

Basic Trends in the Development of Methods for Obtaining Polyfluoroolefins

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Abstract

Analysis of the new approaches to the synthesis of perfluoroolefins and the conditions for performing thermal decomposition of difluorochloromethane and perfluoroalkyl iodides for the synthesis of tetrafluoroethylene and hexafluoropropylene is carried out. Essential simplifications of the technology are stressed. It is established that the production of tetrafluoroethylene is affected by the presence of chlorine and oxygen, the material of reactor walls (quartz glass) and diluter (overheated water vapour). The mechanism of thermolysis is discussed from the viewpoint of the decisive role of difluorocarbene. The possibilities of dehalogenation and dehydrohalogenation of polyfluorohalogenoalkanes in the synthesis of perfluoroolefins and perfluorobutadiene are demonstrated. Decarboxylation of perfluorocarboxylic acids in the production of terminal perfluoroolefins are discussed.

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1. INTRODUCTION

Development of organofluorine chemistry started from the creation of convenient and economical methods of fluorine introduction into organic molecules and the synthesis of a series of freons and biologically active compounds, and is permanently continuing. The development is stimulated by the increasing need of technology for the materials with new properties,

improved consumer qualities and the ability to operate in severe environment [1–6]. Prerequisites for domestic and medical applications of new materials containing fluorine atoms have been created. During the past years, due to the unique properties of fluorinated organic compounds, a number of new directions of their use appeared; in turn, this stimulated the development of technologies for the production of a series of key fluorine-containing interme-

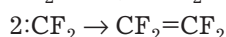
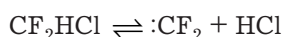
diate products. In particular, wide application was won by industrial perfluoroolefins [7–9] and a number of their oligomers [6] the distinguishing feature of which is clearly exhibited electrophilic reactivity. Due to the specific effect of fluorine atoms on the unsaturated system, perfluoroolefins comprise the basis of one of the areas of organofluorine chemistry investigating their interaction with nucleophilic reagents. This not only broadens our knowledge in olefin chemistry but brings us to the discovery of their unique properties. Investigation of the processes involved in the interaction of perfluoroolefins with nucleophilic reagents turned out to be fruitful both in the theoretical aspect and in practice because it allows deep insight into the properties of the olefin system and at the same time provides access to many organofluorine compounds. Increasing requirements to polymer materials determine the importance of carrying out investigations of the monomers containing fluorine and oxygen atoms (for instance, perfluoroalkylvinyl ethers, hexafluoropropylene oxide *etc.*) and stimulate search for optimal and industrially sound methods of obtaining key perfluoroolefins: tetrafluoroethylene, hexafluoropropylene, 1,1-difluoroethylene, trifluorochloroethylene. Numerous investigations involving existing methods allowed developing a stable operative technology which has already been implemented commercially in many countries. In spite of significant success in this area, the questions concerning the development of economical methods of obtaining perfluoroolefins are still urgent. During the recent years, attempts have been directed mainly to the search for more economical and simple conditions of realization of the thermolytic method that involves decomposition of difluorochloromethane.

In the present review, the major attention is paid to the analysis of the accumulated experimental material concerning the methods of obtaining the most available and widely used perfluoroolefins, as well as the aspects of improvement of the technology of tetrafluoroolefin production, its transformation into hexafluoropropylene.

2. IMPROVEMENT OF THE METHOD FOR PREPARING TETRAFLUOROOLEFIN AS THE BASIC COMPOUND FOR THE PRODUCTION OF FLUORINE-CONTAINING INTERMEDIATE PRODUCTS AND MATERIALS BASED ON THEM

Since the 40s of the 20 century, the major industrial method of obtaining fluorinated olefins is thermal decomposition of fluoro- and fluorochloromethane, ethane and olefins. Pyrolysis of difluorochloromethane is the key process in the synthesis of tetrafluoroethylene used as the initial material for obtaining various fluorinated plastics [6, 10].

The modern interpretation of the notions of thermal decomposition of difluorochloromethane includes the generation of difluorocarbene [11–15]. Its dimerisation leads to the formation of tetrafluoroethylene:



The slowest stage of difluorochloromethane pyrolysis is its thermal dehydrochlorination which is to be considered as the limiting stage of the entire process. The second stage, the recombination of difluorocarbene, proceeds rapidly and is characterized by low activation energy. The rate constants of reactions and their conditions are reported in monograph [15].

Improvement of the process for preparing tetrafluoroethylene became possible only after large-scale investigation of the thermal decomposition of fluorinated compounds. Analysis and results of these investigations were reported in monograph [15]. Only some key moments that played the most important part and were the evidence of the achieved essential simplifications in the technology of tetrafluoroethylene production are considered in the present review [18–20].

The use of catalysts during pyrolysis did not lead to any significant improvement of the technological characteristics of the process because the catalysts got coated with carbon deposits and rapidly lost their activity. Nevertheless, the authors of [16] demonstrated the possibility to use the catalyst based on copper compounds to intensify pyrolysis of difluorochloromethane. The synthesis of tetrafluoroethylene was performed *via* pyrolysis of fluorinated hydrocarbons in the melts of metals and salts [17].

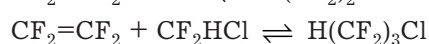
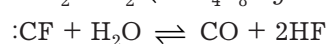
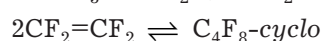
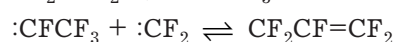
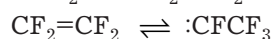
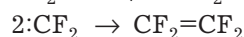
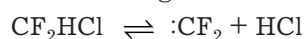
The most efficient operation turned out to be the introduction of a diluent; it is overheated water vapour [7–9, 15, 20–23]. Conversion of the initial raw material and the selectivity of the synthesis of fluoroolefins in the presence of overheated water vapour are much higher than the corresponding characteristics of pyrolysis without water vapour [23]. The authors of [20] established that the pyrolysis of difluorochloromethane in the presence of overheated water vapour proceeds at a temperature of 400 °C, retention time is 0.01–0.1 s, and tetrafluoroethylene is obtained with a high yield. The presence of water vapour has no effect on the reaction of thermal decomposition of difluorochloromethane [24].

To obtain high conversion with respect to the raw material and high selectivity with respect to the monomer, the process is carried out with a large excess of water vapour in order to maintain high process temperature. Rather simple reactor is used: it is shaped as linear pipes arranged in a heated system. Since the prime cost of tetrafluoroethylene production is determined by the cost of initial difluorochloromethane, the major characteristics of the process are conversion of the initial raw material and selectivity of pyrolysis with respect to tetrafluoroethylene. Conversion of difluorochloromethane is determined by pyrolysis temperature and the duration of reagent residence in the reaction zone. Selectivity with respect to tetrafluoroethylene depends on temperature and time of reagent residence in the reaction zone, as well as on the partial pressure of difluorochloromethane vapour. Optimal mode parameters of this pyrolysis process are: temperature 755–900 °C, retention time 0.05–0.01 s, pressure $1.7 \cdot 10^5$ N/m²; dilution degree is 3–4 mol of water per 1 mol of difluorochloromethane. With these technological parameters and displacement mode, the degree of difluorochloromethane conversion is 70–80 %, and the selectivity with respect to tetrafluoroethylene is 95–98 % [23, 25–27].

Overheated water vapour is rather inert towards the reagent and pyrolysis products; it is easily condensable and well separable from the reaction gases. At a temperature of 600–780 °C, dimerisation of tetrafluoroethylene occurs [21], while at 550–700 °C and retention time

of 1–30 s octafluorocyclobutane is also formed [28–30]. Simultaneous formation of tetrafluoroethylene and hexafluoropropylene by means of pyrolysis of difluorochloromethane is possible in the presence of water vapour overheated preliminarily (to 150–250 °C) at 730–760 °C and retention time 0.01–0.2 s [31].

Difluorochloromethane decomposition in water vapour medium can be represented with the following reactions:



It was discovered that the introduction of some additives, for example 1,1,2,2-tetrafluorochloroethane (Freon 124a), causes an increase in the efficiency of difluorochloromethane pyrolysis and the yield of tetrafluoroethylene [15, 25–27]. This method also provides separation of hydrogen chloride and obtaining hydrochloric acid from it, multi-step rectification with the isolation of the fraction of the target product and the fraction containing difluorochloromethane and hexafluoropropylene. Absorption with water is carried out in the column-type apparatus in the counterflow mode. Azeotropic mixtures are collected sequentially: at first, the azeotropic mixture of difluorochloromethane and hexafluoropropylene is isolated at a pressure of 3–8 atm with the boiling point of –42...–38 °C (calculated for atmospheric pressure), then the azeotropic mixture of 1,1,2,2-tetrafluorochloroethane and octafluorocyclobutane at a pressure of 2–7 atm with the boiling point of –15 to 0 °C.

The authors of [10] studied the pyrolysis of difluorochloromethane in the solution of pentafluoroethane proceeding within temperature range 500–700 °C at the retention time of 0.1–60 s and pressure 10–30 atm, in a metal reactor with hydrogen fluoride added as a catalyst, followed by distillation of hydrogen chloride. The degree of difluorochloromethane conversion was 20 %; selectivity of tetrafluoroethylene formation was 99 %.

In a similar manner, the authors of [30] developed a technology of trifluorochloroethylene production by means of thermal decomposition of the isomers of trifluorodichloroethane at a temperature within 700–850 °C in the presence of overheated vapour at the retention time of 0.05–0.3 s and the ratio of initial isomers to water vapour equal to (2–3) : 1. Pyrolysis of chlorotrifluoroethylene at 505–600 °C and retention time 0.5–15 s results in the formation of a mixture of 1,2-dichlorohexafluorobutene-3 and 1,2-dichlorohexafluorocyclobutene-3 (conversion degree was 50–70 %); the technology of separation of these compounds was industrially implemented [32].

The selectivity of the pyrolysis of 1,1-difluoro-1-chloroethane at 800–840 °C with respect to 1,1-difluoroethylene is 98–99 % with almost complete conversion of 1,1-difluoro-1-chloroethane [23].

By means of thermal decomposition of difluorochloromethane in a flow-through quartz reactor within temperature range 650–800 °C in the presence of chlorine as an additive, tetrafluoroethylene may be obtained with a high yield [18]. It was established that thermal decomposition of difluorochloromethane is realized in all the cases as the first-order process with respect to difluorochloromethane. The addition of chlorine to difluorochloromethane undergoing thermal decomposition on a fresh quartz wall leads to a decrease in activation energy by 29 kJ and an increase in decomposition rate by a factor of 2 in comparison with the decomposition of pure difluorochloromethane under the same conditions [16, 18]. The products of decomposition exhibit an increased content of difluorochloromethane, difluorodichloromethane and 1,2-dichlorotetrafluoroethane. Tetrafluoroethylene obtained using this method gives the polymerisation product with a high yield; this product meets all the requirements of the standard [10]. The obtained results may be interpreted on the basis of radical chain mechanism of difluorochloromethane decomposition.

3. OTHER METHODS OF TETRAFLUOROETHYLENE SYNTHESIS

The direct synthesis of tetrafluoroethylene from carbon and fluorine in the volume of the

electric arc was developed by the researchers from DuPont Company (the USA) in 1950–1960. The yield of the target product turned out to be not high; various carbon sources were used as the raw material, including organic fluorinated compounds. It was shown that the process runs through the stage of formation of fluorocarbon radicals at temperatures 1800–1900 °C and time of retention in the reaction zone 0.0001–10 s. The best acceptable conditions of tetrafluoroethylene synthesis with the yield of 80–90 % with almost quantitative consumption of the initial raw material are as follows: temperature 2000–500 °C, contact time 0.01–1 s, pressure 1–30 mm Hg. Analysis of these works was presented in monograph [15].

The data concerning the use of different kinds of physical action on the reagents in the synthesis of tetrafluoroethylene are presented in Table 1. The formation of turbulent plasma in a substantial part of the reactor volume and, as a consequence, dissociation of metal fluoride (provided that only fluorine is present but other halogens are absent) leads to the formation of the gas mixture of the metal and reactive fluorine. The interaction of this mixture with carbon particles gives the precursor of tetrafluoroethylene; its slaking allows one to obtain tetrafluoroethylene [34, 35].

Difluorocarbene plays a key role in all the above-considered processes. It may be assumed that in other cases involving the generation of difluorocarbene during the decomposition of fluorinated organic compounds and polymers based on them tetrafluoroethylene will be formed, too. This assumption was confirmed for the plasma-chemical decomposition of organofluoric compounds. In spite of the fact that the yield of tetrafluoroethylene does not exceed 48 %, this method may become the basis of the alternative industrial technology.

Vat residue formed in the production of tetrafluoroethylene contain highly fluorinated compounds of wide range (Freon 318c, 124, 226 *etc.*) [39]. Some of them are of separate interest (for example Freon 318c), while others may serve as a raw material for the synthesis of new organofluoric compounds. For instance, hexafluorochloropropane for which the method of isolation from the vat residue was implemented on the industrial scale is the raw mate-

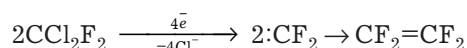
TABLE 1

Synthesis of tetrafluoroethylene using high-temperature pyrolysis of fluorinated organic compounds under physical action

Physical action	Process characteristics	Yield of $\text{CF}_2=\text{CF}_2$, % (accompanying compounds)	References
High-frequency plasma	Initial $\text{CF}_4 + \text{H}_2$ $\text{CF}_3 \cdot \rightarrow \cdot\text{CF}_2 + \text{F} \cdot$ $2:\text{CF}_2 \rightarrow \text{CF}_2=\text{CF}_2$	$[\text{C}_3\text{F}_2\text{H}_2, \text{C}_4\text{FH}, \text{C}_4\text{H}_2, \text{C}_2\text{F}_3\text{H}]$	[33]
Turbulent plasma	Organofluoric compounds $2:\text{CF}_2 \rightarrow \text{CF}_2=\text{CF}_2$	$\text{CF}_4, \text{C}_2\text{F}_2, \text{C}_2\text{F}, \text{F}$	[34, 35]
Plasma or direct-current arc	C 1-10 (mainly $\text{C}_2\text{F}_5\text{H}$ or CHF_3), inert gas (Ar, HF, CO, N_2 , CF_4 , CO_2) at a pressure of 0.1-2 atm, time of contact 0.002-0.1 s, temperature 1727 K Pyrolysis of $\text{C}_2\text{F}_5\text{H}$ (800 °C, time of contact 0.01 s, atm. pressure), conversion 100 % Pyrolysis of CHF_3 Carbon dust + F_2 , ratio C : F = 1 : 2 $2:\text{CF}_2 \rightarrow \text{CF}_2=\text{CF}_2$	66.9-75.8 $[\text{CF}_4, \text{C}_2\text{F}_6, \text{CHF}_3, \text{C}_3\text{F}_6]$ 82 $[\text{CF}_4, \text{C}_2\text{F}_6]$	[36, 37]
Plasma of CF_4			
CO_2 laser	During pyrolysis of CHF_3 , pressure range 0.4-4000 Pa 0.4-4000 Pa Pyrolysis of hexafluoroethane Pyrolysis of pentafluoroethane Two routes of reaction: $\text{C}_2\text{F}_5\text{H} \rightarrow \text{C}_2\text{F}_4 + \text{HF}$ $\text{C}_2\text{F}_5\text{H} \rightarrow \cdot\text{CF}_3 + \text{CHF}_2$ Photolysis of radicals in the laser generation region During thermolysis of polytetrafluoroethylene thermolysis of $\text{C}_6\text{F}_6, \text{C}_6\text{F}_5\text{H}$ $\text{CF} \cdot, \cdot\text{CF}_2$ (at 249 nm) Perfluorocyclohexane Decafluorocyclopentane Perfluorinated ethers $\text{CH}_4 + \text{SF}_6$	$\text{C}_2\text{F}_4, \text{CF}_3\text{CF}=\text{CF}_2,$ oktafluorocyclobutane 64 80 $[\text{CF}_3\text{CF}_2\text{O}, \text{CF}_2\text{O}]$ $[\text{CS}_2, \text{CF}_4]$	[38] [36]

rial for the production of Freon 227a. The authors of Patent [40] propose a method for isolating tetrafluoroethylene from a mixture contains both high- and low-boiling impurities. This method is based on the distillation treatment in several stages.

The authors of [41, 42] showed that electrolysis of dichlorodifluoromethane on a lead electrode at the voltage of 1.5 V in acetonitrile results in the formation of tetrafluoroethylene with a yield of 43.2 %; this compound may be easily separated from other side products. It is assumed that tetrafluoroethylene is formed through dimerisation of difluorocarbene:



However, one cannot exclude also dimerisation of difluorochloromethyl radical, resulting in the formation of 1,2-dichlorotetrafluoroethane. The latter is transformed during electrolysis into tetrafluoroethylene due to chlorine reduction:



It should be stressed that difluorocarbene was detected in the electrolysis of dichlorodifluoromethane in the presence of 2,3-dimethyl-2-butene when the interaction of the latter with difluorocarbene leads to the formation of 1,1-difluoro-2,2,3,3-tetramethylcyclopropane:

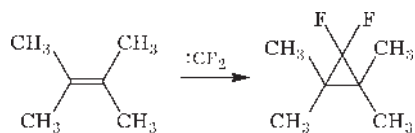






TABLE 2

Fluorination of polychloroolefins with potassium fluoride in the presence of perfluoroperhydrophenanthrene (PFC) [45]

Initial substrate	Reaction conditions	Product	Yield, %
Hexachlorobuta-1,3-diene	PFC, THTD, 190 °C, 15 h, atm. pressure	Hexafluorobuta-1,3-diene	60
	PFC, 18-crown-6 ether, 190 °C	Hexafluorobuta-1,3-diene	55
	PFC, 18-crown-6 ether, 190 °C, 4 h, atm. pressure	$\text{CF}_3-\text{C}\equiv\text{C}-\text{CF}_3$	
2,3-Dichlorohexafluorobut-2-ene 	PFC, 18-crown-6 ether, 190 °C, 48 h	Octafluorobut-2-ene	90
	PFC, 18-crown-6 ether, 190 °C, 15 h		68
	PFC, THTD, 190 °C, 15 h, atm. pressure		
	PFC, 18-crown-6 ether, 190 °C, 15 h		
	PFC, 18-crown-6 ether, 190 °C, 120 h, autoclave		

Trifluoroethylene may be obtained by thermal dehydrofluorination of fluorine-containing ethanes. The process is carried out in a reactor made of nickel-chromium alloy after preliminary treatment of its inner surface with pyrolysis products, in the presence of water vapour at a temperature within the range 650–900 °C [15]. The authors of [43] describe a method of obtaining trifluoroethylene on the basis of the interaction of CF_3CClFX ($X = \text{H}, \text{Cl}, \text{F}$) with hydrogen in the presence of catalysts: Ru, Ni, Cu, and Cr metals, metal halogenides and oxides.

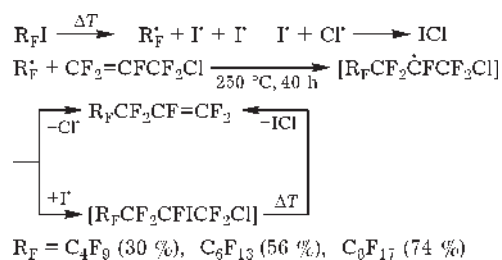
To synthesise perfluorinated olefins, exchange of a halogen atom at the double bond in halogenated olefin $\text{R}^2\text{CCl}=\text{CClR}^3$ ($\text{R}^2, \text{R}^3 = \text{F}, \text{alkyl}, \text{fluoroalkyl}$) under the action of alkaline metal fluoride in dimethylformamide or N-methylpyrrolidone is used [44]. The authors of [45] demonstrated the efficiency of chlorine exchange for fluorine in hexachlorobut-3,4-diene, octachlorocyclopentene and hexachlorocyclobutene through the action of potassium fluoride in the presence of a perfluoroperhydrophenanthrene (PFC) (Table 2).

4. METHODS OF THE SYNTHESIS OF TERMINAL PERFLUOROOLEFINS

Thermal transformations are characteristic also for perfluoroalkyl iodides, though the latter compounds are thermally stable up to 300 °C, while above this temperature they decompose with the formation of perfluoroolefins [46].

In the presence of iodotrifluoromethane, perfluoroalkenes-1 are formed with a low yield from hexafluoropropylene [47, 48]. The authors of [49] proposed an efficient method of obtaining terminal perfluoroolefins that involves heating perfluoroalkyl iodides with perfluoroallyl chloride at 180–250 °C and atmospheric pressure. This method is used to obtain terminal perfluoroolefins with the purity of 99 %. It is necessary to stress the fact that temperature rise to 200–250 °C does not cause an increase in conversion degree, while the presence of a CuI or peroxide (Trigonox 145) does not affect an increase in the yield of terminal perfluoroolefin. Isomerisation of the latter into the internal perfluoroolefin does not take place.

The reaction is likely to proceed according to the following scheme:



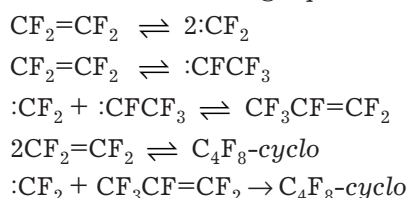
5. THERMAL TRANSFORMATIONS OF TETRAFLUOROETHYLENE. SYNTHESIS OF HEXAFLUOROPROPYLENE

Kinetics and mechanism of the thermal decomposition of tetrafluoroethylene have been investigated in detail, which is to a high extent due to the production of hexafluoropropylene on its basis. This compound is the raw material for the production of a number of fluorinated materials, first of all hexafluoropropylene oxide [15]. The main products of pyrolysis of tetrafluoroethylene at medium temperatures are represented by perfluorinated compounds with the number of carbon atoms equal to 4 – perfluorocyclobutane, perfluorobut-1-ene, perfluorobut-2-ene and perfluoroisobutylene. In extremely small amounts (up to 1 %), also CF_4 , C_2F_6 , C_3F_8 are formed, along with the products of tetrafluoroethylene polymerisation, and carbon black (the product of complete decomposition). With temperature rise, hexafluoropropylene becomes the major prod-

uct of pyrolysis. In addition, the formation of octafluorocyclobutane takes place. It is purified from tetrafluorochloroethane admixture in an absorption column by treating with the aqueous solution of inorganic salts in which the concentration of chloride and fluoride anions ($CaCl_2$, NaF) is 1–100 mg/l [29].

To obtain hexafluoropropylene, pyrolysis of tetrafluoroethylene at a temperature of 700–900 °C without hydrogen in the reaction zone of a turbulent reactor the inner walls of which are mechanically coated with nickel or nickel alloy containing 8 % of chromium [50]. The reaction zone has a shape of a spiral with a volume of 0.04 m³. Good results were obtained with the use of Inconel 617 alloy (55 % Ni, 22 % Cr, 12.5 % Co, 1.2 % Al) at 825 °C and retention time 2.5 s.

On the basis of data obtained in experiments and calculations, a kinetic model of the synthesis of hexafluoropropylene during gas-phase pyrolysis was built up. The key stage of this model is the generation of thermodynamically most stable difluorocarbene. Thermal decomposition of tetrafluoroethylene can be represented with the following equations:

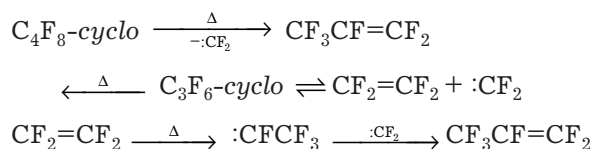


The double bond of fluorinated olefins gets destroyed much simpler than the corresponding bond of hydrocarbon analogues, which is confirmed by the data listed below:

Olefin	C=C bond rupture energy, kJ/mol
$CF_2=CF_2$	293–295
$CFCl=CFCl$	428
$CH_2=CH_2$	710

Taking into account substantial decrease in the energy of C=C bond in comparison with non-fluorinated analogues, one clearly sees the mechanism of perfluorocyclobutane formation through dimerization of tetrafluoroethylene [51]. Quite contrary, the routes of hexafluoropropylene formation in the thermolysis of tetrafluoroethylene remained unclear for a long time and were interpreted ambiguously. Thus, in the

opinion of the author of [52], the formation of hexafluoropropylene occurs due to thermal isomerization of hexafluorocyclopropane, while the authors of [53, 54] relate its formation to actual olefin-carbene isomerization of tetrafluoroethylene followed by recombination of carbene :CFCF_3 with difluorocarbene:

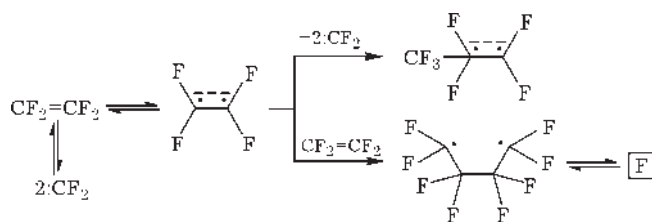


The formation of difluorocarbene during the gas-phase pyrolysis (327–927 °C) of tetrafluoroethylene occurs in the elementary reaction of decomposition of the biradical structure. This singlet 1,2-biradicaloid reacts with difluorocarbene to form hexafluoropropylene. The construction of octafluorocyclobutane system from tetrafluoroethylene occurs through the addition of this biradical structure to tetrafluoroethylene molecule with the formation of 1,4-biradical, followed by closing the four-membered ring [55, 56] (Scheme 1).

To elevate the selectivity of the process with respect to hexafluoropropylene at the same degree of tetrafluoroethylene conversion, it is necessary to increase pyrolysis temperature and decrease contact time. Thus, it was established in [15] that temperature rise to 850 °C and decrease of retention time to 0.03–0.05 s causes an increase in selectivity with respect to hexafluoropropylene to 70 % for the degree of tetrafluoroethylene conversion 65–70 %. This is higher by 20 % in comparison with pyrolysis at 770 °C. With an increase in retention time, the yield of hexafluoropropylene increases. For example, for retention time equal to 1 s, the yield of hexafluoropropylene is 45 %, while total yield of tetrafluoroethylene and hexafluoropropylene exceeds 70 %. The authors of monograph

[15] recommend the following conditions for obtaining hexafluoropropylene: temperature 850 °C, retention time 1 s, degree of dilution of the initial raw material with water vapour 0.5–1.0. In the opinion of those authors, the most promising raw material for pyrolysis is not tetrafluoroethylene which is expensive, but difluorochloromethane to be subjected to two-step pyrolysis. At the first stage, pyrolysis of difluorochloromethane in the presence of water vapour occurs, with an increase in conversion degree to 80–85 %, which ensures substantial decrease in the amount of return difluorochloromethane. At the second stage, after separation of hydrogen chloride, pyrolysis of the remaining difluorochloromethane, formed tetrafluoroethylene and side products in the presence of water vapour or without it is performed. During hexafluoropropylene isolation by means of rectification, unreacted tetrafluoroethylene is returned to the second-stage pyrolysis, while octafluorocyclobutane is isolated as the commercial product or returned to pyrolysis at the second stage. This approach is based on sequential separation by means of extractive rectification and adsorption of the fraction containing the target products, difluorochloromethane, hexafluoropropylene and closely boiling admixtures [57]. Purification of hexafluoropropylene is important technological operation. An approach using sulphur trioxide SO_3 in gas-phase and liquid-phase versions at temperatures 0–50 °C [58] allowing one to exclude trifluorochloroethylene admixture from commercial hexafluoropropylene was developed.

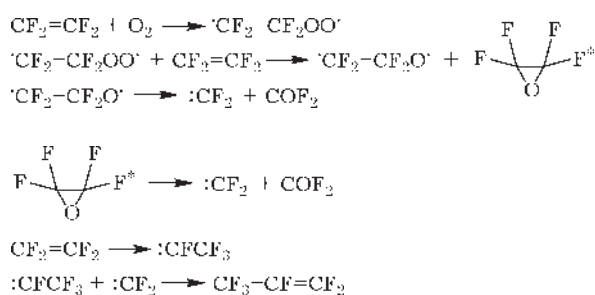
The authors of [59] proposed and industrially realized a non-conventional ecologically sound method of concentrating hexafluoropropylene using the membrane method to the concentration above the azeotropic point; in combination with rectification, this allows one to



Scheme 1.

obtain commercial hexafluoropropylene with the purity above 99.9 %. An experimental-industrial membrane apparatus was developed on the basis of the modified hollow fibre Graviton. In real technological mixtures based on return Freon 22 containing 2–6.5 mol. % hexafluoropropylene, 3–7 mol. % (total) trifluorochloroethylene, tetrafluoroethylene and Freons 12, 318 and 114, the use of two-step membrane scheme allows one to obtain the outflow containing 45–50 mol. % of hexafluoropropylene.

It was established that hexafluoropropylene is formed in the pyrolysis of tetrafluoroethylene at 800 °C in the presence of molecular oxygen [60]. This discovery was the basis of the approach to the development of the corresponding technology of hexafluoropropylene production (involving pyrolysis of tetrafluoroethylene). The effect of oxygen concentration on the selectivity of the process with respect to hexafluoropropylene and the degree of tetrafluoroethylene conversion were determined [60]. It was established on the basis of the experimental data that with the use of oxygen in the amount of 1–5 % (by volume) with respect to tetrafluoroethylene, the degree of tetrafluoroethylene conversion increases by 30 %, while the selectivity of the process with respect to hexafluoropropylene increases by 20–35 % in comparison with pyrolysis without oxygen. The assumed mechanism of tetrafluoroethylene thermal decomposition in the presence of oxygen is shown in the following scheme:



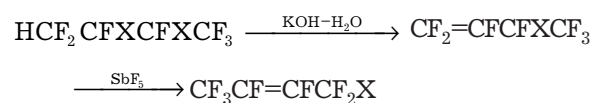
The addition of oxygen in the amount <1 % (by volume) is insufficient for the formation of the necessary amount of peroxy biradicals $\cdot\text{CF}_2-\text{CF}_2\text{OO}\cdot$. In the case when a large amount of oxygen is used (>5 % by volume), pyrolysis is accompanied by the destruction of initial tetrafluoroethylene, which is confirmed by the

presence of carbon dioxide, hexafluoroethane, carbonyl fluoride in reaction products [60].

Pyrolysis of a mixture of tetrafluoroethylene and trifluoromethane (Freon R23) at 700–1000 °C, duration of contact between reagents 0.01–14 s and trifluoromethane/tetrafluoroethylene ratio 0.1 : 5, leads to the formation of hexafluoropropylene with a high yield [61]. Perfluoroisobutylene, $\text{CF}_3\text{CF}=\text{CFCF}_3$, $\text{C}_2\text{F}_3\text{H}$, CF_3CHCF_2 , $\text{CF}_3\text{CF}_2\text{CF}=\text{CF}_2$ are formed as impurities in small amounts; they are separated during purification of the target product using the standard methods.

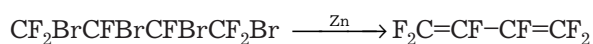
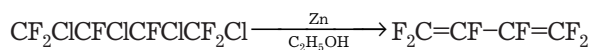
6. SYNTHESIS OF PERFLUOROOLEFINS BY DEHALOGENATION AND DEHYDROHALOGENATION OF POLYFLUORINATED ALKANES

Fluoroolefins may be obtained by splitting off hydrogen halide from fluorocarbons at a temperature within 200–500 °C in the presence of catalysts (for example, salts of transition metals). This method is rather widely used not only in laboratory practice but also on the industrial scale because the process runs selectively with the high yield of target products. Thus, pentafluoropropylene was obtained by passing hexafluoropropane through a flow reactor at 200–500 °C in the presence of chromium trifluoride [62]. Aqueous solutions of alkalis may also be used for these purposes. For example, the system $\text{KOH}-\text{H}_2\text{O}$ turned out to be efficient for obtaining perfluorobutenes [63–65]:



X = Br, Cl

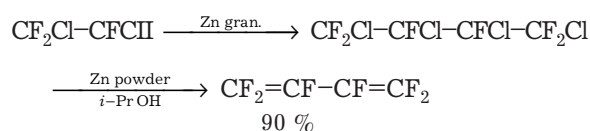
One of the approaches to the synthesis of conjugated olefins is based on the use of the processes of dechlorination and debromination of fluorochlorohydrocarbons under the action of zinc in ethanol [66] or in a polar organic solvent [67]. Dechlorination of 1,2-dichlorohexafluorobutene-3 with zinc in a polar solvent at 37–50 °C leads to the formation of hexafluorobutadiene:



Under heating 1-chloro-2,2,3,3-tetrafluorocyclobutane in the presence of bases (NaOH, CaCl₂) at a temperature of 50 °C for 14 h, 3,3,4,4-tetrafluorocyclobutene was obtained with the yield of 91 % [68]. Incompletely fluorinated olefins may be obtained also by dehydrochlorination. For example, CF₂ClCH₂CF₃ on the catalyst (active coal) at 250–270 °C within 2 h (retention time 58 s) forms CF₂=CHCF₃ with the yield 76.6 % and selectivity 97.9 % [69].

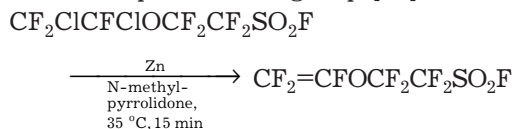
Dehalogenation carried out in the presence of metals or organometallic compounds like XCF₂CFXCF₂CFXCF₂X leads to the formation of octafluoro-1,4-pentadiene [70], while under the action of zinc in soda in the presence of copper salt as a catalyst, 1,2,3,4-tetrachlorohexafluorobutane forms hexafluoro-1,3-butadiene with a high yield [71].

Technologically convenient method of synthesis of perfluorobutadiene has been developed. It consists in condensation of trifluorodichloroiodoethane under the action of granulated zinc at 20 °C without any solvent in the presence of catalytic amounts of ethyl acetate into polyfluoro-polychlorobutane, which is transformed with the yield 90 % into perfluorobutadiene without preliminary treatment [72, 73]:



Compounds having more complicated composition with chlorofluoroalkyl fragments can be used for dechlorination reaction, too. For ex-

ample, the action of metal zinc in dimethylformamide or N-methyl-2-pyrrolidone on polyfluorochloroalkanesulphofluoride leads to the formation of unsaturated bond and conservation of sulphofluoride group [74]:

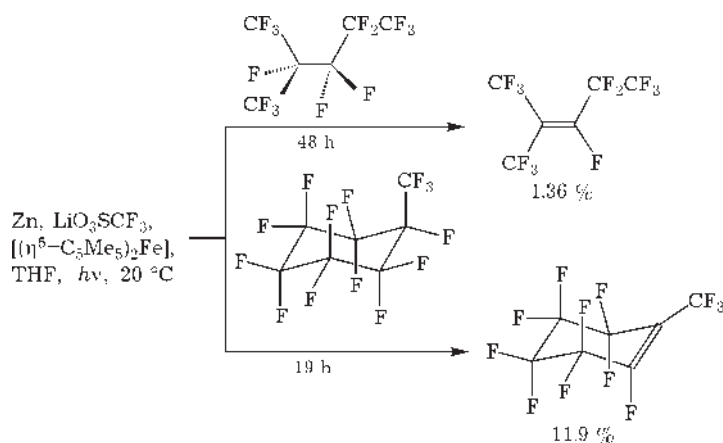


The resulting monomer is used to synthesize polymers applied as solid electrolytes, electrodes *etc.* For example, its copolymerisation with vinylidene fluoride leads to the formation of a polymer that forms a solid electrolyte after treatment with lithium carbonate [75].

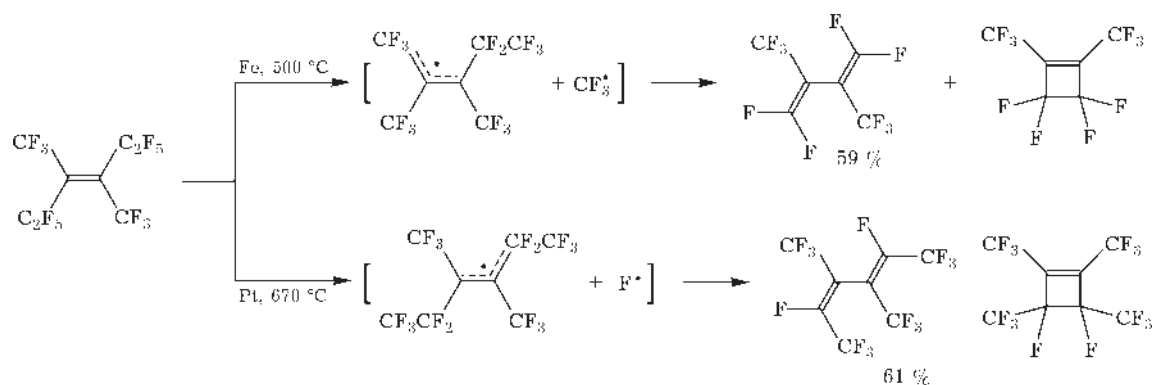
Dehalogenation of the compounds having the composition CF₂Z¹XFZ²(CF₂)_nCXYOCFZ³CF₂Z⁴ (X = H, F, Cl, Br, I; n = 1–3; Z¹–Z⁴ = Cl, Br, I; n = 1–3) in dimethylformamide in the atmosphere of inert gas at 50–55 °C and pressure 3 MPa leads to the formation of fluorine-containing dienes CF₂=CF(CF₂)_nCXYOCF=CF₂ [75, 77]. For n = 1 and X = Y = Cl, the yield of diene was 62 %.

At the same time, defluorination of perfluoroalkanes proceeds very difficultly. For example, the action of metal zinc in the presence of [(η⁵-C₅Me₅)Fe] and LiO₃SCF₃ (lithium triflate) on perfluoromethylcyclohexane gives the products containing unsaturated bonds with a very low yield [78] (Scheme 2).

Not only perfluoroalkanes but also perfluoroolefins undergo defluorination at high temperatures. Reactions proceed in the presence of metals and lead to the formation of perfluoro-



Scheme 2.



Scheme 3.

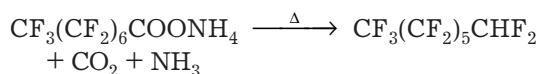
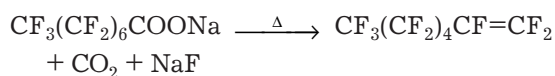
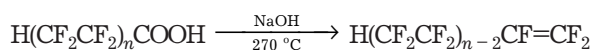
dienes. It should be kept in mind that at high temperatures further transformations of dienes leading to the formation of cyclic compounds, as side products are possible. For example, depending on the nature of a metal, perfluoro-3,4-dimethylhex-3-ene (tetramer of tetrafluoroethylene) forms dimers of different structures that are further on transformed into the derivatives of cyclobutene [79] (Scheme 3).

Similar defluorination occurs also with perfluorocycloalkenes [80].

7. SYNTHESIS OF PERFLUOROOLEFINS BY DECARBOXYLATION AND DECARBONYLATION OF PERFLUOROCARBOXYLIC ACIDS

Poly- and perfluorinated carboxylic acids like $\text{H}(\text{CF}_2\text{CF}_2)_n\text{COOH}$ ($n = 1-5$) and R_fCOOH decompose at high temperatures, as a rule, forming to major products – 1H-perfluoroalkane and terminal perfluoroolefin. For perfluorooctanoic acid as an example, the kinetics of thermal decomposition into 1H-perfluoroheptane and perfluoro-1-heptene at temperatures 355–385 °C was investigated by means of NMR spectroscopy (gas-phase measurements) (Table 3) [81].

At the same time, thermal decomposition of sodium salts of polyfluorinated carboxylic acids proceeds preferentially with the formation of terminal perfluoroolefins [82, 83]. This formed the basis of the method for obtaining olefins with long perfluorinated chain; the yields of polyfluoroolefins are stable and approach quantitative ones.



$$E_a = 154 + 11 \text{ kJ/mol}; \log (A/s^{-1}) = 13.6 + 1.2$$

Other salts, for example ammonium salt of perfluorooctanoic acid, give only polyfluoroparaffin as a result of pyrolysis in glass [81]. The authors of patent [84] proposed a method for obtaining new mixtures of perfluoro-, α -chloroperfluoro- and α,ω -dichloroperfluoroalkanes by decarboxylation of perfluoro- and ω -chloroperfluorocarboxylic acids with potassium hydroxide at a temperature up to 60 °C, followed by the action of potassium persulphate at 90–95 °C. The ratio of the mixture of acids to po-

TABLE 3
Kinetics of thermal decomposition of perfluorooctanoic acid

Temperature, °C	$k, 10^{-3} \text{ min}^{-1}$		
	$\text{CF}_3(\text{CF}_2)_6\text{COOH}$	$\text{CF}_3(\text{CF}_2)_5\text{CHF}_2$	$\text{CF}_3(\text{CF}_2)_4\text{CF}=\text{CF}_2$
355	5.0 ± 0.7	7.0 ± 1.8	1.8 ± 0.9
370	9.2 ± 0.7	11.1 ± 1.2	4.3 ± 0.9
385	26.4 ± 3.1	23.0 ± 2.1	8.9 ± 4.5

tassium persulphate is 1 : 0.6, while the mixtures of acids are 1 : 1. The following mixtures of acids were used:

- 1) perfluorooenanthic and ω -chloroperfluorooenanthic;
- 2) perfluorooenanthic and ω -chloroperfluoropelargonic;
- 3) perfluoropelargonic and ω -chloroperfluorooenanthic;
- 4) perfluoropelargonic and ω -chloroperfluoropelargonic;
- 5) ω -chloroperfluorooenanthic and ω -chloroperfluoropelargonic.

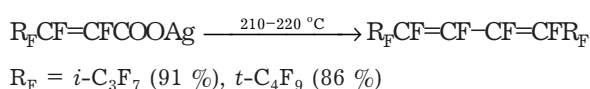
The products of decarboxylation are powders; their structure was not reported in [84]. Nevertheless, the authors of that work proposed to use the resulting products for manufacturing plastic skis.

Good results were obtained by decarboxylation of halogenoanhydrides of perfluorocarboxylic acids and their alkyl esters in the presence of catalysts – oxides of Mf, Cr, Ba, Zn, Al, Ni, Si, promoted by 20–50 % of alkaline metal halides, at 100–300 °C. The yield of terminal perfluoroolefins reaches 95 % [85].

The reactions of α,β -unsaturated perfluorocarboxylic acids, accompanied by decarboxylation, open the way to the synthesis of various compounds of ethylene and acetylene series [86]. For example, thermal decomposition of sodium salts of α,β -unsaturated perfluorocarboxylic acids in ethylene glycol leads to the formation of 1-hydroperfluoroalkenes-1, while thermolysis of silver salts of these acids leads

to the formation of perfluorinated α -dienes, perfluoroalkanes and the products of dimerization of radicals formed by oxidative decarboxylation of the initial salts [86, 87] (Scheme 4).

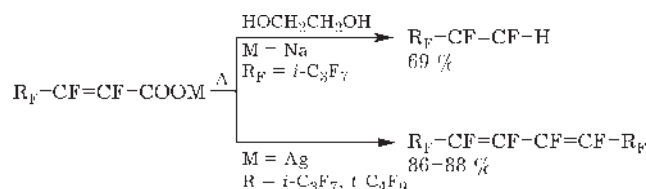
The authors of [88] used the indicated approach to synthesize perfluorinated conjugated dienes using silver salts of unsaturated perfluorocarboxylic acids. It was established that the decomposition of silver salts of perfluoro-4-methylpent- and perfluoro-4,4-dimethylpent-2-enic acids leads to the formation of perfluorodienes in the form of (1E,3E)-S-cis isomers with the yield of 87–89 % [88]:



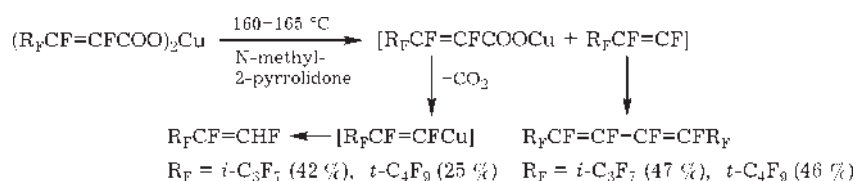
Thermal decomposition of copper (Cu^{2+}) perfluoroalkenylcarboxylates in high-boiling organic solvents, for example in N-methylpyrrolidone or sulfolan (tetramethylene sulphone), leads to the formation of a mixture of 1,3-dienes and 1-hydroperfluoroalkenes-1 [87, 88] (Scheme 5).

Esters of perfluorocarboxylic acids undergo decarboxylation at 100–300 °C in the presence of catalysts (oxides of magnesium, calcium, barium, zinc, nickel), which results in the formation of perfluoroolefins or perfluoroalkylvinyl esters with the yield of ~95 % [88].

At the same time, when passed over heated Al_2O_3 , fluoroanhydrides of perfluorocarboxylic acids undergo decarboxylation with the formation of perfluoroalkanes. In the case when the sources of halide ions are present in the



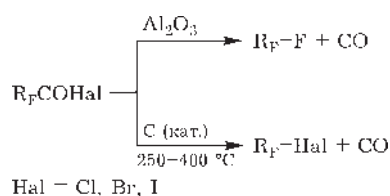
Scheme 4.



Scheme 5.

system (for example, alkaline metal halides or haloids), thermolysis of chloroanhydrides of perfluorocarboxylic acids leads to the formation of haloidoperfluoroalkanes. Thus, pyrolysis in a flow reactor under atmospheric pressure and 250–350 °C in the presence of potassium iodide leads to the formation of iodoperfluoroalkanes with the yield of 80–85 %, while heating of a mixture of fluoroanhydrides of perfluorinated acids with bromine at 300–450 °C on activated carbon results in the formation of bromoperfluoroalkanes [86].

It should be noted that under these conditions chloro- and bromoanhydrides of the corresponding acids do not transform, so it is necessary to use activated carbon to carry out this process. In this case, the products of reaction are chloro- and bromoperfluoro-paraffins [86]:



Thermal reactions of sodium and potassium salts of perfluorinated carboxylic diacids (temperature 150–250 °C) give rise to decarboxylation and the formation of monoacids with the end difluoromethyl group. For thermal decarboxylation of potassium salts of the acids having the structure $\text{KOOCCF}_2\text{-R}_F\text{-CF}_2\text{COOK}$, obtained by oxidative polymerization of tetrafluoroethylene with oxygen under UV irradiation [88], the kinetics of the reaction was investigated [89–92]. It was established that the process temperature affects the rate of decarboxylation (k_s):

Temperature, °C	140	160	180	200
$k_s, 10^5 \text{ s}^{-1}$	1.1	7.2	51	220

Arrhenius parameters E_a and A for the reaction were calculated using these data; they were found to be 3 kcal/mol and $3.6 \cdot 10^{12} \text{ s}^{-1}$, respectively [92].

8. CONCLUSION

The data presented in the review provide evidence of permanently increasing attention of researchers to the problem of mastering the

method of tetrafluoroethylene production and development of the approaches to its transformations into hexafluoropropylene and other organofluoric compounds. These processes have clear advantages and actual possibilities to be applied in industrial technologies. Implementation of this methodology allows one to expect the discovery of new reactions and transformations leading to the synthesis of fluorinated compounds. Of course, the aspects connected with the realization of new ideas and approaches are interesting not only for researchers working in the area of chemistry of fluorinated organics but also for experts in the area of organic synthesis. It is necessary to stress that perfluorinated organic compounds in some cases serve as convenient and sometimes unique models for formulating and solving a number of fundamental problems of theoretical organic chemistry.

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