

Joint Fluorination of Alkansulfofluorides and Tertiary Amines Illustrated by Example of Octanesulfofluoride and Ethylbenzenesulfofluoride.

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Introduction.

Due to their unique properties perfluorinated organic compounds attract the attention of different lines of industry, including instrument-making and engineering industries, metallurgy, medical and chemical industries. They can be used in many fields of science and technology. However the high cost of perfluorinated products impedes their wide distribution and application.

The working out of more economically sound, low cost and simple obtaining technology of perfluorinated organic compounds, both possessing functional groups or heteroatom in their composition and not possessing them is a very urgent problem. The electrochemical fluorination method is a most preferable one to obtain these compounds, because unlike other perfluorinated compounds obtaining methods it has a number of advantages. The first advantage is an opportunity to obtain perfluorinated organic compounds preserving the original functional group and also to fluorinate (rather successfully) organic compounds with rather long hydrocarbon radicals (C=7 - 8). The second weighty but not lesser argument in favour of electrochemical fluorination is the fact, that exhaustive or full fluorination passes till isolation of fully fluorinated compound in one apparatus named electrolyzer. The third advantage is that anhydrous hydrogen fluoride is directly used as fluorine source and therefore synthesis phases of elemental fluorine or its carriers, for example cobalt trifluoride, are excluded.

Before the main perfluoroalkanes synthesis method was the hydrocarbon fluorination method using elemental fluorine or its carriers. However, the late works regarding obtaining of per fluoromethylcyclohexane and perfluoropentane and others show, that perfluoroalkanes can be obtained using electrochemical fluorination method and often they are obtained with higher yields.

Most perspective and popular in demand perfluorinated organic compounds for industrial application are perfluoroalkansulfofluorides and perfluorinated tertiary amines.

Perfluoroalkansulfofluorides are used as source material for surfactants synthesis, as mixture component in fire-fighting compositions, as source material at synthesis of perspective electrolytes for chemical sources of current [1-3]. Fluorine-containing surfactants are very effective agents, greatly lowering the surface tension at their low content in solution. Surfactants are characterized by high resistance, and perfluorinated derivatives of alkansulfo acids can form stable foam even in the presence of strong oxidizer like chromic and sulphuric acids and they sustain high temperatures [2,3]. Due to these characteristics surfactants are used in fire-fighting compositions, in pools of electrochemical metal plating and at electrochemical refining of nickel and chrome.

Perfluoroalkansulfofluorides are source material for obtaining of perfluoroalkansulfoacids, which are super acids and are used for organic synthesis. .

Perfluorinated tertiary amines field application is no less wide. They are known and popular in demand as unique dielectrics-heat transfers, gas carrying liquids in blood substitutes and in other important fields of science, technology and economy. One of possible perfluorinated tertiary amines fields of application is their use as media for transportation of value breed fry.

It is known, that alkansulfofluorides and many other organic compounds do not conduct current in anhydrous hydrogen fluoride. That's why they are subject to electrochemical fluorination in the presence of electrolytic additive.

If sodium fluoride is an electrolytic additive, then that influences the yield of target compound, due to the known influence of NaF on product yield [1], probably because of serious increasing of anodes corrosion and resinification of source organic compounds in electrolyte, that also doesn't make this process commercially paying.

If mercaptans, for example n-butylmercaptan, are electrolytic additives, then their main drawback is a strong , obnoxious, specific odor. This fact also prejudices the opportunity of their commercial use according to the ecological standards. It should also be noted, that mercaptans undergo electrochemical fluorination very well and their perfluorinated analogues are formed in large quantities in crude material. As their commercial application is limited, then after isolation of target product the remaining part of the crude material, containing perfluorinated compounds of hexavalent sulphur, is expelled that no doubt makes the production process more expensive and less paying.

In our opinion the method that we worked out allows as much simply and effective as possible to solve this problem and improve a whole number of electrochemical fluorination process indices among them:

1. Electrochemical fluorination process in the presence of tertiary amines (namely triethylamine, triethylamine, tripropylamine, tributylamine and pyridine) as electrolytic additives results in rather high yield of target product and it takes long time. The additive of mentioned amines allows to heighten anodic current density in the electrochemical fluorination process (from 0,001 - 0,002 A/cm² to 0,03 A/cm²), that greatly increases electrolyzer productivity. The low current densities could have been used to decrease the process of destructive fluorination. However, the application of low current densities decreases the destruction by 5-10% but at that the productivity decreases by 10 ten and more times.
2. The application of additives mentioned above allows to carry out the periodical (once in 5-6 hours), but not the continuous organic inflow of electrolyte, which is especially important for industry.
3. Widely used in industry, medicine, electrotechnics etc. perfluorinated tertiary amines are formed as by-products of electrolysis.
4. Such compounds as perfluorooctane, perfluoropropane, perfluorobutane, which can find or already have found their application for many industrial branches are formed as by-products (because of destruction) of reaction..

All above said allows to lower the cost price of perfluorooctansulfofluoride electrochemical synthesis.

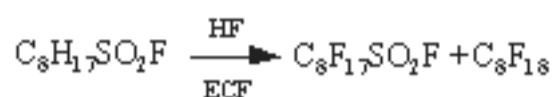
Experiments

The experiments were carried out in electrolyzer of Simons type [4] volume equal 0,7 l. Current density was 0,03 A/cm², initial concentration of octanesulfofluoride (OSF) was 10%,

and electrolytic additive was 2,5%. OSF was being added every hour according to calculated expenditure index. The electrolytic additive was added according to the voltage increase, i.e. when it was rising up to 6,5 V, another 2,5% of electricity-conductive compound were added into electrolyte.

At every stage (in 200 A/hours) of electrolysis the analyses of electrolyte for anhydrous hydrogen fluoride and amine content were held, chromatographic analysis of gaseous phase, pouring and crude material analysis were also carried out. The main components of anodic gas were: CF_4 , NF_3 , C_2F_6 , C_3F_8 , SO_4F_4 etc. An average composition of crude material is listed in table 2.

The main co-reactions passing at anode :



where $RH = (C_2H_5, C_3H_7, C_4H_9, C_3H_5)$, and also C_5H_5N - pyridine

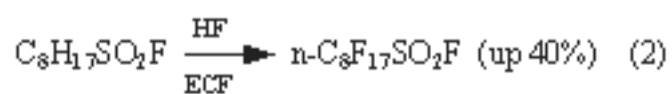
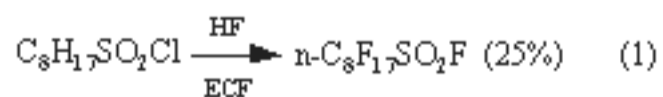
Surfactants Synthesis Methods.

Isolated from anhydrous hydrogen fluoride crude material was sent for rectification, where corresponding fluoroanhydride was isolated with purity equal to 97,0 - 99.0 %. This crude material was rectified at packed column, filled with glass coils with length and diameter equal to 2 mm, height of column was 42 cm, diameter 18 mm, the process was carried out at cube temperature in the range st. 70 to 110°C, the residual pressure was changing from 65 to 19 mm Hg. The product was analyzed using method of GL chromatography. GL chromatography analysis was carried out using Russian apparatus "Tsvet-100" with thermal conductivity detector, at column, filled with silochrom-80 with 20% α, β -cyanacetophenone.

Monomethylethanolamine (MMEA) and monoethylethanolamine (MEEA) was also subject to rectification in vacuum at packed column with the height 42 cm and diameter of 18 mm. The process was controlled using refractive index, which is 1,4390 for monomethylethanolamine and 1,4400 for monoethylethanolamine at 20°C.

Results and discussion

Usually perfluorooctanesulfluoride is obtained by electrochemical fluorination of octanesulfochloride (OSC) or octanesulfofluoride (OSF) :



In first case, formula (1), electrolysis with 25% yield takes small period of time, then the yield greatly decreases, probably because of chlorine participation in the process [5]. This makes this process commercially unprofitable.

In the second case, which is more close to our process, sodium fluoride or mercaptane (most often n-butylmercaptan is used) can be used as electrolytic additive, because octanesulfofluoride doesn't carry current in anhydrous hydrogen fluoride. But this method is

characterized by disadvantages, that were mentioned above.

TABLE 1. MAIN TECHNOLOGICAL CHARACTERISTICS OF OCTANESULFOFLUORIDE AND DIFFERENT TERTIARY AMINES ELECTROCHEMICAL FLUORINATION PROCESSES:

	The addition of co-fluorinated amine				
Electrolysis characteristics	Triallylamine	Triethylamine	Tripropylamine	Tributylamine	Pyridine
Addition of OSF, gr.	327	234	214	83	33
Addition of amine, gr.	115	98	133	132	66
Total addition of organics, gr.	442	332	347	215	99
Obtained crude material, gr.	542	195	285	189	138
Time of Electrolysis, hours	106	65	78	69	26
Current density, A/cm ²	0,03	0,03	0,03	0,03	0,03
Quantity A*hours	1584	975	1133	984	390
Quantity A*hours/liter	2400	1477	1718	1490	590,5
Yield of crude (current)%	52	37	46	36	58

TABLE 2. AVERAGE % CONTENT OF THREE MAIN COB COMPONENTS, WHICH WAS OBTAINED BY ELECTROLYSIS OF OCTANESULFOFLUORIDE AND DIFFERENT TERTIARY AMINES

	MAIN CRUDE COMPONENTS, % wt.		
Amine added	Perfluorooctanesulfonyl fluoride	Perfluoroamine	Perfluorooctane
Triethylamine	42	26	17
Tripropylamine	57	12	20
Tributylamine	45	25	12
Triallylamine	50	24	14
Pyridine	15	55*	10

*% content of perfluoroamine electrolysis main product is indicated, here perfluoropentane.

As it was mentioned before, ethylbenzene sulfofluoride also was a raw material for perfluoroalkansulfo fluoride synthesis besides octansulfofluoride. We had showed the opportunity of ethylbenzene sulfofluoride and tertiary amines joint fluorination by example of

ethylbenzene sulfofluoride and pyridine electrochemical fluorination (table 3).

Table 3. The main technological characteristics of perfluoroethylbenzene sulfofluoride electrochemical synthesis together with pyridine electrochemical fluorination.

Time of electrolysis (hours)	Current density (A/cm ²)	Quantity A*Hours	Quantity A*hours/l	Organic mixture addition (g)	Crude material (g)	Yield acc. current %
48	0,03	727	1102	146	234	47

Besides chromatographic analysis of gas and liquid phase we had carried out the analysis of products obtained by nuclear magnetic resonance method. Obtained data is listed in table 4.

TABLE 4. NMR ¹⁹F Spectra of FSO₂C₈F₁₇ probe (hexafluorobenzene as internal and external standard)

N	Shift, ppm	Intensity				Compound structure
		Probe #1		Probe #2		
		Sum	IF	Sum	IF	
1	46,7	1,19	1,19	1,22	1,22	¹ FSO ₂ C ¹² F ₂ C ¹⁴ F ₂ C ¹⁷ F ₂ C ¹⁸ F ₂ C ¹⁹ F ₂ C ²⁰ F ₂ C ²¹ F ₂ C ¹¹ F ₃
2	46,6	0,26	0,26	0,11	0,11	(C ⁷ F ₃) ₂ C ²⁴ FC ¹³ F ₂ C ¹⁴ F ₂ C ¹⁵ F ₂ C ¹⁶ F ₂ C ¹² F ₂ SO ₂ ² F
3	-61,2	0,11		0,27		
4	-67,9	0,34		0,0		
5	-69,5	1,03	0,17	0,21	0,04	(C ⁵ F ₃) ₂ C ²³ FC ¹³ F ₂ C ¹⁵ F ₂ C ¹⁶ F ₂
6	-70,0	0,34	0,05	0,21	0,03	(C ⁶ F ₃) ₂ C
7	-71,4	1,44	0,24	1,09	0,18	(C ⁷ F ₃) ₂ C ²⁴ FC ¹³ F ₂ C ¹⁴ F ₂ C ¹⁵ F ₂ C ¹⁶ F ₂ C ¹² F ₂ SO ₂ ² F
8	-79,7	0,34	0,11	0,16	0,05	C ⁸ F ₃
9	-80,4	0,42	0,14	0,1	0,03	C ⁹ F ₃
10	-80,6	0,48	0,16	0,17	0,06	C ¹⁰ F ₃
11	-80,7 d 8 Hz	5,39	1,80	5,19	1,73	¹ FSO ₂ C ¹² F ₂ C ¹⁴ F ₂ C ¹⁷ F ₂ C ¹⁸ F ₂ C ¹⁹ F ₂ C ²⁰ F ₂ C ²¹ F ₂ C ¹¹ F ₃
12	-107,4	3,82	1,91	3,93	1,96	
13	-113,6	0,43	0,21	0,44	0,24	(C ⁷ F ₃) ₂ C ²⁴ FC ¹³ F ₂ C ¹⁴ F ₂ C ¹⁵ F ₂ C ¹⁶ F ₂ C ¹² F ₂ SO ₂ ² F
14	-119,0	3,83	1,91	3,6	1,80	¹ FSO ₂ C ¹² F ₂ C ¹⁴ F ₂ C ¹⁷ F ₂ C ¹⁸ F ₂ C ¹⁹ F ₂ C ²⁰ F ₂ C ²¹ F ₂ C ¹¹ F ₃
15	-119,2	0,52	0,26	0,42	0,21	(C ⁷ F ₃) ₂ C ²⁴ FC ¹³ F ₂ C ¹⁴ F ₂ C ¹⁵ F ₂ C ¹⁶ F ₂ C ¹² F ₂ SO ₂ ² F
16	-119,8	0,50	0,25	0,4	0,2	
17	-120,3	3,47	1,74	3,05	1,50	¹ FSO ₂ C ¹² F ₂ C ¹⁴ F ₂ C ¹⁷ F ₂ C ¹⁸ F ₂ C ¹⁹ F ₂ C ²⁰ F ₂ C ²¹ F ₂ C ¹¹ F ₃
18	-120,5	3,47	1,74	3,05	1,50	
19	-120,7	3,47	1,74	3,05	1,50	

20	-121,6	3,44	1,72	3,05	1,50	
21	-125,4	3,70	1,85	3,39	1,70	
22	-183,5 d 20 Hz	0,12	0,12	0,03	0,03	
23	-183,9 d 20 Hz	0,24	0,24	0,09	0,09	
24	-185,1	0,28	0,28	0,18	0,18	(C ⁷ F ₃) ₂ C ²⁴ FC ¹³ F ₂ C ¹⁴ F ₂ C ¹⁵ F ₂ C ¹⁶ F ₂ C ¹² F ₂ SO ₂ ² F

1. Two different perfluoroalkylsulfurides in proportion of 4:1 are discovered in probe, the intensity of signals #1 and #2 indicates this fact. In the probe there are the same alkylsulfurides in proportion 9:1.

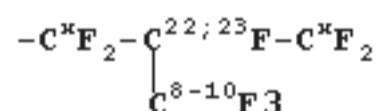
2. In the probe there is n-perfluorooctanesulfuride of C¹¹F₃C¹²F₂C¹⁴F₂C¹⁷F₂C¹⁸F₂C¹⁹F₂C²⁰F₂C²¹F₂SO₂¹F structure as the main component, to which in spectra signals with the top formula indices correspond.

3. In the probe there are 2-trifluoromethylsubstituted perfluoroalkylsulfurides, what the signals ## 4-7 indicate, meeting (CF₃)₂C-group and what the signals ##22-24 indicate, meeting >CF-group at intensity proportion of these signals close to 6:1.

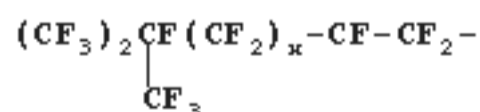
4. In the probe there is iso-perfluorooctanesulfuride isomer (perfluoro-6-methylheptanesulfuride with structure (C⁷F₃)₂C²⁴FC¹³F₂C¹⁴F₂C¹⁵F₂C¹⁶F₂C¹²F₂SO₂²F) as second by intensity of signal.

5. Because of signals ##12 and 14 of fluorine atoms chemical shifts of perfluorooctanesulfuride are close with iso-perfluorooctanesulfuride signals there intensity are too high relatively signals 17-19.

6. The presence of signals 8-10 typical for CF₃-group in spectra and signals 22,23 typical for >CF-group are evidence of isomer presence not only in 6 position but also with structure



7. Signal 6 of (CF₃)₂C-group also can to correspond to isomer structure with two ramification



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