New approaches to the nitrogen fluoride synthesis

Message 2. Fluorination of some hydroxylamines.

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In the monograph [1] the hydroxylamines fluorination process is not mentioned at all as nitrogen fluorides obtaining method, that's why we have made an attempt to study the opportunity of nitrogen fluoride and oxyfluoride using the example of interaction of fluorine with sulfuric hydroxylamine and hydroxylamine-o-sulpho-acid (HASA). Hydroxylamine-o-sulpho-acid in our opinion is a convenient model reagent, which is able to delocalize the charge in molecule and thus is more resistant to different destructive processes. In other literature the works regarding the obtaining of nitrogen fluorides and oxyfluorides by fluorination of hydroxylamines are absent.

In the work [2] it is informed that at fluorination of hydroxylamine hydrochlorides and o-methylhydroxylamine the interaction products were only nitrous oxide (yield up to 60%) and anhydrous hydrogen fluoride. At fluorination of o-methylhydroxylamine the formation of some nitrogen fluoride is also noted.

In the article [2] the reaction has been studied only in heterogeneous conditions and its results indicate the fact that heterogeneuos fluorination of hydroxylamines passes according to the scheme of cross-linking fluorination with formation of intermediate unstable derivatives of hydrazine and azo-compounds like it takes place at heterogeneous fluorination of urea and other amines and imines [3].

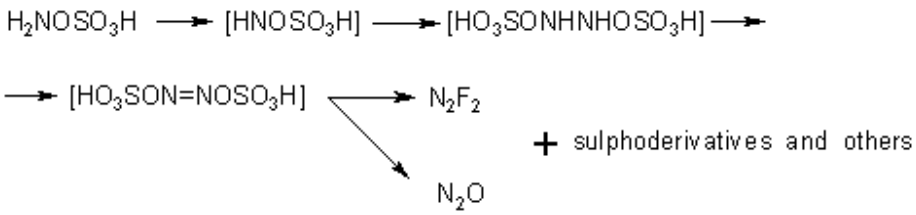
Heterogeneous fluorination of hydroxylamine-o-sulpho-acid was carried out in nickel autoclave or in stainless steel flow reactor separately as well as in mixtures with sodium fluoride.

The carrying out conditions of the experiments and the combination of reaction gaseous products are listed in the table.

It was stated experimentally that at heterogeneous fluorination in autoclave as well as in flow reactor the reaction main products were nitrous oxide and difluorodiazines, the total content of which in reaction products was 91-93% in the flow reactor and in autoclave was about 83% (not including sulfoderivatives). At that under the action of concentrated fluorine in autoclave the biggest relative contents of difluorodiazines (N_2F_2 : N_2O = 0.75) is noted, which in flow reactor using diluted fluorine essentially lowers when temperature increases. (from 0,48 at 6^0C to 0,39 at 40^0C).

At the same time the contents of nitrogen trifluoride slightly increases when temperature goes up (from 3,7 to 4,2 % mol.). At dilution of hydroxylamine-o-sulpho-acid with sodium fluoride in ratio of 1:1 the situation sharply changes: at the same total yield of azo-derivatives (about 92%) the proportion N_2F_2 : N_2O = 0,11, but the formation of nitrogen trifluoride is almost absent.

Both difluorodiazines and nitrous oxide are the destruction products of intermediate azo-compounds, which are formed according to the scheme of cross-linking fluorination:

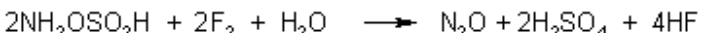


That's why it can be considered that the process of heterogeneous fluorination of hydroxylamines is similar to the heterogeneous fluorination of amines and imines [3].

The formation of nitrogen trifluoride takes place only in o-substituted hydroxylamines (hydroxylamine-o-sulpho-acid and o-methylhydroxylamine), though its yield is not big. As it was expected hydroxylamine-o-sulpho-acid appeared to be a more convenient reagent for direct nitrogen fluoride synthesis than un-substituted hydroxylamine, but relatively small yield of difluorodiazines and nitrogen trifluoride doesn't allow to consider its heterogeneous fluorination as perspective synthesis method of nitrogen trifluoride.

As long as results of fluorination of amines, imines and ammonia salts solutions sharply differ from their heterogeneous fluorination, then we had studied the fluorination of hydroxylamine-o-sulpho-acid solutions with fluorine-helium mixtures, in water, sulphuric and fluorosulfonic acids. The fluorination of sulfuric hydroxylamine aqueous solution was carried out for comparison of results with literature data. The results of research are listed in the table.

The main nitrogen-containing product of the reaction at fluorination of hydroxylamine and hydroxylamine-o-sulpho-acid aqueous solutions is nitrous oxide, forming according to the reactions:



$$2NH_2OH + 2F_2 \longrightarrow N_2O + H_2O + 4HF$$

The content of nitrous oxide in a few cases reached 99%. At the same time few essential patterns of relationship can be noted. The nitrogen trifluoride yield is not high and doesn't exceed several percents in all studied cases. This indicates that as in the case of heterogeneous fluorination the main path is the process of structuring with further destruction of intermediate azo-derivatives. The ratio between difluorodiazines and nitrous oxide at the final stage of destruction process is mainly determined by process carrying out conditions (reactor material, reaction temperature, concentration and time of reagent's contacting).

The fluorination of hydroxylamine-o-sulpho-acid solutions was carried out in the stainless steel reactors, nickel or fluorocarbon polymer coated steel reactors. Fluorine-helium mixture was fed using bubbler to under the solution layer, and gaseous products of reaction were accumulated in the vacuum-processed reservoir. During some experiments the selection of gas phase for the analysis was held directly from the reactor. In the stainless steel reactors and with fluorocarbon polymer coating the formation of difluorodiazines is not discovered. The contents of nitrous oxide is 89-90% and it depends a little on other process carrying out conditions. The experiments N 8 and 9 (see table) was exceptional cases, when essential concentration of difluorodiazines and nitrous oxide was detected.

Relatively high yield of difluorodiazines is observed in the nickel reactor, catalytic influence of vessel's walls, containing nickel fluorides that as is well known are effective catalysts of fluorination processes, explains this fact. The confirmation of this version is the fact that during the fluorination process the vessel wall was being intensively destroyed. In 10-15 experiments the inner surface of the reactor reminded of fine-grained abrasive material.

When temperature of reaction goes up the yield of difluorodiazines increase in the beginning, and then decrease again, reaching the maximum at temperature of 40-50^0. The further temperature rise up to 60-80^0 sharply decreases the yield of difluorodiazines, that can be explained by the speeding up of the intermediate azo-contents hydrolysis:

$$[HO_3SON{=}NOSO_3H] + H_2O \longrightarrow N_2O + 2H_2SO_4$$

The lowering of reagent's concentration results in increasing of difluorodiazines yields, that is obvious from the comparison experiments 13-17, 14-18, 15-16. The increasing of reagent's contacting time doesn't influence the formation of difluorodiazines.

The highest yield of difluorodiazines at fluorination of hydroxylamine-o-sulpho-acid aqueous solutions was managed to obtain in nickel reactor at 45^{0}C, hydroxylamine-o-sulpho-acid concentration 5% mass. and with using of 5% fluorine-helium mixture (ratio N_2F_2 : N_2O is about 0,4).

The largest temperature interval is studied at fluorination of hydroxylamine-o-sulpho-acid solutions in fluorosulphonic acid. At that it is determined that at temperature from -50^{0}Ñ to 0^{0}C the yield of difluorodiazines doesn't change at all further according to the temperature increase to about 60^{0}C increase of total nitrogen fluoride yield takes place, and then on one hand the share of structuring processes sharply increases and on the other hand acid's hydrolysis of intermediate structures also increases. This results in abrupt lowering of nitrogen fluorides yield and increase of nitrous oxide yield. The wear of rector's surface is more than during of aqueous fluorination process.

At fluorination of hydroxylamine-o-sulpho-acid solutions in sulphuric acid even at moderate temperatures and small concentrations of reagents the main gaseous reaction products were sulphur oxides and sulfur fluorooxides, and though the proportion N_2F_2 : N_2O was roughly equal the detailed study of this reaction was not of practical interest.

Thus the most important from the point of view of nitrogen fluoride synthesis is the reaction of fluorination of hydroxylamine-o-sulpho-acid solutions in fluorosulphonic acid when using the nickel reactor.

The results of fluorine and hydroxylamine-o-sulpho-acid interaction in different conditions testify that fluorination of o-substituted hydroxylamines can be considered as one of the obtaining methods of some nitrogen fluorides.

N	**Reaction conditions**					**Products distribution, % mol.**						**P.S.**
	Conc. HASA, % mass.	F_2 conc., % mol.	T,^{o}C	Solvent	Reactor material	NO+ N_2+ O_2	NF_3	N_2F_2	N_2O	SO_2F_2	SO_2	
1	2	3	4	5	6	7	8	9	10	11	12	13
1	100	100	20-60	-	nickel	7	2,4	19,7	26,3	44,6	-	autoclave
2	100	20	6	-	stainless steel	4,5	3,7	34,1	57,7	-	-	flow reactor
3	100	20	40	-		5,2	4,2	25,4	65,2	-	-	
4	50	20	10	-		7,4	0,1	8,9	82,2	1,4	-	HASA+NaF
5	10	20	0	H_2O	stainless steel	8,1	2,7	traces	89,2	-	-	
6	30	20	5			1,9	1,6	traces	96,5	-	-	
7	5	5	50			0,2	0,3	1,0	98,5	-	-	
8	30	10	0-5	H_2O	teflon	31,1	1,6	9,0	58,3	-	-	
9	5	10	0-5			43,6	1,4	traces	55,0	-	-	
10	3	10	0-5			3,5	0,4	traces	95,5	0,6	-	= 100 s

11	3	10	0-5			10,4	1,5	-	82,7	4	1,4	= 240 s
12	30	10	5			1,7	0,3	2,9	95,1	-	-	
13	10	10	45			traces	-	6,2	93,8	-	-	
14	10	10	60			1,2	-	2,3	96,5	-	-	
15	5	10	0	H_2O	nickel	1,9	0,4	traces	96,8	0,9	-	
16	5	5	0			8,5	0,3	3,4	87,8	-	-	
17	5	5	40			20,0	0,4	28,2	69,4	-	-	
18	5	5	60			2,2	0,5	17,7	79,6	-	-	
19	5	5	20	H_2O	nickel	0,2	0,7	traces	99,1	-	-	NH_2OH*
20	5	5	45			-	-	6,7	93,3	-	-	0,5 H_2SO_4
21	20	20	-50			13,7	traces	86,3	-	-	-	
22	20	20	0			13,2	traces	86,8	-	-	-	
23	20	20	40	HSO_3F	nickel	5,8	18,6	75,6	-	-	-	
24	20	20	80			4,2	2,8	62,6	30,4	-	-	
25	20	20	120			3,4	traces	42,9	53,7	-	-	
26	20	20	155			2,0	traces	34,2	52,4	11,4	-	
27	5	5	60	H_2SO_4	nickel	1,3	0,1	3,3	3,2	45,2	46,8	

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