a nickel boat. This boat was placed in a 12" long nickel reactor which was flushed with dry nitrogen for 0.5 hours. Then fluorine mixed with nitrogen in approximately a 1:25 ratio was passed over the sample for 2 hours. The nitrogen was gradually reduced over an hour's time until pure fluorine was passing over the sample at 2 cc/min. These conditions were maintained for 30 hours more. The fluorine was stopped and the reactor flushed with nitrogen for 0.5 hours.

The material obtained in the boat was a white solid. The material did not melt to 300^o, but HF evolution was noted during heating. The mass spectrum at 100^o showed essentially a background spectrum with a large peak at 20 m/e. The X-ray pattern of the product material was characteristic of sodium bifluoride, $NaHF_2$. The material after heating was also X-rayed and proved to be NaF. The values obtained were compared to known values in Inorganic Index to the Powder Diffraction File. Chemical analysis of the product also confirmed the presence of $NaHF_2$.

(2) During the initial experiments it was difficult to isolate or separate pure products. It appeared that the fluorination was being carried out under very drastic conditions, and, therefore, to understand the process of fluorination and to see whether we could control the degradation reaction at certain levels of fluorination, we have conducted experiments under a variety of new conditions. It is of special interest to see if we can partially fluorinate these compounds. With this in mind, sodium acetate was refluorinated. It was fluorinated with different concentrations of fluorine diluted with dry nitrogen. The dilutions used were with the proportions of fluorine to nitrogen of 1:1, 1:5, and 1:10. With the most dilute concentration (1:10) the reaction product showed no C-F bonds in the infrared absorption spectra. Fluorination with 1:5 and 1:1 mixtures for one hour and two hours duration also showed the absence of C-F bonds in the reaction products. This work led us to collect the gaseous volatile products that are produced during the reaction. Subsequently a system was set up so that the volatile products could be collected at different temperatures. The cold traps were made from copper tubing 3/8". Each trap had two valves at the end so that any one trap could be separated from the system independent of the other.

Finely powdered sodium acetate, about 15 grams, was placed in a nickel boat which was then introduced into the reactor. The outlet of the reactor was connected to a series of traps (U-tubes). The first one contained sodium fluoride to absorb the hydrogen fluoride produced during the reaction. This trap was kept at 0°C (ice water bath). The outlet of this trap was connected to two more traps. Both of these traps were held at -79°C (carbon tetrachloride and dry ice bath). The outlet of the third trap was connected to a trap filled with charcoal to absorb any unreacted fluorine, the outlet of this trap was connected to a drying tube to prevent the absorption of moisture from the atmosphere by these cold traps. The fluorinations were run for 4, 6, and 8 hours. The rates of flow of fluorine were 10, 15, and 20 cc/min respectively. After the reaction time the flow of fluorine was shut off and nitrogen was passed to purge the system and remove any unreacted fluorine from the traps for about two hours. After the purging, the valves were closed and the traps were removed and connected to the mass spectrometer for analysis. The volatile gaseous products from one of the traps were transferred to an IR cell.

The infrared absorption spectrum indicated the presence of a molecule with $>C{=}O$ and $\geqslant C{-}F$ bonds.

The results of one of the six mass spectral runs are reported as typical. All the six runs were essentially identical and indicated the presence of the same species in all these runs. It seems clear that CF_3COOF, as well as other fluoro-<u>organic</u> species resulted from reaction of $NaC_2H_3O_2$ and F_2.

Solids were also found after the reaction, and the major residue was sodium bifluoride, $NaHF_2$.

(3) The reactions were carried out in the 400 ml Parr bomb fitted with a pressure-vacuum gauge and a valve connection for filling and evacuation. In a typical run 0.3 g (.00366 moles) of NaAc were placed in the bomb. The vessel was evacuated for 3 hours. Then, fluorine was admitted at 5 cc/min for 64 min (.01428 moles). The vessel was closed and allowed to stand 24 hours. Initially, the pressure in the reactor was 16" of vacuum and after 24 hours the pressure was 15" vacuum. An infrared spectrum of the volatiles at 10 mm pressure showed the intense bands of CF_4 as being the only species. However, a high pressure spectrum (110 mm) showed the presence of CO_2 to be unmistakably present. No other carbonyl species such as CF_3COF or COF_2 were noted. The mass spectrum confirmed the infrared data. The reaction appears to be:

$$CH_3CO_2Na + 4F_2 \rightarrow CF_4 + CO_2 + 3HF + NaF$$

Thus, it appears that complete fluorination and degradation to unwanted species was the result and shorter reaction times and possibly smaller amounts of fluorine are indicated to be areas of further investigation of this sealed bomb reaction.

e. The Reaction of Adipic Acid with Fluorine.

Adipic acid was finely powdered and a weighed amount was placed in a nickel boat which was then introduced into the nickel reactor. Fluorinations

Table I

Mass Spectrum of ($CH_3COONa + F_2$) Reaction

Mass no.	Probable species
35	OF
36	C_3
44	CO_2
48	C_4 or O_3
50	CF_2
51	CHF_2
54	OF_2
55	C_3F
63	C_2HF_2
73	---
93	C_3F_3
95	$C_2F_2O_2H$
97	CF_3CO
107	$C_4F_3H_2$
116	CF_3COF
118	C_5F_3H
132	$C_2F_4O_2$

of adipic acid have been carried out under a variety of conditions to learn the effects of temperature, time of fluorination, and concentration of fluorine gas on the process. A summary of the various experimental conditions is presented in Table II.

In all the experiments the reaction product was a viscous material (a mixture of liquids and solids) containing some dark material indicative of charring or decomposition. The amount of the dark material increased with the duration of fluorination or with increased concentration of fluorine. Gas chromatography indicated the presence of at least seven different components. The reaction product thus obtained (viscous material) could not be separated into pure components by chromatographic or by standard separation techniques. Attempts to separate the product into pure components by distillation were not very successful. At 58°C some bubbles were observed, but not enough to be collected as a pure component. The rest of the material darkened on further heating. At about 100°C the material became dark brown. An IR of the material indicated the presence of a $>C{=}O$ group, as well as of $\geq C{-}F$ bonds.

f. The Reaction of Malonic Acid with Fluorine.

Malonic acid (1 gram) was placed in a nickel boat which was then introduced into the nickel reactor. The system was flushed with dry nitrogen for 0.5 hours to remove any moisture from the reactor. Then fluorine was allowed to pass at 5 cc/min. The duration of fluorination was 2 hours in the first experiment, 4 hours in the second and 6 hours in the third experiment. After this period the flow of fluorine was cut off and dry nitrogen was allowed to pass to flush the system. After 0.5 hours the product was removed from the reaction chamber. In all the experiments the product was a viscous material (semi-solid mass) indicating a charring of the material. Various tests including the IR spectrum indicated an extremely low level of fluorination.

g. The Reaction of Fluorine with Diglycolic Acid, $HO_2CCH_2OCH_2CO_2H$.

After discussions with the project director, it was decided that some emphasis should be placed on fluorination of (1) mono- and dibasic acid with -O- linkages in the backbone of the molecule, (2) polyphenyl and related ethers, and (3) tertiary amines.

Thus, diglycolic acid was selected as the initial compound to be investigated. 1.1 g of finely powdered diglycolic acid was placed in a nickel boat. The boat was inserted in the reactor. The reactor system was flushed with dry nitrogen for one hour. Down stream from the reactor were two cold traps held at -95°C to collect the volatile species. After flushing, the N_2 flow was shut off and undiluted fluorine was allowed to pass through the reactor at 5 cc/min for 6 hours. After six hours, F_2 was shut off and N_2 was passed at 10 cc/min for an hour to expel the remaining unreacted fluorine from the system. The traps were closed off and isolated from the system. These collected samples were subjected to IR, mass spectrometry and gas chromatography. The solid diglycolic acid after fluorination had become a clear viscous liquid.

The IR spectrum of the viscous liquid which remained in the boat indicated

Table II

Conditions for Fluorinations of Adipic Acid

Experiment	Temperature °C	Rate of flow of fluorine cc/min	Rate of flow of nitrogen cc/min	Time (hours)
A	25	2	---	1
B	25	5	---	1
C	-78	5	---	4
D	-78	3	5	6
E	-78	3	---	6
F	25	8	---	18
G	25	2	10	24
H	25	3	---	24

a weak C-H bond in the 3000 cm^{-1} region, a very broad C-F stretching region from 900-1450 cm^{-1}, three apparent C=O stretching bands at 1600 cm^{-1}, 1695 cm^{-1} and 1855 cm^{-1} were observed. The amount of viscous liquid was very small (< 50 mg).

Room temperature as well as -78° fluorinations were run and the reaction has yielded the same types of products in each case. In the reactor a viscous liquid remained after fluorination and some volatiles were collected at -78° in cold traps downstream. The viscous material left in the reactor was incompletely fluorinated. The infrared spectrum indicated some C-F stretching modes but it also contained intense C-H stretching frequencies as well as unchanged carbonyl frequencies from the starting acid. The material in the reactor was evidently reduced in reactivity by virtue of the formation of the viscous liquid on the surface. This in turn reduced the ability of the fluorine to diffuse into the material and to effect complete fluorination. The presence of large amounts of HF was noted in this liquid. Upon standing in a desiccator, some of the liquid solidified but no change in the infrared of this material could be detected. Attempted separation on a gas chromatograph produced only an extremely broad and unseparated peak.

The volatiles from the reactions were collected at -95°C. These were stripped from the traps and degassed on a standard Pyrex vacuum line. The amount obtained was extremely small. The bulk of the material was a gas which sublimed upon warming from -196°. The gas chromatograph indicated the presence of at least seven species in the volatile fraction. The relative amounts of the peaks as well as the reproducibility of peaks under similar conditions would vary from run to run. The mass spectrum of the material included large peaks for CO_2^+, CF_3OF^+ and $C_2F_5O_3^+$ (Table III). Lowering the ionizing voltage indicated a number of parent species. The fluorinations appear to have degraded much of the starting material into volatile, fragment fluorocarbons and CO_2, although partially fluorinated C_4-species were observed.

h. The Reaction of Fluorine with Diphenyl Ether at -78°.

One of the objectives of the project was to provide a perfluorinated hydrocarbon material containing di-functional groups, and also a $\geqslant$C-O-C$\leqslant$ linkage. From the results of diglycolic acid studies, it is clear that the acid functional group (-COOH) had been changed, (sometimes to a $-\mathrm{C}\lessgtr^{O}_{F}$ group), and it appeared that the $\geqslant$C-O-C$\leqslant$ bond was often cleaved--a mass spectrum of the volatile species collected in the cold traps downstream from the reactor indicated the presence of lower molecular weight fragments. Thus if one would like to have the $\geqslant$C-O-C$\leqslant$ bond in the fluorinated molecule, it seemed necessary to understand the effect of direct fluorination on some simple ether molecules. With this in mind, diphenyl ether was obtained and fluorinated.

A few drops of diphenyl ether were placed in a nickel boat so as to form a thin layer. The weight of this diphenyl ether was found to be 0.3 g. This boat was placed in the nickel reactor. The reactor was then cooled and held at -78°C (dry ice bath) during the fluorination reaction. The system, including the collecting traps which were held at -95°C, was flushed with dry nitrogen for half an hour. Then a 1:10 fluorine-nitrogen gas mixture was passed over the sample for 2.5 hours. The system was then flushed with dry nitrogen to remove any unreacted fluorine and hydrogen fluoride gas from the

Table III

Mass Spectral Studies

Mass no.	Intensity	Possible species
44	s	CO_2
47	s	COF
50	s	CF_2
51	vs	O_2F
66	m	C_4O
67	m	C_4F_2
69	s	CF_3
85	s	CF_3O
86	m	C_4F_2
87	m	C_4F_2H
94	w	$C_2F_2O_2$
97	w	CF_3CO
101	m	CF_3O_2
103	w	C_4OF_2H
106	w	CF_3OF
119	m	C_2F_5
132	w	$C_2F_4O_2$
136	w	$C_4O_3F_2H_2$

reactor, for an hour. The cold traps were closed and removed. The materials collected in these traps were stripped and degassed on a vacuum line. No volatile compounds were found in these traps. The IR spectra of the starting material and the fluorinated material remaining in the boat were almost identical, thereby indicating that apparently no fluorination had occurred. This could be attributed to: (1) too low a concentration of fluorine, (2) too short a reaction time or (3) possibly the reaction temperature was too low. Therefore, an experiment was performed with a higher concentration of fluorine and at room temperature (25°C). The time of reaction was kept constant.

i. The Reaction of Diphenyl Ether with Fluorine at 25°C.

The experimental procedures were identical to those in the above experiment, except that the reactor was held at room temperature (25°C). The concentration of fluorine in this experiment was 1:5 fluorine-nitrogen. The reaction time was again 2.5 hours. The material in the boat was found to be charred--a brown particulate matter was suspended in a clear liquid.

Up to this point direct fluorinations had been carried out mainly on finely divided solid materials, but many of the compounds of interest especially with -O- linkages in the backbone of the molecule were liquids. Hence a reactor for the fluorination of liquid materials was designed and constructed. This reactor was to be used for the fluorination of liquids as well as for solutions or suspensions. Provisions for stirring the liquids or suspensions to be fluorinated have been provided in the design of the reactor. The speed of stirring can also be varied according to the need during the fluorination. The fluorination could be carried out over a wide range of temperatures by simply immersing the reactor in a furnace for high temperature fluorination or in cold baths for low temperature fluorination.

j. Fluorination of 2-Ethoxyethyl Acetate

(1) 2.07 g of 2-ethoxyethyl acetate was placed in the reactor which was flushed with dry nitrogen for one half hour. The reactor was held at room temperature. A fluorine-nitrogen mixture was passed at 5.25 cc/min through the reactor for four hours. After this time the flow of fluorine was cut off. The system was flushed with nitrogen for one hour. The IR of the pure and the fluorinated product were almost alike. However, a broadening was noticed in the C=O region.

(2) 5.6 g of 2-ethoxyethyl acetate were placed in the reactor. Nitrogen was passed through at 25 cc/min. Thereafter an F_2:N_2 mixture of 2:20 was passed for 20 min. The concentration of fluorine was raised to 3:20. The reaction was stopped after 2 hours due to a mechanical problem in the rotation mechanism. The product was a viscous liquid having a pale blue color, most likely due to the copper inlet tube being below the liquid level, which reacted with the HF. The IR spectra of the product showed that the bulk of the material was 2-ethoxyethyl acetate. Some broadening of the C=O was observed, whereas very little if any C-F stretching modes were present.

k. Fluorination of 3-Oxoglutaric Acid.

In a typical run 0.5 g of 3-oxoglutaric acid was placed in the reactor.

The system was flushed with dry nitrogen for one half hour. After which fluorine, diluted with nitrogen in the ratio of 1:10, was passed for 22-1/2 hours. The reaction was carried out at room temperature. After 22-1/2 hours the flow of fluorine was cut off and dry nitrogen allowed to pass through so as to purge the system. The product was mostly volatilized with traces of burned residue.

l. Fluorination of 2-Oxoglutaric Acid.

(1) In the first experiment 0.8 g of 2-oxoglutaric acid were placed in the reactor. It was fluorinated with 1:6 diluted fluorine-nitrogen mixture for 6 hours at room temperature. After the reaction, the product had completely volitilized, primarily as CF_4 and CO_2, as evidenced by the IR spectra and the mass spectrum of the collected volatile species.

(2) In the second experiment 2-oxoglutaric acid was fluorinated with lower concentration of fluorine and for a shorter duration of time. 0.5 g of 2-oxoglutaric acid was fluorinated with 1:8 fluorine-nitrogen mixture. The reaction time was 4 hours. In this experiment too, the products were all volatilized, primarily as CF_4 and CO_2 as evidenced by IR spectra and the mass spectrum of the volatile materials collected.

m. Fluorination of Methoxyacetic Acid.

(1) 3.1 g of methoxyacetic acid were placed in the liquid reactor. The reactor was flushed with nitrogen for 30 min. Then, fluorine at 2 cc/min and nitrogen at 25 cc/min were passed through the reactor. For 30 min the fluorine flow was raised to 5 cc/min. After another 30 min the reactor was noticeably warmer. It was immersed in an ice water bath. After 3 hours the reaction was stopped and the system was flushed for 30 min. The reactor contained a colorless liquid. The mass spectrum showed only a minimal amount of fluorine present, as well as the absence of C-F stretching mode in the IR spectrum.

(2) The same precedures as in Run No. 1 were used with the exception of increasing the fluorine flow to 10 cc/min. The reactor was cooled to -7 to -10° by an ice-salt water cold bath. At the end of 3 hours no material was found in the reactor, and the gaseous products collected consisted primarily of CF_4 and CO_2 as evidenced by IR and mass spectra.

(3) The concentration of fluorine was decreased to 1:10 (F_2 at 3 cc/min + N_2 at 30 cc/min). The reactor was at $-45^{\circ}C$ by means of an acetonitrile-liquid nitrogen slush bath. The time of reaction was 3-1/2 hours. A liquid product was obtained. The IR and mass spectra were essentially identical to the starting material, indicating absence of fluorine in the product.

n. Fluorination of p-Methoxyphenoxyacetic Acid.

(1) 1.3 g of solid material were placed in a nickel boat. This was inserted into a reactor and flushed with nitrogen for 0.5 hours. Then $F_2:N_2$ in a ratio of 1:2 was passed for 6.75 hours. The product was a pale brown solid. Little, if any, fluorination was shown by infrared studies.

(2) 1.2 g of p-methoxyphenoxyacetic acid was placed in the

reactor and flushed with nitrogen, and then a mixture of F_2N_2 in the ratio of 5:10 was passed for 48 hours. The product was a dark brown solid. IR spectra showed a strong C-F band and marked decrease in the C-H band. The carbonyl region had decreased significantly and the remaining peak was extremely broadened. The weight of the material after reaction was 1.91 g. Attempted purifications of this solid material by recrystallizations and sublimations did not produce any pure identifiable materials. Subsequent infrared and mass spectra showed mixtures of fluoro- and hydrocarbon species but no isolated pure species. The TLC of the product indicated the presence of some starting material and a broad non-resolved region moving more slowly up the plate. Thus, the material appeared to be too little fluorinated on short exposures and apparently moderately crosslinked on long exposures with loss of functionality. It is evident that further extensive investigation of time, dilution and flow rates is necessary for the thorough understanding of the process of fluorination of this material.

o. Reactions of Organic Molecules in Fluorine Matrices.

The fluorine reactions studied, together with those intermediate and final products which could be identified from their infrared spectra, are listed in Table IV. It is likely that this list is incomplete since some products gave infrared spectra which were too broad and weak to be useful. Inspection of Table IV shows that fluorine molecules are very inactive at 15 K. Photolysis to produce F-atoms does cause reaction in most cases. These reactions and their products are discussed in the following section.

(1) <u>CH_4</u>. The infrared spectrum of CH_4 in F_2 indicates that there is negligible interaction between F_2 and CH_4. But upon photolysis, bands belonging to H_3CF appeared whose production was attributed to the reactions:

$$F_2 \xrightarrow{h\nu} 2F\cdot$$

$$CH_4 + F\cdot \longrightarrow \cdot CH_3 + HF$$

$$\cdot CH_3 + F\cdot \longrightarrow FCH_3$$

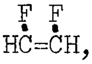
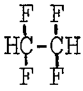
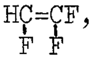
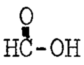
Upon warming this matrix other fluorinated methane molecules were formed, i.e., H_2CF_2, HCF_3 and CF_4.

(2) <u>C_2H_6</u>. The infrared spectrum of C_2H_6 in F_2 indicates that no reaction between the trapped species and the host matrix took place. Upon photolysis bands belonging to $H_2FC\text{-}CH_3$, $F_3C\text{-}CH_3$, $F_3C\text{-}CF_2H$ and $FH_2C\text{-}CH_2F$ were produced along with some other unidentified products.

(3) <u>C_2H_4</u>. Trapping of ethylene in an F_2 matrix provided the only case of apparent reaction between fluorine molecules and a matrix isolated species. Immediately after ethylene was trapped in F_2 the infrared spectrum indicated that only ethylene was present. The fundamental frequencies of ethylene were in essential agreement with those of the gaseous phase literature values except for relative intensities. A second scan of the matrix showed new bands in the C-F stretch region and a reduction of ethylene bands. These new bands increased in intensity upon photolysis but disappeared upon warming the matrix. This seems to indicate that C_2H_4 reacts

Table IV

Fluorine Reactions Studied via Matrix Isolation Technique

Reactions	Products (Identified)	Comments
$CH_4 + F_2$	CH_4	no reaction
$CH_4 + F\cdot$	H_3CF, H_2CF_2, HCF_3, CF_4	photolysis
$C_2H_6 + F_2$	C_2H_6	no reaction
$C_2H_6 + F\cdot$	$FH_2C\text{-}CH_3$, $F_3C\text{-}CH_3$, $F_3C\text{-}CF_2H$, $FH_2C\text{-}CH_2F$	
$C_2H_4 + F_2$	$F_3C\text{-}CH_2F$, unidentified products	time dependent
$C_2H_4 + F\cdot$	C_2F_6	photolysis
$C_2H_2 + F_2$	C_2H_2	no reaction
$C_2H_2 + F\cdot$	$HC{\equiv}CF$,  $H\overset{F}{C}{=}\overset{F}{C}H$,  $H\underset{F}{\overset{F}{C}}\text{-}\underset{F}{\overset{F}{C}}H$, C_2F_6,  $H\underset{F}{C}{=}\underset{F}{C}F$, $F_3C\text{-}CF_2H$	photolysis
$H\overset{O}{C}\text{-}OH + F_2$	 $H\overset{O}{C}\text{-}OH$	premixed at room temperature
$H\overset{O}{C}\text{-}OH + F\cdot$	HF, CO_2, unidentified products	photolysis

with F_2 at ~15 K to form an unstable free radical. Other products were CF_3-CH_2F and C_2F_6.

(4) C_2H_2. After observing the interesting complications in the $C_2H_4 + F_2$ reaction, we were surprised to find that we were able to isolate C_2H_2 in F_2 without any observable reaction. Upon photolysis of the matrix bands belonging to $HC{\equiv}CF$, $HFC{=}CFH$, HCF_2-CF_2H, $HFC{=}CF_2$, F_3C-CF_2H and C_2F_6 were observed.

(5) HCOOH. Both monomeric and dimeric formic acid were isolated in F_2 matrix with no observable reaction.

This work has demonstrated the feasibility of using pure fluorine matrices as a reactive matrix whose reactivity can be simply controlled via photolysis with production of fluorine atoms and followed via observing the changes of concentration of reactants and products. The most important thing was that we were able to observe some of the intermediate products of the reactions and this would enable us to confirm some of the proposed mechanisms of fluorination.

The nature of intermediate products brought about by photolysis and reaction with the above hydrocarbons suggests that most reactions involve stepwise addition of fluorine atoms. The reaction with ethylene is an interesting exception and suggests a very high reactivity to the fluorine molecule in special cases.

SECTION III

DIRECT FLUORINATION OF POLYETHYLENE FILMS

1. Background

The fluorination of a readily moldable polymer such as polyethylene is a desirable method of producing a chemically-resistant surface because of the fluorocarbon coating. The use of a film of uniform thickness and known surface area and weight provides an easily monitored sample for studies of rates of reaction with fluorine. Previous fluorinations of polyethylene film reported by Schonhorn and Hansen (26) and Rudge (27) did not list kinetic data. More recently, Okada and Makuuchi (28) reported the fluorination of a polyethylene powder to be proportional to the 0.28th power of time over a range in temperature from -196 to 80°C. The reaction is generally shown as:

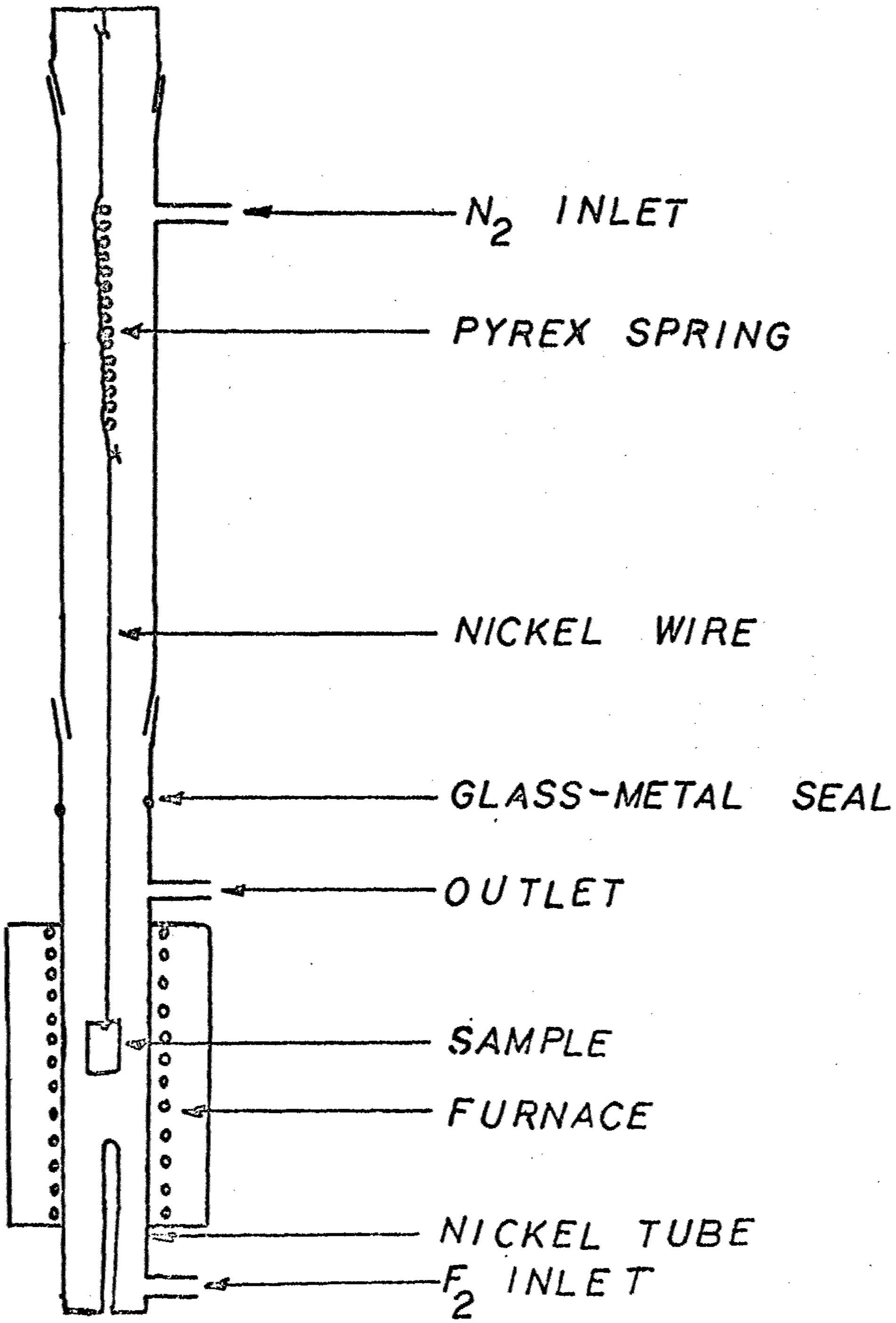
$$\left(CH_2 \right)_n + 2nF_2 \longrightarrow \left(CF_2 \right)_n + 2nHF$$

Completely neglected in this simplistic reaction is chain shortening by production of volatile species such as CF_4 or crosslinking of the carbon backbones to form a perfluorinated interconnected outer layer. The formation of fluorinated free radicals is generally accepted as being responsible for these two types of behavior. Some of the property changes have been evaluated by Schonhorn and Hansen (26). Because more data and information were necessary for a real understanding of the direct fluorination of polymers, especially polyethylene, we undertook this kinetic study of the rate of fluorination.

2. Apparatus and Experimental

Conventional polyethylene film was cut into 1.0 x 2.0 cm rectangles. The thickness of the film was 0.0114 cm (4.5 mil). A hole as small as possible was made in the sample in order to be able to suspend the sample in the reactor by a 2 mil nickel wire. The sample and wire were hung from a Pyrex spring. The spring constant was determined prior to each run. The reaction chamber consisted of a 1" I.D. nickel tube. This tube was connected by a Swagelock union to a 1" Pyrex glass tube. An inlet at the top of the glass section was used for blanketing the Pyrex spring with dry nitrogen to protect it from fluorine attack. Fluorine was admitted through a 1/4" inlet at the very bottom of the nickel section. A common outlet for the nitrogen and fluorine was in the middle of the reactor. The lower nickel section could be heated by a Kanthal wire-wound furnace. A 0.6 cm nickel tube, closed at one end was used as a thermocouple well. It was sealed into the bottom of the reactor and extended to the center of the furnace. A chromel-alumel thermocouple was used to measure the temperature. The extension of the spring was measured by means of a cathetometer capable of measuring changes of 0.01 mm. No temperature corrections for the spring were necessary since it was maintained at constant (room) temperature. Readings were taken at suitable intervals of time. A diagram of the apparatus is shown in Figure 2.

In a typical experiment, the reactor was first flushed with dry nitrogen



FLUORINATION APPARATUS FIG. 2

for two hours. Then, with the reactor heated to the desired constant temperature, the nitrogen through the furnace was stopped and undiluted fluorine at a flow rate of 5 cc/min was admitted into the bottom of the reactor. As reaction progressed, the polyethylene film increased in weight. At the conclusion of the run, the fluorine was shut off and the reactor flushed once again with nitrogen. The fluorine flow was measured by a monel Haystings-Raydist mass flow/meter, Model LP-50. The nitrogen flow was measured with a previously calibrated glass flow meter.

3. Results

Polyethylene films have been successfully fluorinated at various temperatures from 25-50°C. The samples all survived the direct fluorinations with no burning or external evidence of charring. The temperature was not raised above 50° to avoid the possibility of burning. After reaction at all temperatures, the samples became more translucent. They appeared to be somewhat stiffer than the unfluorinated film. The surface coating did not appear to flake off with moderate flexing of the samples. The initial introduction of fluorine over the sample undoubtedly includes a dilution of the fluorine. Thus, data corrections were used to offset the initial time of the start of the reaction. This was chosen to be 30 minutes after the beginning introduction of fluorine. The reactions at all temperatures appeared to be smooth with regular increases of weight per unit time. The reproducibility of the results was checked and was found to be within 10%. The weight increase per unit area with time is illustrated in Figure 3.

The room temperature fluorinations (24.5°) show extreme linearity of weight gain up to the maximum time measured of 10,000 minutes. As the temperature was increased, the linearity of the rate of weight increase was good until longer times were measured ($T \sim 4000$ min). After this a slightly lower rate of reaction was observed. The calculated linear rate constants for the polyethylene film-fluorine reactions are shown in Table V. The k values are listed in mg/cm^2/min units.[1] The activation energy computed by a least squares method for the data gives a value of 15.90 kcal/mole. As shown in the data an increase of temperature from 25-50°C brings about a 2-1/2 fold increase in the rate of fluorination. Further work in this area of fluorination is recommended to find optimum conditions for fluorinations of moldable plastics.

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[1] Figure 3 shows graphically the weight increase per unit time at the different temperatures.

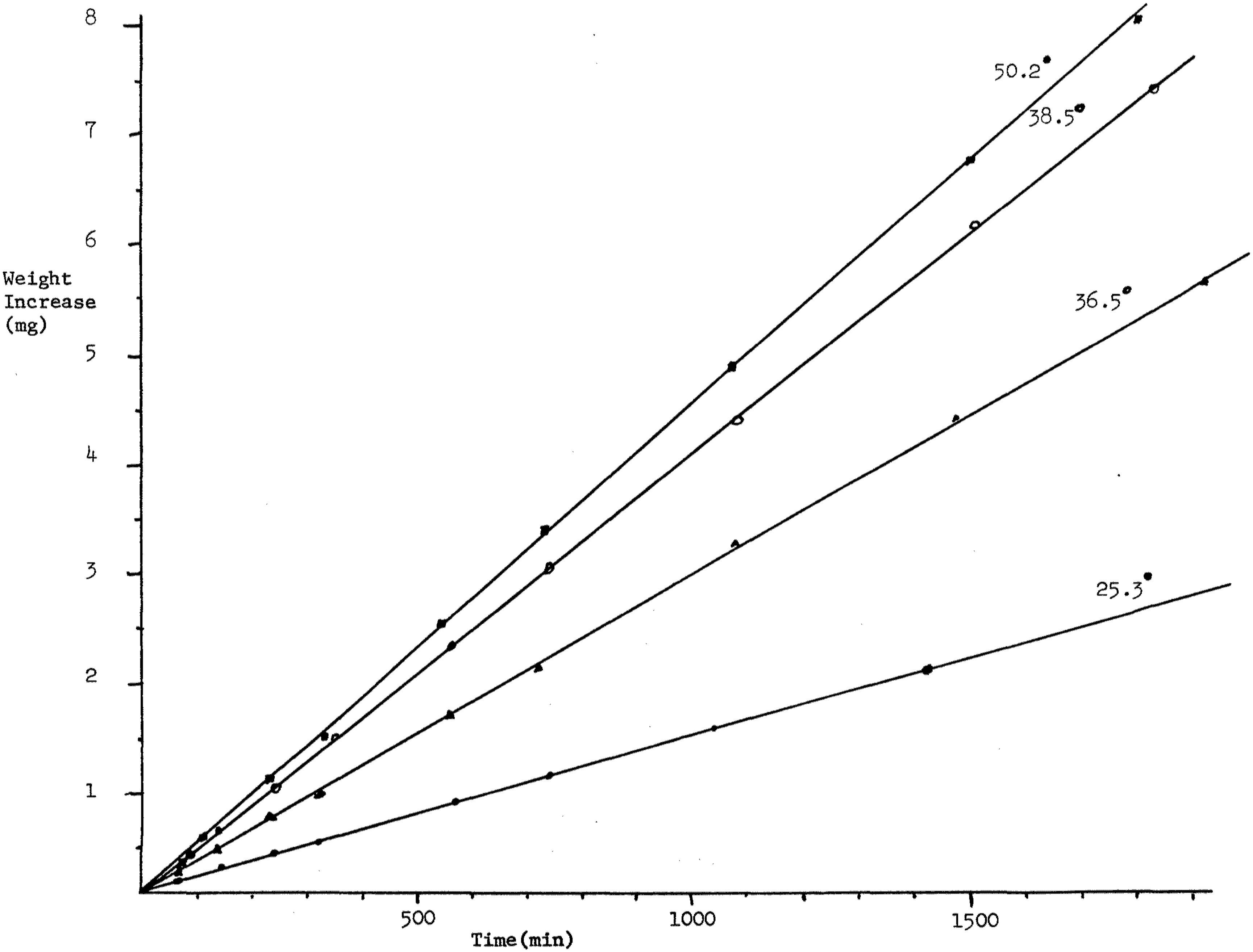

Figure 3. Increase in Weight of Polyethylene Film vs Time

Table V

Rate Constants

T(^{o}C)	K (mg/cm/min) x 10^{-4}
25	4.73
36.5	7.26
38.5	10.23
50	10.12

ΔH_a = 15.9 Kcal

SECTION IV

DISCUSSION

1. General

The main purpose of this work was to investigate the possibility of preparing perfluoro-organic molecules containing difunctional groups, especially with a heteroatom in the backbone of the molecule. This was to be attempted by direct fluorination of specifically chosen starting materials such as dibasic acids, esters, etc., since these materials could then, hopefully, be used as building blocks for perfluorinated polymers. Other areas of study were to include fluorination of polymeric materials and the preparation of perfluoro model compounds. To best fulfill the aim of this work the following categories of compounds and specific materials were selected as follows:

(1) Mono-acids
    a. o-toluic acid
    b. m-toluic acid
    c. p-toluic acid

(2) Dibasic-acids
    a. malonic acid
    b. adipic acid
    c. diglycolic acid

(3) Salts of acids
    a. sodium acetate

(4) Acids with ether linkages
    a. methoxyacetic acid
    b. 2-ethoxyethylacetate
    c. p-methoxyphenoxy acetic acid
    d. 2-oxoglutaric acid
    e. 3-oxoglutaric acid

(5) Ethers
    a. diphenyl ether

(6) Polymers
    a. polyethylene

(7) Small hydrocarbon molecules for reactions in F_2-matrices

2. Problems

From the results of the direct fluorinations of the compounds and materials listed above, it is evident that the direct production of a perfluoro-molecule from the analogous hydrocarbon is not a simple task. The preparation of the perfluoro-materials is hindered by a variety of problems. Some of the problems include:

a. The highly exothermic reaction produced by replacing a C-H bond with a C-F bond. This excess energy can be detrimental by causing possible C-C scission which is followed by either further production of C-F bonds or the crosslinking of the free radicals. This crosslinking mechanism inevitably appeared whenever the starting and final materials were solids. In the cases where volatiles resulted from fluorination, the appearance of lower molecular weight molecules such as CO_2 and CF_4 were in evidence. In some cases, such as when the starting material became charred, both degradation and crosslinking probably occurred. To overcome these difficulties, a variety of procedures were used:

(1) Dilution of the F_2 with dry inert gases such as N_2 or He.

(2) Coupled with the dilution of reactants, a shorter reaction time was utilized. The usual effect of dilution and shortened times was an incompletely fluorinated product.

(3) The temperature of the reactor was lowered by immersing it in a variety of cold baths. In spite of all these controllable variables, the resulting products were all complex mixtures.

b. A second problem is controlling the attack of fluorine on specific sites on the starting molecules. It appeared that the acid functions were being decarboxylated at a faster rate than replacement of C-H by C-F. The subsequent randomness of C-H replacement made it difficult to remove all C-H without unwanted side reactions such as fragmentation, crosslinking, and decarboxylation. Another possible reaction is simply the evolution of O_2.

c. As a result of the previous problems the largest problem was that of sorting and isolating the fluorinated raw product into pure components. Recrystallizations, sublimations, T.L.C., and G.C. methods did not resolve the mixtures into pure components in most of the experiments.

d. Another area of uncertainty is related to the possible side effects of impurities in the fluorine gas supply (mainly O_2, N_2, and HF) or to the negative catalytic effects of reaction products, especially HF. Indirect evidence suggests that O_2 present at low levels can lead to free radicals and to excessive crosslinking. According to a private communication form Dr. Leo A. Wall of the National Bureau of Standards, the thermal stability of some perfluoropolytetrafluoroethylenes prepared by this technique was lowered because of peroxy-impurity sites and/or crosslinking via oxygen.

3. Results

While the large scale conversion of functional hydrocarbons into perfluorinated materials has not yet been wholly successful, a number of positive results have come out of this investigation.

a. It has been shown that contrary to many previous reports, many organic solid and liquid materials can be safely fluorinated.

b. While the resulting materials may not contain the pure perfluorinated end products, this does not preclude the possibility of potential valuable compounds that such a mixture might contain and/or other ones. Thus, it might be possible that partially fluorinated materials could be utilized in a variety of ways. These could include use as fluorocarbon lubricants, as comparatively non-oxidizing additives or possibly as thermal degradation stabilizers. This type of use could arise after limited treatment of the crude material (such as removal of HF adhering to the material).

c. Polymeric materials such as polyethylene and natural rubber have been shown to be amenable to surface fluorination with relative ease. A noticeable decrease in surface energy in the case of the natural rubber lends itself to a variety of useful applications. The polyethylene too showed a regular increase in the degree of fluorination with time and the kinetics could be followed quite nicely. This treatment also improves the surface properties of the polyethylene with respect to solvent resistance. This treatment is especially interesting in that plastic materials can be given chemical resistance after being molded, an advantage over the inert but difficult-to-mold Teflon and similar polymers.

d. The matrix isolation work has demonstrated the feasibility of using pure fluorine as a reactive matrix. The reactivity can simply be controlled by photolysis with production of F atoms and followed by observing the changes of concentration of reactants and products. The most important thing is that one can observe some of the intermediate products of the reactions and, thus, elucidate the mechanism(s) of fluorination. The nature of the intermediates produced by photolysis indicates that most fluorination reactions involve stepwise addition of F atoms.

4. Summary

In summary, direct fluorination techniques would appear to have a great potential for the synthesis of organic molecules, although charring, fragmentation, crosslinking and impurity effects may lead to poor yields and undesirable products. The variation of reaction conditions, especially of temperature, would appear to be important in future investigations. The production of fluorocarbon coatings on polyethylene, polypropylene, natural rubber and similar materials leads to an unusual number of properties including low surface energy and chemical inertness. The fluorination of organic species with functional groups is, apparently, hard to control yet small yields of perfluorospecies are indicated. Partially fluorinated species are also produced and it is interesting to note the report of preparing 5-fluorouracil by direct fluorination is ~64% yield (29). Direct fluorination techniques will have a significant impact on fluoro-organic chemistry in this decade!

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13. ABSTRACT

This report contains results on the direct fluorination of a variety of organic compounds and materials. The compounds studied included: ortho-toluic acid, meta-toluic acid, para-toluic acid, sodium acetate, diglycolic acid, diphenyl ether, 2-ethoxyethylacetate, 3-oxoglutaric acid, 2-oxoglutaric acid, methoxyacetic acid. These materials have been fluorinated at low concentrations of fluorine and at a variety of temperatures. Invariably with extremely low fluorine concentrations, the resulting products contained very little fluorinated material. Under extreme conditions the materials tended to degrade. Polyethylene has been surface fluorinated and the kinetics of the process have been studied. The rate was determined as indicated by weight gain as a function of time. Natural rubber samples were surface treated with fluorine and appear to survive acceptably. Matrix isolation studies of organic molecules in fluorine matrices are also reported. The species studied were methane, ethane, ethylene, acetylene, and formic acid. It was found that fluorine atoms, prepared <u>in situ</u> by photolysis, lead to various fluorinated derivatives.

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