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# Technology for the preparation of perfluoro-organic compounds

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## Abstract

Fluorination by elemental fluorine of fluorine-containing alkenes, alkanes, ethers and tertiary amines was investigated, aimed at obtaining the perfluorinated analogs. The factors affecting yield of the target compounds were studied. Elements of technology were elucidated.
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## 1. Introduction

Owing to the possession of unique properties, such as extremely high chemical and thermal stability, useful dielectric and thermophysical properties, and the ability to dissolve gases in large amounts, perfluoro-organic compounds can be widely applied in medicine, electric power technology, energetics, electronics, navigation techniques, chemical industry, and even in fishing industries [1,2]. These perfluoro-organic compounds are generally linear or cyclic perfluorocarbon compounds often containing such atoms as nitrogen and oxygen. However, use of these materials is restricted by their high cost, which to a great extent is determined by the absence of convenient manufacturing technology.

Industry employs two methods for obtaining perfluoro-organic compounds: reaction of hydrocarbons (paraffins and ethers) with higher transition metal fluorides, mostly with $CoF_3$, and electrochemical fluorination of hydrocarbons in anhydrous hydrogen fluoride (ethers and tertiary amines) [3]. Both these methods are characterized by low productivity and poor yield of the target compounds, by formation of wastes difficult to be utilized and often including highly toxic compounds and it is necessary to remove the incompletely fluorinated compounds completely. All methods require purification of final products by complicated technology, increasing the product cost. However, during purification, loss of the perfluoro-organic compound cannot be avoided, and a problem of reduction of yield arises. When using a fluoride of a metal of high oxidation state, low productivity is connected with low content of active fluorine, e.g., 16.38% in $CoF_3$. The content is in practice even lower, approximately 2.5–3.2%, owing to the formation of a dense $CoF_2$ film on the $CoF_3$ surface, which decelerates the fluorination process. A by-product is easily formed by decomposition. Among the attempts to enhance the process of fluorination with $CoF_3$ we must mention fluorination in a fluidized bed [1,2]: the more dense $CoF_2$ falls to the reactor bottom, where it is refluorinated to $CoF_3$. In some plants, worm reactors are used: in one part $CoF_2$ is fluorinated, while in another $CoF_3$ is used for the fluorination of a hydrocarbon. In both the methods the fluorine consumption is slightly higher, but the whole process gives low yield (20–40%) and the amount of waste is large.

The method of electrochemical fluorination employed in production of perfluorinated ethers and trialkylamines, is characterized by an even lower yield (7–25%) compared to $CoF_3$, low productivity, and much waste. The electrolysis productivity is not constant: it initially increases (induction period), then remains stable, and then decreases due to corrosion of anodes and contamination by tarry reaction by-products. Improvement of the electrochemical fluorination process was attempted by employing porous anodes. Owing to the extended surface the electrolyzer productivity increases, but their period of use becomes shorter due to rapid corrosion and tarring.

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Perfluoro-organic compounds are prepared by substituting hydrogen atoms of an unfluorinated or partially fluorinated, saturated or unsaturated organic compound having a particular skeleton with fluorine atoms. The fluorinating means adopted in the present work uses fluorine gas. In fluorination with elemental fluorine the yield is a few percent only, and the main products are low-molecular weight fluorinated alkanes. This is a result of the high energy of C–F bond formation (448–507 kJ/mol) exceeding that of C–C bonds (347 kJ/mol) [4], which leads to fragmentation of the carbon framework. The high heat of reaction in conjunction with low dissociation energy of fluorine ($D$(F–F)=157 kJ/mol) results in effective branching of the reaction chain process and in even higher heat evolution. To avoid this, a special technique is applied: fluorination with a low temperature gradient [5], 25–100-fold dilution of fluorine, and aerosol fluorination [6], giving fluorinated compounds in higher yield, but these methods have low productivity, are complicated, and do not yet proceed on a laboratory scale.

According to our earlier investigations [7–11] that conform to published observations [12], compounds containing fluorine atoms are capable of being electrochemically fluorinated to form perfluorinated products in satisfactory yields. As has been shown [3], polyfluorinated compounds containing 1–3 hydrogen atoms can be fluorinated up to perfluoro compounds in high yields. In the present work we consider this problem and some questions on fluorination with elementary fluorine for gas-phase fluorination and fluorination from two-phase gas–liquid of perfluorinated olefins, polyfluorinated paraffins, fluorine-containing ethers and tertiary amines.

## 2. Results and discussion

The procedure employed consists in controlled fluorine addition to the substrate with a flow rate low enough to prevent heating of the reaction mixture by more than 1.5°C and increase in fluorine partial pressure by more than 0.02 MPa (“adiabatic” fluorination) (cf. [14–16]). The liquid phase of the starting mixture is contacted in a counter-current manner with the fluorine gas (liquid-phase absorption column system, “adiabatic” fluorination). In each experimental series besides polyfluorinated compounds their hydrocarbon analogs were also involved in the fluorination. The principal experimental results are listed in Tables 1–4.

Considering the results, we may note that polyfluorinated compounds convert to the perfluorinated in high yield, while fluorination of hydrocarbons results in very low yields of perfluorinated products. This obviously is connected with decrease in both heat of fluorination (Table 5) and fluorination rate (like the rate of any halogenation) upon fluorine replacement for hydrogen atoms in hydrocarbons. This leads to decrease in the rate of heat evolution and improves the conditions of heat transfer.

Elongation of the carbon chain leads to increase of the fluorination conditions: while lowest olefins ($C_2$–$C_4$) are fluorinated at −40°C to −10°C, higher olefins ($C_8$–$C_{12}$) require 120°C, and fluorination time rises from 0.5 to 48 h. This may be connected with the vibrational and rotational energy of the whole molecule, which depends on the carbon chain length.

Dialkyl ethers are more stable compared to olefins, paraffins and trialkylamines to fluorine action. This

Table 1
Fluorination of perfluoroolefins slight excess of $F_2$

| Olefin | Target compounds (yield, %) | Other products of reaction (yield, %) | Temperature (°C) start–end | Time process (h) |
|---|---|---|---|---|
| $CF_2=CF_2$ | $C_2F_6$ (92.0) | $CF_4$ (8.0) | −40 to 40 | 0.5 |
| $CF_2=CF_2$ | $C_2F_6$ (46.5) | $CF_4$ (46.5) | −25 to 25 | 0.5 |
| $CF_2=CF–CF_3$ | $C_3F_8$ (98.5) | $CF_4$ (1.0); $C_2F_6$ (0.5) | −27 to 20 | 1 |
| $CF_2=CF–C_2F_5$ | $C_3F_8$ (76.5) | $CF_4$ (18.5); $C_3F_8$ (5.0) | −15 to 15 | 1 |
| $CF_2=CF–C_2F_5$ | $C_4F_{10}$ (1.5) | | −10 to 0 | 2.3 |
| $CF_3–CF=CF–CF_3$ | $C_4F_{10}$ (0.5) | $C_3F_8$ (0.5) | −10 to 0 | 2.3 |
| $CF_3–CF=CF–C_2F_5$ | $C_5F_{12}$ (87.5) | $CF_4$ (9.5); $C_2F_6$ (2.0); $C_3F_8$ (0.5); $C_4F_{10}$ (0.5) | 0–60 | 4 |
| $(CF_3)_2C=CFCF_3$ | $(CF_3)_2CFC_3F_7$ (83.5) | $CF_4$ (12.0); $C_2F_6$ (33.5); $C_3F_8$ (0.5); $C_4F_{10}$ (0.5) | 0–80 | 10 |
| $(CF_3)_2CF–CF=CFCF_3$ | $(CF_3)_2CFC_3F_7$ (80.0) | $CF_4$ (13.5) $C_2F_6$ (1.5); $C_3F_8$ (3.5); $C_4F_{10}$ (1.5) | 0–100 | 12 |
| $C_9F_{18}$<br>Mixture<br>Isomers<br>Tetramer | $[(\tilde{N}F_3)_2CF]_2CFC_2F_5$ (62.5) | $CF_4$ (15.3); $C_2F_6$ (7.5); $C_3F_8$ (3.5); $C_4F_{10}$ (3.0); $C_5F_{12}$ (2.0) | 20–140 | 22 |
| $C_{12}F_{24}$ | $C_{12}F_{26}$ (54.0) | $CF_4$ (26.5); $C_2F_6$ (7.5); $C_3F_8$ (6.5); $C_5F_{12}$ (3.5); $C_6F_{14}$ (2.0) | 20–160 | 40 |
| $CH_2=CH_2$ | $C_2F_6$ (7.5) | $CF_4$ (85.5); $C_2F_6$ (6.0); $C_3F_8$ (0.5); $C_2F_5H$ (1.0) | −40 to 30 | 1.5 |

Tetramer hexafluoropropylene

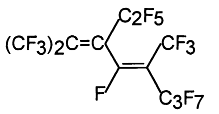


Table 2
Fluorination of polyfluorinated paraffins

| Paraffins | Target compounds (yield, %) | Other products (yield, %) | Conditions | | |
|---|---|---|---|---|---|
| | | | Temperature reaction (°C) start–end | Time (h) | $F_2$/substrate molar ratio |
| $CF_3H$ | $CF_4$ (99.5) | $C_2F_6$ (0.5) | −25 | 0.5 | 1.1 |
| $C_2F_5H$ | $C_2F_6$ (92.5) | $CF_4$ (7.0); $C_3F_8$ (0.5) | 20–40 | 1.5 | 1.1 |
| $CFH_2CF_3$ | $C_2F_6$ (5.5) | $CF_4$ (94.5) | −20 | 0.4 | 0.3 |
| $CFH_2CF_3$ | $C_2F_6$ (44.5) | $CF_4$ (1.5); $C_2F_5H$ (4,5); $C_3F_8$ (0.5), $CFH_2CF_3$ (49.0) | 45–60 | 2.5 | 1.1 |
| $CFH_2CF_3$ | $C_2F_6$ (96.5) | $CF_4$ (2.5); $C_3F_8$ (0.5); $C_2F_5H$ (0.5) | 45–60 | 5.0 | 2.1 |
| $CFH_2CFH_2$ | $C_2F_6$ (8.0) | $CF_4$ (31.5); $CHF_2CF_3$ (1); $CHF_2CHF_2$ (59.5) | 0–20 | 0.6 | 0.46 |
| $CHF_2CHF_2$ | $C_2F_6$ (40.5) | $CF_4$ (2.5); $CHF_2CF_3$ (6.5); $C_3F_8$ (0.5) | 40–60 | 2.5 | 1.15 |
| $CHF_2CHF_2$ | $C_2F_6$ (84.0) | $CF_4$ (4.0); $C_2F_5H$ (12,0) | 40–60 | 5 | 2.1 |
| $CHF_2C_2F_5$ | $C_3F_8$ (9.0) | $CF_4$ (5.0); $C_2F_6$ (1.5) | 60–70 | 3.6 | 1.05 |
| $CF_3CHFCF_3$ | $C_3F_8$ (86.0) | $CF_4$ (11.0); $C_2F_6$ (3.0) | 60–70 | 4.0 | 1.05 |
| $CF_3CHFCF_3$ | $C_3F_8$ (95.5) | $CF_4$ (4.0); $C_2F_6$ (0.5) | 45–90 | 5.0 | 1.05 |
| $CF_3CFHCFHC_2F_5$ | $C_5F_{12}$ (41.0) | $C_3F_8$ (1); $C_2F_6$ (1); $C_2F_5CHFC_2F_5$ (4.5); $CF_3CHFCHFC_2F_5$ (45.5); $CF_3CHFC_3F_7$ (4.0), $CF_4$ (3.0) | 50–100 | 7 | 1.1 |
| $CF_3CFHCFHC_2F_5$ | $C_5F_{12}$ (90.5) | $CF_4$ (6.0); $C_2F_6$ (2.0); $C_3F_8$ (1.0); $C_4F_{10}$ (0.5) | 50–120 | 9 | 2.15 |
| $C_3F_8$ | $C_3F_8$ (50) | $CF_4$ (80.5); $C_2F_6$ (13.5); $CF_3CHF–CF_3$ (1.0) | −30 to 10 | 6 | 12.2 |

Table 3
Fluorination of partially fluorinated ethers

| Substrate | Target compounds (yield, %) | Other products (yield, %) | Conditions | | |
|---|---|---|---|---|---|
| | | | Temperature (°C) start–end | Time process (h) | $F_2$/substrate molar ratio |
| $CF_3CF{=}CFOCH_3$ | $C_3F_7OCF_3$ (45.5) | $CF_4$ (32.5); $C_2F_6$ (14.5);$C_3F_8$ (2.0); $C_3F_7OCHF_2$ (0.5); $C_3F_7OCH_2F$ (0.5) | −30 to 80 | 12 | 4.15 |
| $(CF_3)_2C{=}C(OCH_3)C_2F_5$ | $(CF_3)_2CFCF(C_2F_5)OCF_3$ (91.5) | $CF_4$ (2.0); $C_2F_6$ (0.5)$(CF_3)_2CFCF(C_2F_5)OCHF_2$ (3.5); $(CF_3)_2CFCF(C_2F_5)OCH_2F$ (2.0) | −30 to 80 | 14 | 4.1 |
| $CF_3CF{=}CFOC_2H_5$ | $C_3F_7OC_2F_7$ (45.5) | $CF_4$ (32.5); $C_2F_6$ (14.5); $C_2F_5H$ (4.1) | −30 to 80 | 16 | 6.2 |
| $CFH_2OCFH_2$ | $CF_3OCF_3$ (8.5) | $CF_2HOCFH_2$ (6.0); $CF_2HOCF_2H$ (24.5); $CF_3OCFH$ (6.5);$CF_3OCF_2H$ (1.5); $CF_4$ (4.5); $C_2F_6$ (1,5); $CFH_2OCH_2F$ (50.0); $O_2$ (1.5) | −10 to 25 | 8 | 2.3 |
| $CFH_2OCFH_2$ | $CF_3OCFH_2$ (92.5) | $CF_4$ (3.5); $C_2F_6$ (1.5); $O_2$ (0.5); $CF_3OCHF_2$ (2.0) | −10 to 80 | 12 | 4.2 |
| $C_4HF_8OC_4F_9$ | $C_4F_9OC_4F_9$ (57.5) | $CF_4$ (20.0); $C_2F_6$ (3.5); $C_3F_8$ (3.0); $C_4F_{10}$ (8.5); $O_2$ (7.5) | 20–150 | 6 | 1.1 |
| $C_4F_8$ $HOC_4F_9$[a] | $C_4F_9OC_4F_9$ (97.5) | $CF_4$ (1.0); $C_2F_6$ (0.5); $O_2$ (0.5); $C_4F_{10}$ (0.5) | 250–300 | 0.2 | 1.1 |
| $CH_3OCH_3$ | $CF_3OCF_3$ (9.5) | $CF_4$ (28.0); $CF_3CHF_2$ (2.0); $CF_2HOCF_2H$ (17.0); $CF_3OCFH_2$ (4.5); $O_2$ (3.5); $CH_3OCH_3$ (36.0) | −30 to 45 | 6 | 3.8 |
| $CH_3OCH_3$ | $CF_3OCF_3$ (33.0) | $CF_4$ (62.0); $O_2$ (4.5); $CF_3OCF_2H$ (0.5) | 0–45 | 6 | 3 |

See footnote of Table 4.

Table 4
Fluorination of polyfluorotrialkylamines

| Amine | Target compounds (yield, %) | Other compounds (yield, %) | Temperature (°C) start–end | Time (h) | $F_2$/substrate molar ratio |
|---|---|---|---|---|---|
| $C_2F_5N(HCFCF_3)_2$[a] | $(C_2F_5)_3N$ (63.5) | $N_2$ (10.0); $CF_4$ (20.5); $C_2F_6$ (6.0) | 100–150 | 15 | 2.5 |
| $C_2F_5N(CFCF_3)_2$ | $(C_2F_5)_3N$ (97.5) | $N_2$ (1.0); C F (1.0); CF (0.5) | 260–360 | 0.1 | 2.1 |
| $C_3F_7N(HCFC_2F_5)_2$[a] | $(C_3F_7)_3N$ (51.0) | $N_2$ (14.5); $CF_4$ (0.5); $C_2F_6$ (4.5); $C_3F_8$ (6.5) | 100–170 | 17 | 2.8 |
| $(C_3F_7)N(HCFC_2F_5)_2$ | $(C_3F_7)_3N$ (97.0) | $N_2$ (1.7); $CF_4$ (0.5); $C_2F_6$ (0.5); $C_3F_8$ (1.0) | 280–390 | 0.1 | 2.1 |
| $(C_4F_9)N(HCFC_3F_7)_2$ | $(C_4F_9)_3N$ (95.5) | $N_2$ (1.5); $CF_4$ (1.0); $C_2F_6$ (0.5); $C_3F_8$ (0.5); $C_4F_{10}$ (0.5) | 300–410 | 0.1 | 2.1 |
| $C_5F_{12}N(CFHC_4F_9)_2$ | $(C_5F_{12})_3N$ (91.0); | $N_2$ (2.0); $CF_4$ (2.0); $C_2F_6$ (0.5); $C_3F_8$ (1.5); $C_5F_{12}$ (2.0); $C_4F_{10}$ (1.0) | 340–440 | 0.1 | 2.2 |
| $(C_2H_5)_3N$ | $(C_2F_5)_3N$ (1.0) | $CF_4$ (60.5); $N_2$ (18.0) | −35 to 20 | 14 | 20.5 |

[a] Gas-phase fluorination using $CoF_3$.

Table 5
Heats and specific heats of fluorination of some fluoro-organic compounds[a]

| Compound | Molecular weight | Heat of fluorination (kJ/mol) | Specific heat of fluorination (kJ/mol) |
|---|---|---|---|
| $CF_2=CFCF_3$ | 150 | 630 | 4.20 |
| $(CF_3)_2C=CFC_2F_5$ | 300 | 630 | 2.10 |
| $C_9F_{18}$ | 450 | 630 | 1.40 |
| $CF_2H–CFHCF_3$ | 152 | 945 | 6.21 |
| $CF_3CFHCFHC_2F_5$ | 252 | 945 | 3.75 |
| $(CFH_2)_2O$ | 82 | 1870 | 22.8 |
| $CH_3OCF=CFCF_3$ | 162 | 2045 | 12.62 |
| $(CH_3)_2OC_6F_{11}$ | 312 | 2045 | 6.55 |
| $CH_3NC_6F_{11}$ | 325 | 3460 | 10.65 |
| $(CH_3)_2NC_9F_{19}$ | 475 | 3476 | 7.28 |
| $(CH_3)_2 NC_6F_{11}$ | 325 | 3476 | 10.7 |
| $(CH_3)_2NC_9F_{13}$ | 363 | 2844 | 7.83 |
| $C_6F_{13}N(CH_3)CH_2F$ | 381 | 2370 | 6.22 |
| $C_6F_{13}N(CH_3)CHF_2$ | 399 | 1896 | 4.75 |
| $C_6F_{13}N(CH_3)CF_3$ | 417 | 1422 | 3.4 |
| $C_6F_{13}N(CH_2F)CF_3$ | 435 | 948 | 2.18 |
| $C_6F_{13}N(CHF_2)CF_3$ | 453 | 474 | 1.04 |
| $(CH_3)_2NC_6F_{17}$ | 475 | 3476 | 7.31 |
| $(CH_3)_2NC_9F_{19}$ | 513 | 2844 | 5.54 |
| $C_9F_{19}N(CH_3)CH_2F$ | 531 | 2370 | 4.46 |
| $C_9F_{19}N(CH_3)CHF_2$ | 549 | 1896 | 3.45 |
| $C_9F_{19}N(CH_3)CF_3$ | 417 | 1422 | 2.5 |
| $C_9F_{19}N(CH_2F)CF_3$ | 585 | 948 | 1.62 |
| $C_9F_{19}N(CHF_2)CF_3$ | 603 | 474 | 0.79 |
| $C_3F_7OCF(CF_3)OCHFCF_2N(CH_3)_2$ | 495 | 2844 | 5.74 |
| $C_3F_7OCF(CF_3)OCHFCF_2N(CH_3)CH_2F$ | 513 | 2370 | 4.61 |
| $C_3F_7OCF(CF_3)OCHFCF_2N(CH_3)CHF_2$ | 531 | 1896 | 3.57 |
| $C_3F_7OCF(CF_3)OCHFCF_2N(CH_3)CF_3$ | 549 | 1422 | 2.59 |
| $C_3F_7OCF(CF_3)OCHFCF_2N(CH_2F)CF_3$ | 567 | 948 | 1.67 |
| $C_3F_7OCF(CF_3)OCHFCF_2N(CHF_2)CF_3$ | 585 | 474 | 0.81 |

[a] Heats and specific heats of fluorination are from the present work.

probably is caused by the influence of oxygen. Therefore fluorination of dimethyl ether yields up to 33% of the perfluorinated product, while the yield of perfluorinated compounds in the fluorination of olefins and paraffins is 7.5% or lower, yield of perfluorinated tertiary amines in the fluorination of their hydrocarbon analogs is 1% only.

Fluorination of the partly fluorinated dialkyl ethers (Table 3) proceeds with greater selectivity than polyfluorinated alkanes (Table 2). While fluorination of dihydroperfluoroalkanes after adding 1 mol of fluorine results in 10% content of monohydro derivatives, addition of half the amount of the total required fluorine to sym-difluorodimethyl ether gives 68% of sym-tetrafluorodimethyl ether. Contacting the mixture formed with excess molecular fluorine at a temperature of 25–250°C converts the partially fluorinated organic compounds to perfluoro-organic compounds.

Tertiary amines containing one perfluorinated group are the least stable of all with respect to fluorine, obviously due to the high heat of reaction [13]. For achieving successful fluorination, the initial step should be performed under mild conditions: effective stirring, deep cooling, low fluorine flow rate. Upon substitution of fluorine for hydrogen, the heat of fluorination changes, and fluorination requires more rigid conditions. The yield of tertiary perfluorinated amines achieved is 53–85%.

Fluorination of any polyfluorinated compounds except some low molecular weight olefins and paraffins also results in formation of incompletely fluorinated compounds and products of destructive fluorination, with some starting materials. The content of incompletely substituted products in direct fluorination is substantially lower than in electrochemical fluorination and fluorination with $CoF_3$, where it can be 30%.

For extending the method of direct fluorination of polyfluoro compounds to an industrial scale we performed additional investigation using tube-type and large reactors, in the gas phase and in perfluorinated solvents. The results of fluorination of hexafluoropropene in a tubular reactor with simultaneous passing of hexafluoropropene and fluorine are given in Table 6. The process in the gas phase does not give complete conversion of hexafluoropropene and is accompanied by a degradative process. Yields of perfluorinated products are about 91–92%. Use of inert solvents decreases degradation considerably, owing to the 10-fold increased thermoconductivity of the reaction mixture [17] and the absence of local overheating at the points of contact of the components. The yield of perfluorinated products can

Table 6
Fluorination of hexafluoropropene to perfluoropropane (I) in a tubular reactor

| Condition reactions | | | Contents of reaction mixture (yield, %) (disregarding solvent) |
|---|---|---|---|
| Temperature (°C) start–end | Solvent | Time (min) | |
| −26 to 22 | | 20 | (I) 1 (91.7); $CF_4$ (6.2); $C_2F_6$ (1.7); $CF_2=CFCF_3$ (0.4) |
| −26 to 22 | | 40 | (I) (92.0); $CF_4$ (6.2); $C_2F_6$ (1.7); $CF_2=CFCF_3$ (0.1) |
| −26 to 10 | | 40 | (I) 1 (92.1); $CF_4$ (6.2); $C_2F_6$ (1.7) |
| −26 to 22 | $(C_2F_5)_3$ N | 10 | (I) (98.0); $CF_4$ (1.2); $C_2F_6$ (0.5); $CF_2=CFCF_3$ (0.5) |
| −26 to 10 | $(C_2F_5)_3N$ | 20 | (I) (98.4); $CF_4$ (1.3); $C_2F_6$ (0.3) |
| −26 to 10 | $C_5F_{12}$ | 20 | (I) (98.7); $CF_4$ (1.0); $C_2F_6$ (0.2) |
| −26 to 10 | $C_3F_8$ | 20 | (I) (99.9); $CF_4+C_2F_6$ (0.1) |
| −15 to 10 | $C_3F_8$ | 20 | (I) (97.5); $CF_4$ (2.1); $C_2F_6$ (0.4) |
| −26 to 10 | $C_3F_8$ | 10 | (I) (95.7); $CF_2=CFCF_3$ (4.3) |
| −26 to 10 | $CF_2=CFCF_3$ | 20 | (I) (94.4); $CF_4$ (4.1); $C_2F_6$ (1.5) |

be 99.9%. Short carbon chain perfluorinated solvents used instead of long-chain compounds depress additional degradation processes, owing to, in our opinion, to higher solubility of fluorine and better heat transfer. Use of hexafluoropropylene as a solvent, although it decreases the degradation process compared to the gas phase, does not exclude it completely, probably due to high concentration of dissociated fluorine molecules in the presence of the excess perfluoroolefin. An important role is thus played by the temperature of the fluorination process, with its increase, decomposed starting materials are increased. If the temperature is lower than 120°C, it is almost impossible to perfluorinate the partially fluorinated organic compound obtained at 0–25°C, and it is impossible to obtain the intended perfluoro-organic compound in a high yield.

Fluorination of long-chain perfluoroolefins in the gas phase requires more rigid conditions compared to those for hexafluoropropene. For $C_5$ olefins it is 20–40°C, and $C_9$ olefins it is 120–160°C. Table 7 contains the results of fluorination of some perfluoroolefins in the gas phase.

Despite the somewhat lower specific heat of fluorination, the gas phase fluorination of higher perfluorinated olefins proceeds with considerable degradation. In contrast with published observations [6], no influence of catalysts on the reaction mixture composition was observed in our experiments. Probably poor heat exchange is the most important factor. Increase in the flow rate of components in the fluorination of perfluoromethylpent-2-ene and perfluorononene led to uncontrolled rise in temperature with much degradation.

Fluorination of higher fluorolefins in the liquid phase proceeded more successfully. In Table 8 we show the results of liquid-phase fluorination of unsaturated compounds when the final product is used as a perfluorinated solvent. The temperatures thus remain low, but the yield of the target products grows to 80–90%. Though degradation is observed, it is not so great as in the case of fluorination in the gas phase. These results are characteristic for linear, and cyclic perfluoroolefins. As seen, the yield of target compounds is reduced on lengthening the carbon chain. Although the solvent affects the degradation processes, the influence is less than in the case of low-boiling olefins. Methoxy perfluoroolefins thus remain in the liquid phase at lower temperatures in comparison with the corresponding

Table 7
Gas-phase fluorination of some perfluoroolefins (time of contact 40 min)

| Olefin | Target compounds | Temperature (°C) start–end | Contents of reaction mixture (yield, %) |
|---|---|---|---|
| $CF_3CF=CFC_2F_5$[a] | $C_5F_{12}$ (II) | 20–40 | (II) (86.5); $CF_4$ (8.9); $C_2F_6$ (2.1); $C_3F_8$ (1.1); $CF_3CF=CFC_2F_5$ (1.4) |
| $CF_3CF=CFC_2F_5$ | $C_5F_{12}$ (II) | 20–40 | (II) (87.0); $CF_4$ (8.9); $C_2F_6$ (2.1); $C_3F_8$ (1.4); $CF_3CF=CFC_2F_5$ (0.6) |
| $CF_3CF=CFC_2F_5$[b] | $C_5F_{12}$ (II) | 20–40 | (II) (87.6); $CF_4$(8.6); $C_2F_6$ (1.8); $C_3F_8$ (1.2); $CF_3CF=CFC_2F_5$ (0.8) |
| $CF_3CF=CFC_2F_5$[c] | $C_5F_{12}$ (II) | 20–40 | (II) (87.7); $CF_4$ (8.8); $C_2F_6$ (1.7); $C_3F_8$ (1.2); $CF_3CF=CFC_2F_5$ (0.6) |
| $(CF_3)_2C=CFC_2F_5$ | $(CF_3)_2CFC_3F_7$ (III) | 60–90 | (III) (63.8); $CF_4$ (23.5); $C_2F_6$ (7.1); $C_3F_8$ (3.8); $(CF_3\ )_2C=CFC_2F_5$ (1.8) |
| $(CF_3)_2C=CFC_2F_5$[b] | $(CF_3)_2CFC_3F_7$ (III) | 60–90 | (III) (64.4); $CF_4$ (23.1); $C_2F_6$ (7.0); $C_3F_8$ (3.7); $(CF_3)_2C=CFC_2F_5$ (1.8) |
| $(CF_3)_2C=CFC_2F_5$[c] | $(CF_3)_2CFC_3F_7$ (III) | 60–90 | (III) (64.2); $CF_4$ (23.1); $C_2F_6$ (7.0); $C_3F_8$ (3.8); $(CF_3)_2C=CFC_2F_5$ (1.9) |
| $C_9F_{18}$[b] mixture isomers | $[(CF_3)_2CF]_2CFC_2F_5$ (IV) | 120–160 | (IV) (50.3); $CF_4$ (26.5); $C_2F_6$ (7.7); $C_3F_8$ (3.1); $C_9F_{18}$ (12.4) |
| $C_9F_{18}$[c] mixture isomers | $[(CF_3)_2CF]_2CFC_2F_5$ (IV) | 120–160 | (IV) (50.8); $CF_4$ (26.6); $C_2F_6$ (7.6); $C_3F_8$ (2.9); $C_9F_{18}$ (12.1) |
| $C_9F_{18}$[c] mixture isomers | $[(CF_3)_2CF]_2CFC_2F_5$ (IV) | 120–160 | (IV) (50.6); $CF_4$ (26.6); $C_2F_6$ (7.5); $C_3\ F_8$ (3.11); $C_9F_{18}$ (12.2) |
| $C_9F_{18}$ mixture isomers | $[(CF_3)_2CF]_2CFC_2F_5$ (IV) | 180–250 | (IV) (24.4); $CF_4$ (59.3); $C_2F_6$ (9.6); $C_3F_8$ (4.9); $C_9F_{18}$ (1.8) |

[a] Non-controllable temperature.
[b] Catalyst $CuF_2$.
[c] Catalyst $CoF_3$.

Table 8
Fluorination of perfluoroolefins in the liquid phase slight excess of $F_2$

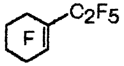
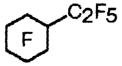
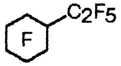
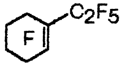
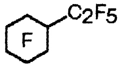
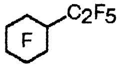
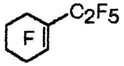
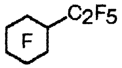
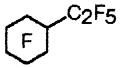
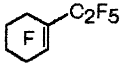
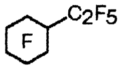
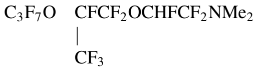
| Initial olefins | Target compound | Temperature (°C) start–end | Solvent | $F_2$–olefin molar ratio | Concentration of olefin (mass%) | Contents of reaction mixture (disregarding solvent) (yield, %) |
|---|---|---|---|---|---|---|
| $CF_3CF{=}CFC_2F_5$ | $C_5F_{12}$ (II) | 0–40 | $C_5F_{12}$ | 1.05 | 20 | (II) (94.8); $CF_4$ (2.1); $C_2F_6$ (0.4); $C_3F_8$ (0.2); $CF_3CF{=}CFC_2F_5$ (2.5) |
| $CF_3CF{=}CFC_2F_5$ | $C_5F_{12}$ (II) | 0–60 | $C_5F_{12}$ | 1.05 | 20 | (II) (96.7); $CF_4$ (2.0); $C_2F_6$ (0.4); $C_3F_8$ (0.2); $CF_3CF{=}CFC_2F_5$ (0.7) |
| $CF_3CF{=}CFC_2F_8$ | $C_5F_{12}$ (II) | 0–60 | $C_5F_{12}$ | 1.1 | 10 | (II) (97.0); $CF_4$ (1.8); $C_2F_6$ (0.4); $C_3F_8$ (0.2); $CF_3CF{=}CFC_2F_5$ (0.6) |
| $CF_3CF{=}CFC_2F_8$ | $C_2F_{12}$ (II) | 0–60 | $C_5F_{12}$ | 1.1 | 10 | (II) (97.4); $CF_4$ (1.6); $C_2F_6$ (0.2); $C_3F_8$ (0.2); $CF_3CF{=}CFC_2F_5$ (0.6) |
| $(CF_3)_2C{=}CFC_2F_5$ | $(CF_3)_2CFC_3F_7$ (III) | 45–80 | $(CF_3)_2CFC_3F_7$ | 1.05 | 20 | (III) (86.3); $CF_4$ (8.6); $C_2F_6$ (1.6); $C_3F_7$ (0.9); $(CF_3)_2C{=}CFC_2F_5$ (2.6) |
| $(CF_3)_2C{=}CFC_2F_5$ | $(CF_3)_2CFC_3F_7$ (III) | 45–80 | $(CF_3)_2CFC_3F_7$ | 1.05 | 10 | (III) (90.4); $CF_4$ (4.9); $C_2F_6$ (1.4); $C_3F_8$ (0.7); $(CF_3)_2C{=}CFC_2F_5$ (2.6) |
| $(CF_3)_2C{=}CFC_2F_5$ | $(CF_3)_2CFC_3F_7$ (III) | 45–80 | $C_5F_{12}$ | 1.05 | 19 | (III) (91.4); $CF_4$ (5.2); $C_2F_6$ (1.1); $C_3F_8$ (0.5); $(CF_3)_2C{=}CFC_2F_5$ (1.8) |
| $C_9F_{18}$ mixture isomers | $[(CF_3)_2CFC_2F_5$ (IV) | 60–140 | $[(CF_3)_2CF]_2CFC_2F_5$ | 1.15 | 20 | (IV) (82.8); $CF_4$ (9.1); $C_2F_6$ (2.0); $C_3F_8$ (1.8); $C_9F_{18}$ (4.3) |
| $C_9F_{18}$ mixture isomers | $[(CF_3)_2CFC_2F_5$ (IV) | 60–160 | $[(CF_3)_2CF]_2CFC_2F_5$ | 1.3 | 20 | (IV) (84.9); $CF_4$ (9.3); $C_2F_6$ (2.1); $C_3F_8$ (2.0); $C_9F_{18}$ (1.7) |
| $C_{12}F_{24}$ perfluoropropylene tetramer | $C_{12}F_{26}$ (V) | 60–160 | $C_{12}F_{26}$ | 1.2 | 20 | (V) (70.8); $CF_4$ (13.4); $C_2F_6$ (2.2); $C_3F_8$ (1.6); $C_6F_{14}$ (4.0); tetramer (7.5) |
| $C_{12}F_{24}$ perfluoropropylene tetramer | $C_{12}F_{26}$ (V) | 60–180 | $C_{12}F_{26}$ | 1.45 | 20 | (V) (74.3); $CF_4$ (14.2); $C_2F_6$ (3.1); $C_3F_8$ (1.9); $C_6F_{14}$ (4.2); tetramer (2.3) |
| $C_{12}F_{24}$ perfluoropropylene tetramer | $C_{12}F_{26}$ (V) | 60–180 | $(CF_3)_2CFC_3F_7$ | 1.45 | 20 | (V) (76.2); $CF_4$ (13.5); $C_2F_6$ (3.0); $C_3F_8$ (1.4); $C_6F_{14}$ (3.8); tetramer (2.1) |
|  |  (VI) | 40–100 |  | 1.1 | 20 | (VI) (88.4); $CF_4$ (3.3); $C_2F_6$ (2.0) |
|  |  (VI) | 40–120 |  | 1.25 | 20 | (VI) (90.7); $CF_4$ (3.5); $C_2F_6$ (2.1) |
|  |  (VI) | 40–140 |  | 1.4 | 20 | (VI) (90.9); $CF_4$ (3.7); $C_2F_6$ (2.2) |
|  |  (VI) | 40–140 | $C_5F_{12}$ | 1.3 | 20 | (VI) (91.6); $CF_4$ (3.2); $C_2F_6$ (2.1) |

Table 9
Liquid-phase fluorination of methoxy- and *N*, *N*-dimethylamino derivatives of perfluoroolefins

| Starting substrates | Target compounds | Temperature (°C) start–end | Solvent concentration (mass%) | $F_2$/substrate molar ratio | Reaction products (yield, %) |
|---|---|---|---|---|---|
| $CH_3OCF{=}CFCF_3$ | $CF_3OC_3F_7$(VII) | −26 to 10 $C_3F_8$ | 10 | 4.2 | VII (87.4); $O_2$ (2.6); $CF_4$ (3.5); $C_3F_8$ (0.7); $C_3F_7OCF_2H$ (3.4); $C_3F_7OCFH_2$ (2.2), $C_2F_6$ (0.2); |
| $CH_3OCF{=}CFCF_3$ | $CF_3OC_3F_7$ (VII) | −26 to 10 $C_3F_7OCF_3$ | 10 | 4.2 | VII (85.5); $O_2$ (2.6); $CF_4$ (4.9); $C_3F_8$ (0.9); $C_3F_7OCF_2H$ (3.5); $C_3F_7OCFH_2$ (2.3); $C_2F_6$ (0.3); |
| $CH_3OCF{=}CFCF_3$ | $CFOC_3F_7$ (VII) | −26 to 0 $C_3F_7OCF_3$ | 10 | 4.6 | VII (92.1); $O_2$ (2.7); $CF_4$ (5.1); $C_3F_8$ (1.0); $C_3F_7OCF_2H$ (1.1); $C_3F_7OCFH_2$ (0.4); $C_2F_6$ (0.3); |
| $CH_3OCF{=}CFCF_3$ | $CF_3OC_3F_7$ (VII) | −26 to 0 $(C_2F_5)_3N$ | 10 | 4.7 | VII (87.9); $O_2$ (2.9); $CF_4$ (6.2); $C_3F_8$ (1.2); $C_3F_7OCF_2H$ (1.1); $C_3F_7OCFH_2$ (0.3); $C_2F_6$ (0.4); |
| $(CF_3)_2C{=}C(OCH_3)C_2F_5$ | $(CF_3)_2CFCF(OCF_3)C_2F_5$ (VIII) | −30 to 80 $C_5F_{12}$ | 10 | 4.2 | VIII (92.8); $O_2$ (1.3); $CF_4$ (2.2); $(CF_3)_2CFCF(C_2F_5)OCHF_2$ (1.9); $(CF_3)_2CFCF(C_2F_5)OCH_2F$ (1.3); $C_2F_6$ (0.5); |
| $(CF_3)_2C{=}C(OCH_3)C_2F_5$ | $(CF_3)_2CFCF(OCF_3)C_2F_5$ (VIII) | −30 to 80 $(CF_3)_2C{=}C(O\ CH_3)C_2F_5$ | 10 | 4.6 | VIII (94.7); $O_2$ (1.2); $CF_4$ (2.9); $C_2F_6$ (0.5); $(CF_3)_2CFCF(C_2F_5)OCHF_2$ (0.9); $(CF_3)_2CFCF(C_2F_5)OCFH_2$ (0.5) |
| $(CF_3)_2C{=}C(OCH_3)C_2F_5$ | $(CF_3)_2CFCF(OCF_3)C_2F_5$ (VIII) | −30 to 80 $(CF_3)_2CFCF(OCH_3)C_2F_5$ | 10 | 4.2 | VIII (91.4); $O_2$ (1.8); $CF_4$ (3.1); $C_2F_6$ (0.6); $(CF_3)_2CFCF(C_2F_5)OCHF_2$ (2.0); $(CF_3)_2CFCF(C_2F_5)OCH_2F$ (1.1); |
| $(CF_3)_2C{=}C(NMe_2)C_2F_5$ | $(CF_3)_2CFCF(N(CF_3)_2)C_2F_5$ (IX) | −30 to 80 $C_5F_{12}$ | 5 | 8.8 | IX (24.5); $N_2$ (18.6); $CF_4$ (42.3); $(CF_nH_{3-n})_2NCF(C_2F_5)CF(CF_3)_2$ (10.8) $n{=}0{-}3$; $C_3F_8$ (0.6); $C_2F_5$ (3.2); |
| $(CF_3)_2C{=}C(NMe_2)C_2F_5$ | $(CF_3)_2CFCF(N(CF_3)_2)C_2F_5$ (IX) | −30 to 80 $(C_2F_5)_3N$ | 5 | 8.8 | IX (25.1); $N_2$ (18.5); $CF_4$ (42.2); $C_2F_6$ (3.1); $C_3F_8$ (0.6); $(CF_nH_{3-n})_2NCF(C_2F_5)CF(CF_3)_2$ (10.5) |
| $(CF_3)_2C{=}C(NMe_2)C_2F_5$ | $(CF_3)_2CFCF(N(CF_3)_2)C_2F_5$ (IX) | −30 to 80 $(C_2F_5)_3N$ | 5 | 10.5 | IX (32.0); $N_2$ (18.9); $CF_4$ (42.3); $C_2F_6$ (3.0); $C_3F_8$ (0.8); $(CF_nH_{3-n})_2NCF(C_2F_5)CF(CF_3)_2$ (3.0) |
| $[(CF_3)_2CF]_2C{=}C(NMe_2)CF_3$ | $[(CF_3)_2CF]_2CFCF(CF_3)N(CF_3)_2$ (X) | −30 to 80 $(C_2F_5)_3N$ | 5 | 9.1 | X (27.2); $N_2$ (15.4); $CF_4$ (37.9); $C_2F_6$ (2.6); $C_3F_8$ (0.5); $[(CF_3)_2CF]_2CFCF(CF_3)N(CF_nH_{3-n})_2$ $n{=}0{-}3$ |
| $[(CF_3)_2CF]_2C{=}C(NMe_2)CF_3$ | $[(CF_3)_2CF]_2CFCF(CF_3)N(CF_3)_2$ (X) | −30 to 80 $[(CF_3)_2CF]_2CFCF(CF_3)N(CF_3)_2$ | 5 | 10.6 | X (31.4); $N_2$ (31.4); $N_2$ (15.7); $CF_4$ (38.2); $C_2F_6$ (2.1); $C_3F_8$ (0.6); $[(CF_3)_2CF]_2CFCF(CF_3)N(CF_3)_2$ (8.0) |
|  $C_3F_7O\underset{\underset{CF_3}{\vert}}{CF}CF_2OCHFCF_2NMe_2$ |  $C_3F_7\underset{\underset{CF_3}{\vert}}{OCF}CF_2OCF_2CF_2N(CF_3)_2$ (XI) | −30 to 80 | 5 | 10.2 | (XI) (85), $C_3F_8$ (10), $CF_4$ (0.5) |

perfluoroolefins and the yield of perfluorinated compounds is high (87–93%), and is characteristic for fluoroolefins with various number of carbon atoms. However, for amines with $NMe_2$ groups there is a high degree of decomposition of starting materials. Use of a wider temperature range for fluorination has not resulted in an increase in yield of perfluorinated products. The use of perfluorinated solvents for fluorination does not greatly influence the processes (Table 9). Fluorination of enamines and ethers containing multiple bonds in the carbon chain proceeds predominantly at the C=C double bond; subsequently substitution of hydrogen atoms begins to occur (Table 9). Taking into account the high heat of fluorination, we suggest that it is not worthwhile to investigate gas-phase fluorination of such compounds.

The results of fluorination of polyfluorinated compounds of different classes (Tables 7–9) show that liquid-phase fluorination gives perfluorinated compounds in 70–90% yield. The fluorination proceeds over a wide temperature range, with ethers and tertiary amines in particular, and this should be taken into consideration in the development of technology. We suggest that it is most convenient to employ reactors in a circuit, each working over a rather narrow temperature range. Despite the fact that in short carbon chain perfluorinated solvents the yield of target products is higher than in long-chain solvents, we suggest that in industrial technological processes it is best to use the target compound, or corresponding crude material, as the solvent, to reduce the number of compounds in use and simplify isolation of the final product. As noted above, the product of fluorination of a polyfluorinated compound contains also the products of fluorination, the products of incomplete fluorination, and the starting material. Useful content is lower than in electrochemical fluorination or fluorination with

Table 10
Heats of fluorination of some polyfluorinated compounds

| Compound (Mw) | Heat of fluorination (kJ/mol) | Specific heat of fluorination (kJ/g) | Solvent (g) | Concentration (wt%) | Heat of fluorination (kJ/mol) | Specific heat (kJ/g) |
|---|---|---|---|---|---|---|
| $CF_3CF{=}CFC_2F_5$ (250) | 630 | 2.52 | $C_5F_{12}$ | 0.6 | 3.78 | 0.013 |
| $(CF_3)_2C{=}CFC_2F_5$ (300) | 630 | 2.10 | $(CF_3)_2CFC_3F_7$ | 2.9 | 18.27 | 0.054 |
| $C_9F_{18}$ mixture isomers (450) | 630 | 1.4 | $C_9F_{20}$ | 2.0 | 12.6 | 0.026 |
| $CFH_2OC_3F_7$ (218) | 946 | 4.34 | $CF_3OC_3F_7$ | 0.4 | 3.8 | 0.015 |
| $CF_2HOC_3F_7$ (236) | 946 | 2.00 | $CF_3OC_3F_7$ | 1.1 | 5.2 | 0.020 |
| $CH_2FOCF(C_2F_5)CF(CF_3)_2$ (368) | 946 | 2.57 | $CF_3OC_6F_{13}$ | 0.5 | 4.7 | 0.012 |
| $CHF_2OC_6F_{13}$ (386) | 473 | 1.22 | $CF_3OC_6F_{13}$ | 0.9 | 4.25 | 0.010 |
| $C_6F_{13}N(CFH_2)_2$ (399) | 1892 | 4.74 | $(CF_3)_2NC_6F_{13}$ | 3.0 | 56.8 | 0.12 |
| $C_6F_{13}N(CF_2H)_2$ (435) | 946 | 2.17 | $(CF_3)_2NC_6F_{13}$ | 3.0 | 28.3 | 0.06 |
| $C_9F_{19}N(CFH_2)_2$ (549) | 1892 | 3.44 | $C_9F_{19}N(CF_3)_2$ | 4.0 | 75.7 | 0.12 |
| $C_9F_{19}N(CF_2H)_2$ (585) | 946 | 1.61 | $C_9F_{19}N(CF_3)_2$ | 4.7 | 44.5 | 0.072 |

Table 11
Catalytic fluorination of polyfluorinated compounds in solution

| Starting compounds | Solvent catalyst | Temperature fluorination (°C) | Contact time (min) | Mixture reaction products up to (after) (yield, %) |
|---|---|---|---|---|
| $CF_3CF{=}CFC_2F_5$ | $C_5F_{12}$ $CuF_2$ | 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) |
| $(CF_3)_2C{=}CFC_2F_5$ | $C_6F_{14}$ $CuF_2$ | 230–320 | 7 | $(CF_3)_2C{=}CFC_2F_5$ 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) |
| $C_9F_{18}$ mixture isomers | $C_9F_{20}$ $CuF_2$ | 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 (0.1) |
| $C_9F_{18}$ mixture isomers | $C_9F_{20}$ $CoF_3$ | 240–320 | 10 | $C_9F_{20}$ 97.5 (99.5); $CF_4$ 0.2 (0.2); $C_2F_6$ 0.2 (0.2); $C_3F_8$ 0.1; (0.1); $C_9F_{18}$ 2.0 (0) |
| $CF_2HOC_3F_7$+$CFH_2OC_3F_7$ | $CF_3OC_3F_7$ $CuF_2$ | 230–340 | 8 | $CF_3OC_3F_7$ 98.1 (99.6); $CF_4$ 0.2 (0.2); $C_2F_6$ 0.1 (0.1); $C_3F_8$ 0.1 (0.1); $CFH_2OC_3F_7$ 0.4 (0); $CF_2HOC_3F_7$ 1.1 (0) |
| $CHF_2OC_6F_{13}$+$CH_2FOC_6F_{13}$ | $CF_3OC_6F_{13}$ $CuF_2$ | 260–340 | 10 | $CF_3OC_6F_{13}$ 98.2 (99.3); CF4 0.2 (0.3); $C_2F_6$ 0.1 (0.1); $C_3F_8$ 0.1 (0.1); $CHF_2OC_6F_{13}$ 0.9 (0.1); $CH_2FOC_6F_{13}$ 0.5 (0.1) |
| $CHF_2OC_6F_{13}$+$CH_2FOC_6F_{13}$ | $CF_3OC_6F_{13}$ $CoF_3$ | 240–300 | 9 | $CF_3OC_6F_{13}$ 98.2 (99.5); $CF_4$ 0.2 (0.2); $C_2F_6$ 0.1 (0.1); $C_3F_8$ 0.1 (0.1); $CHF_2OC_6F_{13}$ 0.9 (0); $CH_2FOC_6F_{13}$ 0.5 (0) |
| $C_6F_{13}N(CFH_2)_2$+$C_6F_{13}N(CF_2H)_2$ | $C_6F_{13}N(CF_3)_2$ $CoF_3$ | 260–320 | 10 | $C_6F_{13}N(CF_3)_2$ 93.6 (99.2); $CF_4$ 0.2 (0.5); $C_2F_6$ 0.1 (0.2); $C_3F_8$ 0.1 (0.2); $C_6F_{13}N(CFH_2)_2$ 3.0 (0); $C_6F_{13}N(CF_2H)_2$ 3.0 (3.0) |
| $C_9F_{19}N(CFH_2)_2$+$C_9F_{19}N(CF_2H)_2$ | $C_9F_{19}N(CF_3)_2$ $CoF_3$ | 280–360 | 12 | $C_9F_{19}N(CF_3)_2$ 91.4 (98.9); $CF_4$ 0.2 (0.6); $C_2F_6$ 0.1 (0.3); $C_3F_8$ 0.1 (0.2); $C_9F_{19}N(CFH_2)_2$ 4.0 (0); $C_9F_{19}N(CF_2H)_2$ 4.2 (0) |

Table 12
The purification of perfluorinated compounds by absorption on activated carbons BAU-2 and SKT

| Substrates | Main product | Cleaning reagent | Contact time (min) | Original contents of impurity up (molar mass%) | Contents of on impurity after absorption |
|---|---|---|---|---|---|
| $CF_3CF{=}CFC_2F_5$ | $C_5F_{12}$ | BAU-2 | 8 | 0.6 | 0.1 |
| $CF_3CF{=}CFC_2F_5$ | $C_5F_{12}$ | BAU-2 | 12 | 0.6 | 0 |
| $CF_3CF{=}CFC_2F_5$ | $C_5F_{12}$ | SKT | 6 | 0.6 | 0 |
| $CFH_2OC_3F_7$ | $CF_3OC_3F_7$ | BAU-2 | 8 | 0.4 | 0.2 |
| $CF_2HOC_3F_7$ | $CF_3OC_3F_7$ | BAU-2 | 16 | 1.1 | 0.5 |
| $CFH_2OC_3F_7$ | $CF_3OC_3F_7$ | BAU-2 | 16 | 0.4 | 0.1 |
| Ñ$F_2HOC_3F_7$ | $CF_3OC_3F_7$ | BAU-2 | 16 | 1.1 | 0.2 |
| $CFH_2OC_3F_7$ | $CF_3OC_3F_7$ | BAU-2 | 48 | 0.4 | 0.1 |
| $CF_2HOC_3F_7$ | $CF_3OC_3F_7$ | BAU-2 | 48 | 1.1 | 0.1 |
| $CFH_2OC_3F_7$ | $CF_3OC_3F_7$ | SKT | 20 | 0.4 | 0 |
| $CF_2HOC_3F_7$ | $CF_3OC_3F_7$ | SKT | 20 | 1.1 | 0 |
| $CF_2HOC_3F_7$ | $CF_3OC_6F_{13}$ | SKT | 20 | 0.9 | 0 |
| $CFH_2OC_3F_7$ | $CF_3OC_6F_{13}$ | SKT | 20 | 0.5 | 0 |

transition metal fluorides [18], mixture of over $10^{-3}$% makes the exploitation of the perfluorinated compounds more difficult. We showed earlier that the products of incomplete fluorination may be further fluorinated, using various catalysts. Owing to the higher stability of such compounds, lower heat of fluorination, and the low concentration in solution, there appears the possibility of gas-phase fluorination of these compounds using a catalyst. In Table 10 are given calculations of the heat of fluorination for some of these compounds and their solutions; Table 11 contains the results of solution fluorination using the catalysts $CoF_2$ and $CoF_3$. Table 11 shows that the compounds with the longest carbon chain can be best fluorinated over a $CoF_3$ catalyst.

When the fluorination products contain little incompletely fluorinated compounds (less than 1.5%), simple absorbtion methods can be used for purification. We investigated purification on activated carbons BAU-2 and SKT. Table 12 shows the results of sorbtion of purification of some compounds.

## 3. Conclusion

Perfluorinated compounds can be obtained in satisfactory yields from partially fluorinated compounds employing ordinary technologies of fluorination using 100% elemental fluorine on the gas–liquid surface. This method was used for industrial scale experimental technology for producing series of compounds: perfluoropropane, perfluoromethylpent-2-ene, perfluorodiisopropylpropane, and perfluoromethoxypropane. The methodology allows use of molecular fluorine as an ordinary reagent and to apply it in very different technological processes for obtaining perfluorinated organic compounds. However, to realise the complexity of mechanism of the fluorine reactivity and principal components of fluorination technology, further investigations are required. Simplification of technology will reduce considerably the cost of perfluorinated products and will extend the application of this class of compound in various spheres.

## 4. Experimental

### 4.1. General

UV spectra were recorded on an SF-16 spectrophotometer, fluoride ion was determined with a fluoroselective EG-GI electrode, reaction mixtures were analyzed on a Tsvet-100 chromatograph with a thermal conductivity detector, the helium flow rate was 60 $cm^3$/min; the columns used were either 2 m column, liquid phase $\alpha,\alpha,\alpha$-tris(cyanoethyl)acetophenone (20%), solid-phase Silochrom (80%) (for the long carbon chain compounds), or 3 m, liquid-phase mineral oil (15%), solid-phase $\alpha$-silica gel. For identification of products, IR and $^{19}F$ NMR spectra were compared with those of authentic samples. No new organofluorine compounds were prepared, so the identities of all the products are based on the results of $^{19}F$ NMR analysis.

The conditions for catalytic fluorination have been described earlier [12]. Industrially produced fluorine was applied, it contains 97% of $F_2$, 1.4% of $N_2$, 1.5% of HF, 0.1% of $CF_4$. Flow fluorinations were performed with ca. 10% (by volume) fluorine-in-nitrogen mixture using apparatus employed earlier for fluorinating aqueous substrates, except that product cold traps were removed.

Industrially produced perfluoroolefins $C_2$–$C_4$, $C_6$ and $C_9$ were used. The content of the main reactant was 99.9% or higher. Perfluoropent-2-ene was prepared by condensation of tetrafluoroethylene with hexafluoropropylene [19], perfluoroethylcyclohexene by desulfofluorination of perfluoroethylcyclohexylsulfofluoride obtained electrochemically [20], 2,3-dihydrodecaperfluoropentane by catalytic hydrogenation of perfluoropent-2-ene [19]. The partially fluorinated dialkyl ethers were prepared by reaction of perfluoroolefins with alcohols [8], sym-difluorodiethyl ether was obtained directly in the reactor from formaldehyde and hydrogen fluoride and used as a solution [21]. Monohydro and dihydro derivatives of perfluorodibutyl ether, perfluorotriethyl-, perfluoro-tripropyl-, perfluorotributyl-, and perfluorotripentylamines were isolated by rectification from the products of electrochemical fluorination of corresponding hydrocarbon derivatives. Trimer hexafluoropropylene was prepared by the reaction of perfluoro-2-methylpent-2-ene with $P(NEt_2)_3$ [22]. Fluorinations with elemental fluorine were carried out in both "open" (using ca. 1:9 (v/v) $F_2$–$N_2$ blends) and "closed" (neat $F_2$, at <20 mm Hg pressure) systems using a steel reactor, as described previously except that no cold traps were placed in the exit line. During fluorination experiments, careful control of the rate of uptake of fluorine (and hence reaction temperature) is essential to prevent the onset of potentially "runaway" free-radical mechanisms.

### 4.2. *General procedure of fluorination of partially fluorinated compounds ("adiabatic fluorination")*

Fluorination was performed in a 0.2 l reactor made of 12X18HIOT steel, equipped with valves for input of the substrate, fluorine inlet and sample take off, with pressure gauge, magnetic stirrer, jacket for cooling and heating, and thermocouple sleeve. The reactor was kept in a steel protecting box. In the reactor was placed the reactant (0.01 mol), solvent (when required, 120–150 ml) and after attaining the required temperature, fluorine was added with stirring, at a rate low enough to prevent heating the mixture by more than 1.5°C and non-consumed fluorine accumulation to a pressure 0.02 MPa. When the fluorine consumption finished, the reactor was heated at 10–20°C/h to complete the reaction (the excess fluorine not disappearing for 6 h, as tested with KI paper).

### 4.3. *Gas-phase fluorination*

Fluorination of hexafluoropropene and decafluoropentene was performed in two consecutive reactors made of 12X18HIOT steel, constructed as vertical tubes of 300 mm length and 30 mm diameter, having jackets for controlled cooling. The bottom sections were equipped with inlets for fluorine and olefin, 20 mm from each other. The head sections had sampling valves. The reaction mixture from the first reactor was passed through a cooled pipe to the bottom of the second reactor, to which fluorine admission was also provided. The system was equipped with a pressure gauge and provided working up to 0.1 MPa. To the first reactor, cooled to a certain temperature, the fluorine and olefin flows were introduced at controlled rates, with fluorine to olefin ratio 0.3–0.5:1. The reaction mixture from the first reactor was passed to the second, cooled to a given temperature, and fluorine was also admitted, in a 0.55–0.75:1 ratio. The reaction products from the head of the second reactor passed through a valve to a column filled with $Ca(OH)_2$ and then to a cooled receiver. In the case of liquid-phase fluorination, solvent was condensed at the end reactor 1.

### 4.4. *Fluorination of polyfluorinated compounds $C_5$–$C_{12}$*

The fluorination was performed in two 0.25 l reactors made of 12X18HIOT steel, one with jacket for controlled cooling, another with controlled heating. Each reactor was equipped with a magnetic stirrer, reflux condenser, bubbler for fluorine inlet and outlet for gaseous sampling. To the first reactor was passed the fluorinated compound and solvent, and on achieving the required temperature, while stirring, fluorine began to pass through the bubbler at a given flow rate. When fluorine consumption ceased (fluorine passed through) the reaction mixture was transferred by pressure to the second reactor, and fluorine passage was continued while heating the mixture. After completing the fluorine pass, the reaction mixture was washed with water and dried over silica gel. Gas-phase catalytic fluorination has been described earlier [18].

### 4.5. *Sorbtion purification*

A column made of 12X18HIOT steel 25 mm diameter and 500 mm height was filled with activated carbon (BAU-2 or SKT). The studied liquid was admitted to the column head, sampling rate was controlled by the bottom valve. The eluent was collected in a receiver and analyzed (Table 12).

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