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New approaches to the synthesis of nitrogen trifluorides.

Message 1
Synthesis of nitrogen trifluorides by direct fluorination of ammonium salts

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In spite of seeming simplicity and abundance of different methods of nitrogen trifluoride synthesis the choice of technically reasonable and economically rational ways still remains a difficult task. This task is defined by concrete conditions of nitrogen trifluoride application, technological opportunities and technical experience of producer, the availability of necessary materials and raw materials. Methods of simple nitrogen trifluoride synthesis are mostly in full analyzed and described in monograph [1]. According to information from literature one of most explored and common ways of nitrogen trifluoride synthesis is heterogeneous fluorination of ammonium salts. However heterogeneous process of ammonium salts fluorination is hard to control because of difficulties with heat removing, which are caused by high exothermicity of the process.

In their times the works of V. Grakanskas [2] regarding direct fluorination of urea aqueous solutions and other amines made a revolution in fluorine chemistry. We thought it would be extremely interesting to check the principal opportunity of obtaining nitrogen trifluoride by direct fluorination of aqueous solutions of ammonium salts.

The process was carried out in bubbling reactor at temperature ranging from 0°C to 80°C, where the concentration of fluorine was 10-30% and concentration of salt 10-30%. Ammonium fluoride, ammonium bifluoride, ammonium chloride, ammonium carbonate and ammonium fluorosulphate were used as objects of fluorination. The results obtained allow us to make a conclusion, that NH_4 - cation is resistant to fluorine and that the nature of anion in this process doesn't influence the behavior of cation. Solid diluents (for example, sodium fluoride, which also acted as hydrogen fluoride acceptor) and metal cuttings were put into reaction mixture to improve the conditions of heat removing and rising of controllability of ammonia salts fluorination heterogeneous process.
For the same purposes we used suspensions of ammonia salts in different types of liquids inert to fluorine: chlorofluorocarbon liquids, fluorinated manometric liquids, perfluoropolyethers, perfluorinated oligomer acids and perfluoroalkylamines. The main characteristics of these liquids you can find in reference book [3].

As we expected the media didn't influence much the conditions of fluorination. Along with that it was established that direct fluorination of ammonia salt suspension can be of practical interest of simple nitrogen trifluoride synthesis.

Thus nitrogen trifluoride mainly forms during fluorination of ammonia fluoride suspension (temperature 20-80°C); tetrafluorohydrazine forms during fluorination of ammonium chloride (20-100°C), tetrafluorohydrazine and nitrogen trifluoride form simultaneously during fluorination of ammonium chloride diluted by sodium fluoride ; during fluorination of ammonia carbonate the main products of reaction were nitrogen and carbon dioxide with low content of nitrogen trifluoride. The experimental data obtained shows that the process of fluorination of ammonia salts is described by the following scheme:

$$\begin{aligned}
&NH_4F + 3F_2 \rightarrow NF_3 + 4HF\\
&2NH_4F + 3F_2 \rightarrow N_2 + 8HF\\
&4NH_4Cl + 10F_2 \rightarrow N_2F_4 + N_2 + 2Cl_2 + 16HF\\
&4NH_4Cl + 11F_2 \rightarrow 2NF_3 + N_2F_4 + 4HCl + 12HF
\end{aligned}$$

The yield of nitrogen trifluoride depends on fluorine concentration, reaction temperature and period of reagent contacts. At temperature below 80-100°C the reaction goes very slowly (though the interaction already takes place at room temperature and even lower it) however when temperature is increasing the destruction processes with formation of nitrogen and hydrogen fluoride intensify. Every salt has its own temperature optimum. Thus during fluorination of different suspensions of ammonium fluoride maximum yield of NF_3 reached about 70% at 40°C and at fluorine concentration 20% ; during fluorination of ammonium chloride maximum yield of tetrafluorohydrazine was about 20% at temperature of 80°C and at fluorine concentration 35%.

The main method of nitrogen trifluoride synthesis is electrochemical fluorination of ammonium bifluoride, though this method is not applicable everywhere because of unavoidable organofluorine admixtures formed during this process, they are absolutely inadmissible during using of the product, for example in electronics. That's why it was important to explore the process of direct fluorination of ammonium salts melts with the use of elemental fluorine. It is technically possible only for ammonium bifluoride, which unlike other ammonium salts is stable at melting point [4]. The process was carried out in nickel bubbling reactor at temperature up to 300°C and fluorine concentration ranging from 20 to 100%. It is shown that the fluorination process of ammonium bifluoride is described by two equations analogously to suspension fluorination:

$$\begin{aligned}
&NH_4F\ HF + 3F_2 \rightarrow NF_3 + 5HF\\
&2NH_4F\ HF + 4F_2 \rightarrow N_2 + 10NF
\end{aligned}$$

Three factors influence decisively the fluorination process of melt: the temperature of reaction, period of reagent contact and media acidity.

When temperature rises over 150-200^{o}C the quantity of nitrogen increases noticeably in reaction products. When temperature is much lower and contact period is less than 50 seconds the conversion reduces.

The acidity of melt increases according to generation of anhydrous hydrogen fluoride. At that the yield of nitrogen noticeably reduces and yield of base product increases. During the start moment nitrous oxide is also present in reaction gas. It disappears according to moisture expenditure.

$$NH_4F\ HF + 4F_2 + H_2O \rightarrow N_2O + 2HF,$$

According to increasing of melt acidity the yield of nitrogen trifluoride gradually increases, reaches maximum (from 67 to 85%) and then decreases again.

Averaged mixture of reaction gas: 24% of nitrogen, 2% of nitrous oxide and 74% of nitrogen trifluoride. Maximum content of nitrogen trifluoride reaches 87% (with 13% of nitrogen as admixture), that allows to use such mixture for example for tetrafluorohydrazine production without additional purification. To obtain refined nitrogen trifluoride the process of separating such mixtures is not a technical difficulty.

For increasing of summary yield of desired nitrogen trifluoride the reaction of nitrogen formation was suppressed by acidification of melt during the start period and also by using of reactor with zones, where fluorine and calculated quantity of ammonia for excessive anhydrous hydrogen fluoride absorption and keeping the optimum level of acidity.

According to information from [5] during fluorination of ammonia gas in flow reactor at cupreous catalyst nitrogen trifluoride (up to 20%), tetrafluorohydrazine (2-10%) are formed, though the process is not stable and difficult to control.

We had tried to carry out the fluorination of ammonia solution by diluted fluorine (20-30%) at low temperatures (-70 - -60^{o}C). Methylen chloride was used as dissolvent, in which ammonia is good to dissolve. In mentioned conditions we failed to obtain nitrogen trifluoride in appreciable quantities, the main products of reaction were nitrogen and ammonium fluoride.

Conclusions

1.Ammonium cation is resistant to fluorine action not depending on anions nature.

2.Ammonium salt suspension fluorination in inert media may be used for preparative purposes for nitrogen trifluoride and tetrafluorohydrazine synthesis.

3.During fluorination of ammonium bifluoride melt the nitrogen trifluoride forms with high yield. The reaction may be used for development of technology of high purity nitrogen trifluoride producing.

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