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SHORT COMMUNICATION

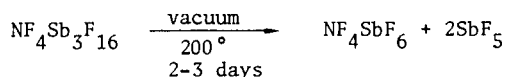
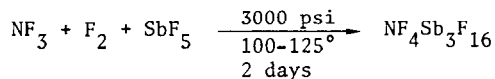
Improved Syntheses of NF_4BF_4 and NF_4SbF_6

Karl O. Christe, Carl J. Schack, and Richard D. Wilson

Rocketdyne, a Division of Rockwell International,
Canoga Park, California 91304

In view of the importance of NF_4^+ salts for solid propellant $\text{NF}_3\text{-F}_2$ gas generators [1], improved syntheses of NF_4BF_4 and NF_4SbF_6 were required.

Two methods have previously been reported for the synthesis of $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$ involving the use of either high pressure and temperature [2,3] or uv-irradiation [4]. Of these, the thermal method is more convenient for larger scale production. According to Tolberg et al. [2,3] the most favorable reaction conditions are:

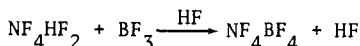
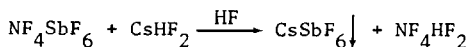
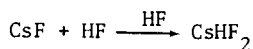


The resulting product contained an appreciable amount of Monel salts and was removed from the reactor by cutting it open with a hacksaw and scraping out the hard clinkered product. Based on recent work done in our laboratory [1], temperatures (250-260°), higher than those reported by Tolberg, are required for the vacuum pyrolysis of $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$ to NF_4SbF_6 within a reasonable time period.

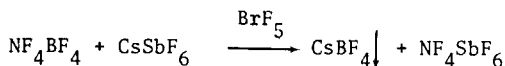
We have now found that most of the drawbacks of the above procedure can be avoided by directly synthesizing NF_4SbF_6 . For this purpose, NF_3 , F_2 , and SbF_5 in a 2:2:1 mol ratio are heated in a Monel cylinder to 250° for 72 hours. The size of the cylinder is chosen in such manner that at the completion of the reaction the autogenous pressure is about 70 atm. The excess of NF_3 and F_2 is removed under vacuum at room temperature and the desired NF_4SbF_6

product is extracted from the Monel cylinder with anhydrous HF using about 50 ml of liquid HF per 100 g of NF_4SbF_6 . Since, contrary to a previous report [3], the formed Monel salt impurities (about 5%) are quite insoluble in anhydrous HF, they can be easily removed from the product by incorporating a porous Teflon filter (Pall Corporation) into the HF solution transfer line. Based on elemental and spectroscopic analyses and the observed material balances, the resulting product was shown to be essentially pure NF_4SbF_6 .

Several methods have previously been reported for the synthesis of NF_4BF_4 . This salt can be prepared either directly from NF_3 , F_2 , and BF_3 using glow discharge [5,6], bremsstrahlung [7] or ultraviolet radiation [4,8], or indirectly from NF_4SbF_6 using a metathetical process [3,9]. Of these, the metathetical process is most amenable to the larger scale production of NF_4BF_4 utilizing existing technology. The original metathetical NF_4BF_4 process [3] involved the following steps:



Since the crude product, thus obtained, contained much CsSbF_6 , its NF_4BF_4 content was increased by extraction with BrF_5 . The use of BrF_5 resulted in the following side reaction:



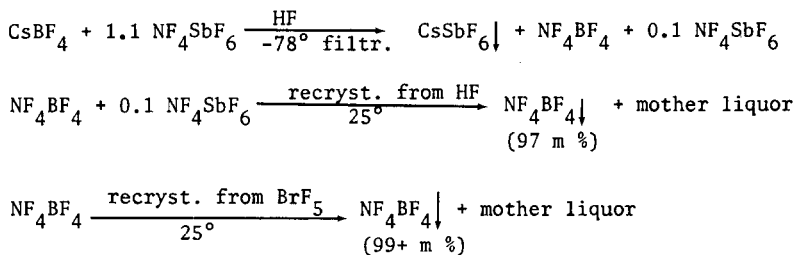
The composition of the final product was reported [3] to be: 91.5% NF_4BF_4 and 8.5% NF_4SbF_6 . In addition to the requirement of BrF_5 as a recrystallization solvent, this process suffers from the following disadvantage. Highly concentrated solutions of NF_4HF_2 in HF are unstable decomposing to NF_3 , F_2 , and HF. This can cause a pressure build up in the metathesis apparatus which in turn can render filtration steps more difficult.

This process was somewhat improved upon [9] by substituting CsF by AgF. This modification eliminated the BrF_5 extraction step and resulted in a product of the composition (mol %): NF_4BF_4 (89), $\text{NF}_4\text{Sb}_2\text{F}_{11}$ (7.9), AgBF_4 (3.1). However, the process still involved the handling of concentrated NF_4HF_2 solutions. Furthermore, the cost of silver salts is rather high and therefore requires their recycling in high yields.

We have now found that NF_4BF_4 of at least 97 mol % purity can be prepared by a simpler process using anhydrous HF at different temperatures as the only solvent. Furthermore, we have shown that the purity of the NF_4BF_4

can be raised to above 99 mol % by a single recrystallization from BrF_5 . The cesium content in both products was shown to be less than 0.1 mol %, the principal impurity being NF_4SbF_6 .

Our improved process consists of the following steps:



The important features of our process are:

- (i) The use of CsBF_4 instead of CsHF_2 eliminates one step and avoids the complications caused by NF_4HF_2 .
- (ii) The use of a 10 mol % excess of NF_4SbF_6 decreases the solubility of CsSbF_6 by the common ion effect.
- (iii) Carrying out the CsSbF_6 filtration step at -78° decreases the SbF_6^- concentration since the solubilities of SbF_6^- salts in anhydrous HF decrease with decreasing temperature much more rapidly than those of BF_4^- salts. Furthermore, the amount of NF_4BF_4 , retained in the CsSbF_6 filter cake by absorption of a certain volume of mother liquor, is minimized owing to the decreased solubilities.
- (iv) Since NF_4BF_4 and NF_4SbF_6 have comparable solubilities in HF at room temperature, the 10% excess of NF_4SbF_6 used in the CsSbF_6 precipitation step can be removed as mother liquor by recrystallization from HF at room temperature. Unfortunately, the solubilities in HF at room temperature are so high that a significant percentage of the mother liquor is retained by the NF_4BF_4 precipitate. This problem can be minimized by using for this recrystallization a solvent in which these NF_4^+ salts are less soluble. Thus, a single recrystallization from BrF_5 raised the product purity above the 99 mol % level. Other suitable solvents could be used to replace BrF_5 in this step. The mother liquors of the recrystallization steps can be easily recycled into the CsSbF_6 precipitation step, thus avoiding the loss of any NF_4^+ values.

In summary, the combination of the two improved processes for the syntheses of NF_4SbF_6 and NF_4BF_4 , respectively, results in a relatively

simple and economical process for the production of NF_4BF_4 in a purity of about 97 mol %. Furthermore, it was demonstrated for the first time that high purity (99+ mol %) NF_4BF_4 can be prepared by metathesis.

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