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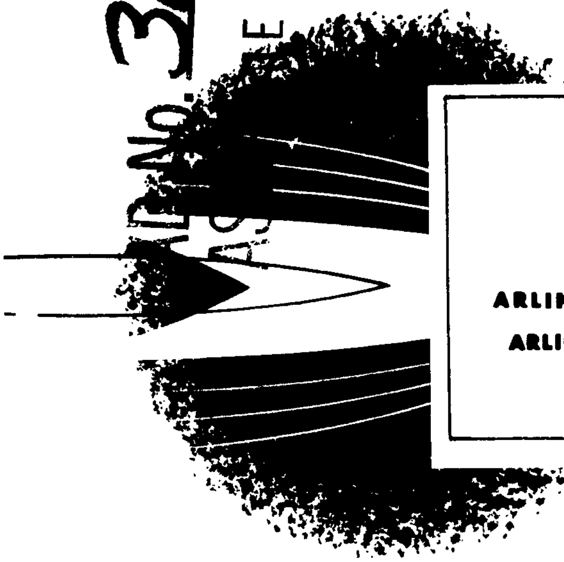

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RESEARCH IN NITROPOLYMERS AND THEIR APPLICATION TO SOLID PROPELLANTS

Contract Nonr-2655(00)

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Chemical Division

Aerojet-General CORPORATION
AZUSA, CALIFORNIA — THE GENERAL TIRE — SACRAMENTO, CALIFORNIA
A SUBSIDIARY OF THE GENERAL TIRE & RUBBER COMPANY

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15 July 1960

Report No. 0235-01-7
(Quarterly)

RESEARCH IN NITROPOLYMERS AND THEIR APPLICATION TO SOLID PROPELLANTS

Contract Nonr 2655(00)

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AEROJET-GENERAL CORPORATION
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ABSTRACT

The nuclear-magnetic-resonance spectrum of the product of the reaction of tetrafluorohydrazine with the sodium salt of dinitroethane was consistent with the structure N,N-difluoroamino-1,1-dinitroethane contaminated by 1,1-dinitroethane. The amount of this impurity indicated was consistent with carbon-hydrogen analysis. Removal of the contaminant by chromatography reduced the impact stability to below 1 cm/2 kg.

The reaction of the sodium salt of 1,1-dinitrobutane with tetrafluorohydrazine gave a product which appeared to be N,N-difluoro-1-amino-1,1-dinitrobutane.

The reaction of sodium 2-propanenitronate with tetrafluorohydrazine under several experimental conditions gave 2,3-dinitro-2,3-dimethylbutane as the principal product; 2-(difluoroamino)-2-nitropropane was not isolated.

Salts of the following nitro compounds reacted with tetrafluorohydrazine, although the products were not identified: 2,2-dinitroethanol, 1-chloro-1-nitroethane, 1-nitroethane, and butyl nitramine. The sodium salt of nitroform did not appear to react with tetrafluorohydrazine.

The direct fluorination of the potassium salt of butylnitramine in aqueous solution gave N-fluorobutylnitramine.

The fluorination of dipotassium perchlorylamide resulted in the uptake of approximately 2 moles of fluorine per mole of salt.

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CONTRACT FULFILLMENT STATEMENT

This quarterly report is submitted in partial fulfillment of Contract Nonr 2655(00).

I. INTRODUCTION

The objective of this work is to develop new methods for preparing fluoronitro compounds and other high-energy materials, and to evaluate these materials for military applications.

II. TECHNICAL PROGRESS

A. REACTION OF TETRAFLUOROHYDRAZINE WITH NITRONATE SALTS (K. Baum)

1. Discussion

A study of the reaction of nitronate salts with tetrafluorohydrazine was initiated during the previous report period.* The reaction of the sodium salt of 1,1-dinitroethane with tetrafluorohydrazine in methanol gave a liquid which was distilled at 32 to 33°C/0.5 mm and had an impact stability of 5 cm/2 kg. The infrared spectrum contained peaks in the NF region at 9.8, 10.55, and 11.5 microns (μ), and the material rapidly oxidized potassium iodide reagent.

Subsequently, the reaction was repeated and an identical product was obtained. The cryoscopic molecular weight in benzene was found to be 168, which is consistent with the compound difluoroamino-1,1-dinitroethane (mol wt 171).

The proton nuclear-magnetic-resonance (NMR) spectrum of this adduct showed singlets at +90 cps (2.25 ppm) and +26 cps (0.65 ppm) and a doublet at +113 cps (2.82 ppm), using water as the standard. The area ratio of the latter bands, approximately 1 to 3, and the splitting of the 113-cps band support the assignment of these two bands to 1,1-dinitroethane, which must account for 24

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*See Aerojet-General Report 0235-01-6, 18 April 1960, p. 2 (Confidential).

mole% of the sample according to the relative areas of the 90- and 113-cps bands. The lower field of the singlet methyl band agrees with the structure of N,N-difluoroamino-1,1-dinitroethane.

The presence of 1,1-dinitroethane is also consistent with the carbon-hydrogen analysis of the adduct, although the nitrogen and fluorine analyses cannot be rationalized. However, difficulty was encountered in analyzing known NF compounds for these elements.

Analysis (%): Calculated for $C_2H_3N_3O_4F_2$: C, 14.04; H, 1.75; N, 24.56; F, 22.20. Calculated for 76 mole% of $C_2H_3N_3O_4F_2$, 24 mole% of $C_2H_4N_2O_4$: C, 15.7; H, 2.04; N, 25.2; F, 18.2. Found: C, 16.14; H, 1.86; N, 28.90, F, 6.4.

In order to remove the 1,1-dinitroethane, this sample was chromatographed on neutral alumina, using methylene chloride as the elutant. It was found that under these conditions 1,1-dinitroethane was absorbed strongly on the alumina and gave a brilliant yellow color. Using the length of column colored by a sample of pure 1,1-dinitroethane as a rough indication of the amount of 1,1-dinitroethane present in the product yielded results comparable to those of the NMR analysis. The impact stability of the chromatographed product was below 1 cm/2 kg (RDX = 30 to 35 cm), although that of the impure material, containing 25 mole% (17.5 wt%) of 1,1-dinitroethane, was 5 cm/2 kg. There is thus a strong possibility that the sensitivity of this class of compounds might be modified by slight changes of structure, or by the addition of desensitizers.

One method by which the stability might be increased is the use of a longer alkyl side-chain. The synthesis of 1,1-dinitrobutane was therefore carried out by the oxidative nitration of 1-nitrobutane.* The sodium salt of 1,1-dinitrobutane was then treated with tetrafluorohydrazine for 24 hours, using methanol as the solvent. A product was obtained which was distilled at 65 to 67°C/1.5 mm. This material, with an impact stability of about 20 cm/2 kg (charring only), contained some unreacted starting material, as indicated by the

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*Aerojet-General Report 622, 26 June 1952, p. 60 (Confidential).

infrared spectrum. Chromatography on alumina apparently removed this impurity and reduced the impact stability to 8 to 10 cm/2 kg. The product reacted instantly with potassium iodide reagent and showed infrared peaks at 9.8 and 11.2 μ.

Attempts were also made to synthesize NF compounds by the reaction of salts of mononitro compounds with tetrafluorohydrazine. Workers at Rohm & Haas had examined briefly the reaction of sodium 2-propanenitronate with tetrafluorohydrazine in aqueous ethanol and found the coupling product, 2,3-dinitro-2,3-dimethylbutane.* A mechanism involving a one-electron transfer from the nitronate salt was suggested.

This reaction was repeated using methanol as the solvent. A preliminary experiment, using the same reaction conditions that were employed for the addition of tetrafluorohydrazine to salts of gem-dinitro compounds, yielded only 2,3-dinitro-2,3-dimethylbutane. If this product results from a one-electron-transfer mechanism to yield 2-nitropropyl radicals which then couple, it might be possible to trap this free-radical intermediate with tetrafluorohydrazine under suitable experimental conditions. Thus, reducing the salt concentration would slow the coupling reaction, while increasing the pressure of tetrafluorohydrazine would favor the trapping of the free radical.

The reaction was therefore repeated, with the concentration of the salt of 2-nitropropane reduced by a factor of 7 (to 0.15 M) and the pressure of tetrafluorohydrazine increased by a factor of 8 (to 200 psi). No product corresponding to the difluoroamine adduct was isolated, although the solvent (methanol) that was removed by distillation showed some oxidizing power. The yield of coupling product was 50%. An identical experiment using ethanol as the solvent gave a 63% yield of coupling product, as well as a small amount of liquid, bp 63 to 68°C, which showed oxidizing power. Vapor-phase chromatography of this material showed mainly acetone. It is possible that this material

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*Rohm & Haas Report P-58-25, Part II, 25 January 1959, p. 7 (Confidential).

contained a compound, such as the acetone adduct of difluoroamine, which might decompose on the column.

Preliminary studies were made of the reaction of tetrafluorohydrazine with the salts of other nitro compounds. The sodium salt of 2,2-dinitroethanol was prepared in situ by adding an equivalent of sodium methoxide to a solution of 2,2-dinitro-1,3-propanediol in methanol. This salt was treated with tetrafluorohydrazine for 20 hours at ambient temperature; the excess tetrafluorohydrazine was then removed and the solvent was distilled. Methylene chloride was added to the residue and an oil separated. The supernatent solution was then stripped to give another viscous liquid, which showed infrared absorption characteristic of hydroxyl (3 μ), nitro (6.4 μ), and possibly NF (9.8 μ). The infrared spectrum of the methylene-chloride-insoluble material appeared qualitatively similar, although the hydroxyl peak was much weaker than that of the soluble material, and the nitro peak was stronger. The insoluble material bubbled slowly on standing at room temperature, showing instability. An attempt to distill a portion of the soluble fraction led to decomposition. In order to prepare a stable derivative, this alcohol was subsequently treated with paraformaldehyde in the presence of concentrated sulfuric acid. The infrared spectrum of the product no longer showed hydroxyl absorption

The salt of 1-chloro-1-nitroethane produced an oily residue that did not show NF absorption as well as another product that codistilled with methanol. The latter product was concentrated using a Heli-Pak column to remove most of the methanol. The concentrate showed infrared absorption at 9.8 μ.

The salt of 1-nitroethane gave a small amount of liquid, bp 27°C/1 mm, which showed a small peak at 10 μ. The residue showed a strong peak at 10.3 μ and small peaks at 9.7, 9.8, and 11.2 μ.

The salt of butyl nitramine produced a viscous residue which showed infrared absorption characteristic of butyl nitramine, as well as new peaks in the NF range. This product reacted slowly with potassium iodide reagent.

There was no evidence of reaction in one experiment using sodium nitroform as the starting material.

2. Experimental

a. Reaction of 2-Nitropropane with Tetrafluorohydrazine

(1) A 175-ml pressure bottle containing 2.96 g (0.0333 mole) of 2-nitropropane, 0.0333 mole of sodium methoxide, 5 g of tetrafluorohydrazine, and 25 ml of methanol was stored at ambient temperature for 2 days. The gases were then released and 75 ml of methylene chloride was added. The salts were filtered off and the solvent was removed using a semi-micro Heli-Pak column; 2,3-dinitro-2,3-dimethylbutane remained as a residue after this distillation, mp 208°C, after a recrystallization from ether.*

(2) A 175-ml pressure bottle containing a magnetic stirrer was loaded with 2.96 g (0.0333 mole) of 2-nitropropane, 0.0333 mole of sodium methoxide, and 150 ml of methanol. The bottle was connected by means of stainless-steel tubing and a valve to a 75-ml stainless-steel bomb, and the system was evacuated. Tetrafluorohydrazine (10 g) was then condensed into the bomb and was transferred at ambient temperature, with stirring, into the pressure bottle. The pressure rose to 200 psi, but dropped to 100 psi after 2 days. The gases were vented and the methanol was vacuum-distilled through a Heli-Pak column at 34°C/200 mm. Some liquid (20 ml) was collected in the Dry Ice trap during this distillation; the liquid showed oxidizing power to potassium iodide, although redistillation established that it was mainly methanol. The solid residue of the former distillation was slurried with 25 ml of methylene chloride and was filtered, and the precipitate was washed with 10 ml of methylene chloride. The combined washings were stripped to give 1.5 g (0.0085 mole, 50% yield) of 2,3-dinitro-2,3-dimethylbutane, mp 205 to 210°C.

(3) This reaction was repeated with ethanol as the solvent, using sodium ethoxide as the base. After 24 hours, the gases were

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*L. W. Seigle and N. B. Haas, <u>J. Org. Chem.</u>, 5, 100 (1940).

vented and the liquid was distilled through a 1-ft Heli-Pak column. A 0.3-g sample was collected with bp 63 to 68°C, followed by 1.1 g with bp 70 to 72°C. Both fractions oxidized potassium iodide, and the infrared spectra were almost identical, with peaks at 3.0, 3.4, 3.5, 5.9, 6.2, 7.0, 7.3, 7.8, 9.2, 9.6, 11.3, 11.7, and 14.0 μ. A vapor-phase chromatogram indicated mainly acetone, but eight other components, with both higher and lower boiling points than acetone, were also indicated. The remaining ethanol was distilled off, leaving 1.84 g (0.0105 mole, 63% yield) of 2,3-dinitro-2,3-dimethylbutane.

b. Reaction of 1,1-Dinitrobutane with Tetrafluorohydrazine

A pressure bottle containing 4.93 g (0.0333 mole) of 1,1-dinitrobutane, 0.0333 mole of sodium methoxide, and 9 g of tetrafluorohydrazine was kept at ambient temperature for 24 hours. The bottle was then vented and the methanol was distilled off. The residue was stirred with 25 ml of methylene chloride and was filtered. The solvent was removed from the filtrate, leaving an oil, which was then distilled to yield 2 g of liquid, bp 65 to 67°C/ 1.5 mm. This material oxidized potassium iodide solution and had an impact stability on glass cloth of about 20 cm/2 kg, with charring only. The infrared spectrum of this product indicated that 1,1-dinitroethane was present. The chromatographing of this material on a 28 by 2-cm column of neutral alumina, using methylene chloride as the solvent, gave 0.8 g of liquid that appeared, on the basis of the infrared spectrum, to be free of starting material. The impact stability of the chromatographed product was 8 to 10 cm/2 kg.

c. Reaction of Sodium 2,2-Dinitroethanol with Tetrafluorohydrazine

Each of two 175-ml pressure bottles was loaded with 11.06 g (0.0666 mole) of 2,2-dinitro-1,3-propanediol, 75 ml of methanol, 0.0666 mole of sodium methoxide, and 10 g of tetrafluorohydrazine. The solutions were stirred magnetically for 20 hours and the gases were then released. The contents of the bottles were combined, and the methanol was distilled until the volume of solution remaining was about 50 ml. Methylene chloride (100 ml) was added and the precipitate that formed was filtered off. An additional 300 ml of methylene chloride was added, and an emulsion formed which was broken by centrifuging the mixture. A small amount of methanol was added to the precipitate (which consisted of an oil and inorganic material), and the salts were filtered off. After the methanol was removed from the filtrate, 3.9 g of oil remained. This material decomposed after standing at room temperature for several days.

The methylene chloride solution was then stripped to give 11.1 g of oil, which had infrared peaks at 3.0 (s), 3.45 (m), 3.6 (m), 6.35 (s), 6.8 (s), 7.4 (s), 7.6 (s), 8.2-4 (s), 8.8 (s), 9.6 (m), 9.8 (m), and 10.5 (w) μ. This oil oxidized potassium iodide. An attempted vacuum distillation of a portion of this oil caused gas evolution and was discontinued.

An attempt was made to prepare a formal derivative of this alcohol. A solution of 5 g of the above oil in 10 ml of methylene chloride was placed in a 25-ml three-necked flask equipped with a magnetic stirrer, a condenser with a drying tube, and an additional funnel, and was cooled with an ice bath. Concentrated sulfuric acid (5 ml) was added dropwise, with stirring, at a rate slow enough to keep the temperature below 10°C. Paraformaldehyde (0.5 g) was then added, and the mixture was stirred at ambient temperature for 1 hour. The methylene chloride layer was separated, was washed to pH 7 with saturated sodium bicarbonate solution, and was then stripped. The residue was dried at 0.1 mm Hg at ambient temperature. The infrared spectrum of this oil had a strong peak at 6.4 μ and medium peaks at 3.5, 5.8, 6.9, 7.6, 8.4, 8.7, 9.0, 9.6, 10.0, 10.5, 10.9, 11.9, and 12.4 μ. A bulb-to-bulb distillation yielded a few drops, bp 90 to 95°C/0.1 mm.

The methanol removed from the original N_2F_4 reaction mixture by simple distillation had an odor indicating that another product was present. Redistillation of this solvent through a Heli-Pak column yielded a liquid, bp 55 to 56°C/150 mm, which had infrared peaks at 3.0, 6.1, 9.0, 9.8, and 11.0 μ.

d. Reaction of 1-Chloronitroethane with Tetrafluorohydrazine

A pressure bottle containing 3.65 g (0.0333 mole) of 1-chloronitroethane, 50 ml of methanol, 0.0333 mole of sodium methoxide, and 5 g of tetrafluorohydrazine was kept at ambient temperature for 2 days. After the bottle was vented and the solvent was removed, 100 ml of methylene chloride was stirred with the residue. The solution was filtered and stripped of solvent to leave 1.5 g of an orange-colored oil. Redistillation of the original solvent using a Heli-Pak column gave a residue which distilled slightly higher than methanol (bp 34 to 35°C/145 mm). This material oxidized potassium iodide and gave strong infrared absorption at 3.7 μ (OH) and 9.8 μ (NF).

e. Reaction of Nitroethane with Tetrafluorohydrazine

A pressure bottle charged with 2.5 g (0.0333 mole) of nitroethane, 25 ml of methanol, 0.0333 mole of sodium methoxide, and 5 g of tetrafluorohydrazine was kept at ambient temperature for 24 hours. The gases were then released and the methanol was distilled off at 35°C/200 mm, using a semi-micro Heli-Pak column. When a few milliliters of liquid remained in the pot, 75 ml of methylene chloride was added and the inorganic residue was filtered off. The methylene chloride and the remaining methanol were then distilled off, leaving 2.0 g of liquid. This liquid was distilled, bp 26 to 30°C/1 mm, leaving a residue. The distillate gave strong infrared peaks at 6.5, 6.65, 7.24, and 7.53 μ, and only weak absorption at 10 μ in the NF region. The residue absorbed strongly at 6.5, 8.4, 9.0, 10.3, and 11.2 μ.

f. Reaction of Butylnitramine with Tetrafluorohydrazine

A pressure bottle charged with 3.93 g (0.0333 mole) of butylnitramine, 0.0333 mole of sodium methoxide, 25 ml of methanol, and 5 g of tetrafluorohydrazine was kept at ambient temperature for 11 days, during which a white precipitate gradually formed. The bottle was then vented and the precipitate was filtered off. After the methanol was distilled off under vacuum and 50 ml of methylene chloride was added to the residue, a gel formed. The addition of 50 ml of water dissolved the residue. The methylene chloride layer was separated, was dried over sodium sulfate, and was stripped of solvent. The residue, an oil, was heated to 70°C at 0.3 mm Hg in an unsuccessful distillation attempt, and an attempted crystallization from ether was likewise unsuccessful. This oil slowly oxidized potassium iodide reagent, whereas butylnitramine, as a control, did not react. The infrared spectrum contained peaks characteristic of butylnitramine, as well as new peaks at 9.1, 9.6, 9.8, 10.3, and 11.1 µ.

g. Reaction of Nitroform with Tetrafluorohydrazine

A mixture of 5 g (0.033 mole) of nitroform, 0.033 mole of sodium methoxide, 25 ml of methanol, and 5 g of tetrafluorohydrazine in a pressure bottle was kept at ambient temperature for 3 days. The solution remained homogeneous during this period. The bottle was then vented and 75 ml of methylene chloride was added. A yellow salt (apparently sodium nitroform) precipitated and was filtered off. The solvents were distilled off through a Heli-Pak column, leaving a 0.5-g residue of nitroform.

B. DIRECT FLUORINATION OF PRIMARY NITRAMINES (V. Grakauskas)

1. Discussion

It was found previously that the sodium salt of ethylenedinitramine reacted with elementary fluorine in aqueous solution to yield a liquid which was very sensitive to impact. Although the infrared spectrum indicated that this product was N,N'-difluoro-N,N'-dinitroethylenediamine, the sensitivity precluded further investigation.*

In order to obtain a less-sensitive N-fluoronitramine which could be characterized more fully, the potassium salt of butylnitramine was fluorinated under similar conditions. A water-insoluble liquid phase separated during the fluorination. The organic phase was then washed with sodium bicarbonate solution and water, and was distilled at reduced pressure. The infrared

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*Aerojet-General Report 0235-01-5, 15 January 1960, p. 3 (Confidential).

nitro peak was shifted from 6.34 μ for butylnitramine to 6.19 μ for the product. New absorption in the NF region appeared at 9.60, 10.05, and 11.30 μ. The results of elemental analysis also confirmed the structure of N-fluorobutylnitramine.

Analysis (%): Calculated for $C_4H_9N_2FO_2$: C, 35.29; H, 6.66; N, 20.58; F, 13.96. Found: C, 34.39; H, 6.24; N, 21.44; F, 14.30.

The impact stability of this product was 25 cm/2 kg, whereas RDX fires at 30 cm/2 kg on the same tester.

2. Experimental - Preparation of N-Fluoro-n-butylnitramine

A stream of fluorine (2 to 3 liters/hour) diluted with helium (10 liters/hour) was passed at 5 to 7°C, with stirring, into a solution of 11.8 g of n-butylnitramine (0.1 mole) in 200 ml of distilled water containing 0.1 mole of potassium hydroxide. The reaction was continued for 60 to 75 minutes, during which about 3 to 4 liters of fluorine gas was consumed. A pale-yellow oil began to separate from the clear reaction mixture at the beginning of fluorination, and the amount of material gradually increased. At the end of the reaction, the mixture was transferred into a separatory funnel and the organic material (about 13 g) was separated from the aqueous solution. The product was washed first with two 70-ml portions of saturated aqueous sodium bicarbonate and then several times with water. The material was dried over anhydrous sodium sulfate and was filtered, and the clear colorless filtrate was distilled at 40 to 50°C/0.1 to 0.3 mm to yield 10 g of clear liquid, n_D^{25} 1.4040, with an impact sensitivity of 25 cm/2 kg.

C. FLUORINATION OF DIPOTASSIUM PERCHLORYLAMIDE (N. W. Thomas)

1. Discussion

Dipotassium perchlorylamide, K_2NClO_3, was prepared by the method of Engelbrecht and Atzwanger.* A preliminary attempt to fluorinate an

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*A. Engelbrecht and H. Atzwanger, J. Inorg. Nucl. Chem., 2, 348 (1956).

aqueous solution of this material resulted in an uptake of fluorine in an amount which roughly corresponds to 2 moles of fluorine per mole of the salt. However, the products of the reaction have not been established.

The desired product, prechloryldifluoroamine, would be valuable as a liquid oxidizer as well as a chemical intermediate.

2. Experimental

a. Preparation of Dipotassium Perchlorylamide

About 2.9 ml (23 g) of liquid ammonia and 2.7 ml (4.9 g) of perchloryl fluoride were successively condensed in a 5-liter round-bottom flask. This mixture was evaporated and condensed several times and was then allowed to stand overnight at room temperature. No condensible gases remained after this treatment. The solid contents of the flask were treated at room temperature with alcohol saturated with potassium hydroxide until the vapors of ammonia were no longer detected.

The solid was removed by filtration and was dried; the yield was 5.4 g with an impact stability of 74 cm/2 kg (RDX = 36 cm). This crude mixture of KF and K_2NClO_3 was used in the subsequent reaction. It was strongly oxidizing toward acidified potassium iodide solution.

b. Fluorination

Three and one-half grams of the crude KF and K_2NClO_3 mixture was treated with 35 ml of distilled water in a three-necked flask; a solid was present at room temperature. The reaction flask was connected to a trap at -15°C, followed by a tee connected to an infrared gas cell and a -78°C trap that was connected, in turn, to a trap containing potassium iodide solution. The contents of the reaction flask were stirred and cooled to 5°C, and a helium (10-liter/hour) and fluorine (2-liter/hour) gas stream was bubbled through the flask. Assuming the crude salt mixture to be 1:1 $KF:K_2NClO_3$, it was estimated that 18 minutes should elapse before the first signs of fluorine would be evident at the potassium iodide trap; the first signs of fluorine were noted after 20