

Obtaining of Perfluoroalkylsulphofluorides from Sultones

(finale part)

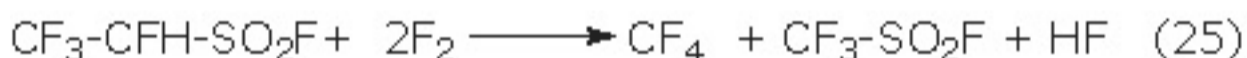
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α -HTFESF, taken in molar excess to elemental fluorine was supposed to use as an alternative. α -HTFESF molecule has one hydrogen atom, locating at α -position to sulphonyl group, which on the one hand is stabilized by trifluoromethyl group, and on the other hand it has the poorest bond in energy terms carbon - sulphur (285 KJ/mole). According to thermodynamical estimations the thermal effect of fluorination reaction is equal to 423,3 KJ/mole.

Along with reaction **23** at carrying out radical-chain mechanism of fluorination reactions **24** and **25** also take place



All of them are characterized by destruction according to bonds of carbon- sulphur and carbon- carbon, by increasing of fluorine expenditure in 1,5 - 2 times and by process temperature growth. At that, the energy of carbon-carbon bond exceeds the energy of carbon - sulphur bond at 1,5 times, which affects the proportion of quantity of by-products, formed according to reactions **24**, **25** and **26** (table 8).

In RSC Applied Chemistry a unit for direct fluorination, functioning at dynamic mode, was made to study main regularities of direct gas-phase fluorination of α -HTFESF.

Laboratory reactor is made of nickel tube (diameter - 38 mm and length 1300 mm), filled with copper chips and it is the reactor of ideal displacement. Reactor unit is conditionally separated into three heated areas:

- the evaporator; serves for evaporating of starting material,
- the chamber used to mix the starting compound and fluorine,
- the reactor itself; it provides enough contacting time for reacting compounds.

The evaporator is connected to dosing apparatus, composed of collecting metering device for α -TFESF, light and gaseous nitrogen cylinder, for steady charge of starting materials. After fluorinating reactor the products of synthesis get into collector, chilled to temperature within minus 15 minus 90 °C, through neutralizing reservoir. Gas

chromatographic analysis of products of fluorination was carried out at reactor's entering to assigned mode of exploitation and out of collector upon finishing the tests and thermostating to room temperature. Liquid products of reaction (mainly mixture of anhydrous hydrogen fluoride and α -HTFESF) were collected into entrainment separator, chilled with cold water. The conversion rate of starting material was determined by concentration of starting compound and anhydrous hydrogen fluoride. Based on data of laboratory tests a pilot model unit of gas-phase direct fluorination (output is equal to 500 kg/year) was projected and made at JSC "Halogen" (Perm).

During preliminary tests at laboratory reactor (volume 1,5 l) of ideal displacement, it was stated, that carrying out the fluorination process without diluting provokes significant destruction of starting compounds and products of fluorination (up to 93 - 96 %) . At that the selectivity amounts to 3-3,5 % at 100% conversion of raw materials (Table 8 # 1), and temperature inside fluorinating reactor increases by 20 -30 °C. Lowering of fluorine amount fed into concerning α -HTFESF results in gradual increasing of selectivity from 30% to 60% depending on α -HTFESF excess (table 8 # 2-4). Conversion of starting material at that drops proportionally to the amount of fluorine fed. This testifies, that starting α -HTFESF can be used as solvent for the fluorination process with further return of product that had not reacted into cycle.

Table 8. *The Results of Preliminary Tests at Direct Fluorination Unit, volume 1,5 l, Temperature - 403K, Feed rate α -HTFESF - 0,25g/min.*

#	Charge mole/mole α -HTFESF /F ₂	Dilution Mole/mole		Ratio products/ destruction, % (mass.)	Conversion,%	Selectivity, %
		F ₂ /N ₂	α -HTFESF /HF			
1.	1:1,02	-	-	7:93	100	3,5
2.	1:0.88	-	-	29:71	90	30
3.	1:0.75	-	-	48:52	75	50
4.	1:0.58	-	-	60:40	60	60
5.	1:1.03	1:2.1	-	83:17	90	83
6.	1:1.03	1:1.5	-	79:21	90	80
7.	1:1.02	1:1.76	-	85:15	95	85
8.	1:1.02	1:0.7	-	59:41	70	60
9.	1:0.99	-	1.4:1	80:20	98	80
10.	1:1.00	-	1.4:1	85:15	100	85
11.	1:1.00	-	1:1	95:5	97	95
12.	1:1,00	-	1:1.5	98:2	83	98

In spite of 75% mole excess of α -HTFESF the selectivity of fluorination process doesn't exceed 60% (table 8, # 4). The selectivity of direct fluorination increases greatly (up to 85%) when using nitrogen (table 8, # 5-7). Losses of finished product with exit gases at 50% dilution of fluorine by inert amount approximately 45-50%. These losses can be avoided when using additional unit of compression, that will to a great extent complicate the technology and increase the cost price of PFASF. Using of undiluted fluorine allows simplifying of the unit of crude products collection.

Anhydrous hydrogen fluoride introduction into reactor (table 8, # 9-12) provokes

decreasing of destruction by 95% under the other equal conditions. It's obvious, that amount of anhydrous hydrogen fluoride correlates with amount of fluorine suppressed, and taking into account the One Electron Transfer Theory the optimal proportion of HF : F₂ should be 1 : 1. I.E. The molar proportion of components going to be synthesized (α-HTFESF : HF : F₂) must ideally correspond with stoichiometry. Decreasing of concentration of anhydrous hydrogen fluoride down to 0,71 mole per one mole of fluorine leads to decreasing of selectivity by 15-20% and increasing up to 1,5 mole per one mole of F₂ results in conversion of starting materials, that must be connected with increasing of inhibitory action of HF and lowering of fluorinating rate (table 8 # 12).

Thus, one of the factors, determining selectivity of fluorination of α-HTFESF is concentration of anhydrous hydrogen fluoride.

The results of direct fluorination in reactor of 11.5 l volume are listed in Table 9. At increasing of anhydrous hydrogen fluoride concentration in α-HTFESF in the range of 7 - 20 % of mass its mole excess increases twice towards main reagents: α-HTFESF and fluorine, and conversion of α-HTFESF decreases to 47-48%. Practically, by increasing concentration of anhydrous hydrogen fluoride in starting mixture twice the fluorinating rate decreases twice. The selectivity of the process, caused by both amount of starting product, fluorinated in the range of reaction volume and after it changes slightly. That means, that fluorine in the excess of anhydrous hydrogen fluoride beyond the reactor doesn't take part in the destructive fluorination of starting raw material, and together with other uncondensed products gets into the neutralizing unit.

The excess of anhydrous hydrogen fluoride after reactor increases in terms of **23, 24** reactions stoichiometry by one mole taking into account α-HTFESF formed as a result of fluorination and ranges from 1,74 in # 1 (Table 9) to 2,89 in # 5 (Table 9).

Table 9. Fluorination in Reactor of 11,5 l. Anhydrous Hydrogen Fluoride Concentration Impact. Temperature - 393K, Feed Rate of α-HTFESF 1,2 g/min.

#	α-HTFESF:HF:F ₂ mole/mole/mole	C(HF) % (mass.)	Ratio Products/ Destruction	α-HTFESF Conversion %	Selectivity,%
1	1,0:0,74:0,94	07,44	94,5 : 05,5	94,23	94,0
2	1,0:0,89:0,93	08,80	92,4 : 7,6	69,00	92,4
3	1,0:1,14:0,94	11,00	90,3 : 9,7	59,84	90,3
4	1,0:1,40:0,94	13,20	87,8 : 12,1	47,56	87,8
5	1,0:1,89:0,93	17,00	89,3 : 10,6	48,00	89,4
6	1,0:5,00:0,93	35,00	93,0 : 7,0	10,00	93,0

Fluorination Products after reactor are cooled to 15-20°C, that forwards deceleration of

fluorination, including a destructive one (selectivity decreases by 5 %).

Temperature is another important factor that determines fullness of reaction passing and selectivity of fluorination.

During preliminary tests at model set it was found, that at equal consumption of raw material and by lowering temperature within the range of 40K the number of destruction products increases from 3 to 30%. At that the α -HTFESF conversion rate scarcely changes and conforms to amount of fluorine fed (Table 10).It can be explained by decreasing of fluorination rate at temperature lowering, as a result of which starting products do not have enough time to react at volume specified, beyond limits of which fluorinating conditions are not kept. You can increase the selectivity of fluorination at low temperatures either by decreasing weight hour space velocity of starting material feeding or by increasing the length of reactor.

We have installed a heated column filled with sodium chloride between the reactor and cooler to remove the unreacted fluorine and to estimate the rate of its conversion. Fluorination products do not interact with sodium chloride and fluorine gets into substitution reaction isolating elemental chlorine. The obtained mixture of bifluoride and sodium chloride was analyzed for content of ions chloride and ions fluoride using method of liquid chromatography.

Table 10. Results of Direct Fluorination at Temperature Alterations

#	\hat{O}, \hat{E}	α -HTFESF:HF:F ₂ mole/mole/mole	Ratio Products/ Destruction	α -HTFESF Conversion %	Selectivity,%
1	373	1 : 1,1 : 0,7	75,7 : 24,3	68,4	75,7
2	373	1 : 1,1 : 0,7	70,3 : 29,7	67,8	70,3
3	373	1 : 1,1 : 0,5	93,4 : 06,6	50,6	93,4
4	383	1 : 1,1 : 0,7	83,1 : 16,9	66,6	83,1
5	383	1 : 1,1 : 0,7	85,4 : 14,6	68,4	85,4
6	383	1 : 1,1 : 0,6	95,9 : 04,1	60,0	95,6
7	393	1 : 1,1 : 0,7	89,5 : 10,5	70,0	89,5
8	393	1 : 1,1 : 0,6	92,8 : 7,2	60,0	92,8
9	403	1 : 1,1 : 0,7	88,7 : 11,3	70,0	88,7
10	403	1 : 1,1 : 0,8	97,8 : 02,2	79,0	97,7

11	413	1 : 1,1 : 0,7	93,2 : 6,8	70,0	93,2
12	423	1 : 1,1 : 0,7	90,3 : 9,7	70,0	90,0

Comparing the results of fluorination, listed in table 10, and referred to equal temperatures it's becoming obvious that optimal temperature mode of fluorination is within the range of 393-403K and it is determined by proportion of starting components and raw materials feed rate.

The obtained PFESF crude product was subject to purifying by neutralization and then was rectified at packed column. Following that they had obtained product containing 99,98% of main compound, which was used to obtain lithium and potassium salts and perfluoroethylsulfonic acid. The grade of obtained salts after re-crystallization amounted to 99,99%.

Series of experiments regarding studying of macrokinetic mechanisms was conducted to create mathematical model of direct gas-cycle fluorination of α -HTFESF. The result obtained are under processing.

1. The studies conducted had confirmed a real opportunity of creating the alternative PFESF obtaining technology.

2. The suggested synthesis method is based on using the local raw materials and typical commercial equipment.

3. New main patterns of behavior of obtaining "sultone" method of monohydropolyfluoroalkylsulphonyl fluoride with the yield up to 92% were studied to work out commercial technology.

4. During studying of gas-phase fluorination of α -HTFESF we can see the opportunity of selective finishing fluorination of functional derivatives with preserving carbon-sulphur bond. At that the yield of PFESF was within the range from 93 to 97%, selectivity amounted to 95% at the rate of conversion of 97%.

5. The PFESF synthesis method created by authors allows significant decreasing the net cost of suggested analogues.

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