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FLUORINE GENERATOR SOLID INGREDIENT DEVELOPMENT

FINAL REPORT

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ROCKETDYNE DIVISION
ROCKWELL INTERNATIONAL CORPORATION
6633 CANOGA AVENUE
CANOGA PARK, CALIFORNIA 91304

AUTHOR: ROSS I. WAGNER

September 1975

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AIR FORCE ROCKET PROPULSION LABORATORY
DIRECTOR OF SCIENCE AND TECHNOLOGY
AIR FORCE SYSTEMS COMMAND
EDWARDS, CALIFORNIA 93523

FOREWORD

This final report was prepared by the Pocketdyne Division, Rockwell International Corporation, 6633 Canoga Avenue, Canoga Park, California 91304 for the Air Force Rocket Propulsion Laboratory, Edwards, California 93523 and covers work from 1 July 1974 to 30 June 1975 conducted under Air Force Contract F04611-74-C-0035, Job Order No. 197000HM.

The project monitor was Capt. Ronald E. Channell. This program was conducted by the Exploratory Chemistry Unit of the Energy Systems and Technology Organization, Advanced Programs, with Dr. B. L. Tuffly serving as Program Manager and Dr. Ross I. Wagner as project engineer. Major contributors to the program were Dr. Carl J. Schack (UV process evaluation) and Mr. Richard D. Wilson (metathetical process evaluation and UV process scale-up and synthesis). Dr. Victor H. Dayan was responsible for analyses and Drs. Karl O. Christe, Arthur E. Axworthy, Louis R. Grant and Frederick D. Raniere contributed significantly as consultants.

This effort was sponsored by the Air Force Rocket Propulsion Laboratory, Edwards, CA., the Air Force Weapons Laboratory, Kirtland Air Force Base, New Mexico, and the Naval Surface Weapons Center, Silver Springs, Maryland.

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Francisco Q. Roberto
FRANCISCO Q. ROBERTO, GS-15, Chief
Formulation and Ingredient Section

Robert L. Geisler
ROBERT L. GEISLER, GS-14, Chief
Propellant Development Branch

FOR THE COMMANDER

Charles R. Cooke
CHARLES R. COOKE, Chief
Solid Rocket Division

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An evaluation of two processes for synthesis of NF_4BF_4 was conducted to determine achievable product purity and potential scalability of each. The ultraviolet induced reaction of NF_3, BF_3 and F_2 produced 99-100 mole percent pure NF_4BF_4 at 1 g/hr in silica equipment. Metathesis of thermally prepared $NF_4SbF_6 \cdot x\ SbF_5$ with AgF in anhydrous HF followed by treatment with BF_3 produced 185 g quantities of NF_4BF_4 of 83 mole percent purity which could be raised to 93 mole percent by fractional crystallization. (Continued)

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The UV process was scaled-up to achieve a production rate of 2.90 g/hr of 99 mole percent $NF_4^{\urcorner}BF_4^{\urcorner}$ with an 84 percent conversion of reactants. Although process optimization was not achieved due to insufficient time, approximately 0.32 Kg $NF_4^{\urcorner}BF_4^{\urcorner}$ was produced and delivered to the Air Force.

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SUMMARY

EVALUATION OF ALTERNATE SYNTHESIS TECHNIQUES - PHASE I, TASK 1

Two preparative methods for NF_4BF_4 of substantially different concept were evaluated for achievable product purity and scalability. The two preparative methods evaluated were (1) the UV-induced reaction of NF_3, BF_3 and F_2, and (2) the metathetical conversion of $NF_4SbF_6 \cdot xSbF_5$ to NF_4BF_4.

An evaluation of the UV-induced synthesis of NF_4BF_4 established that high purity (minimum 99 mole percent) material could be prepared on a small scale in a silica reactor at a rate, ~1g/hr during short reaction times, potentially capable of providing the material at a practical production rate. The most important process parameters established during these studies were (1) cryogenic temperatures, (2) high UV intensity, (3) the mode of addition of reactants to maintain exposure to the radiation, and (4) the mole ratios of the reactants.

The metathetical process was evaluated and the maximum purity obtained for the NF_4BF_4 was 93 mole percent. It was established that: (1) TlF was better than AgF as a precipitant for SbF_6^-; (2) NF_4BF_4 prepared using AgF rather than TlF was of higher purity because of the more complete removal of excess metal fluoride in the second step of the process (i.e., formation of $AgBF_4$); (3) Cl^- ion could not be used to remove additional metal fluoride from the product because of incompatibility with NF_4^+; and (4) the major impurity $NF_4SbF_6 \cdot xSbF_5$ was, in fact, less soluble than NF_4BF_4 rendering purification by crystallization unfeasible.

On the basis of these experimental evaluations, the UV process was selected for scale-up.

SYNTHESIS SCALE-UP - PHASE I, TASK 2

A large-scale UV reactor was designed and fabricated using 347 stainless steel and Teflon-gasketed sapphire windows as materials of construction. By use of those conditions established under Task 1, the production rate objective of 80g NF_4BF_4/week of 99 mole percent purity was achieved. This objective was fulfilled even though optimization of the process parameters was not realized.

LARGE-SCALE SYNTHESIS OF NF_4BF_4 - PHASE II

Investigation of the process parameters of the UV process was continued during production of a total of 0.37 kg of NF_4BF_4. Despite the successful preparation and delivery of 0.24 kg of 99 mole percent NF_4BF_4 to the Air Force during this phase, only qualitative data correlating product formation rate with process variables were obtained. This inability to achieve quantitative data was primarily the result of reactor design deficiencies not readily correctable within the contractual time frame. However, evidence was obtained that, under certain conditions, NF_4BF_4 was synthesized at 2.90g/hour with a conversion of 84 percent.

INTRODUCTION

A solid-propellant fluorine generator would have obvious logistic advantages over conventional gas storage or cryogenic liquid supply systems for the fluorine required to operate a C.W. chemical laser based on a DF lasing species. Ideally, a practical solid-propellant fluorine generator requires a compatible oxidizer-fuel-binder combination that provides a completely gaseous exhaust containing only stable, non-reactive, and non-deactivating co-products. A potential system which meets these ideal requirements is that based on the oxidizer NF_4BF_4 in combination with a fluorocarbon fuel binder.

The purpose of the work described herein was to develop a process for the synthesis of high purity (99 mole percent minimum) NF_4BF_4 which would provide sufficient quantity of this oxidizer to permit its evaluation as an ingredient in a solid-propellant fluorine generator. Specific objectives were: (1) to evaluate two synthetic processes for NF_4BF_4 of substantially different concept; (2) to select on the basis of product purity and potential scalability one process and experimentally demonstrate its scalability to the production level of at least 80g/week; and (3) to produce and deliver to the Air Force 0.24 Kg of high purity NF_4BF_4.

Of the four processes for preparation of NF_4BF_4 known at the inception of this work, the two selected for evaluation were: (1) the UV-induced combination of NF_3, BF_3, and F_2 (Ref. 1) and (2) the metathesis of $NF_4SbF_6 \cdot xSbF_5$ (Ref. 2) with $AgHF_2$ (Ref. 3) and treatment of the resulting NF_4HF_2 with BF_3. The UV process was selected on the basis of its high potential for producing directly a high purity product and the assumption that the production rate could be raised from the previously observed milligram quantities to a practical level. The metathetical process was chosen because it represented the most advanced (Ref. 3) preparative method in terms of production rate, and conventional purification techniques might raise the purity to the required level. Of the remaining two processes, γ-irradiation (Ref. 4) and glow discharge (Ref. 5 and 6) both were rejected because of the projected difficulty of scale-up.

DISCUSSION OF RESULTS

UV PROCESS - PHASE I, TASK 1

At the inception of this contract, only one reference to a UV-induced synthesis of NF_4BF_4 was known (Ref. 1). This reaction, which involved UV irradiation of an equimolar mixture of NF_3, F_2 and BF_3, offered a potential means for acquiring pure NF_4BF_4 by a single step process. However, in the single reported experiment on which this synthesis was based, only 1 to 2 mg of product was obtained when the reaction was conducted in a sapphire tube reactor at ~90 psig and ambient temperature. Although this amount of NF_4BF_4 was produced rapidly, further increase in the amount of product did not occur on continued exposure to the UV source. The exceedingly low conversion of the gaseous reactants to NF_4BF_4 was attributed to deposition of solid product on the sapphire reactor walls. This deposit if opaque to UV light might preclude sufficient transmission of light energy required for further reaction.

The major scaleup problem associated with the UV-induced synthesis of NF_4BF_4 appeared to be development of a method by which a UV-transparent window could be kept free of product. Several possible solutions to this problem were considered, and the one that appeared to be the simplest was the use of HF as a solvent for the NF_4BF_4. Since HF is both UV-transparent (Ref. 7) and an excellent solvent for NF_4BF_4 (Ref. 2), it was proposed that its presence in the gaseous reaction mixture would cause the solid coating to deliquesce, drain off, and thereby maintain window UV transparency. With this approach in mind, the first of several reactors was designed, fabricated and used in the small scale UV-induced reactions for the purpose of evaluating this method for the production of pure NF_4BF_4.

UV Reactor Design (Small Scale)

The initial UV reactor consisted of a 8.5-inch Teflon test tube of 195 ml volume to which was attached a 2-inch diameter sapphire window with appropriate attachments for evacuation and gas filling. Before any experiments were conducted in the presence of HF, the experimental conditions required to synthesize

NF_4BF_4 in the new reactor had to be defined. Although conditions were found which produced NF_4BF_4 in this Teflon-sapphire reactor, none of the product was ever found to coat the window. A reactor of similar design in which stainless steel was used in lieu of Teflon was found to give similar results. These results differed from those previously reported by Christe et al. (Ref. 1). Although reactions were investigated under conditions of high pressures and ambient temperature (see Appendix I), such reactions produced no NF_4BF_4. Under the conditions whereby NF_4BF_4 was produced temperatures were lower than ambient and the product was formed away from the window. Hence, experiments using HF were unnecessary and were never attempted.

As the program progressed, it became obvious that the geometry of the reactor was far from optimum, and materials other than Teflon or Kel-F would be needed for construction of the reactor. Under the influence of the UV-derived fluorine atoms, Teflon was severely degraded as evidenced by shrinkage, embrittlement, stress cracking and formation of CF_4. Kel-F appeared to undergo an even more rapid degradation of physical properties with concomitant formation of perfluoroalkyl chlorides.

Since the use of HF was not required to maintain the sapphire window transparency, fused silica was used to construct the second type of reactor. This reactor was a 3-inch diameter bulb fitted with an O-ring joint and Fischer-Porter needle valve for evacuation and introduction of the gaseous reactants. Although surface attack of the silica did occur (Eq. 1), weight loss of the

$$SiO_2 + 2F_2 \rightarrow SiF_4 + O_2 \qquad (1\ )$$

reactor (with a 100 watt UV source) was only about 1 mg/hr and no byproducts were found to contaminate the NF_4BF_4. The lightweight silica bulb allowed gravimetric determination of the extent of reaction to be made conveniently in place of the manometric method which was used with the much heavier Teflon- or stainless-steel sapphire reactors. In addition to the more accurate method of measuring the NF_4BF_4 formation rate, the diameter of the silica bulb allowed the UV source to be placed closer to the temperature-controlled reaction zone. This led to a significant improvement in the formation rate of NF_4BF_4.

The third reactor design provided a further improvement in geometry by incorporating a 3-inch diameter, flat window in the shallow (1-1/4 inch) silica reactor. This permitted the light source to be even closer to the reaction zone, and reflection losses were decreased as well. Both of these factors contributed to additional increases in the NF_4BF_4 formation rates.

Reaction Parameters

A number of variables, not necessarily independent, were considered for study to determine their effect on the rate of formation of NF_4BF_4. They were (1) temperature, (2) UV light intensity, (3) mode of addition of reactants, (4) reactant mole ratios, (5) pressure, (6) catalysts, and (7) use of HF to dissolve NF_4BF_4 coated on the reactor window. Of these only the last was not investigated, since NF_4BF_4 was not found to coat the window as reported in the original UV-initiated synthesis. Selected experiments which illustrate the effect of a given parameter on the NF_4BF_4 formation rate are presented in the tables accompanying the discussion of that parameter. Complete data for each of the eighty-four experiments conducted during the evaluation phase of the UV-induced synthesis of NF_4BF_4 are tabulated in Appendix I.

Effect of Temperature. Because of the obvious economic advantages of an ambient temperature process over one requiring refrigeration, a number of unsuccessful attempts were made to synthesize NF_4BF_4 at ambient temperature by the UV-initiated method. Typical experiments which indicate the effect of temperature on the rate of formation of NF_4BF_4 are listed in Table 1. Unless otherwise noted, comparable conditions were used in the tabulated experiments.

It is apparent from experiments 1, 5 and 12 (which used the same reactor) that as temperature is decreased the formation rate of NF_4BF_4 is increased. This effect is most pronounced at cryogenic temperatures and has been rationalized as the result of stabilization of a reaction intermediate. The dramatic rate increase shown in experiments 36 and 55, when compared with 13 and 14, clearly emphasized the need for cryogenic temperatures, if a high production rate of NF_4BF_4 were to be achieved. The somewhat larger and seemingly anomalous rate observed at -115 C compared with that at -140 C is in reality the effect of intermittent addition of larger amounts of BF_3 (vide infra).

TABLE 1. EFFECT OF TEMPERATURE ON NF_4BF_4 FORMATION RATE

Experiment No.	Reaction Temp., ° C	Photolysis Time, hrs.	Mole Ratio		Pressure Range (during photolysis), mm	Reactor Used(a)	NF_4BF_4 Formation Rate, mg/hr
			BF_3/NF_3	F_2/NF_3			
1	amb.	18	1	1	~650	TS	0
5	-78	10	1	2	700-690	TS	Trace
13(b)	-115	2	3.3	0.9	800-500	SB	3.5
14(b)	ca. -140	2	1.1	0.25	500-350	SB	1.7
12	-186	8	1	2	~250	TS	8
55	-186	2	1	0.83	370-350	SB	34.5
36	-196	2	1	0.5	220-165	SB	33

(a) TS = Teflon-sapphire; SB = silica bulb

(b) Reactants introduced intermittently during photolysis rather than before photolysis as in other experiments (Refer to Appendix I for details).

Effect of UV Intensity. A series of experiments (64 and 39-42, Table 2) was conducted in which the intensity of the UV source was diminished by insertion of stainless steel screens between the light source and the photolysis zone. The percent transmittance of the screens was measured spectrometrically at both 578 µm and 400 µm. The average of the two values (approximately 1 percent difference) was used as the percent transmittance of the screens. The NF_4BF_4 formation rate was not found to be proportional to intensity (percent transmittance) raised to a constant power. The values for n in the equation $R = kI^n$ (where R is rate and I is intensity) were 0.426, 0.561, and 0.720 for screens with 49.5, 36.3, and 33.0 percent transmittance, respectively.

The apparent curvature of the plot of log R vs log I may be only an artifact arising from geometric factors. The three screens used had the following characteristics: 49.5% transmittance (T), 64 mesh, wire diameter (w)/hole width (h) = 0.224; 33.0% T, 35 mesh, w/h = 0.735; and 36.3% T, 150 mesh, w/h = 0.556. The percent transmittance of the screens was measured virtually normal to the plane of the screen by the nearly parallel light beam in the spectrophotometer. In contrast, the UV light irradiating the reaction zone in the photolysis experiments approximated a divergent cone with a apical angle of 60°. The amount of light passing a screen will decrease as the angle of incidence decreases, and for a given angle of incidence will decrease most with thick screens, i.e., when w/h is largest. The observed correlation of the rates of formation of NF_4BF_4 with light intensity (assuming normal incidence) is as expected for the geometries involved. From these considerations, the rate of NF_4BF_4 formation would be expected to increase by a factor somewhat greater than the maximum observed, i.e., $R > kI^{0.426}$.

With all factors other than UV lamp wattage held reasonably constant, the NF_4BF_4 formation rate was almost directly proportional to the power input (Table 2, experiments 67, 69 and 75). The decrease in NF_4BF_4 formation rate with distance between lamp and photolysis zone (Table 2, experiments 61 and 67) more closely approximates that expected from a point source ($\propto 1/d^2$) than from a linear source ($\propto 1/d$).

TABLE 2. EFFECT OF UV INTENSITY ON NF_4BF_4 FORMATION RATE[(a)]

Experiment No.	Pressure Range (during photolysis), mm	Reactor Used[(b)]	Lamp to Condensed Reactant Distance, cm	Percent Transmission	NF_4BF_4 Formation Rate, mg/hr
64	130-70	SB	12	100	30
39	85-50	SB	12	49.5	21.5
40	80-45	SB	12	49.5	23
41	80-55	SB	12	36.3	17
42	80-50	SB	12	33.0	13.5
61	115-70	SF	9[(c)]	100	71
67	210-100	SF	7.5[(c)]	100	110
69	~200	SF	7.5[(c)]	100	1004
75	~175	SF	7.5[(c)]	100	1172

(a) All experiments were conducted at -196 C for 2 hours in the same reactor using a $NF_3/BF_3/F_2$ reactant mole ratio of 1/1/0.17, respectively.

(b) SB = silica bulb; SF = silica flat-windowed reactor (see Appendix I).

(c) Experiments 67 and 61, 100 watt Hanovia (lamp B); experiment 69, 1000 watt G.E., lamp BH6; experiment 75, 1000 watt III lamp BH6-1-B; other experiments, 100w Hanovia (lamp A).

Mode of Addition of Reactants. Three modes of reactant addition were evaluated: (1) addition of all reactants before initiation of photolysis, (2) continuous introduction of reactants during photolysis, and (3) intermittent addition of reactants during photolysis. The photolysis is best conducted at cryogenic temperatures and under these conditions the BF_3 and NF_3 are found almost entirely in the condensed phase, while F_2 is distributed between the condensed and gaseous phases. The rate at which the reactants are introduced, as well as the order of introduction (if not premixed), affects the physical state of the condensed phase. While not all of the parameters were held constant in the experiments listed in Table 3, the range over which these vary is not sufficient to invalidate comparison of NF_4BF_4 formation rates.

The rate of NF_4BF_4 formation is greater when condensation is effected rapidly (2-3 minutes in mode B, Table 3) as can be seen by comparing Experiments 32 and 27. In the latter experiment condensation occurred over a 60 minute period prior to photolysis and the rate of NF_4BF_4 formation was decreased from 27 to 14 mg/hr. However, if the slow condensation is carried out continuously during photolysis (Experiment 29), the rate is increased to 19 mg/hr indicating the beneficial effect of the continuous mode of addition.

Intermittent addition of reagents should combine the best features of both the pre-photolysis and continuous modes in that rapid condensation of each increment would occur and fresh reagents would be added during the photolysis period. Comparison of Experiments 58 (addition before photolysis) and 11 (intermittent addition during photolysis) does not appear to support the hypothesis that intermittent addition is the best mode. However, other experiments conducted at a higher UV intensity (vide infra) do verify the hypothesis, and the apparent anomaly observed here presumably arises because the sequence of reactions leading to NF_4BF_4 is inhibited by swamping with fresh reagents. In the series of experiments of varying photolysis time wherein all reagents were added before photolysis (Experiments 69, 71, 72 and 74), the NF_4BF_4 formation rate decreased drastically with time. The average hourly rate during the last two hours of the three hour photolysis decreased from an initial 1 g/hr rate (during the first 0.25 hr) to less than 20 percent of this value. Intermittent addition of reagents under comparable conditions (Experiment 84) maintained the average NF_4BF_4 formation rate in a 4 hour photolysis at nearly

TABLE 3. EFFECT OF MODE OF ADDITION OF REAGENTS ON NF_4BF_4 FORMATION RATE[(a)]

Experiment No.	Photolysis Time, hrs	Mole Ratio		Mode of Reactant Addition[(b)]	Pressure Range (during photolysis), mm	Reactor Used	UV Lamp Type	Average NF_4BF_4 Formation Rate, mg/hr
		$\frac{BF_3}{NF_3}$	$\frac{F_2}{NF_3}$					
32	2	4.67	0.56	B	200-120	SB	H(A)	27
27	1	4.67	0.56	B[(c)]	350-185	SB	H(A)	14
29	1	4.67	0.56	C	350-190	SB	H(A)	19
58	2	1	0.30	B	180-120	SB	H(A)	37.5
11	3	1	0.29	I	150 ± 20	SB	H(A)	20
69	0.25	1	0.17	B	~200	SF	GE	1004
71	0.5	1	0.33	B	~225	SF	GE	888
72	1	1	0.33	B	200-175	SF	GE	804
74	3	1	0.43	B	500-225	SF	GE	391
84	4	1	0.21	I	~200	SF[(d)]	GE	647

(a) All experiments were run at -196 C.

(b) B, before photolysis; C, continuous during photolysis; and I, intermittent addition.

(c) All reactants were introduced exactly as in Experiment 29 but before photolysis.

(d) Reactor inlet in center of photolysis zone.

double the value of the 3 hour photolysis where reagent addition preceded photolysis. A conversion of 83 percent was observed in Experiment 84 based on the limiting reactant (F_2).

These data suggested that maximization of the NF_4BF_4 formation rate over extended times (as would be required in a production process) would best be accomplished by intermittent addition of reagents to the photolysis zone. Sufficient time should be allowed between additions to permit optimum utilization of the reagents in each increment.

Effect of Reactant Mole Ratios. Equimolar amounts of NF_3, BF_3 and F_2 are required to prepare NF_4BF_4 by the UV-initiated synthesis. However, since the reaction mechanism is unknown, the rate-determining step might be favored by a deviation from the stoichiometric ratio.

From a practical experimental standpoint, sequential condensation of the three gaseous reagents into a reactor at -196 C should proceed from the least volatile to the most volatile, i.e., BF_3, NF_3 and, finally, F_2. Condensation of BF_3 alone, or even when premixed with NF_3, tends to form a rather compact solid mass due to prior liquefaction. However, if the condensation occurs in a fluorine atmosphere, the condensation rate is slowed somewhat so that a porous solid structure results. The structure of the condensed phase appears to affect the NF_4BF_4 formation rate, perhaps, as a result of varying ease of mass transport of the liquid BF_3-NF_3-F_2 solution through the porous solid BF_3.

In Table 4 the relative effects of an excess of one of the three starting materials on the rate of formation of NF_4BF_4 is illustrated. The most detrimental ingredient when in excess was NF_3, which inhibited NF_4BF_4 formation completely. Less drastic in its effect was excess F_2, but much of this reagent is in the gaseous phase. An excess of BF_3 appears either to be without effect or possibly may even increase the rate of NF_4BF_4 formation based on extrapolation from experiments in a different reactor. No directly comparable experiment in the same reactor using a stoichiometric ratio was conducted.

Effect of Pressure. In all of the experiments which were designed to test the effect of pressure on the NF_4BF_4 formation rate, the temperature of necessity had to be above cryogenic levels where NF_4BF_4 formation is extremely inhibited.

TABLE 4. EFFECT OF REAGENT MOLE RATIOS ON NF_4BF_4 FORMATION RATE[(a)]

Experiment No.	Pyrolysis Time, hrs	Mole Ratio		Mode of Reactant Addition	Pressure Range (during photolysis), mm	Average NF_4BF_4 Formation Rate, mg/hr
		$\frac{BF_3}{NF_3}$	$\frac{F_2}{NF_3}$			
23	1	1	7.8	C	~350	14
22	2	1	4.4	C	~350	29.5
20	2.5	0.21	0.21	I[(b)]	200-100	0
21	1.75	4.67	0.67	C	300-250	47

[(a)] All experiments were conducted at -196 C in a 3-inch stainless steel reactor with a 2-inch diameter sapphire window and the same 100 watt UV source.

[(b)] One-third of the total F_2 used was added after 1 hour photolysis.

Since low temperatures have proved to be perhaps the most important requirement for successful NF_4BF_4 synthesis, the pressure range which could be studied is quite limited. Pressure becomes a dependent variable determined by both the temperature and the reactant mole ratio. From the available data, no effect on NF_4BF_4 formation rate can be ascribed to pressure alone.

Effect of Catalysts. In some of the first experiments where Kel-F components were used in the reactors, the formation of small amounts of ClF_5 was observed. In some of these experiments NF_4BF_4 was also formed and the possibility that ClF_5 was catalyzing the formation of NF_4BF_4 was considered. Addition of ClF_5 to the reaction mixtures was subsequently observed to be ineffective and was discontinued.

METATHETICAL PROCESS - PHASE I, TASK 1

Prior to this contractual effort, NF_4BF_4 had been produced at Rocketdyne in a purity of 86 ± 3 mole percent and 70 percent yield in runs on a 0.8 mole scale. The metathesis was accomplished by the reactions shown in Eq. 2 through 5 . The

$$NF_4SbF_6 \cdot xSbF_5 + AgF \xrightarrow{+HF} NF_4HF_2 + AgSbF_6 \downarrow \qquad (2)$$

$$NF_4HF_2 + BF_3 \xrightarrow{-HF} NF_4BF_4 \qquad (3)$$

major contaminants in the NF_4BF_4 product were found to be $NF_4SbF_6 \cdot xSbF_5$ and $AgBF_4$, and the presence of these impurities was attributed to the following reactions:

$$AgSbF_6 + BF_3 \xrightarrow{+HF} AgBF_4 \downarrow + HSbF_6 \qquad (4)$$

$$HSbF_6 + NF_4BF_4 \xrightarrow{-HF} NF_4SbF_6 \cdot xSbF_5 + BF_3 \uparrow \qquad (5)$$

For the purpose of improving both the yield and purity of the metathetically-derived NF_4BF_4, several process improvements were investigated. These were: (1) attempts to insure the use of water-free HF (the salt is known to hydrolyze readily): (2) preparation of NF_4SbF_6 containing a smaller amount of complexed SbF_5; and (3) the use of SbF_6^- precipitants other than AgF. In addition to these studies, estimates of the solubility of $NF_4SbF_6 \cdot 0.8SbF_5$ and TlF in HF were obtained, as well as the densities of such solutions. These data were required to maximize the batch quantities of NF_4BF_4 prepared in the volume-limited reactor. Finally, investigations were conducted to upgrade the crude NF_4BF_4 by reprocessing, chemical reaction and recrystallization.

Attempted Analysis for Water in HF Solutions

Since NF_4BF_4 is hydrolytically unstable, minimizing the water content of the reagents used in the metathetical synthesis would be expected to give an increased yield of higher purity product. Accordingly, an attempt was made to develop a quantitative analytical method for water in the solvent HF applicable also to reagent solutions in HF. The proposed method was based on the hydrolysis of the thermally produced (and, hence, water-free) salt $NF_4SbF_6 \cdot xSbF_5$. It was expected that NF_3 generated by reaction of a few milligrams of H_2O with this antimony salt could be determined quantitatively using the very strong NF_3 infrared absorbance at 907 cm^{-1}.

The amount of NF_3 formed on reaction of a known quantity of water in HF with an excess of $NF_4SbF_6 \cdot xSbF_5$ was but a few percent of theoretical (see Table 5). To explain these low results, it is postulated that the complex salt in HF behaves as a solution of NF_4SbF_6 and $HSbF_6$, and in the resulting extremely acidic solution the water is protonated almost completely. As a consequence, a reaction between the cations, NF_4^+ and OH_3^+, would not be very probable. In line with this hypothesis, water (completely protonated) when introduced as OH_3SbF_6 (Ref. 8) failed to hydrolyze a significant amount of the NF_4^+ salt (Table 5). In view of these results, no additional work was performed for the analysis of water in HF or its solutions.

TABLE 5 . ANALYSIS OF WATER IN HF(a)

Sample No.	Wt. of HF, g	Wt. of H_2O, mg	Vol. of NF_3, cc	% of Theoretical NF_3 Recovered
1	2.3226	2.30	0.129	4.5
2	1.0155	1.00	0.034	2.7
3	1.4591	1.45	0.099	5.5
4	2.3605	2.38	0.020	0.68
5	9.7	10.74(b)	0.191	1.7

(a) $HF-H_2O$ solution added to known quantities of $NF_4SbF_6 \cdot 0.8\ SbF_5$

(b) Weighed directly as 0.1520g OH_3SbF_6

Solubility and Density Studies. In order to maximize the amount of NF_4BF_4 per batch in the metathetical synthesis from $NF_4SbF_6 \cdot 0.8SbF_5$, the solubility of this starting material and the density of its HF solution were required. The data obtained must be considered as approximate only since the composition of the salt varies slightly with each batch (vide infra, Table 6). The solubility of $NF_4SbF_6 \cdot 0.8SbF_5$ was found to be 5.1 g/g HF at 0.5 C and 8.5 g/g HF at 28.5 C by visual observation of dissolution of weigh quantities of solute and solvent. The density of the latter solution was determined to be 2.4 g/ml.

Data from a similar study of TlF solutions were invalid because the solution was fluorine-dried and only part of the TlF_3 formed precipitated, while the rest remained in solution as complex anionic species.

$NF_4SbF_6 \cdot xSbF_5$ Preparative Studies

The antimony salt, $NF_4SbF_6 \cdot xSbF_5$, is the most readily prepared source of NF_4^+ cation and, as such, was used as the starting material in the metathetical synthesis of NF_4BF_4. Of the several known methods for its preparation, the thermal activation process is the best for preparing relatively large amounts in a minimum time (Eq. 6). The product obtained is a solid with variable

$$NF_3 + F_2 + (x + 1)\ SbF_5 \rightarrow NF_4SbF_6 \cdot xSbF_5 \qquad (6)$$

composition (i.e., x = 3 to 4). The amount of SbF_5 complexed by the NF_4SbF_6, when the salt is used as an intermediate for the synthesis of NF_4BF_4, should be as small as possible since the excess SbF_5 increases the amount of metal fluoride required for the precipitation of $MSbF_6$ (Eq. 2).

Prior to the $NF_4SbF_6 \cdot xSbF_5$ preparative studies conducted under this contract, a number of large-scale runs had been made at 115 C (Runs 1-6, Table 10 , see Experimental Section). The ratio of Sb/N in the product salt was in the range 3-4 and required vacuum pyrolysis at 200 C for 24 hours or longer to distill off the excess SbF_5. The Sb/N ratio of the final product was approximately 1.8-2.0.

In view of the fact that partial depolymerization of the complex anion could be accomplished at 200 C, attempts were made to produce $NF_4SbF_6 \cdot xSbF_5$ with a lower Sb/N ratio directly from the gaseous reactants, without post pyrolysis. This approach was based on the assumption that, at the 115 C reaction temperature, the product with a Sb/N ratio of 3 to 4 may have been stabilized due to crystallization from the fluid mixture. If this assumption were correct, then higher reaction temperatures might yield higher melting salts of lower antimony content.

Several syntheses were conducted at temperatures higher than 115 C. At both 200 and 250 C, the Sb/N ratio of the products remained in the range 3 to 4, and the post preparative pyrolysis step was required to remove excess SbF_5. A slightly greater attack of the Monel reactor at these temperatures was noted by the increased quantity of nickel and copper salts accompanying the

$NF_4SbF_6 \cdot xSbF_5$. An appreciable amount of these relatively insoluble nickel and copper salts were removed by filtration during extraction of the product from the Monel reactor with HF. Analytical data and calculated composition of the products for the high temperature runs are summarized in Table 6 .

Since the higher temperatures were not useful for a direct synthesis of $NF_4SbF_6 \cdot xSbF_5$ with a low Sb/N ratio, all other preparative runs were made at 115 C to provide the starting material for the metathetical synthesis of NF_4BF_4.

$NF_4SbF_6 \cdot xSbF_5$ Metathesis to NF_4BF_4.

To achieve the specified 99-mole percent pure NF_4BF_4 by the metathetical route, the first approach was to substitute thallous fluoride for AgF as the SbF_5 precipitant (Eq. 2). Although NF_4BF_4 had been previously synthesized at Rocketdyne and elsewhere by the metathetical route, the maximum purity of the salt (without post treatment) never exceeded 86 ± 3 mole percent. It was believed that an increase in the purity of NF_4BF_4 could be realized if the Ag^+ ion were replaced in the metathesis by another cation which formed less soluble SbF_6^- and BF_4^- salts. This conclusion was reached on the basis of the knowledge that both $NF_4SbF_6 \cdot xSbF_5$ and $AgBF_4$ are present as contaminants in the NF_4BF_4, and their presence is most likely due to reactions such as represented by Eq. 4 and 5 .

Metathesis Using TlF. Of the metals forming HF-soluble fluorides, only thallium appeared to be a better precipitant candidate for SbF_6^- than silver. The reported solubility data for $TlSbF_6$ in HF (Ref. 9) indicated a solubility almost an order of magnitude less than that of $AgSbF_6$ (0.019M vs. 0.16M; the latter was estimated from antimony analyses of NF_4BF_4) No information, however, had been previously reported either on the solubility of $TlBF_4$ in HF or on the compatibility of NF_4^+ and Tl^+.

A preliminary experiment on a 10 mmole scale demonstrated that little Tl^+ was oxidized to Tl^{+3} by NF_4^+. The evidence for this was that only a small amount of NF_3 was formed during the reaction. Since there appeared to be no Tl^+-NF_4^+ compatibility problem, a 0.2 mole metathesis experiment was conducted in the large-scale reactor (Fig. 1) using TlF in place of AgF. The NF_4BF_4 isolated from this experiment had an antimony content approximately four times less than that using AgF.

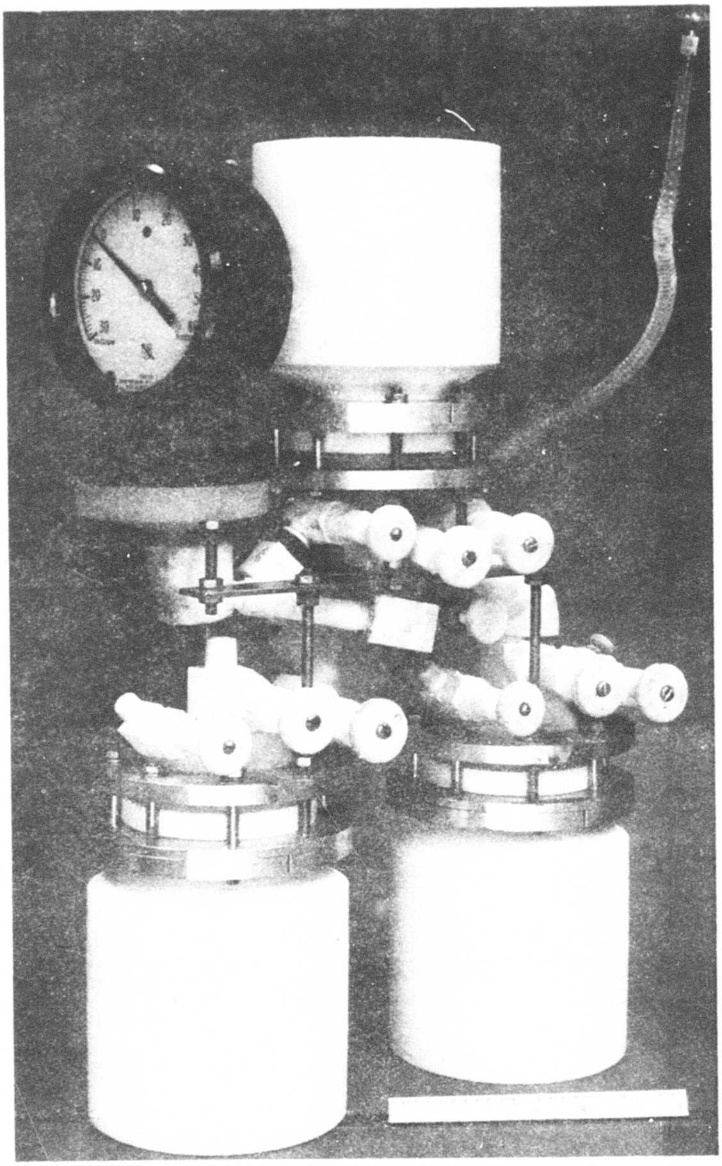

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Figure 1. Metathesis Apparatus

TABLE 6 . ANALYSIS AND COMPOSITION OF HF SOLUBLE $NF_4SbF_6 \cdot xSbF_5$ PREPARATIONS

Run No.	Sample wt, mg	NF_3, µmoles	Sb, µg-at	Ni, µg-at	Cu, µg-at	Sb/N	Calculated Composition $M(SbF_6)_n \cdot xSbF_5$, Mole Percent			
							X	$M = NF_4^+$	$M = Ni^{+2}$	$M = Cu^{+2}$
7	9.2	18.0	33.4	0.30	0.24	1.86	0.75	97.1	1.6	1.3
8[(a)]	6.4	0.54	27.7	6.39	3.54	51.3	0.36	5.2	61.0	33.8
9	10.1	18.0	34.2	1.87	0.31	1.90	0.53	89.2	9.3	1.5
10	12.0	22.0	44.8	1.11	0.24	2.04	0.82	94.2	4.8	1.0

(a) During the post preparative pyrolysis step, the temperature control failed resulting in a temperature excursion and extensive decomposition of the $NF_4SbF_6 \cdot xSbF_5$.

However, the purity of the NF_4BF_4 was found to be lower than that produced by the use of AgF. This lower purity resulted from the presence of appreciable quantities of thallium in the product. The exact form in which the thallium was present is unknown; however, the most likely forms are $TlBF_4$ and/or perhaps soluble Tl^{+3} complexes. The high toxicity of thallium coupled with the fact that attempts to decrease the thallium content of the NF_4BF_4 were unsuccessful (vide infra) eliminated this reagent from further consideration.

Metathesis Using AgF. The scale of the metathetical reaction between AgF and $NF_4SbF_6 \cdot xSbF_5$ was increased from the normal 0.8 mole runs to 1.5 to 2.0 moles of the NF_4^+ salt for the purpose of producing more of the product per batch. Problems associated with the removal of the coproduct $AgSbF_6$ were encountered during these larger scale runs. The precipitation of the larger quantity of $AgSbF_6$ resulted in a heat release that could not be rapidly dissipated by the Teflon equipment. This resulted in a product which contained a large amount of $AgSbF_6$ due to the increased solubility of this coproduct under the experimental conditions used. Sufficient cooling of the $AgSbF_6$-NF_4HF_2 slurry during the filtration step caused the $AgSbF_6$ to precipitate in the filter and plug it.

Because of the marginal thermal stability of NF_4HF_2 formed along with the $AgSbF_6$, long periods between mixing the $NF_4SbF_6 \cdot xSbF_5$ and AgF prior to filtration of the $AgSbF_6$ could not be tolerated. Therefore, the HF solution of AgF was precooled in an ice bath for about 0.5 hour prior to adding it to the HF solution of $NF_4SbF_6 \cdot xSbF_5$, followed by an additional 0.5 hour cooling period before carrying out the filtration step. This procedure worked well when 1.0 mole scale preparations were conducted, and would probably be adaptable to larger scale runs as well.

A second observation that was made during the larger scale runs was that the reaction of the filtrate, from the AgF - $NF_4SbF_6 \cdot xSbF_5$ reaction, with BF_3 required more agitation than was needed in the smaller runs. The required agitation was provided by manually shaking the reactor.

The synthesis and analytical data obtained for three metathetical runs are summarized in Table 7.

TABLE 7 . METATHETICAL NF_4BF_4 PREPARATIONS

Run No.	Reactants, moles			Crude NF_4BF_4, g	NF_4BF_4 Purity mole percent	Percent Yield	Analysis (mg Found)						
	$NF_4SbF_6 \cdot xSbF_5$	AgF	BF_3				Sample	NF_3	B	Sb	Ag	Cu	Ni
9	0.95 (x = 0.89)	2.14	0.82	123.8	63[(a)]	39	382.2	121.6	14.1	64.2	21.4	0.009	0.006
10	1.08 (x = 0.99)	2.22	1.40	164.2	90[(b)]	65	372.1	117.4	18.4	37.8	11.9	0.011	0.015
11	0.94 (x = 0.91)	2.20	1.40	185.0	83[(b)]	89	368.9	118.5	19.1	33.2	7.95	0.009	0.012

(a) Low purity attributed to contamination by $AgSbF_6$ because of non-cooling of the $AgF\text{-}NF_4SbF_6 \cdot 0.95\ SbF_5$ reaction mixture.

(b) HF solution of antimony salt was added to the HF solution of AgF precooled in an ice bath. The reaction mixture was retained in the ice bath for 40 minutes prior to filtration and reaction with BF_3.

Purification of Metathetical NF_4BF_4

Because the purity of the NF_4BF_4 obtained directly from the metathetical reaction could not be increased by any of the approaches attempted, efforts were made to increase the purity of the material by other means. A crystallizer (Fig. 2) was built and used for recrystallizing the NF_4BF_4 from HF. The procedure used for operating the crystallizer is described in the Experimental Section. Attempts were also made to upgrade the purity of the material by reprocessing the NF_4BF_4, and by reaction with HCl in HF. The results of these studies are presented below.

Crystallization Studies. Based on the assumption (since no density data or reliable solubility data were available) that NF_4BF_4 is less soluble than $NF_4SbF_6 \cdot xSbF_5$ in HF, it was believed possible to recover pure NF_4BF_4 by crystallization from an HF solution of the mixed salts. The inseparable mixture that would be obtained after crystallization could then be metathetically reprocessed to enrich it in NF_4BF_4.

Experimentally, $NF_4SbF_6 \cdot xSbF_5$ proved to be less soluble than NF_4BF_4, and, hence, it concentrated in the solid phase during crystallization. When a composite (470 g, calculated to consist of 84 NF_4BF_4, 9.3 $NF_4SbF_6 \cdot 1.1\ SbF_5$, and 6.6 mole percent $AgBF_4$) was taken of the metathetical runs shown in Table 7 and crystallized from HF, the results summarized in Table 8 were obtained. The filter cake

TABLE 8 . CALCULATED COMPOSITIONS* OF ISOLATED FRACTIONS FROM NF_4BF_4 CRYSTALLIZATION

Sample	Weight, g	NF_4BF_4	$NF_4SbF_6 \cdot xSbF_5(x)$	$AgBF_4$	$AgSbF_6$
Composite of Runs 9-11	470	84.1	9.3 (1.1)	6.6	0
Insolubles Runs 9-11	23	5.0	3.6 (1.1)	91.4	0
Crystallized Filter Cake					
Center	180	74.0	23.4 (0.90)	0	3.0
Periphery		75.4	20.1 (0.90)	0	4.6
Filtrate Residue	250	93.0	5.9 (0.90)	0	1.1

*Compositions given as mole percent

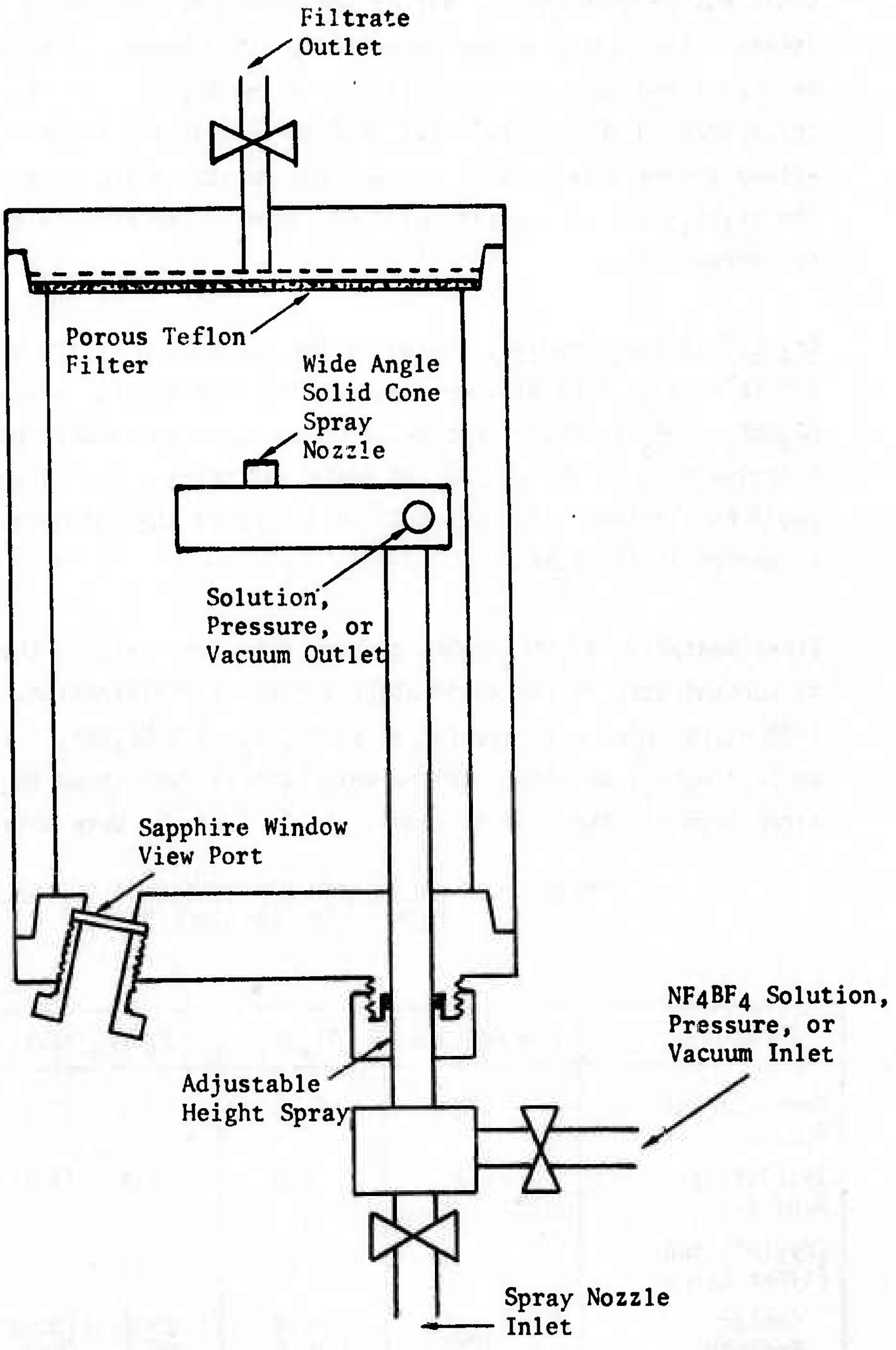

Figure 2. Teflon and Kel-F Concentrator-Crystallizer Schematic

was sampled for analysis in two places - the center, where more efficient washing by the HF spray occurred, and the periphery. The analytical results indicated that the concentration of antimony salt in the saturated solution was too high to provide high purity NF_4BF_4 by evaporation of the crystallization mother liquor. Furthermore, the higher ratio of antimony to boron NF_4^+ salts in the center of the filter cake served as confirmatory evidence for the selective dissolution of the more soluble NF_4BF_4 by the HF wash. Although the filtrate residue analyzed higher in NF_4BF_4 content than the calculated value for the composite, this improvement in purity appeared to be due primarily to removal of the contaminating $AgBF_4$.

Reprocessing of Metathetical NF_4BF_4. An attempt was made to upgrade a 93 mole percent NF_4BF_4 sample by using it as the starting material for the metathetical process. With the lower initial antimony content, the minimum value for antimony should be readily attained in the final product. Since the fluoroantimonate salt is the major impurity in metathetical NF_4BF_4, a decrease in its concentration should yield a significantly purer NF_4BF_4.

In the initial step of the metathetical reaction, all NF_4^+ salts (including NF_4BF_4) were converted to the intermediate bifluoride salts (Eq. 7 and 8).

$$NF_4BF_4 + AgF \xrightarrow{HF} NF_4HF_2 + AgBF_4\downarrow \qquad (7\ )$$

$$NF_4SbF_6 \cdot xSbF_5 + AgF \xrightarrow{HF} NF_4HF_2 + AgSbF_6\downarrow \qquad (8\ )$$

Treatment with BF_3 then produced NF_4BF_4 as in the process starting with the antimony salt alone. Although a 38 percent decrease in the antimony content was achieved, the purity of the NF_4BF_4 recovered was unchanged at 93 mole percent due to an increase in the $AgBF_4$ content.

HCl as a Metal Precipitant. The solubility of AgCl in HF is quite low, and presumably that of TlCl would also be low since much of chemistry and many of the physical properties of Ag^+ and Tl^+ compounds are parallel. The approach used to decrease the Ag^+ or Tl^+ content of metathetical NF_4BF_4 was to saturate the HF solution of the crude NF_4BF_4 with HCl in order to precipitate the metal ion without introducing other contaminants (Equation 9). Partial success was

$$MBF_4 + HCl \xrightarrow{HF} MCl\downarrow + HF + BF_3\uparrow \qquad (9)$$

attained in that the silver content of the product was decreased to about one-fourth its initial value. However, a pressure rise was noted subsequent to the HCl addition and a net loss in weight of nonvolatile solids was observed suggesting that the NF_4^+ ion and HCl are incompatible. As a result of the partial loss of NF_4BF_4 by the reaction postulated in Eq. 10, overall purity of the recovered

$$NF_4BF_4 + HCl \xrightarrow{HF} NF_3 + BF_3 + HF + ClF \qquad (10)$$

product dropped from 93 to about 90 mole percent.

Confirmation of the interaction of NF_4BF_4 with HCl was obtained in a similar treatment of the NF_4BF_4 prepared by metathesis using TlF in place of AgF. Although a small proportion of the thallium content of initial product was rendered insoluble, the destruction of NF_4BF_4 was much more extensive suggesting that not only was HCl oxidized, but that Tl^+ was also oxidized to Tl^{+3} possibly as indicated in Eq. 11. The HCl treatment decreased the purity of the NF_4BF_4

$$Tl^+ + ClF \xrightarrow{HF} Tl^{+3} + Cl^- + F^- \qquad (11)$$

from 88 to about 65 mole percent.

CONCLUSIONS - PHASE I, TASK 1

During Phase I, Task 1, it was possible to demonstrate that pure NF_4BF_4 could be prepared by the UV-induced reaction of NF_3, F_2 and BF_3 at an average rate of 1 g/hr (during short reaction times). In contrast, the metathetical reaction provided NF_4BF_4 of a purity not exceeding 93 mole percent despite efforts to increase the purity by physical or chemical means. On the basis of the simplicity of the UV-induced reaction, its potential for providing the material at a lower cost and the demonstrated synthesis of pure NF_4BF_4, this method was chosen as the one to study during the scale-up task (Phase I, Task 2).

SCALE-UP OF UV PROCESS - PHASE I, TASK 2 AND LARGE SCALE SYNTHESIS OF NF_4BF_4 - PHASE II

For the purposes of convenience and because of overlap of the experimental data, these two work efforts have been combined. During Phase I, Task 2, the objective of demonstrating a scalability of the UV process to achieve a production rate of 80 g/week of NF_4BF_4 of high purity was achieved. During Phase II, this same process was used to produce 0.24 Kg of NF_4BF_4 of 99 mole percent purity which was delivered on schedule.

A description of the UV apparatus used to accomplish these objectives, and a discussion of the process parameters investigated are given in the following sections.

Equipment Design (Large-Scale)

On the basis of the previously described experiments conducted under Phase I, Task 1, an apparatus was designed and fabricated to produce NF_4BF_4 in larger quantity and at higher rates than had been obtained in the preceding experiments. The reactor was constructed of 347 stainless steel (with the exception of a few 300 series stainless steel fittings) and was fitted with a 4-inch diameter sapphire photolysis window and a 1-inch diameter sapphire view port using Teflon gaskets. The reactor and its ancillary equipment are shown schematically in Fig. 3.

Basically, the reactor consists of a windowed chamber, to contain the reactant gases, with an internal liquid nitrogen-cooled flat photolysis surface parallel to the sapphire window. With the exception of this cooled vertical photolysis zone, all other walls of the liquid nitrogen refrigeration system are vacuum jacketed.

Reactant gases are introduced from a pressure regulated supply tank through a timer-operated, solenoid-actuated, pneumatic valve to an integral manifold supplying six 0.0135-inch diameter holes equally spaced around the perimeter of the window. Unreacted gases are vented from the reactor through a solenoid-actuated, pneumatic valve and collected in a liquid nitrogen-cooled catch tank. By actuation of an externally mounted hydraulic ram, a scraper can be made

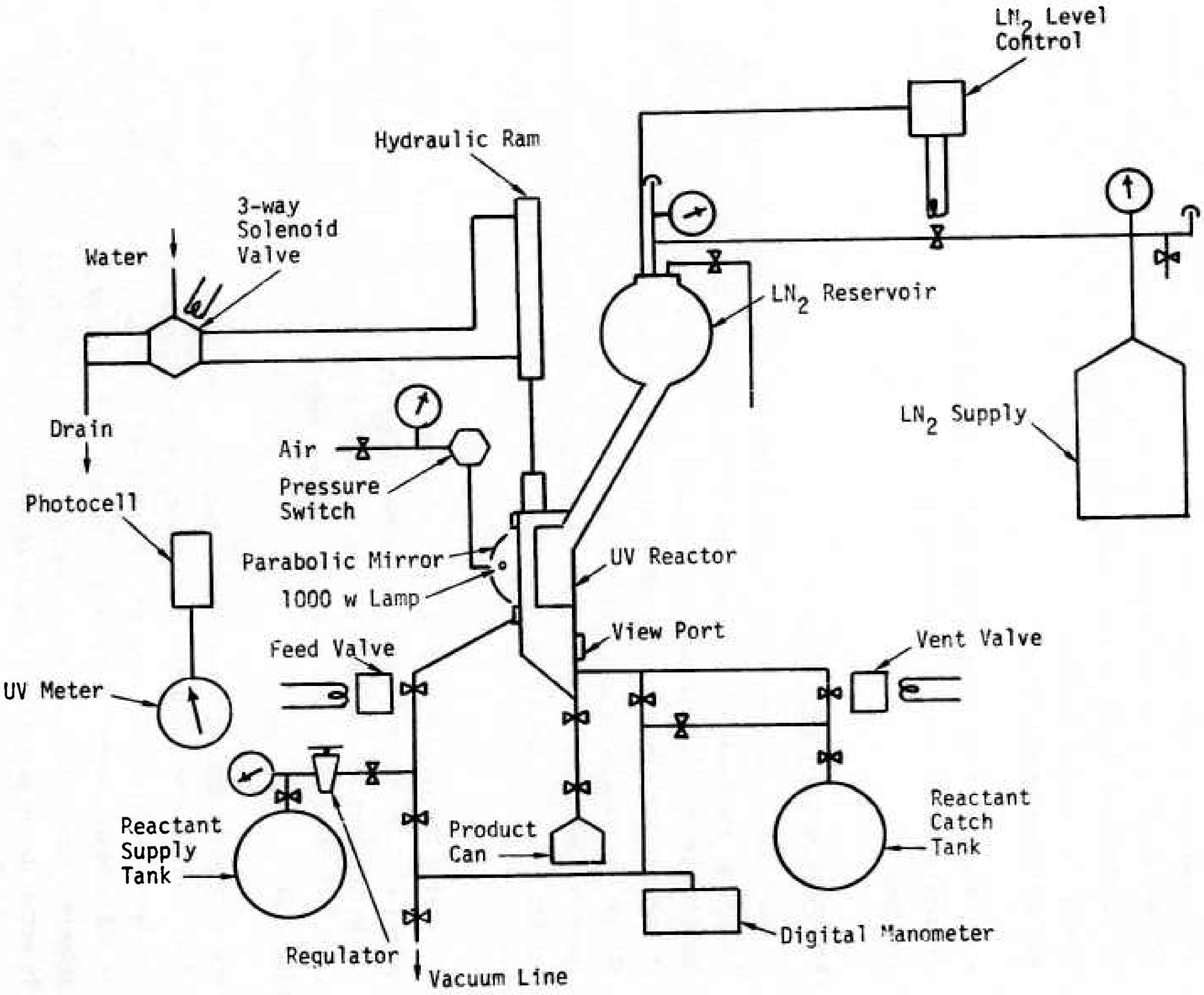

FIGURE 3. UV REACTOR APPARATUS SCHEMATIC

to pass over the photolysis zone to remove adhering unreacted starting materials and NF_4BF_4. The latter is collected in a removable can for transfer to the drybox. Pressures in the reactor, reactant gas feed line, and catch tank are measured with a digital manometer (Validyne, Model 56A).

The UV source is a 1000 watt, high pressure capillary mercury arc lamp (GE BH6) with appropriate air-cooling and power supply. A polished nickel parabolic reflector is positioned around the lamp to maximize the light intensity in the photolysis zone. A relative measure of the UV intensity is determined by an externally mounted photocell.

The refrigeration system consists of a 100-liter liquid nitrogen supply in series with a 14-liter constant level vessel, which permits replenishing the 100-liter supply without interruption of the photolysis process.

Reaction Parameters

From the experiments conducted during Task 1, the relative importance of a number of reaction parameters had been indicated. In the large-scale reactor design, an effort was made to utilize the optimum values for these parameters. However, because of the completely different geometry and partial process automation, some additional parametric factors were introduced. The study of the various process parameters was conducted under Phase I, Task 2 (Synthesis Scale-Up). During the work effort, 80g of NF_4BF_4 of 99 mole percent purity was prepared and delivered to the Air Force and a production rate of 80g/week was demonstrated. These milestones were achieved even though optimization of the process was not complete by the end of this task. Therefore, the optimization studies were continued under Phase II (Large-Scale Synthesis). Even with the additional parametric evaluation, sufficient time was unavailable to obtain data which would accurately define the optimum process conditions for synthesis of NF_4BF_4 in the large-scale reactor.

During the course of this investigation, it became obvious that several important variables could not be controlled and, as a result, the correlations found between reaction parameters and rate of formation of NF_4BF_4 are qualitative. Insofar as it is possible, the influence on the NF_4BF_4 formation rate of each of the parameters studied will be discussed. The data obtained using the large-scale reactor are tabulated in Appendix II. Runs 1-13 were conducted under Phase I, Task 2 and Runs 14-21 under Phase II.

Effect of Temperature. Small-scale experiments indicated the essentiality of cryogenic temperatures if reasonable NF_4BF_4 formation rates were to be achieved. Accordingly, only liquid nitrogen was used as a coolant in the large-scale reactor, but some temperature variation (ca. 10 C temperature rise) was accomplished by pressurization of the cooling system. A total of six runs were made with pressures of 1-1.5 atmospheres above ambient in the liquid nitrogen cooling system. No significant difference could be found between those runs made using pressurization in the cooling system and those conducted at ambient pressure. Since the latter procedure was simpler from an operational standpoint, it was the method of choice.

Effect of UV Intensity. The intensity of the UV radiation at the photolysis surface is a function of (1) the distance from lamp to the photolysis surface, and (2) the UV output of the lamp. In most experiments the lamp was positioned as close as possible (4.2 cm) to the photolysis zone. In three runs the distance was increased primarily to lower the heat load on the cooling system. Comparing runs 3 and 4 (Appendix II), the NF_4BF_4 formation rate decreased more drastically than would be expected from 1.50 g/hour to 0.36 g/hour on increasing the lamp-photolysis surface distance from 4.2 cm to 6.7 cm. These data are of dubious value because of the subsequent (i.e., Run 8) observation of a significant, yet variable, build-up of NF_4BF_4 in the reactor. This uncontrollable factor will be discussed in more detail (vide infra).

During the course of the series of runs, a number of lamps were used. The lamps, operated at 900 volts, exhibit a wide variation in both initial UV intensity and in aging characteristics. The observed range of initial UV intensities for ten new lamps was 0.023-0.034 $\mu w/cm^2$ (at a distance of 85 cm from the lamp) with an average value of 0.027 $\mu w/cm^2$. When the intensity decreased to 0.016 $\mu w/cm^2$ the lamp was replaced. Lamp life varied in the range 13-45 hours (average 27.6, hours). The practice common in industry (where lower intensities are generally used) of increasing operating voltage to maintain UV intensity was impractical in our use because the accompanying much greater increase in infrared radiation added too much heat to the refrigeration load. The inherent variation of

30-50 percent in UV intensity during the life of a lamp rendered correlation of NF_4BF_4 formation rate with other given reaction parameters qualitative.

Effect of Reactant Mole Ratios. In view of the fact that NF_4BF_4 is formed from an equimolar mixture of NF_3, BF_3 and F_2, it was logical to use such a mixture as the starting material in the UV process. No attempt was made to determine the ratio of the starting materials contained in the reactor in "dynamic equilibrium" during the course of a run.

Effect of Mode of Introduction of Reactants. The intermittent mode of addition of the equimolar NF_3-BF_3-F_2 reactant mixture was dictated by the results of the small-scale experiments. To optimize the process, it would be necessary to achieve a balance between a high NF_4BF_4 formation rate with low conversion or a low NF_4BF_4 formation rate with high conversion. Theoretically, a high formation rate should be achieved by frequent renewal of the reactants in the photolysis zone and high conversion by infrequent renewal. The quantity of reactants introduced with each increment must not exceed that which can be converted to products in the time between additions, or both NF_4BF_4 formation rate and conversion will be low.

Comparison of Run 19 with combined Runs 9 and 10 (each of which has approximately the same reactant feed rate, see Appendix II) suggests that doubling the quantity of reactants per increment added and halving the frequency of additions resulted in a 20 percent increase in the NF_4BF_4 formation rate. Further decreases in the frequency of addition resulted in very significant lowering of the NF_4BF_4 formation rate (Runs 20 and 21). An insufficient number of runs of long duration (12-35 hours) were made to define either the frequency of incremental additions or the optimum quantity of reagents introduced per addition. Such data as were obtained are qualitative due primarily to two uncontrolled parameters inherent in the reactor design. These parameters are discussed below.

Effects of Reactor Hold-up of NF_4BF_4 and Reactant Gas Orifice Plugging. The nature of the NF_4BF_4 produced by the UV process is such that the dry powder is not free-flowing. Its angle of repose approaches the vertical. Accordingly, an average of about 5 grams of product accumulated on the 40-degree slope of the reactor bottom before additional product falling from the scraper blade would slide into the collection can. Temperature cycling between runs sometimes dislodged large flakes of product from the photolysis surface which facilitated the accumulation of product (up to 20 grams) in the reactor or complete plugging of the outlet. In any case, the quantity of NF_4BF_4 which accumulated in the reactor was a very substantial, yet variable, percentage of the total produced in all runs. In some runs mechanical removal of product resulted in more reliable formation rate data. The behavior of NF_4BF_4 is postulated to be the result not only of the irregular shape of the solid particles which readily acquire an electrostatic charge, but more importantly, the extremely high HF solubility of the product. A small amount of HF introduced with the F_2, or from trace hydrolysis of BF_3 by atmospheric moisture leaking into the reactor is suspected to promote the observed stickiness and slight caking of the product.

During 75-100 hours of operation, the quantity of reactant gases introduced per increment was observed to decrease to about one-half its initial value as measured by the maximum pressure rise immediately after the addition. This decrease in addition rate of reactants was found to be due to an uneven accumulation of solids in the inlet orifices. Thus, not only did the amount of reactants introduced decrease (at a given pressure differential between reactant feed supply and reactor and a given open valve time), but the distribution of condensed reactants on the photolysis surface became uneven. The result was that correlations of NF_4BF_4 formation rate with incremental reactant feed rates are qualitative in most instances.

Process Efficiency. During the 34-hour run time of Run 19 (Appendix II), the pressure in the 9.5 liter reactant supply tank decreased by 75 psig which is equivalent to 0.66 mole (117 g) NF_4BF_4. The 98.9g NF_4BF_4 synthesized indicated an 84 percent conversion of starting materials to product. Assuming the feed rate in Run 21 to be one-half of that of Run 19, the conversion is calculated to be 97 percent.

Overall conversion for all twenty-one runs is calculated to be 31 percent since 369g NF_4BF_4 (323g delivered, 46g analytical samples, mechanical losses, or discarded as partially hydrolyzed) was prepared from the 1197g of an equimolar mixture of NF_3-BF_3-F_2.

EXPERIMENTAL

REAGENTS

HF Drying

A 12-lb quantity of commercial anhydrous HF (Matheson) was transferred into an evacuated 9.5 l stainless steel, high pressure cylinder fitted with a 1000 psi pressure gage. After cooling to -78 C, approximately 500 mm of non-condensable gas was pumped off. A 500 ml cylinder containing approximately 40 l F_2 at -196 C was then connected to the HF cylinder and, after allowing both cylinders to warm to ambient temperature, the HF was pressurized with F_2 to 100 psi. The F_2 pressure over the HF dropped to 85 psi after standing overnight and remained constant during 1 hour shaking of the HF cylinder. The unused F_2 and O_2 which had been generated were condensed at -196 C in the 500 ml cylinder which was then disconnected. The residual F_2-O_2 mixture was removed from the HF by vacuum pumping for about 3 hrs at -78 C, and then briefly at ambient temperature.

NF_3

NF_3 was obtained from the Rocketdyne plant where it is prepared by electrolysis of NH_4HF_2. Analysis of this material indicated the following composition.

Component	w/o
NF_3	99.5
N_2	0.3
HF	0.1
CF_4	trace < 0.01
N_2O	trace < 0.01
trans-N_2F_2	trace < 0.01
cis-N_2F_2	not detectable
F_2	not detectable

SbF_5

Commercial SbF_5 (Ozark-Mahoning) was distilled at atmospheric pressure under dry nitrogen from glass apparatus into Teflon bottles. Only the center cut (b.p. 148 C) was taken for use, and the liquid was subsequently stored and transferred entirely within a drybox.

All other chemicals were obtained commercially and used as received unless otherwise noted.

UV PROCESS

Small-Scale UV Experiments

The pre-photolysis procedure generally used to prepare NF_4BF_4 on a small-scale by the UV process was as follows. A part (or all when smaller amounts were used) of the F_2 was introduced at -196 C into an evacuated reaction vessel. The UV lamp was then turned on to permit the system to reach thermal equilibrium (5 to 10 minutes). Measured amounts of NF_3 and BF_3 (either premixed or separately) were then quickly introduced by using pressures higher than the internal F_2 pressure. Additional F_2, if necessary, was then added. Deviations from this procedure are noted in Appendix I for individual experiments.

Unless otherwise noted in Appendix I, the procedure for continuous or intermittent addition of reagents differed only in that, after introducing part of the reactants, the flow of the remaining gases into the reactor was either (1) controlled with a needle valve and monitored by pressure measurements, or (2) by rapid addition at varying times during photolysis. Details of individual experiments are given in Appendix I.

Large-Scale UV Preparations

Operation of the large-scale UV-reactor employed the following procedure. An equimolar mixture of $NF_3/BF_3/F_2$ was introduced into the evacuated photolysis cell, which was cooled on the internal working face to -196 C, until the pressure (F_2 partial pressure) rose to the preselected working range (~500 mm). The UV lamp was turned on and the feed cycle timer circuit was activated to admit additional incremental amounts of the equimolar gas mixture from a pressure regulated supply. The reactant gas feed rate was governed by the time that the solenoid activated pneumatic inlet valve was open, the pressure differential between the reactor and supply, and the time between inlet valve activations. At approximately 15 minute intervals, a hydraulic ram was manually activated to drive a scraper blade across the internal working face of the reactor and thereby dislodge the mixture of NF_4BF_4 and unreacted starting materials. The unreacted starting materials volatilized and the increase in cell pressure was reduced to the preselected value by bleeding the unreacted materials into a catch tank at -196 C. The solid product was deposited in a doubly-valved removable collection vessel under the photolysis cell. At the conclusion of a run, the bulk of the liquid nitrogen refrigerant was pressure-transferred from the apparatus. As soon as the refrigerant was depleted, the cell pressure began to rise and the feed cycle timer circuit was deactivated. The pressure in the photolysis cell was maintained just below atmospheric by controlled release of the volatilized unreacted gases to the catch tank. The lamp was turned off when the pressure stabilized. The product collection vessel was then evacuated and transferred to a drybox to remove the product. Details for individual runs are tabulated in Appendix II.

METATHETICAL PROCESS

Attempted Analysis for Water in HF Solution

A sample of F_2-dried HF was added to an evacuated, tared Teflon tube containing 5 μl H_2O. The weighed solution was then partitioned in an evacuated system into three analytical samples by pouring part of it into two other tared Teflon tubes. The three samples were in turn allowed to react with an excess of $NF_4SbF_6 \cdot 0.8SbF_5$ in HF solution. The NF_3 generated was pumped through a -196 C trap into a -210 C trap and then warmed and expanded into an IR cell of known volume. The amount of NF_3 was calculated from the measured absorbance of the 907 cm^{-1} band which had been calibrated against known NF_3 pressures. A fourth experiment was conducted and the NF_3 was pumped through a -126 C trap into the -210 C trap without significant change in the amount of NF_3 obtained. A result comparable to those obtained using water was obtained when the salt, OH_3SbF_6, was used as the water source.

Solubility and Density of HF Solutions of $NF_4SbF_6 \cdot 0.8SbF_5$

A 0.2345g sample of $NF_4SbF_6 \cdot 0.8SbF_5$ was dissolved in HF at ambient temperature in a Teflon ampoule fitted with a Teflon valve. The solvent was removed under vacuum to leave a solid which weighed 0.2363g after pumping for 1 hr at ambient temperature. In an independent experiment, approximately 3g of $NF_4SbF_6 \cdot 0.8SbF_5$ was dissolved in HF at ambient temperature in a Teflon ampoule equipped with a Teflon filter and valve. After filtering out Monel chips and the relatively insoluble $M(SbF_6 \cdot xSbF_5)_2$ salts (M = Cu, Ni), the filtrate was observed to be just slightly turbid in a second tared, volume-calibrated Teflon ampoule. HF was gradually pumped away and crystallization of the salt was induced by supercooling the ampoule tip. The slurry was allowed to warm slowly with agitation in a water bath, the temperature of which was measured with an Anshutz thermometer. The temperature at which the last crystal dissolved was noted as was the volume of the solution. The solution weight was subsequently determined at ambient temperature. The weight of dissolved salt was determined by complete removal of solvent under the conditions described above.

$NF_4SbF_6 \cdot xSbF_5$ Preparative Studies

A typical preparation of $NF_4SbF_6 \cdot xSbF_5$ (Run 16, Table 9) was conducted as follows. A 1000 ml Monel high pressure (3500 psi) cylinder was charged with 602g (2.78 moles) SbF_5 in a drybox. After fitting the cylinder with a Monel pressure gage and valve, 167g (2.35 moles) NF_3 and 98.1g (2.58 moles) F_2 were condensed in the cylinder at -196 C. When the mixture had warmed to ambient temperature (pressure 1600 psi), the cylinder was placed in a 115 C oven for 24 hrs. The pressure was observed to be 2550 psi (after 4.5 hrs in oven) and 1900 psi (1125 psi at ambient temperature) as it was removed from the oven. The unreacted NF_3-F_2 mixture (149 g) was removed from the cylinder at ambient temperature and recovered for reuse. Infra-red analysis of the recovered NF_3-F_2 mixture indicated that the mole ratio NF_3/F_2 remained in the range 1.0-1.1.

The crude product was pyrolyzed under dynamic vacuum in a 200 C oven for 24 hrs and excess SbF_5 (204 g) was distilled through an electrically heated line to a -78 C trap for recovery and subsequent reuse. A 100 ml quantity of

TABLE 9 . $NF_4SbF_6 \cdot xSbF_5$ PREPARATIONS

Run No.	NF_3, Moles	F_2, Moles	SbF_5, Moles	Temp., °C	Reaction Time, hrs	Sb/N[a] Initial	Sb/N[a] Final	Pyrolysis Time, hrs	Product Wt., g Crude	Product Wt., g HF Sol.	Product Wt., g HF Insol.
1	1.96	2.14	2.05	115	29	3.73	1.83	90	280	(b)	(b)
2	1.94	2.16	2.04	115	70	3.71	2.05	40	305	(b)	(b)
3	1.97	2.01	2.03	115	25.5	4.17	2.25	40+(c)	288	(b)	(b)
4	1.80	1.98	1.92	115	54	3.74	1.80	51	257	(b)	(b)
5	2.01	2.18	2.27	115	24	3.37	1.67	48+(c)	315	(b)	(b)
6	2.13	2.40	2.44	115	69	3.14	1.84	72	397	(b)	(b)
7	2.17	2.41	2.16	200	5	3.93	1.87	48	283	260	14
8	2.17	2.41	2.15	200	21.5	3.61	[2.02](d)	44	189	32(e)	153
9	1.90	2.13	2.12	250	5	3.35	1.99	48	342	298	38
10	1.85	2.05	2.10	250	24	2.87	2.06	44	398	360	35
11	2.31	2.59	2.79	115	23	3.40	2.06	44	450	430	21
12	2.29	2.56	2.78	115	22	3.19	2.10	44	493	--	--
13	2.32	2.61	2.72	115	22	3.01	1.92	24	481	--	--
14	2.38	2.61	2.73	115	24	2.78	1.89	17+(f)	510	--	14
15	2.33	2.60	2.89	115	23.5	3.00	1.99	28	520	--	19
16	2.35	2.58	2.78	115	24	2.88	1.91	24	503	--	12
17	2.35	2.58	2.79	115	24	2.71	1.93	25	542	--	--

(a)Before and after recovery of excess SbF_5 by 24-48 hour pyrolysis at 200 C.

(b)These preparations, made prior to this contract, were isolated mechanically rather than by HF extraction.

(c)Exact pyrolysis time unknown due to plugging of SbF_5 outlet.

(d)During further heating, temperature control failed resulting in a temperature excursion and extensive decomposition of $NF_4SbF_6 \cdot xSbF_5$.

(e)The major portion of this material may have passed through filter as finely divided solid.

(f)Exact pyrolysis time unknown due to power failure while unattended.

F_2-dried HF was added to the 503 g of crude product in the cylinder, and the mixture was mechanically shaken for 1 hr. The resulting slurry of copper and nickel salts was pressurized to 50 psi with nitrogen and pneumatically transferred to a 1070 ml Teflon container equipped with a Teflon filter. The slurry was pressure-filtered into a second Teflon container from which the filtrate was used directly in a metathetical reaction with AgF. After vacuum pumping the solvent from the first Teflon container, the weight of the copper and nickel salts was found to be 12 g.

$NF_4SbF_6 \cdot xSbF_5$ Metathesis to NF_4BF_4

Compatibility of Tl^+ with NF_4^+. A preliminary experiment involving the first reaction step of the metathetical process, and conducted in Teflon tubing reactors, was not completely satisfactory in that mechanical hold-up of the TlF-HF solution prevented using an excess of this reagent compared to the amount of $NF_4SbF_6 \cdot 0.8SbF_5$. On adding one-half to three-quarters of the 1.35 ml TlF-HF solution (containing 2.188g or 9.82 mmoles TlF) to 1.76 ml of a HF solution of $NF_4SbF_6 \cdot 0.8SbF_5$ (containing 2.645g $NF_4SbF_6 \cdot 0.8SbF_5$ or 9.62 mg-at Sb), a colorless precipitate formed immediately. After 0.5 hour at ambient temperature, NF_3 (0.44 cc) was collected and determined by infrared spectroscopy to be equivalent to 0.36% of the NF_4^+. After standing at ambient temperature for 6 days, an additional 0.15% of the NF_4^+ was found as NF_3, suggesting that the observed precipitate was $TlSbF_6$ which is stable toward oxidation by NF_4^+.

Metathesis Using TlF. Large-scale reactions were conducted in the metathetical reactor shown in Fig. 1. This reactor is entirely constructed of Teflon and Kel-F including reaction vessels, valves, filters, pressure relief valve (set at 60 psi) and diaphragm pressure gage.

An approximately 0.2 mole scale preparation of NF_4BF_4 was made using TlF as the precipitant for SbF_6^-. A solution of 100 g (0.45 mole) of TlF in 72 g HF was added to a solution of 103 g (0.208 mole)of 89.2% $NF_4SbF_6 \cdot 0.53\ SbF_5$ (Run 9, Table 9) in 44 g HF. The resulting slurry was filtered to remove $TlSbF_6$, which was washed with 25 g HF. The combined filtrate and washings were saturated with BF_3 (19 g, 0.28 mole) to 20 psig. The resulting $TlBF_4$ was filtered, and the filtrate was evaporated to dryness under vacuum. All of the above operations were conducted in the metathetical reactor.

Analyses of the 38.2 g of crude product were performed by hydrolyzing the product on a vacuum line. The NF_3 evolved was estimated by the IR technique. The hydrolyzate was then analyzed for B, Tl, Sb, Ni and Cu by atomic absorption spectrometry. A 0.2660 sample of the product on analysis gave: B, 13.8 mg; Tl, 54.4 mg; Sb, 6.4 mg; Ni, 0.006 mg; and Cu, 0.003 mg. Two samples, 0.0027 g and 0.0094 g, gave on an equivalent basis NF_3 values of 93 mg and 47.5 mg, respectively.

Metathesis Using AgF. For a typical reaction, 300 g AgF was dried in a vacuum oven at 60 C for 4 hrs. The resulting 292.6 g AgF, after transfer to a 1070 ml Teflon container in the drybox, was dissolved in 400 ml of F_2-dried HF and pressure-filtered (20 psi N_2) into a second Teflon container to remove 14 g of insolubles. The resulting HF solution contained approximately 279 g (2.20 moles) AgF.

A HF solution of $NF_4SbF_6 \cdot xSbF_5$ was prepared as indicated (vide supra). Although not analyzed, the solution was estimated to contain approximately 488 ± 3 g of 95-96 mole percent $NF_4SbF_6 \cdot 0.9\ SbF_5$ (ca. 1.8 g-atom Sb) on the basis of other analyses (cf. Tables 6 and 9).

The 583 g of $NF_4SbF_6 \cdot 0.9\ SbF_5$ solution was transferred rapidly under 25 psi N_2 pressure into the AgF solution, which had been cooled for 0.5 hr in an ice bath. After standing in the ice bath for an additional 0.5 hr, the slurry was pressure-filtered to remove $AgSbF_6$ which was then washed quickly with 150 ml HF. The nitrogen in the system was pumped away from the combined filtrate and washings, and gaseous BF_3 (95 g, 1.4 moles) was then added, with moderate shaking during 0.5 hr, until the pressure increased to 20 psi. The resulting slurry was filtered to remove $AgBF_4$, and the filter cake was washed quickly with 50 ml HF. The solvent HF was vacuum pumped from the NF_4BF_4 solution, as well as from the solid $AgSbF_6$ and $AgBF_4$ co-products, during 9 hrs. The weights of the isolated products were NF_4BF_4 185 g, $AgSbF_6$ 534 g, and $AgBF_4$ 88 g.

A 0.3689 g sample of NF_4BF_4 was hydrolyzed in a Teflon ampoule on the vacuum line using approximately 1.5 ml H_2O. The colorless solid turned black as the ice began to sublime, suggesting the oxidation of Ag(I) to Ag(II). The solid foamed vigorously on contact with liquid water to give a black solution (or colloidal suspension), which changed first to a pink solution and then colorless during 0.5-1.0 hr. The resulting NF_3 (37.40 cc) and O_2 (18.55 cc) were separated by condensation of the NF_3 at -210 C (N_2 slush), and collected separately by means of a Sprengel pump system. The observed NF_3/O_2 of 2.02 compared very favorably with the theoretical ratio of 2. The hydrolyzate was analyzed by atomic absorption spectroscopy. Found: B, 19.1 mg; Sb, 33.2 mg; Ag, 7.95 mg; Cu, 0.009 mg; Ni, 0.012 mg. On the basis of these analyses, the NF_4BF_4 was approximately 83 mole percent pure, and was obtained in about 89 percent yield based on the $NF_4SbF_6 \cdot 0.9SbF_5$ used.

Reprocessing of Metathetical NF_4BF_4. The typical metathesis reaction was run in the usual manner using 93 mole percent NF_4BF_4 as the NF_4^+ source rather than $NF_4SbF_6 \cdot xSbF_5$. After the metathesis with AgF, the slurry was cooled in a -78 C bath (rather than the usual 0 C bath) for 1.75 hrs before filtration of the $AgBF_4$-$AgSbF_6$ mixture from the NF_4HF_2 solution. The filtrate was saturated with BF_3 and the $AgBF_4$ was filtered. The NF_4BF_4 isolated from the filtrate, by removal of HF under vacuum, was analyzed hydrolytically. A 0.3357 g analytical sample gave 38.2 cc NF_3, 18.0 mg B, 14.8 mg Sb, and 4.91 mg Ag. From these data, the calculated composition of the product (in mole percent) was 93.0 NF_4BF_4, 4.6 $NF_4SbF_6 \cdot 0.51SbF_5$, and 2.6 $AgBF_4$.

HCl As a Metal Precipitant. A 29 g sample of NF_4BF_4 (93 mole percent purity), was dissolved in 23 g HF in a Teflon container which was then pressurized to 10 psi with HCl (3 g). The pressure rose to 15 psi on standing at ambient temperature for 5 minutes, after which time the mixture was filtered to remove 0.70 g AgCl. The solvent was removed from the filter cake and filtrate under vacuum, and 28 g of HF-soluble, nonvolatile products was recovered. A 0.3446 g sample of the recovered NF_4BF_4 was analyzed and 38.24 cc NF_3, 18.9 mg B, 17.1 mg Sb, and 1.61 mg Ag were obtained after hydrolysis. These values indicated a reduction in purity of the NF_4BF_4 to 90 mole percent.

A 36 g NF_4BF_4 sample of 88 mole percent purity and prepared by use of TlF, was dissolved in 19 g HF and treated with 2.5 g HCl in the same manner as described above. A pressure rise to 12 psi was observed, and only 30 g of

HF-soluble, non-volatile products were recovered after filtration and vacuum drying of the filtrate. The precipitate, TlCl (or $TlCl_3$), weighed 5 g. A 0.3384 g sample gave on hydrolysis 28.53 cc NF_3, 15.7 mg B, 11.1 mg, and 62.0 mg Tl. The purity of the treated NF_4BF_4 was reduced to about 65 mole percent.

Purification of NF_4BF_4 by Crystallization

Three analyzed batches of crude NF_4BF_4 were combined and the resulting composite (470 g) was dissolved in 490 g HF in a Teflon vessel. The resulting solution was filtered and transferred to the Teflon and Kel-F Crystallizer (Fig. 2) where it was observed through a sapphire window to be a colorless, clear solution. The residual material (23 g) remaining on the filter was primarily the relatively insoluble $AgBF_4$ (see Table 10).

Crystallization of NF_4BF_4 from the filtrate (929 g) was initiated by removal of HF under reduced pressure. After pumping for about 0.3 hr, crystals (presumably $AgBF_4$ or possibly $AgSbF_6$) had formed and continued to form slowly as 303 g HF was removed during 4.8 hours. At this point, the cold solution changed rapidly to a thick slurry of crystals (presumed to be NF_4BF_4 but possibly $NF_4SbF_6 \cdot xSbF_5$) which redissolved during 0.75 hr as the mixture warmed to ambient temperature without further removal of HF. An additional 95 g HF (total 398 g) was removed during 2.2 hours after which the crystallizer was inverted to transfer the slurry onto the filter. The vapor pressure over the slurry was 19.3 ± 1.0 inches vacuum (270 ± 25 mm) at 20 C. After cooling the upper portion of the apparatus for several hours at 2-5 C, the slurry was pressure-filtered under 8 psig GN_2. The filter cake was spray-washed with 20 ml HF at ambient temperature under 30 psig GN_2 (flow rate 555 ml/min), and the washings were combined with the mother liquor. Both the filter cake and filtrate were pumped to dryness, weighed and analyzed (see Table 10). A material balance indicated that 17 g of the solids introduced were lost by conversion to volatile products.

TABLE 10. ANALYSES OF CRYSTALLIZED NF_4BF_4

	Runs 9-11, HF Insolubles	Crystallized Filter Cake		Filtrate Residue
		Center	Periphery	
Sample Size, g	1.0119	0.3530	0.4259	0.3654
Found, mg				
NF_3(cc)	--	31.65	38.31	41.42
B	49.8	9.9	12.8	18.8
Sb	23.3	83.8	92.5	28.4
Ag	471	4.8	7.9	2.23
Cu	0.075	0.009	0.009	0.012
Ni	0.185	0.005	0.003	0.001

CONCLUSIONS AND RECOMMENDATIONS

The UV-induced synthesis of NF_4BF_4 from NF_3, BF_3 and F_2 has been developed from a batch process producing milligram quantities to a continuous process producing 2.90 g/hour of 99 mole percent purity with an 84 percent conversion of reactants to product. The process has not yet been optimized because insufficient time was available to complete the parametric investigation. Despite the lack of process optimization, approximately 0.32 Kg of 99 mole percent pure NF_4BF_4 was prepared and delivered to the Air Force on schedule.

For further development work on a solid propellant fluorine generator requiring completely gaseous non-deactivating exhaust products, it is recommended that NF_4BF_4 produced by the UV process be procured on a supply contract. At the present stage of development 100g NF_4BF_4 per week (40 hours) can be produced and obviously this rate could be increased to 300 g/week with a continuous operation. Extrapolation of data used for the design of the process equipment suggests that the NF_4BF_4 production rate could be doubled without changes in the existing equipment. During the course of a supply contract additional runs would be made with increased reactant feed rates to verify this postulate and subsequently optimize the production rate and conversion.

Alternatively, for development work on a solid propellant fluorine generator where formation of a clinker is permissible, utilization of NF_4BF_4 as the oxidizer would be highly advantageous in that the lower formula weight (relative to other NF_4^+ sources) provides a larger proportion of available F_2 per pound of oxidizer. For this application it is recommended that NF_4BF_4 produced by either the UV process or the metathetical process should be utilized. At the present stage of development metathetical NF_4BF_4 (93 mole percent or 84 weight percent) can be produced at the rate of 150 g/week (40 hours). Experience gained on this contract suggests that 300 g/week can be prepared without changes in the existing equipment.

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APPENDIX I. SMALL SCALE UV EXPERIMENTS

Expt. No.	Reaction Temp., °C	Photolysis Time, hrs.	Mole Ratio		Total F_2 Used, cc	Reactant Addition		Pressure Range (during photolysis), mm	Reactor Used(b)	Lamp to Condensed Reactant Distance(c) cm	UV Lamp Type(d)	NF_4BF_4 Weight		Average NF_4BF_4 Formation Rate, mg/hr
			$\frac{BF_3}{NF_3}$	$\frac{F_2}{NF_3}$		Mode(a)	Amounts Added(cc) and Addition Times (min)					mg	Method(e)	
1	amb.	18	1	1	54	B		~650	TS	27	H(A)	0	V	0
16	amb.	0.08	1	1	128	B	-	(105 psig)(f)	S	7	H(A)	0	V	0
6	amb.	5	1	1(g)	140	B	-	~1000	TS	27	H(A)	0	V	0
	-78	42												
5	-78	10	1	2(g)	131	B	-	700-690	TS	27	H(A)	trace	V	trace
2	amb.	15.5	1	9	250	B	-	958-926	TS	27	H(A)	trace	V	trace
	-196	7.5						undetermined						
3	amb.	16.5	1	2.2	161	B	-	978-950	TS	27	H(A)	trace	V	trace
	-196	14						158 ± 10						
7	amb.	64	1	2(g)	140	B	-	968-948	TS	27	H(A)	0	V	0
	-196	16						170 ± 10				95	M	6
8	amb.	1	1	2(g)	140	B	-	978-966	SSS-8	25	H(A)	0	V	0
	-196	9.5						135-115				33	M	3.5
	amb.	7						undetermined				0	M	0
9	amb.	16	1	2	372	B	-	(>31 psig)(f)	SSS-B	25	H(A)	0	M	0
	-196	8						undetermined				120	M	15
	amb.	16										0	M	0
17	-196	10	1	0.5	300	B	-	undetermined	SSS-8	25	H(A)	trace	V	trace
	amb.	2						(85 psia)				0	M	0
	-(h)	3						undetermined				0	M	0
13	-115	2	3.3	0.9	180	I	100 NF_3 + 400 BF_3 + 80 F_2 (initially); 100 BF_3 (15), 6 x 30 BF_3(15 intervals); 50 NF_3 (30), 2 x 25 NF_3(30 intervals); 50 F_2 (30), 25 F_2 (60), 20 F_2 (90)	800-500	SB	12	H(A)	7	G	3.5
14	-140 ± 7	2	1.1	0.25	150	I	400 NF_3 + 650 BF_3 + 50 F_2 (initially); 5 x 40 NF_3(20 intervals); 3 x 33 F_2(30 intervals)	500-350	SB	12	H(A)	3.5	G	1.7
12	-186	8	1	2	140	B	-	~250	TS	27	H(A)	64	M	8
55	-186	2	1	0.83	1000	B	10% F_2 added before NF_3+BF_3	370-350	SB	12	H(A)	69	G	34.5
54	-186	2	1	0.50	600	B	17% F_2 added before NF_3+BF_3	260-230	SB	12	H(A)	75	G	37.5
53	-186	2	1	0.33	400	B	25% F_2 added before NF_3+BF_3	225-150	SB	12	H(A)	69	G	34.5
52	-186	2	1	0.17	200	B	-	230-125	SB	12	H(A)	71	G	35.5
50	-186	2	1	0.17	200	B	-	275-115	SB	12	H(A)	76	G	38
51	-186	2	1	0.08	100	B	-	150-60	SB	12	H(A)	71	G	35.5
18	-196	2	0.21	0.14	200	I	1000 NF_3 + 100 BF_3 + 66 F_2 (initially); 2 x 200 NF_3(45 intervals); 2 x 100 BF_3(30 intervals); 4 x 33 F_2 (25 intervals)	60-40	SB	12	H(A)	49	G	24.5
19	-196	2	0.21	0.29	400	I	1000 premixed NF_3/BF_3 = 14/3 + 200 F_2 (initially); 3 x 100 NF_3/BF_3 and 5 x 50 NF_3/BF_3 (10-15 intervals) 2 x 100 F_2 (30 intervals)	120-60	SB	12	H(A)	low(i)	V	-
20	-196	2.5	0.21	0.21	300	I	1700 premixed NF_3/BF_3 = 14/3 + 200 F_2 (initially);	200-100	SSS-3	12	H(A)	0	V	0

							before NF_3+BF_3							
54	-186	2	1	0.50	600	B	17% F_2 added before NF_3+BF_3	260-230	SB	12	H(A)	75	G	37.5
53	-186	2	1	0.33	400	B	25% F_2 added before NF_3+BF_3	225-150	SB	12	H(A)	69	G	34.5
52	-186	2	1	0.17	200	B	-	230-125	SB	12	H(A)	71	G	35.5
50	-186	2	1	0.17	200	B	-	275-115	SB	12	H(A)	76	G	38
51	-186	2	1	0.08	100	B	-	150-60	SB	12	H(A)	71	G	35.5
18	-196	2	0.21	0.14	200	I	1000 NF_3 + 100 BF_3 + 66 F_2 (initially); 2 x 200 NF_3(45 intervals); 2 x 100 BF_3(30 intervals); 4 x 33 F_2 (25 intervals)	60-40	SB	12	H(A)	49	G	24.5
19	-196	2	0.21	0.29	400	I	1000 premixed NF_3/BF_3 = 14/3 + 200 F_2 (initially); 3 x 100 NF_3/BF_3 and 5 x 50 NF_3/BF_3 (10-15 intervals) 2 x 100 F_2 (30 intervals)	120-60	SB	12	H(A)	low[(i)]	V	-
20	-196	2.5	0.21	0.21	300	I	1700 premixed NF_3/BF_3 = 14/3 + 200 F_2 (initially); 100 F_2 (60)	200-100	SSS-3	12	H(A)	0	V	0
82	-196	1	0.5	0.13	300	C	100 F_2 (initially); 3600 premixed NF_3/BF_3 = 2/1 + 200 F_2 (50)	~300	SF	7.5	GE	490	G	490
21	-196	1.75	4.67	0.67	200	C	200 F_2 (initially); 1730 premixed NF_3/BF_3 = 1/4.67 (105)	300-250	SSS-3	12	H(A)	142	M	47
		1.25	4.67	0.33	100	C	100 F_2 (initially); 1700 premixed NF_3/BF_3 = 1/4.67 (75)							
25	-196	2	4.67	0.56	200	C	200 F_2 (initially); 2040 premixed NF_3/BF_3 = 1/4.67 (120)	350-230	SB	12	H(A)	28	G	14
26	-196	1	4.67	0.56	200	C	200 F_2 (initially); 2000 premixed NF_3/BF_3 = 1/4.67 (60)	350-220	SB	12	H(A)	18	G	18
28	-196	1	4.67	0.56	200	C	200 F_2 (initially); 2000 premixed NF_3/BF_3 = 1/4.67 (60)	350-215	SB	12	H(A)	16	G	16
29	-196	1	4.67	0.56	200	C	200 F_2 (initially); 2000 premixed NF_3/BF_3 = 1/4.67 (60)	350-190	SB	12	H(A)	19	G	19
27	-196	1	4.67	0.56	200	B[(j)]	200 F_2 (initially); 2000 premixed NF_3/BF_3 = 1/4.67 (60)	350-185	SB	12	H(A)	14	G	14
30	-196	2	4.67	0.56	200	C	200 F_2 (initially); 2000 premixed NF_3/BF_3 = 1/4.67 (55)	350-145	SB	12	H(A)	45	G	22.5
31	-196	2	4.67	0.56	200	C	200 F_2 (initially); 2000 premixed NF_3/BF_3 = 1/4.67 (15)	300-115	SB	12	H(A)	52	G	26
32	-196	2	4.67	0.56	200	B	-	200-120	SB	12	H(A)	54	G	27

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APPENDIX I (CONT'D)

Expt. No.	Reaction Temp., °C	Photolysis Time, hrs.	Mole Ratio		Total F_2 Used, cc	Reactant Addition		Pressure Range (during photolysis), mm	Reactor Used(b)	Lamp to Condensed Reactant Distance(c) cm	UV Lamp Type(d)	NF_4BF_4 Weight		Average NF_4BF_4 Formation Rate, mg/hr
			BF_3/NF_3	F_2/NF_3		Mode(a)	Amounts Added(cc) and Addition Times (min)					mg	Method(e)	
33	-196	2	4.67	0.2	65	B	-(k)	70-60	SB	12	H(A)	58	G	29
34	-196	2	4.67	0.2	65	B	-(k)	30-25	SB	12	H(A)	48	G	24
81	-196	1	2.2	0.23	300	C	100 F_2 initially); 3600 premixed NF_3/BF_3 = 1/2.2 + 200 F_2 (60)	375-300	SF	7.5	GE	495	G	495
80	-196	1	1.77	0.15	300	C	200 F_2 + 2600 premixed NF_3/BF_3 = 1/1 (initially); 1000 BF_3 (60)	undetermined	SF	7.5	GE	655	G	655
39	-196	2	1	0.17	200	B	-	85-50	SB	12	H(A) 49.5%T	43	G	21.5
40	-196	2	1	0.17	200	B	-	80-45	SB	12	H(A) 49.5%T	46	G	23
41	-196	2	1	0.17	200	B	-	80-55	SB	12	H(A) 36.3%T	34	G	17
42	-196	2	1	0.17	200	B	-	80-50	SB	12	H(A) 33.0%T	27	G	13.5
23	-196	1	1	7.8	1165	C	1165 F_2 (initially); 300 premixed NF_3/BF_3 = 1/1 (50)	~350	SSS-3	12	H(A)	14	M	14
24	-196	2	1	7.8	1165	B	-(k)	~350	SSS-3	12	H(A)	20	M	10
22	-196	2	1	4.4	660	C	660 F_2 (initially); 300 premixed NF_3/BF_3 = 1/1 (50)	~350	SSS-3	12	H(A)	59	M	29.5
4	-196	1.5	1	2.3	145	B	-	undetermined	ST	7	H(A)	trace	V	trace
56	-196	2	1	1	1200	B	8% F_2 added before NF_3 + BF_3	260-240	SB	12	H(A)	70	G	35
48	-196	2	1	0.67	>800(l)	B	25% F_2 added before NF_3 + BF_3	250-175	SB	12	H(A)	63	G	31.5
49	-196	2	1	0.67	800	B	25% F_2 added before NF_3 + BF_3	275-215	SB	12	H(A)	80	G	40
43	-196	2	1	0.5	600	B	-	220-165	SB	12	H(A)	66	G	33
47	-196	2	1	0.5	600	B	-	190-140	SB	12	H(A)	80	G	40
46	-196	2	1	0.42	500	B	-	175-125	SB	12	H(A)	82	G	41
38	-196	2	1	0.33	400	B	-	145-95	SB	12	H(A)	74	G	37
45	-196	2	1	0.25	300	B	-	125-70	SB	12	H(A)	72	G	36
35	-196	2	1	0.17	200	B	-	100-60	SB	12	H(A)	54	G	27
36	-196	2	1	0.17	200	B	-	110-70	SB	12	H(A)	65	G	32.5
37	-196	2	1	0.17	200	B	-	100-65	SB	12	H(A)	61	G	30.5
64	-196	2	1	0.17	200	B	-	130-70	SB	12	H(A)	60	G	30
44	-196	2	1	0.08	100	B	-	55-30	SB	12	H(C)	57	G	28.5
66	-196	2	1	0.33	200	B	-	180-90	SB	12	H(C)	58	G	29
57	-196	2	1	0.30	600	B	33% F_2 added before NF_3 + BF_3	150-100	SB	12	H(A)	71	G	35.5
58	-196	2	1	0.30	600	B	33% F_2 added before NF_3 + BF_3	180-120	SB	12	H(A)	75	G	37.5
59	-196	4	1	0.30	600	B	33% F_2 added before NF_3 + BF_3	200-125	SB	12	H(A)	145	G	36.2
10	-196	4.5	1	0.67	100	-	100 F_2 + 100 premixed NF_3/BF_3 = 1/1 (initially); 2 x 100 premixed NF_3/BF_3 = 1/1 (210 and 240)	undetermined	SB	12	H(A)	38	G	8.4
11	-196	3	1	0.29	200	I	2 x 50 F_2 + 50 premixed NF_3/BF_3 = 1/1	150 ± 20	SB	12	H(A)	60	G	20

37	-196	2	1	0.17	200	B	-	100-65	SB	12	H(A)	61	G	30.5
64	-196	2	1	0.17	200	B	-	130-70	SB	12	H(A)	60	G	30
44	-196	2	1	0.08	100	B	-	55-30	SB	12	H(C)	57	G	28.5
66	-196	2	1	0.33	200	B	-	180-90	SB	12	H(C)	58	G	29
57	-196	2	1	0.30	600	B	33% F_2 added before NF_3 + BF_3	150-100	SB	12	H(A)	71	G	35.5
58	-196	2	1	0.30	600	B	33% F_2 added before NF_3 + BF_3	180-120	SB	12	H(A)	75	G	37.5
59	-196	4	1	0.30	600	B	33% F_2 added before NF_3 + BF_3	200-125	SB	12	H(A)	145	G	36.2
10	-196	4.5	1	0.67	100	I	100 F_2 + 100 premixed NF_3/BF_3 = 1/1 (initially); 2 x 100 premixed NF_3/BF_3 = 1/1 (210 and 240)	undetermined	SB	12	H(A)	38	G	8.4
11	-196	3	1	0.29	200	I	2 x 50 F_2 + 50 premixed NF_3/BF_3 = 1/1 (initially and 15); 16 x 33 NF_3/BF_3 = 1/1 (10 intervals) 2 x 50 F_2 (60 intervals	150 ± 20	SB	12	H(A)	60	G	20
15	-196	3	1	0.29	112	I	50 F_2 + 200 premixed NF_3/BF_3 = 1/1 (initially); 36 x 15.5 premixed NF_3/BF_3 = 1/1 (5 intervals); 10 x 6.2 F_2 (15 intervals)	75-50	SB	12	H(A)	70	G	23
65	-196	2	1	0.67	800	B	25% added before NF_3 + BF_3	340-250	SF	9	H(B)	165	G	82.5
63	-196	2	1	0.42	500	B	40% F_2 added before NF_3 + BF_3	220-150	SF	9	H(B)	157	G	78.5
60	-196	2	1	0.17	200	B	-	110-70	SF	9	H(B)	135	G	67.5
61	-196	2	1	0.17	200	B	-	115-70	SF	9	H(B)	142	G	71
62	-196	2	1	0.17	200	B	-	150-90	SF	9	H(A)	89	G	44.5
67	-196	2	1	0.17	200	B	-	210-100	SF	7.5	H(B)	220	G	110
68	-196	7	1	0.5	600	B	33% F_2 added before NF_3 + BF_3	260-190	SF	7.5	H(B)	764	G	109
74	-196	3	1	0.43	600	B	17% F_2 added before NF_3 + BF_3	500-225	SF	7.5	GE	1174	G	391
78	-196	1	1	0.33	400	B	25% F_2 added before NF_3 + BF_3	~240	SF	7.5	GE	614	G	614
70	-196	1	1	0.33	400	B	13% F_2 added before NF_3 + BF_3	~175	SF	7.5$^{(m)}$	GE	708	G	708
72	-196	1	1	0.33	400	B	13% F_2 added before NF_3 + BF_3	200-175	SF	7.5	GE	804	G	804
71	-196	0.5	1	0.33	400	B	13% F_2 added before NF_3 + BF_3	~225	SF	7.5	GE	444	G	888
73	-196	1	1	0.33	400	B	13% F_2 added before NF_3 + BF_3	~200	SSS-3	10.5	GE	170	G	170
76	-196	1	1	0.23	300	B	33% F_2 added before NF_3 + BF_3	~350	SF	7.5	GE	705	G	705
79	-196	1	1	0.15	200	B	50% F_2 added before NF_3 + BF_3	~125	SF	7.5	GE	614	G	614

APPENDIX I (CONT'D)

Expt. No.	Reaction Temp., °C	Photolysis Time, hrs.	Mole Ratio BF_3/NF_3	Mole Ratio F_2/NF_3	Total F_2 Used, cc	Reactant Addition Mode$^{(a)}$	Reactant Addition Amounts Added(cc) and Addition Times (min)	Pressure Range (during photolysis), mm	Reactor Used$^{(b)}$	Lamp to Condensed Reactant Distance$^{(c)}$ cm	UV Lamp Type$^{(d)}$	NF_4BF_4 Weight mg	NF_4BF_4 Weight Method$^{(e)}$	Average NF_4BF_4 Formation Rate, mg/hr
69	-196	0.25	1	0.17	200	B	-	~200	SF	7.5	GE	251	G	1004
75	-196	0.25	1	0.17	200	B	-	~175	SF	7.5	III	293	G	1172
77	-196	1	1	0.33	400	C	$NF_3/BF_3/F_2$ premixed	~250	SF	7.5	GE	723	G	723
B3	-196	2	1	0.12	300	C	100 F_2 + 50 premixed NF_3/BF_3 = 1/1 (initially); 5000 premixed $NF_3/BF_3/F_2$ = 1/1/0.083 (13% in 30; 39% in 50; 79% in 60; 100% in 120)	500-175	SF	7.5	GE	1226	G	613
84	-196	4	1	0.21	390	I	50 F_2 + 300 premixed $NF_3/BF_3/F_2$ = 1/1/0.18 (initially); 11 x 380 premixed $NF_3/BF_3/F_2$ = 1/1/0.19 (15 intervals)	~200	SF$^{(n)}$	7.5	GE	2558	G	647

(a) B = Before photolysis
C = Continuous during photolysis (or for time specified)
I = Intermittant addition of specified reactants at time specified

(b) TS = 2" sapphire window on 9" Teflon test tube
SSS-8 = 2" sapphire window on 8" 347 stainless steel tube
SSS-3 = 2" sapphire window on 3" 347 stainless steel tube
ST = 0.5" o.d. x 3" silica tube
SB = 3" diameter silica bulb
SF = 3" diameter flat-windowed x 1.25" silica vessel
S = 1/2" diameter sapphire tube

(c) Or distance to reactor bottom if no condensed phase was present.

(d) H(X) = 100w Hanovia Utility Lamp (letter designation for individual bulbs)
GE = 1000w BH6 High Pressure Mercury Arc Lamp, General Electric
III = 1000w BH6-1-B High Pressure Mercury Arc Lamp, Illumination Industries, Inc.

(e) G = Weight determined gravimetrically (but not corrected for changing tare of silica reactors)
M = Weight calculated from pressure decrease after photolysis (manometric method)
V = Visual estimate

(f) Pressure before photolysis.

(g) ClF_5 also added; Mole ratio ClF_5/NF_3 = 0.15 (Experiment 6); ClF_5/NF_3 = 2.3 (Experiment 5); ClF_5/NF_3 = 0.1 (Experiments 7 and 8).

(h) Temperature cycled between ambient and -196 C twelve times.

(i) Reactor leaked after photolysis and solid product was partially hydrolyzed.

(j) All reactants introduced exactly as in experiment 29 but before photolysis.

(h)-(n) 2" sapphire window on 9" Teflon test tube (j)All reactants introduced exactly as in

(b)TS = 2" sapphire window on 9" Teflon test tube
SSS-8 = 2" sapphire window on 8" 347 stainless steel tube
SSS-3 = 2" sapphire window on 3" 347 stainless steel tube
ST = 0.5" o.d. x 3" silica tube
SB = 3" diameter silica bulb
SF = 3" diameter flat-windowed x 1.25" silica vessel
S = 1/2" diameter sapphire tube

(c)Or distance to reactor bottom if no condensed phase was present.

(d)H(X) = 100w Hanovia Utility Lamp (letter designation for individual bulbs)
GE = 1000w BH6 High Pressure Mercury Arc Lamp, General Electric
III = 1000w BH6-1-B High Pressure Mercury Arc Lamp, Illumination Industries, Inc.

(e)G = Weight determined gravimetrically (but not corrected for changing tare of silica reactors)
M = Weight calculated from pressure decrease after photolysis (manometric method)
V = Visual estimate

(f)Pressure before photolysis.

(g)ClF_5 also added; Mole ratio ClF_5/NF_3 = 0.15 (Experiment 6); ClF_5/NF_3 = 2.3 (Experiment 5); ClF_5/NF_3 = 0.1 (Experiments 7 and 8).

(h)Temperature cycled between ambient and -196 C twelve times.

(i)Reactor leaked after photolysis and solid product was partially hydrolyzed.

(j)All reactants introduced exactly as in experiment 29 but before photolysis.

(k)Premixed NF_3/BF_3 added to reactor before F_2.

(l)Some uncertainty in amount of F_2 but over 800 cc.

(m)Lamp inadvertently placed off center of reactor.

(n)Reactor inlet in center of photolysis zone.

APPENDIX II. LARGE SCALE UV-SYNTHESIS OF NF_4BF_4[a]

Run No.	Pressure Range, mm		Feed Cycle ON(sec)-OFF(min)	Lamp-Cold Face Distance, cm	Estimated Average UV Intensity (cm from lamp) w/cm^2 x 100	Photolysis Time, hours	NF_4BF_4 Average Rate, g/hour
	Reactor	Feed Line					
1	615-692	~838	0.15-0.50	4.2	2.4 (85)	4	0.50
2	267→590[b]	~950	0.15-0.50	9.2	2.5 (80)	2	0.90
3	494-538	~924	0.30-0.50	4.2	2.4 (85)	7	1.50
4	538-569	~985	0.30-0.50	6.7	2.8 (82.5)	2	0.36
5	473-590	~985	0.30-1.00	6.7	2.0 (82.5)	4	1.15
6	446-515	~940	0.30-1.00	4.2	2.0 (85)	3.5	0.97
7	472-583	~964	0.30-1.50	4.2	2.0 (85)	3	1.62[c]
8	333-357	~956	0.30-0.33	4.2	1.8 (85)	1	
9[d]	590→827[b]	~1020	0.30-0.50	4.2	2.2 (85)	7	2.36[c]
10[d]	505-540	~1020	0.30-0.50	4.2	1.8 (85)	7	
11[d]	503-554	~964	0.40-0.50	4.2	2.1 (85)	12.5	1.86[c]
12	495-555	~940	0.30-0.50	4.2	1.8 (85)	15	1.33[c]
13[e]	534-600	~940	0.30-0.50	4.2	3.2 (85)	5	
14	380-430	~958	0.30-0.50	4.2	2.3 (85)	35(12+15+8)	1.43
15	580-650	~920	0.30-0.50	4.2	2.0 (85)	13	1.68[c]
16[d]	600-625	~910	0.30-0.50	4.2	1.8 (85)	13	
17[d]	515-545	~1050	0.30-0.50	4.2	2.4 (85)	13	
18[d,e]	520-550	~1080	0.60-1.00	4.2	1.9 (85)	22(8+14)	0.83[c]
19	480-580	~1080	0.60-1.00	4.2	2.1 (85)	34(11+14.5+8.5)	2.90
20[e]	506-540	~1190	0.60-1.50	4.2	2.1 (85)	23(15+8)	1.72[c]
21	500-540	~1130	0.60-2.00	4.2	2.3 (85)	15(9+6)	1.67[c]

[a] Equimolar NF_3-BF_3-F_2 used as reactant feed mixture for all runs. Product scraped from reactor cold face at 30 min. intervals (Runs 1-8) or 15 min. intervals (Runs 9-18).

[b] Pressure in reactor not relieved after each scraping of reactor cold face.

[c] Includes normal product hold-up of reactor which had been mechanically transferred to NF_4BF_4 receiver.

[d] Reactor cold face normally refrigerated with LN_2 at about atmospheric pressure except for Runs 9, 10 and 11 (20 psig); Run 16 and 18 (22 psig); and Run 17 (14 psig).

[e] Reactor disassembled and washed at conclusion of run.