

ADDITIONAL FLUORINATION OF PARTLY FLUORINATED ORGANIC COMPOUNDS BY ELEMENTAL FLUORINE AS AN OBTAINING METHOD FOR PRACTICAL PURPOSE FLUORINE MATERIALS

D.D. Moldavsky, G.G. Furin*

RSC "Applied Chemistry" 14, Dovrolubov av., Saint-Petersburg, 197198

*** Novosibirsk Institute of Organic Chemistry , Russian Academy of Science 63
Novosibirsk, Ac. Lavrentiev av. 9**

(continuation)

1. Organic Compounds Elemental Fluorine Direct Fluorination

At hydrocarbons' elemental fluorine fluorination the yield of perfluorinated analogues doesn't exceed few percents, low-molecular fluorine containing paraffin's are main products, w explained by high energy of forming C-F (448-507 KJ/mole) bond which exceeds the C-C (KJ/mole) bond energy and leading to fragmentation of hydrocarbonic skeleton [16-18]. High r reaction combined with relatively low dissociation energy of fluorine [D(F-F) 155 KJ/mole] res quick branching of chain process, and if the heat doesn't leak immediately, then the inflam occurs. At the same time using of partly fluorinated compounds as starting materials res obtaining perfluorinated analogues with rather high yield [19, 20]. It's not surprising, because rate of substitution of hydrogen atoms by fluorine increases the molecule deactivates itself mo more. Using special techniques (fluorination applying low-temperature gradient, diluting of fluo 25-100 times, aerosol fluorination) allows obtaining of perfluorinated products of satisfactory though their productivity is low, they are complicated to be implemented for apparatus, and go beyond laboratory frames. Along with that in the work [21] it is displayed, that fluorine con hydrocarbons of high yield can be finally fluorinated by elemental fluorine to perfluorinated ones.

At that fluorination doesn't require special mild conditions: the temperature floats within the starting from -30 (Fluorination of lowest olefins) ending 440°C (Fluorination of monoc dihydroperfluorinated compounds which number of carbon atoms is in between 12-15).

The fluorination process itself could have been a reason, and namely fluorination on the gas separating surface. Liquid-phase fluorination is being studied rather widely [21]. Here informal fluorine solubility in organic solvent gets its importance. Fluorination occurs at fluorine b through hydrocarbon soluted in inert solvent. Many authors consider, that during these process reaction goes in gas phase (in bubbles). The author of the work [22] used such construction apparatus, that provided the prolonged contact between gas (elemental fluorine) and liquid, m the process of fluorination on the gas-liquid separation surface. At that he managed to carry c direct fluorination of hydrocarbons in the temperature range of 0-20°C.

| | | | | | | | | | |
|--|---------|------|------|------|------|-----|-----|------|-----|
| $\text{CF}_3\text{CF}=\text{CFC}_2\text{F}_5$ | 20-40 | 86,5 | | | 8,9 | 2,1 | 1,1 | | 1,4 |
| $\text{CF}_3\text{CF}=\text{CFC}_2\text{F}_5$ | 20-40 | 87,0 | | | 8,9 | 2,1 | 1,4 | | 0,6 |
| $\text{CF}_3\text{CF}=\text{CFC}_2\text{F}_5^a$ | 20-40 | 87,6 | | | 8,6 | 1,8 | 1,2 | | 0,8 |
| $\text{CF}_3\text{CF}=\text{CFC}_2\text{F}_5^a$ | 20-40 | 87,7 | | | 8,8 | 1,7 | 1,2 | | 0,6 |
| $(\text{CF}_3)_2\text{C}=\text{CFC}_2\text{F}_5^a$ | 60-90 | | 63,8 | | 23,5 | 7,1 | 3,8 | | 1,8 |
| $(\text{CF}_3)_2\text{C}=\text{CFC}_2\text{F}_5^a$ | 60-90 | | 64,4 | | 23,1 | 7,0 | 3,7 | | 1,8 |
| $(\text{CF}_3)_2\text{C}=\text{CFC}_2\text{F}_5^a$ | 60-90 | | 64,2 | | 23,1 | 7,0 | 3,8 | | 1,9 |
| $\text{C}_9\text{F}_{18}^b$, isomers mixture | 120-160 | | | 50,3 | 26,5 | 7,7 | 3,1 | 12,4 | |
| $\text{C}_9\text{F}_{18}^c$, isomers mixture | 120-160 | | | 50,8 | 26,6 | 7,6 | 2,9 | 12,1 | |
| $\text{C}_9\text{F}_{18}^d$, isomers mixture | 120-160 | | | 50,6 | 26,6 | 7,5 | 3,1 | 12,2 | |
| C_9F_{18} , isomers mixture | 180-250 | | | 24,4 | 59,3 | 9,6 | 4,9 | 1,8 | |

a - compound $[(\text{CF}_3)_2\text{CF}]_2\text{CFC}_2\text{F}_5$,

b - catalyst CuF_2 ,

c - catalyst CoF_3 ,

d - Observe uncontrolled increasing of temperature when increase the rate of component feedi

According to Table 2 we can conclude, that as hydrocarbonic chain becomes longer the fluor conditions become "more and more severe". Thus, C1-C4 perfluorinated olefins are being fluor at $-40 - -10^\circ\text{C}$, while C8-C12 olefins - at $120-160^\circ\text{C}$, the fluorination period rises from 0,5 hours. It can be associated with values of oscillating and rotational energy of molecule as a which depends on carbon chain length. Fluorinating conditions become severer as molecules b saturated with fluorine. Fluorination of perfluorinated olefins with long carbon chain goes severer conditions compare to hexafluoropropylene, which can be explained by the influe spatial factors. As chain becomes longer, the spatial screening of multiple bond occurs, becau molecules of perfluoroolefines are anfractuious and not linear. An additional energy is required t the molecule into the linear one, that provokes the approaching of multiple bond fluorine. A reason for that is in spatial screening of initial radical center by perfluoroalkyl radicals. As the chain increases the radical center screening grows, the energy spent for oscillations and rotat atoms in R_F group, which makes the fluorinating conditions severer. In table 2 you can find th results of fluorination of some perfluorinated olefins in gas phase. You can see by the table dat as concentration of initial fluoroolefine decreases the fluorinating rate drops and to finish it w to increase the temperature; at that, the yield of destructive fluorination products - perfluor paraffins of shortened carbon chain increases. In spite of that, we observe the high yield of perfluorinated paraffins.

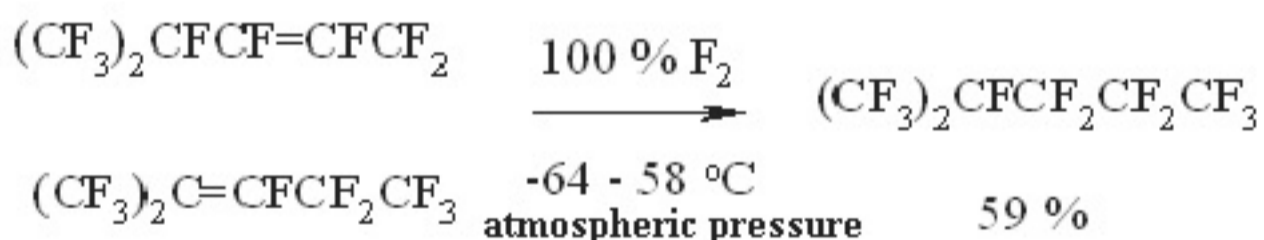
Although using hexafluoropropene as solvent decreases the destructive processes comp process in gas phase, it doesn't suppress them on a whole, which can be connected wit concentration of fluorine atoms, caused by olefine excess. In Table 3 you can see the res hexafluoropropene fluorination in gas-phase and different solvents.

As you can see by the Table 3 data the process carrying out in gas-phase makes dest processes rather notable not providing the total conversion.

Table 3. Conditions and Composition of Hexafluoropropene Elemental Fluorine Fluor Products [6]

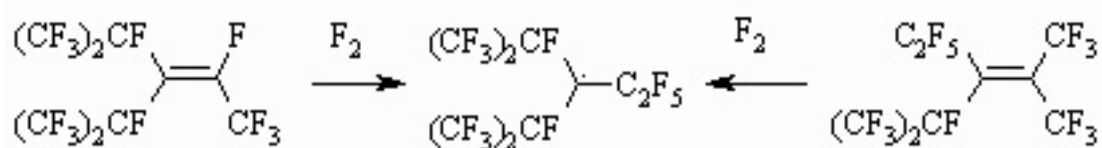
| T, °C | Solvent | Time of contact, min | Reaction mixture, (weight %) | | | |
|-----------|---|----------------------|-------------------------------|-----------------|-------------------------------|------------------------------------|
| | | | C ₃ F ₈ | CF ₄ | C ₂ F ₆ | CF ₂ =CFCF ₃ |
| -26 - -22 | - | 40 | 91.7 | 6.2 | 1.7 | 0.4 |
| -26 - -22 | - | 40 | 92.0 | 6.2 | 1.7 | 0.1 |
| -26 - -10 | - | 40 | 92.1 | 6.2 | 1.7 | |
| -26 - -22 | (C ₂ F ₅) ₃ N | 10 | 98.0 | 1.2 | 0.5 | 0.5 |
| -26 - -10 | (C ₂ F ₅) ₃ N | 20 | 98.4 | 1.3 | 0.3 | |
| -26 - -10 | C ₅ F ₁₂ | 20 | 98.7 | 1.0 | 0.2 | |
| -26 - -10 | C ₃ F ₈ | 20 | 99.9 | 0.1 | 0.1 | |
| -15 - -10 | C ₃ F ₈ | 20 | 97,5 | 2.1 | 0.4 | |
| -26 - -10 | C ₃ F ₈ | 10 | 95.7 | - | 4.3 | 4.3 |
| -26 - -10 | CF ₂ =CFCF ₃ | 20 | 94.4 | 1.5 | 1.5 | |

Nevertheless, the process is rather simple for technological application and doesn't require conditions and equipment and it can be a base for commercial obtaining technology for perfluoro paraffins. We can use the production technology of perfluoropentene and perfluoro -2-methylpentene by elemental fluorine fluorination of perfluoropenten-2-ene and perfluoro-4-methylpent-2-ene, was implemented at an experimental scale at Experimental Plant of RSC of Applied Chemistry, example. We should note, that authors themselves had carried out the successful fluorination of hexafluoropropylene dimers using 100% fluorine in liquid phase [26].



The fluorination of tetrafluoroethylene [27], hexafluoropropene [28], 2-fluoropentene [29] has been carried out the same way. It's better to carry out the process in inert to fluorine solvents, which can be the products of fluorination themselves. In the work [30] it is suggested to use elemental fluorine for detoxication of extremely toxic octafluoroisobutylene, which is generated during pyrolysis of elastomers based on tetrafluoroethylene, instead of perfluorotripentylamine applied for other purposes.

The ease of fluorine adding to multiple C=C bonds is to a great extent determined by steric influence. Thus, fluorine adding by weakly screened multiple bond of tetrafluoroethylene is going through perfluoro-2-butene here requires higher temperature of reaction. [31], and strongly screened multiple bond of perfluoro(1-isopropyl-1-ethyl-2,2-dimethyl)- and (1,1-diisopropyl-2-methyl)-ethylene is on the whole inert to fluorine. Fluorination of these olefins at 300 K stops at the stage of formation of stable (perfluorodiisopropyl-ethyl)methyl radical, which can be distilled without decomposition



1.2. Direct Fluorination of Partly Fluorinated Paraffins, Dialkyl Ethers and T Amines

Final fluorination of CHF_3 and $\text{CF}_3\text{CH}_2\text{F}$ by gaseous fluorine requires high temperature (40–370 °C respectively) and pressure close to 1.5 MPa (Table 4) [6,33]. Different fluoroethanes are finally fluorinated using elemental fluorine [34].

Table 4. Fluorination of Polyfluorinated Paraffins using 100 % [6]

| Paraffin | T, °C | Time, h | F ₂ :Paraffin ratio | Reaction Mixture (yield, % wt.) |
|--|-------|---------|--------------------------------|--|
| CHF_3 | -25 | 0.5 | 1.03 | CF_4 (99.5), C_2F_6 (0.4), CHF_3 (0.1) |
| CF_3CHF_2 | 20-40 | 1.5 | 1.03 | C_2F_6 (92.5), CF_4 (7.0), C_3F_8 (0.9), CHF_2CF_3 (0.1) |
| CH_2FCF_3 | 45-60 | 2.0 | 1.05 | C_2F_6 (44.5), CF_4 (1.5), CHF_2CF_3 (4.5), C_3F_8 (0.4), |
| CHF_2CHF_2 | 0-20 | 0.6 | 0.49 | C_2F_6 (8.0), CF_4 (2.5), CHF_2CF_3 (1.0), C_3F_8 (0.5), CHF_2CF_3 (59.5) |
| CHF_2CHF_2 | 40-60 | 2.5 | 1.05 | C_2F_6 (40.5), CHF_2CF_3 (1.0), C_3F_8 (0.5), CH_2FCF_3 (55.5) |
| CHF_2CHF_2 | 40-60 | 5.0 | 2.05 | C_2F_6 (94.5), CF_4 (4.0), CHF_2CF_3 (1.0), C_3F_8 (0.5), $\text{CHF}_2\text{C}_2\text{F}_5$ (0.5) |
| $\text{CHF}_2\text{C}_2\text{F}_5$ | 60-70 | - | 3.5 | C_3F_8 (93.5), CF_4 (5.0), C_2F_6 (1.0), $\text{CHF}_2\text{C}_2\text{F}_5$ (0.5) |
| $\text{CF}_3\text{CHF}_2\text{CF}_3$ | 45-70 | - | 3.5 | C_3F_8 (95.5), C_2F_6 (0.5), $\text{CF}_3\text{CHF}_2\text{CF}_3$ (0.8) |
| $\text{CF}_3\text{CHF}_2\text{CH}_2\text{C}_2\text{F}_5$ | 50 | - | 7.0 | C_5F_{12} (41.0), CF_4 (3.0), C_2F_6 (1.0), C_3F_8 (1.0), $\text{C}_2\text{F}_5\text{CHF}_2\text{C}_2\text{F}_5$ (1.5), |

| | | | | | |
|--|-------------------|---|------|------|--|
| | 100 | | | | CF ₃ CHFC ₃ F ₇ (1.5), C ₂ F ₅ CHFCHFC ₂ F ₅ (51.0) |
| CF ₃ CHFCHFC ₂ F ₅ | $\frac{50}{100}$ | - | 7.0 | 2.05 | C ₅ F ₁₂ (90.5), CF ₄ (5.0), C ₂ F ₆ (2.0), C ₃ F ₈ (1.0), C ₂ F ₅ CHFCHFC ₂ F ₅ (0.5), CF ₃ CHFC ₃ F ₇ (0.5) |
| CH ₂ FCF ₃ | $\frac{45}{60}$ | - | 4.0 | 2.05 | C ₂ F ₆ (96.5), CF ₄ (2.5), CHF ₂ CF ₃ (0.5), C ₃ F ₈ (0.3) |
| CHF ₂ CF ₂) ₆ CHF ₂ | $\frac{80}{120}$ | - | 12.0 | 2.05 | C ₈ F ₁₈ (88.5), CF ₄ (7.5), C ₂ F ₆ (2.0), CHF ₂ C ₇ F ₁₅ (1.5) |
| C ₃ H ₈ | $\frac{-30}{-10}$ | | 3.0 | 12.5 | C ₃ F ₈ (5.0), CF ₄ (80.5), C ₂ F ₆ (13.5), CF ₃ CHFC ₃ F ₇ (1.0) |

Dialkyl ethers are more resistant to fluorine, than paraffins, olefins and trialkylamines (Ta which probably can be connected to the oxidation level of molecules (dimethyl ether is fluorina to CF₃OCF₃ of 33% yield, while ethylene - up to hexafluoroethane of 7.5% yield) [6].

Table 5. Fluorination of Partly Fluorinated Ordinary Ethers [6]

| Ether | T, °C | Time, h | Ratio F₂ : Ether | Reaction Mixture (yield, % wt.) |
|---|--------------|----------------|------------------------------------|--|
| CF ₃ CF=CFOCH ₃ | -30- 80 | 6.0 | 4.15 | C ₃ F ₇ OCF ₃ (85.0), CF ₄ (9.0), C ₂ F ₆ (2.0), C ₃ F ₈ (2.0), O ₂ (1.0), C ₃ F ₇ OCHF ₂ (0.5), C ₃ F ₇ OCH ₂ F (0.5), C ₃ F ₇ OF (0.1) |
| CF ₃ CF=CFOC ₂ H ₅ | -30- 80 | 16.0 | 6.2 | C ₃ F ₇ OC ₂ F ₅ (45.5), CF ₄ (32.5), O ₂ (3.4), C ₂ F ₆ (14.5), CHF ₂ CF ₃ (4.1), C ₃ F ₇ OF (0.1) |
| (CF ₃) ₂ C=C(C ₂ F ₅)OCH ₃ | -30- 80 | 10 | 4.2 | (CF ₃) ₂ CF(CF(C ₂ F ₅))OCF ₃ (92.8), CF ₄ (28.0), O ₂ (3.5), (CF ₃) ₂ CF(CF(C ₂ F ₅))OCH ₂ F (1.3), C ₂ F ₆ (0.5), (CF ₃) ₂ CF(CF(C ₂ F ₅))OCHF ₂ (1.9) |
| CH ₂ FOCH ₂ F | -30- 80 | 6.0 | 2.1 | CHF ₂ OCHF ₂ (71.5), CF ₄ (2.0), C ₂ F ₆ (1.0), O ₂ (0.3), C ₃ F ₇ OF (0.1), CF ₃ OCF ₃ |

| | | | | | |
|---|-------------|------|------|--|--|
| | | | | | (15.5), CF ₃ OCHF ₂ (3.1), CF ₃ OCHF ₂ (6.5) |
| CH ₂ FOCH ₂ F | -30- 80 | 18.0 | 3.15 | | CF ₃ OCHF ₂ (63.5), CF ₄ (2.5), C ₂ F ₆ (1.5), O ₂ (0.4), C ₃ F ₇ OF (0.1), CF ₃ OCF ₃ (23.5), CHF ₂ OCHF ₂ (4.5), CH ₂ FOCH ₂ F (6.5) |
| CH ₂ FOCH ₂ F | -30- 80 | 6.0 | 4.2 | | CF ₃ OCF ₃ (91.5), CF ₄ (2.5), C ₂ F ₆ (1.5), O ₂ (0.4), CF ₃ OCHF ₂ (2.0), CHF ₂ OCHF ₂ (0.5), CF ₃ OCHF ₂ (2.0) |
| CH ₂ FOCH ₂ F | -30- 80 | 12.0 | 3.8 | | CF ₃ OCF ₃ (92.5), CF ₄ (3.5), C ₂ F ₆ (1.5), O ₂ (0.5), CF ₃ OCHF ₂ (2.0) |
| CF ₃ CF ₂ CF ₂ CHFOC ₄ F ₉ | 20- 150 | 6.0 | 1.1 | | C ₄ F ₉ OC ₄ F ₉ (57.5), CF ₄ (20.0), C ₂ F ₆ (3.5), O ₂ (7.5), C ₃ F ₈ (3.0), C ₄ F ₁₀ (8.5) |
| CF ₃ CF ₂ CF ₂ CHFOC ₄ F ₉ * | 250- 300 | 0.2 | 1.1 | | C ₄ F ₉ OC ₄ F ₉ (97.5), CF ₄ (1.0), C ₂ F ₆ (0.5), O ₂ (0.5), C ₄ F ₁₀ (0.5) |
| CH ₃ OCH ₃ | -30- 80 | 6.0 | 3.8 | | CF ₃ OCF ₃ (9.5), CF ₄ (28.0), O ₂ (3.5), CHF ₂ OCHF ₂ (17.0), CF ₃ OCHF ₂ (4.5), CH ₃ OCH ₃ (36.0) |

*CoF₃- catalyst

However, it should be noted that during final fluorination of partly fluorinated ethers the pro-
going not selectively enough. Thus, the fluorination of HCF₂CF₂OMe using elemental fluorine I
the solution of anhydrous hydrogen fluoride and in the solution of chlorotrifluoroethylene oligor
at room temperature produces mixture of ethers, containing different number of fluorine
[35].

Trialkylamines, containing even one perfluoroalkenyl radical are less resistant to fluorine infl
that is due to highest thermal effect of the reaction: in most favorable case 6 atoms of hy
undergo substitution (Table 6).

Table 6. Polyfluoroalkylamines Fluorination Using Elemental Fluorine [6]

| Amine (Enamine) | T, °C beginning- ending | Time, h | Ratio F₂: Enamine | Target product (yield, % wt.) |
|--|--|--------------------|---|--|
| (CF ₃) ₂ C=C(C ₂ F ₅)N(CH ₃) ₂ ^a | -30- 80 | 16 | 10.7 | (CF ₃) ₂ CF ₂ CF(C ₂ F ₅)N(CF ₃) ₂ (29.5) |
| [(CF ₃) ₂ CF] ₂ C=C(CF ₃)N(CH ₃) ₂ ^a | -30- 90 | 18 | 9.8 | [(CF ₃) ₂ CF] ₂ CF ₂ CF(CF ₃)N(CF ₃) ₂ (35.5) |

| | | | | |
|--|----------|-----|------|-------------------------|
| $C_2F_5N(CH_2CF_2CF_3)_2$ ^b | 100- 150 | 15 | 2.5 | $(C_2F_5)_3N$ (63.5) |
| $C_2F_5N(CH_2CF_2CF_3)_2$ | 260- 360 | 0.1 | 2.1 | $(C_2F_5)_3N$ (97.5) |
| $C_3F_7N(CH_2CF_2CF_2CF_3)_2$ ^b | 100- 170 | 17 | 2.8 | $(C_3F_7)_3N$ (51.0) |
| $C_3F_7N(CH_2CF_2CF_2CF_3)_2$ | 280- 390 | 0.1 | 2.1 | $(C_3F_7)_3N$ (97.0) |
| $C_4F_9N(CH_2CF_2CF_2CF_2CF_3)_2$ | 300- 410 | 0.1 | 2.1 | $(C_4F_9)_3N$ (95.5) |
| $C_5F_{12}N(CH_2CF_2CF_2CF_2CF_2CF_3)_2$ | 340- 440 | 0.1 | 2.2 | $(C_5F_{12})_3N$ (91.0) |
| $(C_2H_5)_3N$ | -35- 20 | 14 | 20.5 | $(C_2F_5)_3N$ |

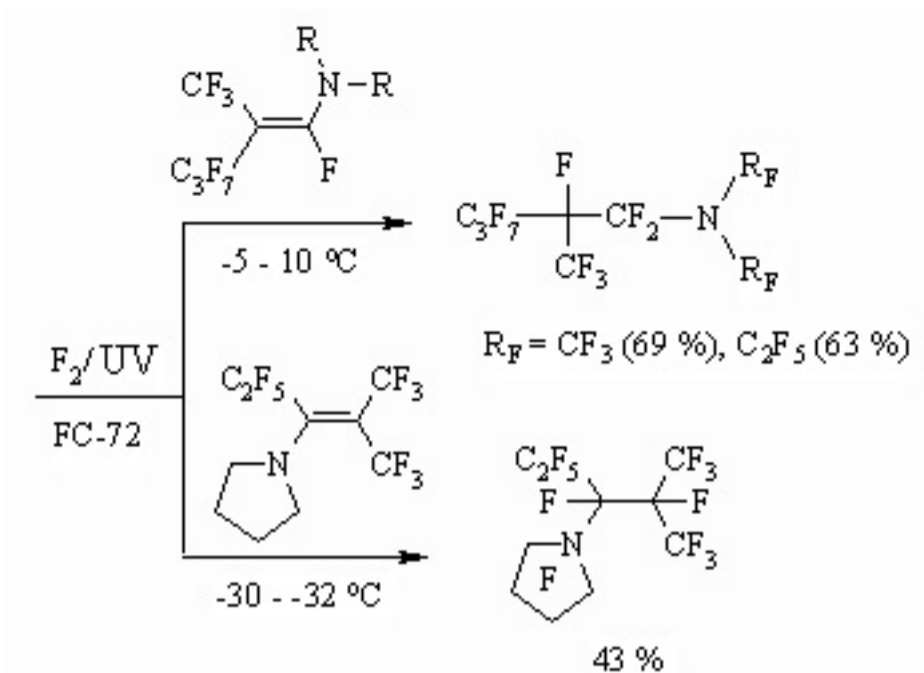
^a Fluorination reaction in $CF_3N(C_2F_5)_2$ (10 %) solution

^b Catalytic (CoF_3) gas phase fluorination

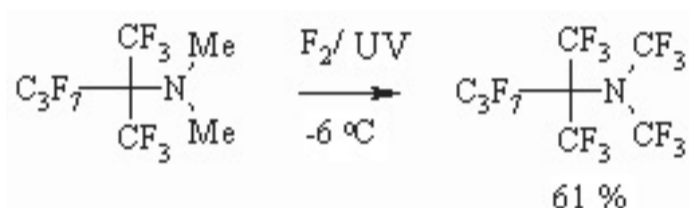
To conduct a successful fluorination we need mild conditions: low temperature, solvent, effective stirring and long period for the process.

At fluorinating of amines and ethers, containing multiple bonds in alkyl chain, at first, multiple bonds are being fluorinated and only then hydrogen atoms are being substituted. While transferring paraffins to dialkyl ethers the selectivity of fluorination is growing: while fluorinating paraffins to dihydroperfluorinated paraffins the content of monohydro derivatives is not high after feeding half mole of fluorine and their content in products of reaction is about 10%, whereas after feeding half quantity of fluorine into α, α' -dimethyl ether the content of products of partial substitution is about 50%. It is stated, that at fluorination of fluorine containing olefines, paraffins and ethers the yield of perfluorinated species is 55-99 %. At fluorination of fluorine containing tertiary amines with two alkyl groups the yield of tertiary perfluorinated amines amounts to 29-35%. As molecule is being saturated with fluorine and as fluorine containing chain is growing the fluorinating conditions are becoming severer. At transfer from polyfluorinated olefines and paraffins to fluorine containing ethers the selectivity of fluorination is growing.

High heat of fluorination of N,N-dialkylamino N-perfluoroalkylenes provokes high compare to fluorine containing compounds dissociation of fluorine molecules, that results in higher molecular fragmentation. The yield of perfluoro-N,N-dimethylhexanes and N,N-dimethylnonanes are 45% and 55% respectively, while at fluorination of hexafluoropropene the yield of octafluoropropane is practically quantitative [25]. High emission of heat at obtaining perfluorinated compounds is a serious problem when working out their obtaining technology of elemental fluorine direct fluorination. Nevertheless even N,N-dimethyl-N-perfluoroalkylenes are fluorinated using elemental fluorine forming corresponding tertiary perfluorinated amines which yield is as minimum as twice exceeding that obtained at electrochemical fluorination. Thus, N,N-dialkyl-N-perfluoroalkylenes are subject to phase fluorination using elemental fluorine at photochemical irradiation forming fully fluorinated tertiary alkylamines [36].



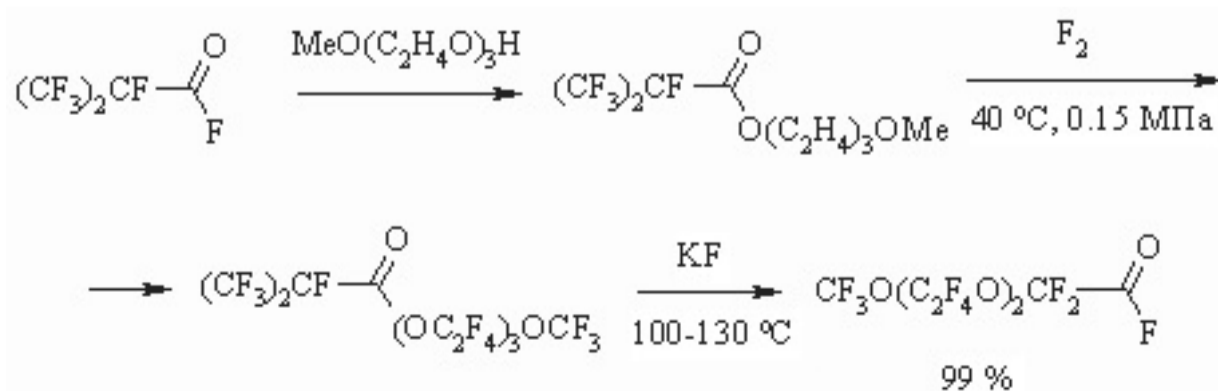
This approach is being implemented as well for partly fluorinated trialkylamines. For example, the formation of [36] perfluoro(N,N-dimethyl-1,1-dimethylbutyl)amine is stated as direct elemental fluorine fluorination of 2-dimethylaminoperfluoro-2-methylpentane [36].



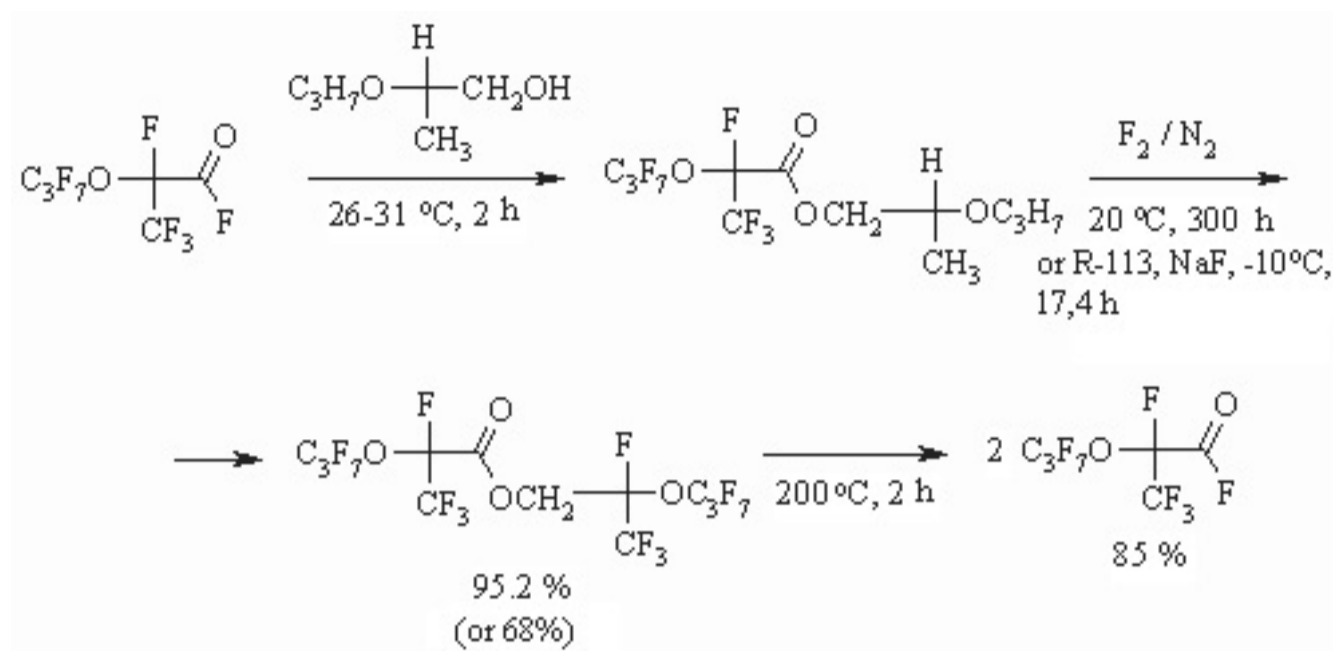
Synthesis of partly fluorinated derivatives doesn't produce any problems and is based on a method developed and produced by the industry for perfluoroolefins [37-39]. The obtained results show that the developed methodology of fluorinating organic compounds on the gas-liquid contact surface with 100% elemental fluorine allows obtaining perfluorinated compounds with satisfactory yields, as compared to usual technological fluorinating techniques. The application of inert solvents decreases destructive processes largely, that is connected to more than tenfold increasing of the reaction mass transfer coefficient [40], absence of local overheating at the point of components' contact. When transition from solvents of longer carbon chain to solvents of shorter carbon chain we observe an additional suppression of destructive processes, that may be connected to higher fluorine solubility in solvents of shorter carbon chain [5,41] and additional improving of heat-exchange.

1.3. Direct Fluorination of Carbonyl Containing Compounds

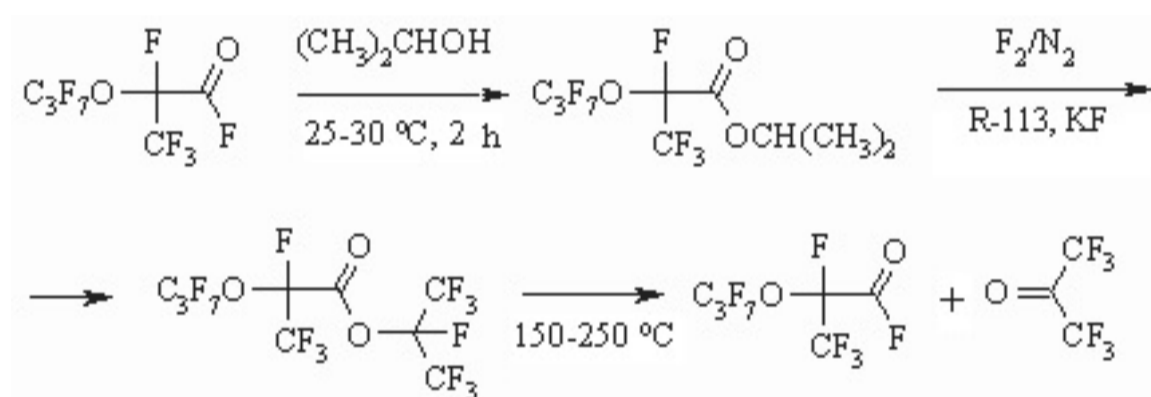
One of the new ways of synthesis for perfluorinated carboxylic acids is based on the following approach. At first we carry out the etherification of available and reasonably priced perfluorinated carboxylic acids using aliphatic alcohol, afterwards the ester is subjected to liquid-phase fluorination by elemental fluorine forming fully fluorinated ester of the corresponding acid. It is decomposed by alkali fluoride at 100-130 °C forming two acids, which are being separated using distillation. The yield of the target products by this method is much higher and it is an alternative for electrochemical fluorination of carboxylic acids [42-46].



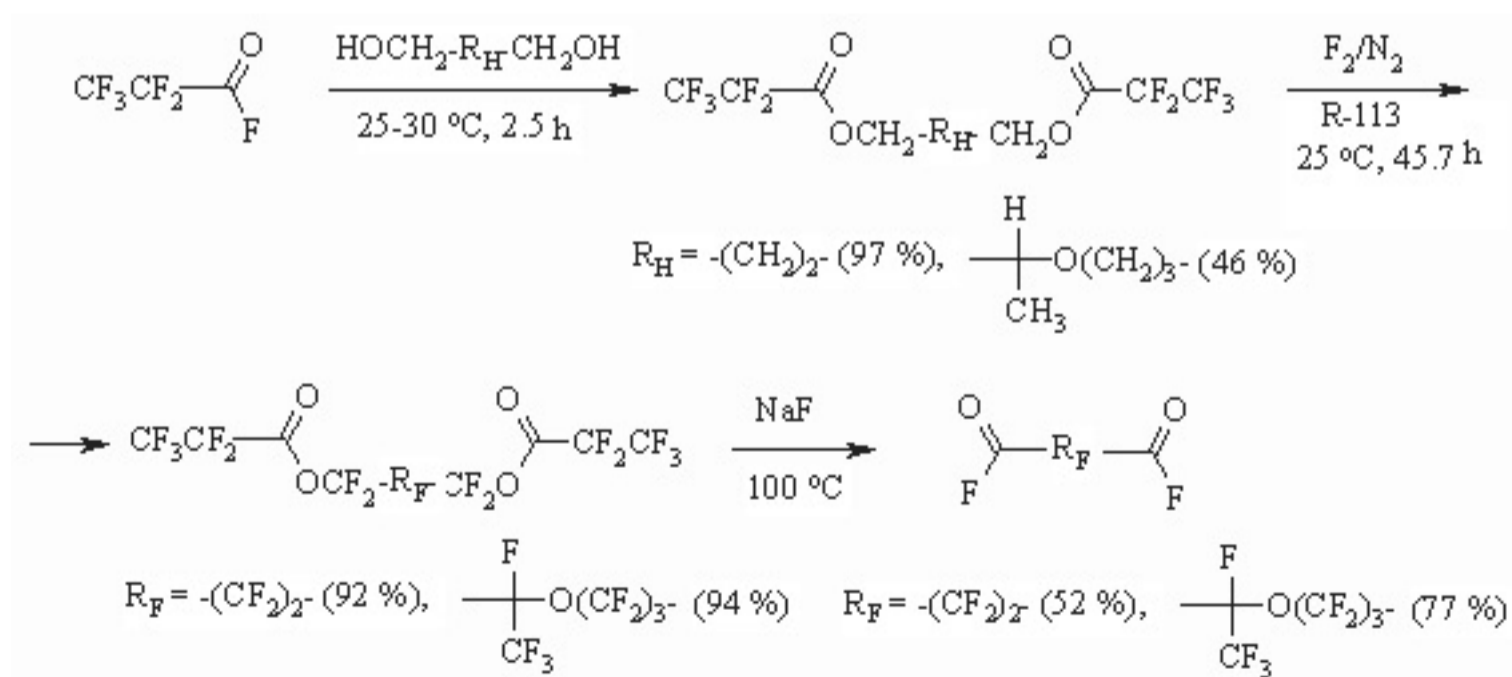
Here it is very important to choose the appropriate perfluorinated carboxylic acid, which can be easily isolated out of mixture of acids. For example, acids' fluoroanhydrides, obtained at dimer and trimerization of hexafluoropropylene oxide are widely used [43, 46, 47]. The presented reaction can be carried out at an industrial scale.



In case of using isopropyl alcohol for this reaction the hexafluoroacetone is formed as a side product [48]. Dissociation of ester bonds is carried out in the temperature range of 150-250°C in the liquid phase without solvent using or during the gaseous phase in a tube, filled with glass, and an alkali-land metal for example KF, NaF or activated carbon [44].

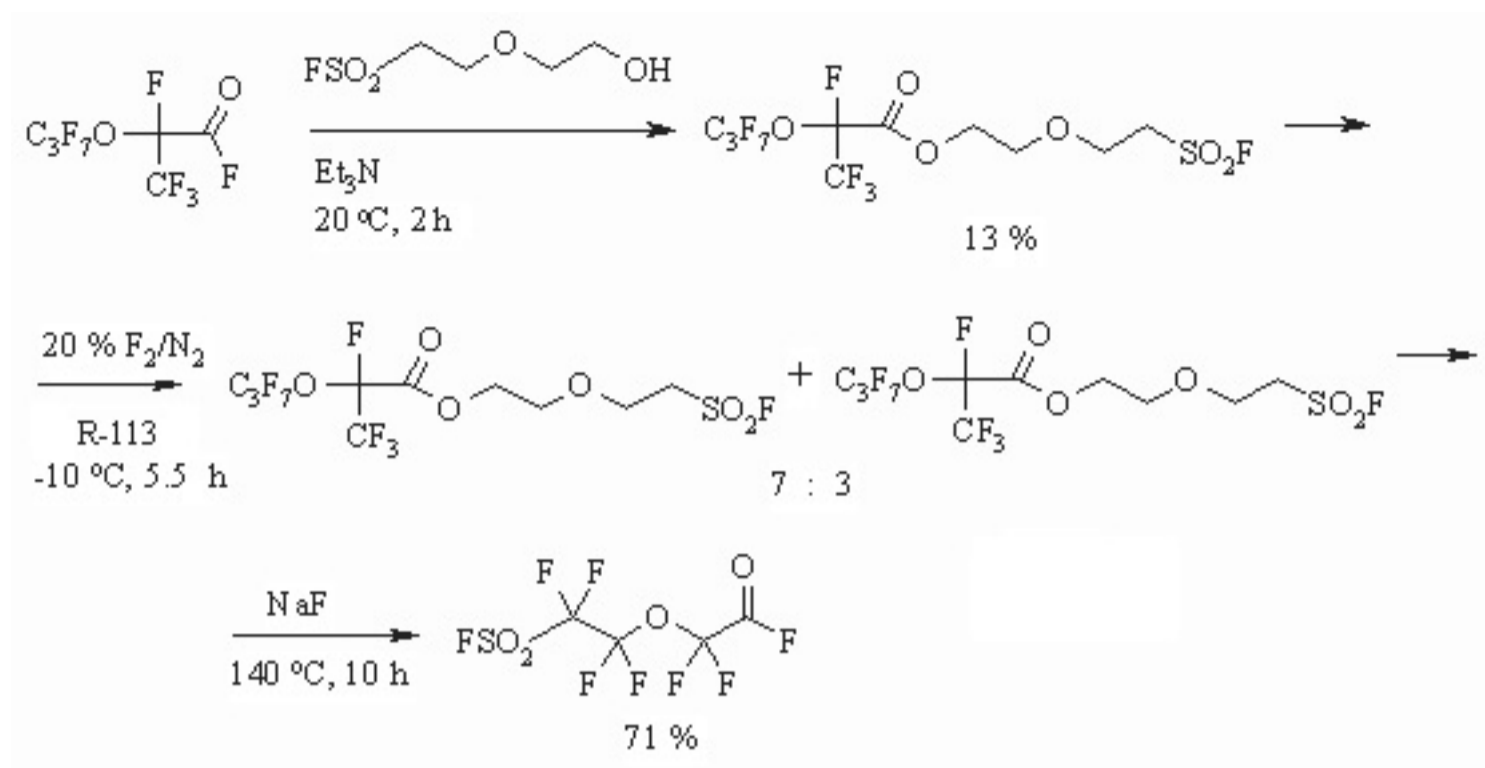


Glycols were introduced into the reaction as well, that allows us to obtain perfluorinated dicarboxylic acids and their derivatives [49].

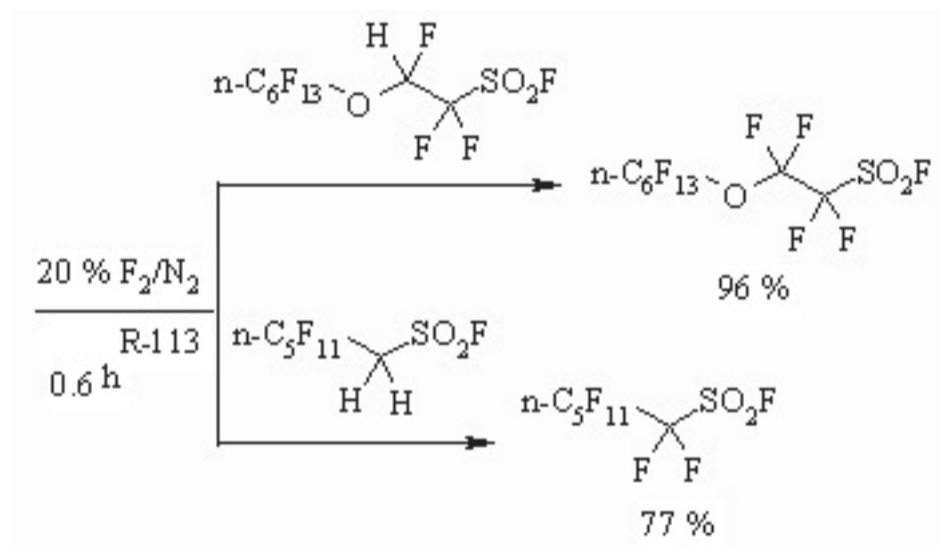


In case of alcohols, possessing SO₂F ending group the fluorination using elemental fluorine is accompanied by substitution of this group by fluorine atom and depends on the length of the chain.

chain [47].

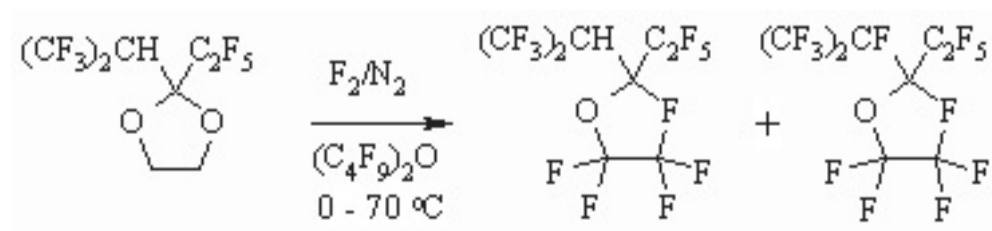


At the same time during influence of elemental fluorine on polyfluorosulphoacids fluoroanhy prove to be resistant and exchange of SO_2F group for fluorine atom doesn't take place but hydrogen atoms are being substituted [47].

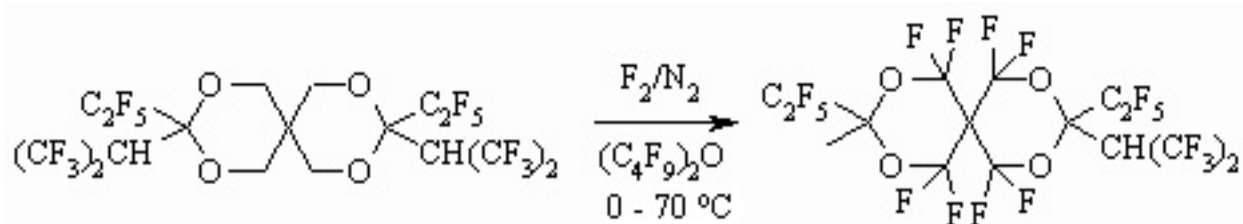


1.4 Heterocyclic Compounds Fluorination

In case of partly fluorinated heterocyclic compounds the influence of fluorine diluted by ni allow obtaining of fully fluorinated compounds. Let's draw just a few examples. Thus, fluorina dioxalane using elemental fluorine, diluted by nitrogen (1:8), is going smoothly forming mixt compounds at consecutive rising of temperature from 0 to 70°C in the solution of perfluoro ester. The hydrogen atom located by the tertiary carbon atom is the most difficult one for the f atom to displace. Severe conditions and excess of fluorine are required to prevent such objects

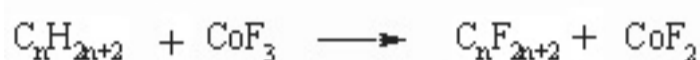


The fluorination of 1,3-dioxane derivative is carried out in the perfluorodibutyl ester as w perfluorinated derivative of 2,4,8,10-tetraoxaspiro[5.5]undecane is produced [50].



1.5. Catalytic Method For Carrying Out The Purification of Mixtures Of Fluorinated Compounds

Cobalt trifluoride is a traditional fluorinating agent for obtaining (incl. commercial prod) perfluorinated organic compounds, especially, parafines and ethers out of hydrocarbo unsaturated analogues [51, 52]. In the reaction process cobalt trifluoride is being resto difluoride:



Fluorinating using cobalt trifluoride is characterized by comparatively low target products' yie (40%), by limited productivity, caused by insignificant concentration of "activated" fluorine (16. %; actual using is 1.2-3 times less) and also by noticeable residue content of hydrogen con and unsaturated compounds (up to 1 wt. %) when the requirements of medicine, radioelec and other branches of industry are $1 \cdot 10^{-3} - 5 \cdot 10^{-4}$ wt %. These particularities make us to k other perfluorinated compounds' obtaining methods.

Catalytic fluorination of fluorine containing organic compounds using elemental fluorine is them. Higher metals fluorides of variable oxidation including nickel, copper and cobalt fluorides [54] are used as catalysts. In the work [55] a comparative fluorinatic monohydroperfluorotripropylamine $C_3F_6HN(C_3F_7)_2$ (I) and monohydroperfluorotributy $C_4F_8HN(C_4F_9)_2$ (II) using cobalt trifluoride and elemental fluorine in the presence of cobalt trif had been studied. Compounds (I), (II) are main technological admixtures at electrochemical ob of perfluorotripropylamine $(C_3F_7)_3N$ and perfluorotributylamine $(C_4F_9)_3N$ respectively. Concen of these admixtures in "crude material" reaches 30 wt %. Fluorination was carried out in the r filled with CoF_3 , at that in first case the mixture of fluorinated compound's vapours and fluorir put into the reactor, and in the second one the nitrogen was fed into the reactor instead of f at the same rate. In Table 7 you can see the results of catalytic fluorination of some hy containing and unsaturated compounds, which can be found in obtained by Electroch Fluorination (**ECF**) method "crude material" as admixtures.

Table 7. Fluorination of Some Fluorine Hydrogen Containing and Unsaturated Compounds Elemental Fluorine at CoF_3 [5]

| Compound | | T, °C | Time, min | A · 10 ⁻⁴ , wt % * | Yield, wt % |
|----------------------|---------------|---------|-----------|-------------------------------|-------------|
| Initial | Target | | | | |
| $C_3F_7CHF-CHF_2$ | C_5F_{12} | 230-280 | 5 | 6 | 94.4 |
| $CF_3CHFN(C_2F_5)_2$ | $(C_2F_5)_3N$ | 270-330 | 5 | 5 | 95.5 |
| $C_3F_6HN(C_3F_7)_2$ | $(C_3F_7)_3N$ | 320-380 | 10 | 6 | 96.0 |
| $C_4F_8HN(C_4F_9)_2$ | $(C_4F_9)_3N$ | 360-410 | 13 | 7 | 93.2 |

| | | | | | |
|----------------------------|---------------------------|---------|----|---|------|
| $C_5F_{10}HN(C_5F_{11})_2$ | $(C_5F_{11})_3N$ | 380-430 | 16 | 8 | 90.1 |
| $C_4F_8HOC_4F_8H$ | $(C_4F_9)_2O$ | 300-350 | 5 | 5 | 96.5 |
| $(C_3F_7)_2CF-CF=CF_2$ | C_9F_{20} | 320-380 | 6 | 5 | 97.0 |
| cyclo- $C_6F_9-C_2F_5$ | cyclo- $C_6F_{11}-C_2F_5$ | 300-360 | 7 | 5 | 96.4 |

A*- residual content of unsaturated and hydrogen containing compounds

It is illustrated by the results of fluorination of CoF_3 and compound (II) at different temperatures (Table 8 and Fig. 1).

Table 8. Final Catalytic Fluorination of Polufluorinated Compounds Solutions [24]

| Compound | Solvent | Catalyst | T, °C | Contact Time, min. | Reaction mixture before fluorination, % |
|------------------------------|-------------|----------|---------|--------------------|---|
| $CF_3CF=CFC_2F_5$ | C_5F_{12} | CuF_2 | 230-260 | 5 | C_5F_{12} , 99.0 (99.4); CF_4 , 0.2 (0.2); C_2F_6 , 0.1 (0.1); C_3F_8 , 0.1 (0.1); $CF_3CF=CFC_2F_5$, 0.6 (0.1) |
| $(CF_3)_2C=CFC_2F_5$ | C_6F_{14} | CuF_2 | 230-320 | 7 | C_6F_{14} , 96.7 (99.4); CF_4 , 0.2 (0.2); C_2F_6 , 0.1 (0.1); C_3F_8 , 0.1 (0.1); $(CF_3)_2C=CFC_2F_5$, 2.9 (0) |
| C_9F_{18} , isomer mixture | C_9F_{20} | CuF_2 | 260-340 | 10 | C_9F_{20} , 97.5 (99.3); CF_4 , 0.2 (0.3); C_2F_6 , 0.2 (0.2); C_3F_8 , 0.1 (0.1); C_9F_{18} , 2.0 (0) |

| | | | | | | |
|---|---|--|------------------|---------|----|--|
| | | | CoF ₃ | 240-320 | 10 | C ₉ F ₂ O, 97.5 (99.5); CF ₄ , 0.2 (0.2); C ₂ F ₆ , 0.2 (0.2); C ₃ F ₈ , 0.1 (0.1); C ₉ F ₁₈ , 2.0 (0) |
| CHF ₂ OC ₃ F ₇ + CH ₂ FOC ₃ F ₇ | CF ₃ OC ₃ F ₇ | | CuF ₂ | 230-340 | 8 | CF ₃ OC ₃ F ₇ , 98.1 (99.6); CF ₄ , 0.2 (0.2); C ₂ F ₆ , 0.1 (0.1); C ₃ F ₈ , 0.1 (0.1); CH ₂ FOC ₃ F ₇ , 0.4 (0); CHF ₂ OC ₃ F ₇ , 1.1 (0) |
| CHF ₂ OC ₆ F ₁₃ + CH ₂ FOC ₆ F ₁₃ | CF ₃ OC ₆ F ₁₃ | | CuF ₂ | 260-340 | 10 | CF ₃ OC ₆ F ₁₃ , 98.2 (99.3); CF ₄ , 0.2 (0.3); C ₂ F ₆ , 0.1 (0.1); C ₃ F ₈ , 0.1 (0.1); CHF ₂ OC ₆ F ₁₃ , 0.9 (0.1); CH ₂ FOC ₆ F ₁₃ , 0.5 (0.1) |
| | | | CoF ₃ | 240-300 | 9 | CF ₃ OC ₆ F ₁₃ , 98.2 (99.5); CF ₄ , 0.2 (0.2); C ₂ F ₆ , 0.1 (0.1); C ₃ F ₈ , 0.1 (0.1); CHF ₂ OC ₆ F ₁₃ , 0.9 (0); CH ₂ FOC ₆ F ₁₃ , 0.5 (0) |
| C ₆ F ₁₃ N(CH ₂ F) ₂ + C ₆ F ₁₃ N(CHF ₂) ₂ | C ₆ F ₁₃ N(CF ₃) ₂ | | CoF ₃ | 260-320 | 10 | C ₆ F ₁₃ N(CF ₃) ₂ , 93.6 (99.2); CF ₄ , 0.2 (0.5); C ₂ F ₆ , 0.1 (0.2); C ₃ F ₈ , 0.1 (0.2); C ₆ F ₁₃ N(CH ₂ F) ₂ , 3.0 (0); C ₆ F ₁₃ N(CHF ₂) ₂ , 3.0 (3.0) |
| | | | | | | C ₉ F ₁₉ N(CF ₃) ₂ , 91.4 (98.9); CF ₄ , 0.2 (0.6); C ₂ F ₆ , 0.1 |

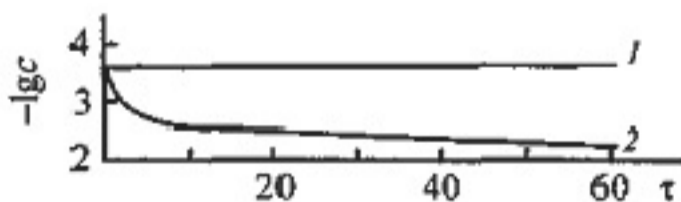
| | | | | | |
|-----------------------|----------------------|---------|------|----|-----------------------------|
| $C_9F_{19}N(CH_2F)_2$ | $C_9F_{19}N(CF_3)_2$ | CoF_3 | 280- | 12 | (0.3); C_3F_8O , 0.1 |
| + | | | 360 | | (0.2); |
| $C_9F_{19}N(CHF_2)_2$ | | | | | $C_9F_{19}N(CH_2F)_2$, 4.0 |
| | | | | | (0); |
| | | | | | $C_9F_{19}N(CHF_2)_2$, 4.2 |
| | | | | | (0) |

Table 9. Fluorination of CoF_3 Hydrogen Containing Admixtures of Perfluorotributylamine (c period is 5 min., start concentration $(C_4HF_8)_3N$ is 17.5 mass.%) [55]

| T, °C | Contents, wt % | |
|----------|------------------------------|-------------------------------------|
| | "active" fluorine CoF_3 | Hydrogen Containing Compounds |
| 200 | 13.0 (79.4) | 7.5 |
| 250 | 13.6 (83.0) | 4.8 |
| 300 | 15.4 (94.0) | 3.2 |
| 350 | 16.0 (97.5) | 2.1 |
| 400 | 16.38 (100) | 0 |
| 450 | 16.38 (100) | 0 |

In Table 9 you can find information on CoF_3 fluorinating process temperature impacts us examples of hydrogen containing admixtures of perfluorotributylamine, obtained by ECF methc obvious, that temperature of 400°C is most effective [56].

Fig. 1

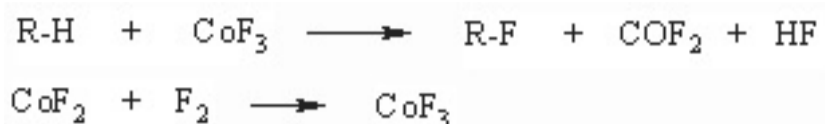


Relative rate of compound (II) fluorination.
 c - compound (II) (mass percent) concentration, τ - time(min)
 Fluorination: 1- $CoF_3 - F_2$ 2 - CoF_3

Curve 2, showing the fluorinating rate of compound (II) CoF_3 is typical for reactions, which s stage goes in fact on the surface of one reagent (in the present case - CoF_3) in the external area. As CoF_3 is being consumed in the surface layer the reaction is transferring to the diffusion with what the seen low drop of the reaction rate is connected [56]. It should be noted, th starting part of the curve 2 is rather difficult to be analyzed and the majority of researches st the kinetics of fluorination of CoF_3 hydrocarbons are usually limited by diffusion area, in which th

lowering is being ignored and taken as constant one [56, 57].

At elemental fluorine fluorination in the presence of CoF_3 (right line 1) the fluorination is going on a standard basis in the external kinetic area due to constant concentration of CoF_3 in the surface which is caused by on-time or even anticipatory fluorine inflow of the fluorine:



The results obtained make the difference in CoF_3 and elemental fluorine with CoF_3 as a fluorinating processes obvious. In first case the fluorinating rate is low and decreases as time goes by, the process is limited by concentration of "activated" fluorine, that hampers its carrying out in an uninterrupted pattern; the residual content of hydrogen containing or unsaturated compounds in the products is quite high ($1 \cdot 10^{-3}$ wt %), and that requires their additional purification. In second case the rate of fluorination is high and constant the process is not limited by the time period in fact, allows us to work using the uninterrupted pattern; the residual content of hydrogen containing compounds is less than $1 \cdot 10^{-3}$ wt % (Catalytic fluorination process has been carried out at the Plant of RSC of "Applied Chemistry").

to be continued