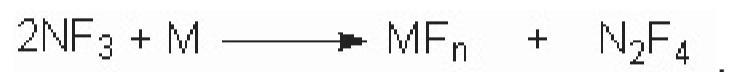


Fluorination of Sulphuric Anhydride Using Nitrogen Trifluoride

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Nitrogen trifluoride is a thermal and chemical stable compound, it is explosive, medium toxic and corrosion inactive. Due to the little chemical activity, belonging to higher non-metals fluorides, it can be related to mild fluorinating agents. Its numerous reactions described by a common equitation are among most studied.



where M- fluorine acceptor: coal, copper, hydrargyrum, arsenic, iron, nitrogen oxyde etc. [1].

We can also find the description of nitrogen trifluoride fluorination of metals, their oxides, chlorides, nitrides and sulphides [2]; non-metals oxides [3], some of oxychlorides and oxyfluorides [4] in literature.

The interaction of nitrogen trifluoride and sulphuric anhydride is described in the article [3]. According to it a nitrogen trifluoride is able to fluorinate sulphuric anhydride forming sulphur fluorides, oxyfluorides of nitrogen and sulphur. In flow reactor at 520 °C and at excess of nitrogen fluoride the $(\text{NO})_2\text{S}_2\text{O}_5\text{F}_4$ and SO_2F_2 (yield 30-35%), and SOF_2 (yield 3-4%), NO , NO_2 and traces of SF_6 are the main products of reaction. At that, the composition of products doesn't depend much on the increasing of contact period from 80 to 230 minutes, only the rate of nitrogen trifluoride conversion changed from 33% to 70%.

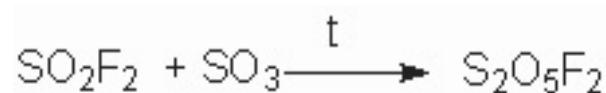
At 230 - 400 °C the mixture of SO_2F_2 and SF_6 is being formed in 62 hours in autoclave, and when nitrogen trifluoride is exceeding its original content twice only SF_6 is formed. At that the nitrogen trifluoride oxidizes to NO and NO_2 .

Thus, here is it actually shown, that composition of interaction products of nitrogen trifluoride and sulphuric anhydride strongly depends on reaction's carrying out conditions.

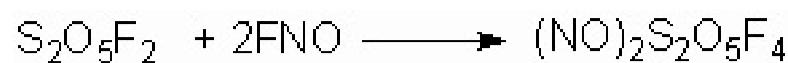
From the reaction's products in a flow system we can see, that the main reaction is a destructive fluorination of sulphuric anhydride till sulphuryldifluoride



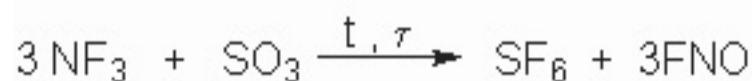
with further formation of pyrosulphuryldifluoride



and its interaction with nitrosyl fluoride



A more full destruction of sulphuric anhydride is going in autoclave at more severe conditions forming sulphur hexafluoride.



Nitrosylfluoride formed is an active fluorinating agent and this explains the presence of nitrogen oxides in reaction's products.

For the purpose of decreasing destruction products share in carrying out the reaction at severe conditions (long period of contact at high temperature) the studying of sulphuric anhydride fluorination reaction using nitrogen trifluoride at more mild conditions was of interest. For that the interaction was carried out in a flow reactor and also at high pressure and different proportion of reagents in autoclave.

In a flow system empty stainless steel pipe of 12 mm diameter served as reactor, it was put into the pipe electrical furnace. Temperature control was done using thermocouple, put into steel pocket. Gaseous nitrogen trifluoride was saturated with sulphuric anhydride by NF_3 bubbling through liquid sulphuric anhydride at 25- 45 °C. The steamy-gaseous mixture obtained was put right into reactor. Reaction products were passed in sequence through traps of - 70 °C and - 196 °C respectively. Then the traps content was evaporated into fully vacuumized collector and analyzed using methods of gas- liquid chromatography and IR-spectroscopy.

When carrying out GLC we used thermal conductivity detector with nickel threads. IR-spectra was taken in cuvettes made of Monel with windows made of calcium and barium fluorides.

The interaction of nitrogen trifluoride with sulphuric anhydride was carried out under pressure in stainless steel autoclave, equipped with manometer, needle valve of fine control and external electrical heating. Fully vacuumized and cooled with liquid nitrogen reactor was filled with calculated amounts of reagents in sequence and after that it was heated up to temperature needed. After a needed exposure at reaction temperature the reactionary gas was put into totally vacuumized vessel, cooled with liquid nitrogen, and then analyzed.

Experimental data is listed in tables 1 and 2.

Table 1. The results of reaction in Flow Reactor

#	Reaction conditions			Products, % mol.						Conversion NF_3 , %
	T, °C	Contact Period, min	Ratio $\text{NF}_3:\text{SO}_3$	NO	NF_3	N_2F_4	SO_2F_2	SOF_2	SF_6	
1	190	3,0	Excess of NF_3	3,3	95,8	0,9	-	-	-	0,0
2	160	8,0	Excess of NF_3	4,0	92,2	0,9	-	2,9	-	3,8
3	280	0,3	Excess of NF_3	2,9	95,0	1,4	0,7	-	-	0,8
4	310	1,3	1:1	3,3	95,3	0,9	0,5	-	-	0,5

5	390	0,8	1:1	3,2	92,7	1,9	0,7	1,5	-	3,2
6	475	0,2	1:1	2,8	75,1	1,0	10,4	10,6	-	21,6
7	540	0,8	1:1	6,6	14,5	2,2	73,3	3,4	-	84,9*
8	590		Excess of SO ₃	6,1	86,8	1,4	-	-	5,7	19,5**

* - Yield of sulphuryldifluoride with the expectation of reacted nitrogen trifluoride is equal to 95%

** - Yield of sulphur hexafluoride with the expectation of reacted nitrogen trifluoride is equal to near 80%

Table 2. The results of reaction in Autoclave

#	Reaction conditions				Products, % mol.						Conversion NF ₃ , %
	T , °C	Pressure, bar	Contact Period, min	Ratio NF ₃ :SO ₃	NO	NF ₃	N ₂ F ₄	SF ₆	SO ₂ F ₂	SOF ₂	
1	100	150	5,7	3,6:1	4,6	94,0	0,2	1,0	0,1	-	1,9
	140	150	4,5	3,6:1	4,7	93,2	-	1,3	0,8	-	2,7
	200	135	6,5	3,6:1	18,2	62,2	1,6	8,7	9,0	0,3	35,1
2	100	385	3,75	2,1:1	4,4	94,9	-	0,7	-	-	0,9
	140	380	9,5	2,1:1	5,5	92,4	-	1,1	1,0	-	3,6
	180	380	7,0	2,1:1	9,4	69,9	-	0,9	0,5	19,3	27,0

In advance thermal stability of sulphuric anhydride was checked in a flow reactor. At temperature up to 600 °C and contact period of 1-2 minutes the decomposition of sulphuric anhydride was not found.

As we see from the tables the interaction of nitrogen trifluoride and sulphuric anhydride in a flow system begins practically at temperature above 160 °C and only T above 400 °C the reaction goes to a great extent reaching conversion of 85% at 540 °C at a comparable little contact period. Thus when rising temperature from 390 °C to 540 °C the conversion increased sharply from 3,2% up to 84,9%. We can also see, that the reaction slows abruptly at excess of sulphuric anhydride. The main fluorination product at excess of nitrogen trifluoride is sulphuryldifluoride, and at excess of sulphuric anhydride the sulphur hexafluoride is mainly formed. The obtained results of researches testify, that decreasing of contact period have not allowed to change the reaction direction in principle. As in the article (3) the main reaction product is sulphuryl difluoride. The new one is only sulphur hexafluoride at excess of sulphuric anhydride.

In autoclave the interaction begins at lower temperature, yet at 100 °C the conversion amounts to about 2%. From the table 2 we can see, that increasing pressure in more than two times from 150 to 380 bar doesn't greatly influence the rate of reaction. The excess of nitrogen trifluoride is much more effective.

Neither in flow reactor, nor in autoclave we have not found the co-valent fluorosulphates, such as pyroxydisulphuryldifluoride, pyrosulphuryldifluoride, fluoride fluorosulphate, which could be expected as a result of sulphuric anhydride fluorination. Probably, S-O-F bonds are

not stable enough for conditions of reaction and only compounds which S-F bond is more stable maintain as a result of fluorination.

References

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- 2) Glemser O., Wegener J., Mews R., Chem. Ber., 1967, 100, N 8, 2474
- 3) Glemser O., Biermann U., Chem. Ber., 100, N 4, 1184
- 4) Glemser O., Biermann U., Chem. Ber., 100, N 8, 2484