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Obtaining of perfluoroalkylsulphofluorides from sultones

(continuation)

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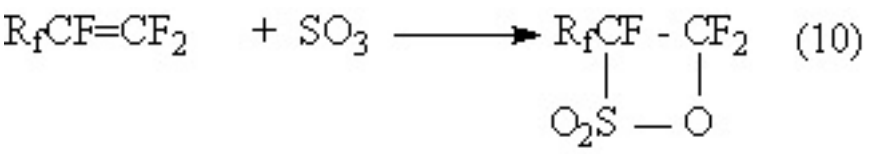
Dithionite method (Table 1 # 3) is of absolute scientific interest due to transforming of ordinary substituents into complicated functional groups, but even at its carrying out in the laboratory we get a long, multistage scheme which includes additional stages of extraction, drying, evaporation and regeneration of solvent. Amongst minuses of the present method we should mark out the following:

- perfluoralkyliodides are expensive and hard to find products; their obtaining according to the works [36,37,38] requires application of rather complicated equipment facilities, as starting compounds: iodine, iodine pentafluoride, fluorine gas provoke active corrosion, and the production itself is highly explosive (the reasons caused the explosions are not studied well enough);
- perfluoroalkylsulphinate sodium chlorination is carried out in aqueous solution, which comes along with a strong corrosion of equipment and pipelines;
- they do not produce sodium dithionite in this country, it is not stable at transportation and storage, which leads to the increasing of consumption rate and lowering of target product yield at the key stage (reaction **8**) by 20% and more;
- one and a half tons of solid waste materials in the form of sodium salts (NaCl, Na_2SO_4, $Na_2S_2O_3$) and 2,5 tons of liquid waste substances in the form of rather toxic organic and fluoroorganic solvents are formed for one ton of finished products. To regenerate and neutralize these waste products we need additional technological equipment.

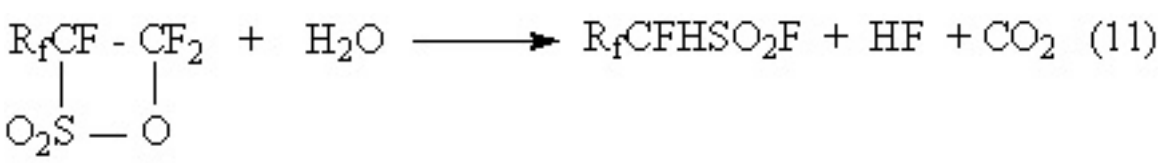
The authors considers the sultones' treatment a simplified and technological method.

According to the works [39-47] the introduction of sulphonyl group can be done at interaction of perfluorolefines and sulphuric anhydride followed by hydrolysis of sultones obtained (table 1, # 5)

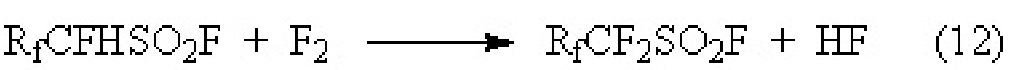
The excessive electron' density of perfluorolefines carbon atoms provides largely a quantitative yield of sultones obtaining reactions (**10**). According to authors data [39, 41] and to experiments' data (table 4) the yield of hexafluoropropane-2--sultone is 96-98%. Linear isomer, 6- and 8-component cyclic sultones and allylfluorosulphate which overall sum ranges from 0,5 to 2% are formed as admixtures. Obtained sultones are hydrolyzed according to reaction **11** up to α-hydropolyfluoroalkylsulphonylfluorides (hereinafter α-HPFASF), which are a starting material for the following exhaustive fluorination (reaction **12**):



$$R_fCF=CF_2 + SO_3 \longrightarrow R_fCF(-O_2S-O)-CF_2 \quad (10)$$



$$R_fCF(-O_2S-O)-CF_2 + H_2O \longrightarrow R_fCFHSO_2F + HF + CO_2 \quad (11)$$



$$R_fCFHSO_2F + F_2 \longrightarrow R_fCF_2SO_2F + HF \quad (12)$$

I. During preliminary tests authors had tested different sultones' synthesis and hydrolysis methods:

- synthesis of sultones under static and dynamic conditions (Table 2, # 1,3),
- synthesis of sultones together with freshly refined sulphuric anhydride and oleum with concentration of free sulphuric anhydride equal to 65% (table 2, # 2).
- hydrolysis of sultone with water dosing into sultone and vice versa (Table 5).

Hexafluoropropene (hereinafter HFP) was used as a starting material to study technological modes of synthesis of PFASF. Comparative results of experiments regarding synthesis and hydrolysis of HFP-2-sultone are listed in the tables 2, 3, 4, 5, 6, 7.

TABLE 2. *Sultone Synthesis*

#	Reactor type	Charging, mole/mole			Conditions of synthesis			Yield%	Impurities,% (mass.)			
		HFP	SO_3	oleum, 65% (mass.)	T,°C	P, bar (initial/ residual)	Time, h		1	2	3	4
1	autoclave	1	1	-	100	19/5	10	96	0,5	2,5	0,5	0,5
2	autoclave	1	-	1	100	19/2	6	61	15	12	2	2
3	tube	1	1	-	100	0,7	0,2	5	0,5	0,5	0,1	0,1

1-perfluoroallylfluorosulphate

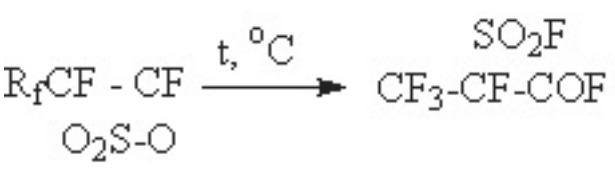
2-tetrafluoropropionic acid

3-sulphuric acid

4-anhydrous hydrogen fluoride

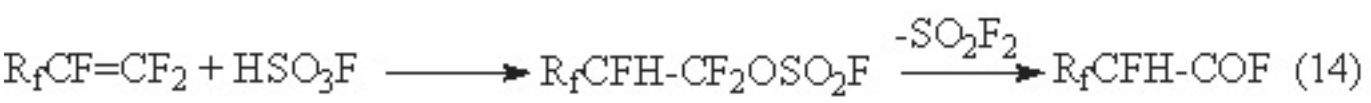
When perfluorolefine is interacting with sulphuric anhydride several competing processes take place (reactions13-17)

-isomerization



$$R_fCF(-O_2S-O)-CF \xrightarrow{t,\ ^oC} CF_3-CF(SO_2F)-COF \quad (13)$$

- forming of fluoroanhydrides - SO_2F_2



$$R_fCF=CF_2 + HSO_3F \longrightarrow R_fCFH-CF_2OSO_2F \xrightarrow{-SO_2F_2} R_fCFH-COF \quad (14)$$

- forming of polyfluoroalkylsulphates

$$R_fCFH\text{-}COF + SO_3 \longrightarrow R_fCFH\text{-}COO\,SO_2F \quad (15)$$

- forming of allylfluorosulphates

$$R_fCF{=}CF_2 + SO_3 \longrightarrow R_fCF{=}CF_2 - OSO_2F \quad (16)$$

- forming of α-hydropolyfluoroacids

$$R_fCHFCOF + H_2SO_4 \longrightarrow R_fCHFCOOH - HSO_3F \quad (17)$$

Reactions **13**, **14**, **15** and **17** take place only in the presence of sulphuric acid in sulphuric anhydride. At that, the number of by-products is in proportion with its concentration in freshly refined sulphuric anhydride, that's why when using commercially produced oleum of free sulphuric anhydride content equal to 65% in sultone's synthesis, as it is suggested in the work [43], leads to lowering of sultone's yield to 35-40%. When using 98% sulphuric anhydride the yield of sultone counts to 96-98%. We should take into consideration, that in first case a rectification unit of sultone's products synthesis is put into operation, and in the second case the need of sulphuric anhydride distillation equipment use is appeared . The difference between boiling points of sultone's synthesis products is in table 3.

Table 3. *Boiling Points of Sultone's Synthesis Products*

Compound	Boiling point, ^oC
HFP-2β-sultone	46.5
$R_FCF{=}CFC\text{-}OSO_2F$	59.0-63.0
$R_FCFH\text{-}COOH$	136 (needs to be specified)
$R_FCFH\text{-}COOSO_2F$	74 / 70 mm Hg

To separate the present mixture we need rectification. The difference of boiling points of sulphuric anhydride (44,88^{o}C) and monohydrate (330^{o}C) is 285^{o}C, so we need a simple distillation to separate this mixture [40].

Table 4. *Results of Laboratory Tests regarding Synthesis of HFP-β-sultone*

#	Charge of reagents SO_3:HFP mole/mole	Conditions of Synthesis	Yield, % (on SO_3)	P.S.		
P, bar (initial/ residual)	T ^{o}C	Time, h				
1	1: 1,01	6 / 4	20-25	48	91	next feeding of HFP after interaction of previous
2	1: 1,06	19 /7	95-98	14,0	77	
3	1: 0,9	14 / 2	95-98	8,5	52	

4	1: 1,05	17,5/4	95-98	5,0	58,0	
5	1: 1,05	17,5 / 9	105-110	12	55,4	
6	1:1,07	10,5 /5	95-98	14,0	98	Double distillation of sulphuric anhydride
7	1:1,07	19,0 / 5	80-95	13	96	Double distillation of sulphuric anhydride
8	1:1,1	19,0/5	80-95	13	95	
9	1:1,2	20 /5	70-95	15	92	
10	1:1,3	20/5	65-95	18	92	
11	1:1,65	20,5 / 9	60-95	24	85	
12	1: 1,1	15 /1,5	60-70	26	85	
13	1:1,1	14,5 / 1	90	7	88	

* - Here a starting pressure is stated at full feeding of monomer and max heating of autoclave/ residual pressure of autoclave at the same temperature (90-100^{o}C).

In the table 4 tests results of sultone synthesis are presented, they allow us to make the following conclusions:

1. Sultones' synthesis is determined by the quality of sulphuric anhydride distillation. Thus, when using double distilled sulphuric anhydride we can obtain maximum yield into sultone that is up to 98% (table 4, # 6, 7). When sulphuric anhydride monohydrate gets into collector by-processes are taking place (table 4, # 2, 8), which result in increasing of the following admixtures: R_FCFH- ÑÎÎH, R_FCFH- ÑÎÎ SO_2F, $R_FCF{=}CF$–OSO_2F, SO_2F_2, $ÑOF_2$. At the stage of hydrolysis they decrease the yield of target product by 10-15%.
2. The completeness of reaction of sultone's synthesis depends on conditions of the process carrying out, i.e. on pressure and temperature. As the main impurities form at temperatures below 60 and above 150^{o}C, then the most preferable is a range of temperatures from + 60^{o}C to + 150^{o}C. However, as preliminary laboratory tests showed, as high as at T above 105 ^{o}C the yield into sultone lowers down to 53%

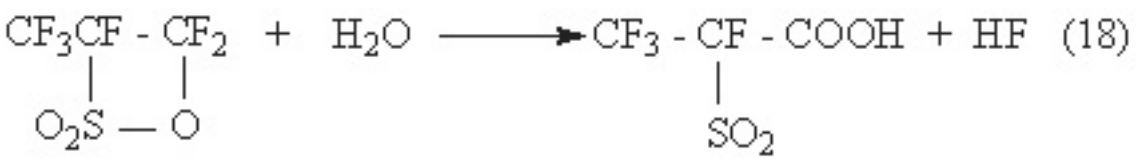
(Table 4, # 5), the increasing of concentration of its decomposition synthesis products in gases testifies the same.

3. Carrying out the process at low temperatures (under 80^{o}C) forwards the decreasing of reaction rate by 2-3 times (Table 4, # 11, 12).
4. The amount of fed monomer must exceed the stochiometrical calculation in 1,1-1,2 times to provide the completeness of conversion of sulphuric anhydride, as at further stage it will forward the acidic hydrolysis of sultone as a result of which the main products of hydrolysis will be acids.

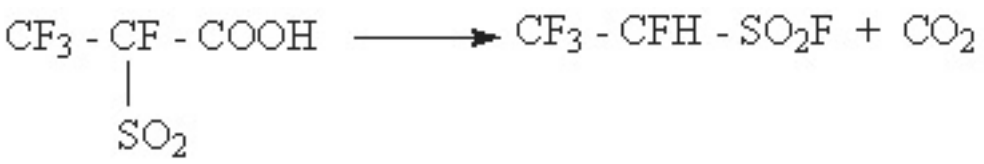
The obtaining technology of α-hydrotetrafluoroethylsulphonylfluoride (α-HTFESF) for exhaustive fluorination provides high yield (by the sum of 2 stages it is up to 92%) and is based on using typical equipment. The special feature of the process is a necessity to use freshly refined sulphuric anhydride and also the necessity to carry out the sultone hydrolysis using apparatus resistant to water containing hydrogen fluoride (graphite, fluorocarbon polymer, nickel steel EI-943), ordinary steel brands are of high corrosion (up to 0,2 g/cm2 per year).

II. Hydrolysis of HFP β-sultone includes 2 consecutively going reactions:

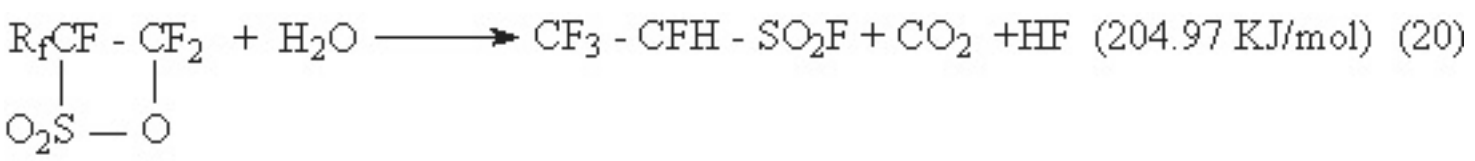
- forming of polyfluoropropionic acid sulphonylfluoride **18**



And its spontaneous decarboxylation forming α-hydrotetrafluoroethylsulphonylfluoride (hereinafter α-HTFESF) according to reaction **19**

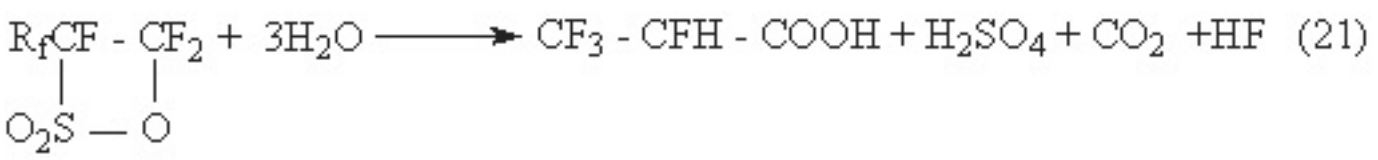


As these two reactions are going simultaneously, then the common summary equitation corresponds to scheme **18** and taking into account the thermal effect it equals to the following:



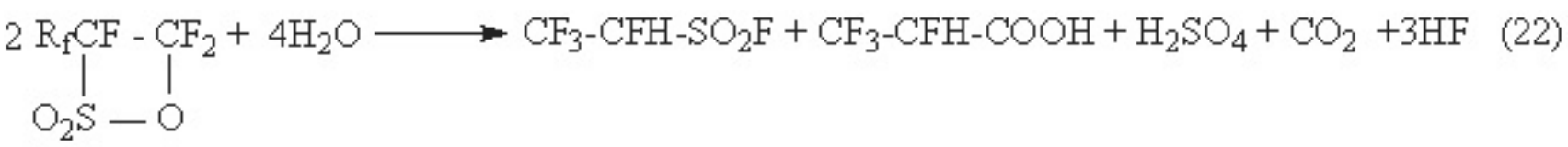
During laboratory tests it was stated, that without well-timed heat removal of sultone hydrolysis reaction we could observe the heating up of reaction mass up to temperature range within + 40 + 60^{o}C. The temperature rise results in formation of by-products, and also in evaporation and carry-over together with carbon dioxide of both initial sultone (b.p.=+46,5^{o}C) and target product of α-HTFESF (b.p.=+62-63^{o}C), that's why in methodical recommendations the temperature interval ranges from 0 to + 10^{o}C. Temperature rise depends on heat removal efficiency.

During the hydrolysis process along with α-HTFESF the hydrogen fluoride is forming, which protonates the reaction mass, that leads to acidic hydrolysis according to reaction **21**



As a result of acidic hydrolysis tetrafluoropropionic (hereinafter TFPA) and sulphuric acids accumulate in reactor along with hydrofluoric acid, the dissociation constant of sulphuric acid determines the rate of following acidic hydrolysis of sultone.

Thus, the summary hydrolysis equitation could be written as scheme **22**



However, stochiometric yield of α-HTFESF according to that reaction is much lower than experimental data (table 2).

At 100-% implementation of that reaction 1 gram-molecule of α-HTFESF is formed out of 2 gram-molecules of sultone, i.e. coefficient of consumption is equal to 2,5, that is in contradiction with experimental data according to which the coefficient of consumption by sultone ranges from 1,4 to 1,6 (theoretical coefficient of consumption according to reaction **18** is 1,25).

According to the methods [39,42] α-HTFESF synthesis is carried out by adding equimolecular amount of water (1:1) into sultone cooled in advance. During preliminary tests it has been stated, that side reaction **21** always takes place, that involves additional water consumption, as a result of which up to 30% of sultone remains unhydrated (table 5, # 1-3).

Table 5

#	Reagents mole/mole	charging	Reagent dosed	Feeding rate, g/min.	T ^{o}C	Yield,%
1.	1:1,02		water	0,13	5-20	70
2.	1:1,26		water	0,13	5 - 15	70
3.	1:1,25		water	0,20	5 - 15	79
4.	1:30,00		sultone	4,70	5 - 10	89

Under conditions of commercial production it will require additional stages of control to correct flows fed for synthesis. Authors has suggested method of hydrolysis, where we use 15-30 times water excess adding chipped ice under laboratory conditions or brine feeding minus 15 under conditions of production to provide intensive reaction heat eliminating, control of temperature range within 2- 5^{o}C and completeness of process passing. At such dilution the concentration of hydrogen ions at aqueous phase changes slightly, that allows to keep rate of direct and side reactions constant (**20, 21**). Besides, sultone is fed into water but not vice versa. That provides literally constant composition for organic and non-organic phases upon finishing the hydrolysis. You can find the results of analysis of aqueous fraction composition depending on proportion of charged reagents and amount of fed for hydrolysis water in table 6.

Table 6. *The Composition of Aqueous Fraction upon Finishing of HFP - 2 β- sultone hydrolysis*

#	Reagents charging mole/mole	Water fraction, g	H^+%	SO_4^{2-}%	F^-%	Polyfluoropropionic acid
1.	1:1,02	5	2,40	6,4	31,8	16
2.	1:1,25	10	1,97	6,3	30,6	14
3.	1:30	300	0,19	0,5	4,0	4,00
4.	1:23	250	0,24	2,16	5,2	5,31
5.	1:16	200	0,22	2,18	5,23	5,36

Concentration of TFPA is determined by disparity of total acidity and acidity, determined by sum of sulphuric and hydrofluoric acids. It is formed during synthesis of sultone according to reactions **3** and **5** (up to 0,5%), and also according to reaction **19** (from 4 to 16%). The rate of TFPA forming significantly influences the yield of target product and depends on a number of factors, including temperature of the process (table 7).

Table 7. *Temperature Effect on the Yield of α-HTFSF.*

#	Reagents charging mole/mole	Sultone's feeding rate g/min	T ^oC	Yield α-HTFSF, %
1.	1:16	1,5	2 - 3	90
2.	1:16	1,5	2 - 4	92
3.	1:16	1,5	5 -10	79
4.	1:16	1,5	5 - 15	67

We have found the proportion between target process rate and TFPA forming rate by target product yield and composition of aqueous fraction. At temperature of 15^{o}C this proportion amounts to 5:1, and upon decreasing temperature to 2 - 3^{o}C the rate of its forming decreases 4,5 times less and proportion of direct and side reactions equals to 22:1.

Sultone's hydrolysis is a exothermal reaction, at which the increasing of temperature results in forming of TFPA up to 16% and decreasing of target product yield by 10-30%, that's why the temperature of the process should not exceed 2-5^{o}C. The process is carried out at water excess of 15-30 times over and at intensive isolation of reaction heat to maintain such temperature mode.

Obtained α-HTFSF raw material contains only water up to 1% as an impurity , other impurities amount to less than 0,01%. The water has been eliminated by drying at zeolites followed by their regeneration using incineration. When needed a simple distillation was done at typical unit, as a result of which a product for exhaustive fluorination was obtained,

containing main compound at a purity of 99,7-99,9%, content of water less than 0,01% (α-HTFSF).

III. Exhaustive fluorination of poly-fluorinated compounds of different classes for commercial production had developed due to successful projects of a number of Russian scientists. Today substitutive fluorination of "residual" hydrogen due to high selectivity of methods suggested passes quantitatively.

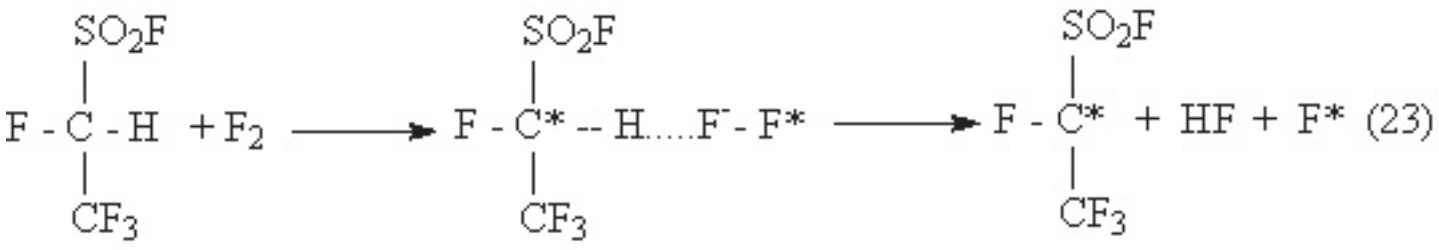
When choosing method of exhaustive fluorination we have analyzed all kinds of methods.

- Electro-Chemical Fluorination (ECF) has no perspectives at non-availability of local produced raw materials and growing energy costs.
- Direct fluorination in perfluorinated solvent under static conditions can not be technologically applied,
- Fluorination using cobalt trifluoride as fluorinating agent and as catalyst for direct fluorination is not economically efficient if taking into account today's prices for cobalt trifluoride,
- Direct gas-phase fluorination at catalytic packing in inert solvent at different temperatures is taken by authors as a main direction for working out the technology.

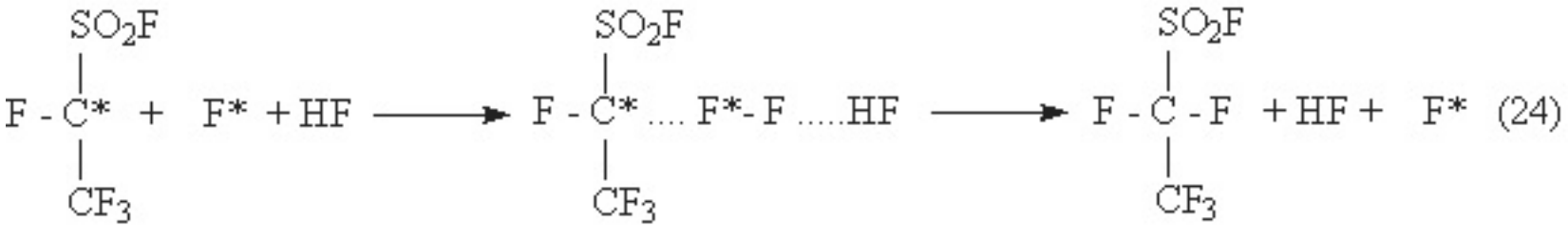
The scientific explanation of manageable process of direct fluorination is based on the conception of localization of direct fluorination acts for the purpose of well-timed isolation of excessive energy of adducts formed. Catalysts of developed surface and active catalyzing agent [49] are worked out for that.

However, somewhat different approach to solve the problem of isolation of excessive energy of intermediate compound exists, namely: using of solvating solvent in complex with heat conducting packing [50,51,52,53]

If we consider compounds reacting with each other as donor-acceptor system [53], where during reaction a total transfer of electron from donor to acceptor (from α-HTFESF to fluorine) occurs according to scheme **23**



Forming negative ion-radical pair, then for its stabilization we'll need proton solvent. This leads to temporary stabilization of transition condition due to which radical components manage to recombine themselves before exit to reaction volume according to scheme **24**



In the process of fluorination anhydrous hydrogen fluoride forms as one of reaction's products, that's why its concentration grow moves the balance to increase of starting materials. Besides that, anhydrous hydrogen fluoride dissolves many organic poly-fluorinated compounds remaining inert to action of oxidants and reducing agents {54] and also its sorption capacity on the surface of transition metals fluorides is high.

To be continued