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The Preparation of Monomers for the Synthesis of Fluorocarbon Polymers by the Oxidation of Fluoro-olefins

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The oxidation reactions of fluoro-olefins are examined: the conditions under which they take place, the characteristic features of the mechanism, and the composition and structure of the products formed. Attention is concentrated on the oxidation reactions of industrial perfluoro-olefins, namely tetrafluoro-ethylene and hexafluoropropene, and also on the methods of synthesis of the most important products of the oxidation of fluoro-olefins - fluorocarbonepoxides and oligomeric perfluoro-polyesters.
The characteristics of the physicochemical properties and the main applications of oxygen-containing products of the oxidation of fluoro-olefins are discussed.
The bibliography includes 154 references.

CONTENTS

I.	Introduction	711
II.	Ionic oxidation reactions of fluoro-olefins	711
III.	Electrochemical and heterogeneous-catalytic oxidation of fluoro-olefins	713
IV.	The oxidation of fluoro-olefins via a radical mechanism	714
V.	Characteristic features of the physicochemical properties and main applications of the fluoro-olefin oxidation products	719

I. INTRODUCTION

Fluorocarbon polymeric materials (plastics, elastomers, and lubricants) play an important role in the application of atomic energy, in machine construction, in chemical industry, and in other branches of the economy by virtue of their high chemical and thermal stability. The chemistry and technology of "second generation" fluoro-polymers, namely oxygen-containing polymers, is nowadays developing vigorously. The introduction of ethers and reactive functional groups into the main chain and into the side groups of fluorocarbon polymers makes it possible to extend significantly the temperature range of their use, while retaining a high chemical stability. A way of synthesising the monomers for oxygen-containing fluorocarbon polymers was discovered in the course of the study of the oxidation reactions of fluoro-olefins.

In contrast to saturated fluorocarbon compounds, which have a high chemical and thermal stability,[1,2] fluoro-olefins are readily oxidised at the double bond via both ionic and radical mechanisms and in this respect show similarity to hydrocarbon olefins. There is also a similarity in the chemical nature of the products of the oxidation of hydrocarbon and fluorine-containing olefins, but the mechanism of the oxidation of fluoro-olefins and the properties of the products have important characteristic features.

Among the products of the oxidation of fluoro-olefins, epoxides and oily products with a perfluoropolyether structure are of greatest practical interest.

Perfluoroepoxides were first obtained approximately 20 years ago by the oxidation of fluoro-olefins by a number of investigators simultaneously[3-9] and this approach to the synthesis of fluorocarbon epoxides still remains virtually the only one available.

The practical importance of fluorocarbon epoxides is indicated by the fact that the manufacture of the most important of these, namely epoxyhexafluoropropane (EHFP), was initiated in the USA in the middle 1960's.[10-12] The perfluoropolyether oils formed in the high-temperature photochemical oxidation of hexafluoropropene, are manufactured on an industrial scale under the trade name "Fomblin" in Italy and under the trade name "PEF" in the USSR.[13] A number of oxygen-containing fluorocarbon materials of practical importance have been obtained on the basis of the oxidation products of fluoro-olefins: solvents, surfactants, thermally and chemically stable fluororubbers with improved frost resistance,[14,15] perfluoropolyether oils and greases with exceptionally effective viscous-temperature characteristics,[13] fluorinated plastics with improved thermal stability,[16] perfluorinated ion-exchange membranes,[17-19] polymers with selective permeability to gases,[20] etc.

The great practical value of the above materials stimulated vigorous investigation of the oxidation reactions of fluoro-olefins. A number of reviews on the synthesis, properties, and applications of fluorocarbon epoxides[21-23] and oxygen-containing fluorocarbon polymers,[10,13,24] involving questions concerning the oxidation of fluoro-olefins, have been published in recent years, but there is no systematic review of the literature data on the oxidation of fluoro-olefins.

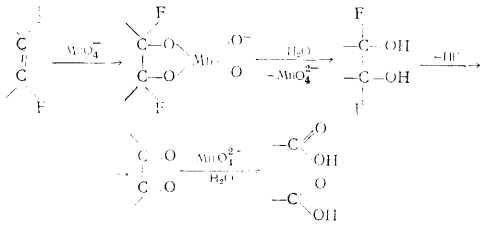
This review discusses what we believe to be some of the most significant questions of the mechanism of the oxidation of fluoro-olefins and the characteristics of the properties of their oxidation products. Attention has been concentrated on the oxidation reactions of two important industrial perfluorinated olefins, namely tetrafluoroethylene (TFE) and hexafluoropropene, with formation of the most important oxidation products—fluorocarbon epoxides.

II. IONIC OXIDATION REACTIONS OF FLUORO-OLEFINS

The oxidation of fluoro-olefins via the ionic mechanism proceeds under mild conditions (atmospheric pressure, room or reduced temperature) in the liquid phase in polar solvents; the oxidants are compounds containing active oxygen: hydrogen peroxide, metal hypohalites, potassium permanganate, etc.

The most important feature of the oxidation of fluoro-olefins via the ionic mechanism is preference for the nucleophilic mechanism due to the increased sensitivity of fluoro-olefins to nucleophilic attack.[25] The epoxidation of fluoro-olefins is accompanied by the simultaneous reaction

leading to the cleavage of the carbon skeleton at the olefin double bond. The first studies were devoted to oxidation processes with dissociation of the double bond and their results have been examined in a review.[25] The most important of these methods involves oxidation with potassium permanganate in neutral or basic aqueous and acetone media. A characteristic feature of such reactions is total hydrolysis of the C–F bonds involving the carbon atoms at the double bond undergoing the dissociation; this entails the formation of carbonyl-containing products: carboxylic acids, CO_2, and ketones:[25]



The hydrolysis of C–F bonds takes place as a consequence of the instability of the intermediate perfluorinated alcohols.[1] The partial conversion of the bound organic fluorine into an inorganic form is a serious technological disadvantage of ionic oxidation processes.

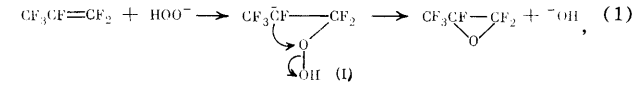
Fluoro-olefins are oxidised by hydrogen peroxide and metal hypohalites in an alkaline medium with preferential formation of epoxides accompanied by side reactions involving oxidation with dissociation of the double bond and also the total hydrolysis of the C–F bonds where the carbon atoms are also part of the double bond undergoing dissociation and the formation of carbonyl-containing products.

The process in which fluoro-olefins are oxidised by an alkaline solution of hydrogen peroxide, developed as early as 1967,[26] still remains one of the main procedures for the synthesis of fluorocarbon epoxides. The oxidation proceeds only in an alkaline medium and the nature of the alkaline agent has no significant influence on the process. KOH, NaOH, NH_4OH, etc. are usually employed. The reaction medium is water; below 273 K, a mixture of water with organic solvents such as methanol and ethanol is used to prevent freezing.[3,26–29] Fluoro-olefins are sparingly soluble in water and alcohol and the reaction therefore proceeds at the interface between the fluorocarbon and aqueous alcoholic phases. The pressure in the system has almost no effect on the oxidation reaction; the process is usually carried out at atmospheric pressure and temperatures between 223 and 323 K;[26] with increase of temperature, the yield of the epoxide diminishes owing to oxidation with rupture of the double bond and with decrease of temperature the rate of epoxidation is appreciably reduced.

An important feature of the method is its universality; it is suitable for the epoxidation of aliphatic fluorocarbon α-olefins,[3,26] internal and cyclic perfluoroalkenes,[30] incompletely fluorinated alkenes,[26] perfluorinated dienes,[31] etc. and the increase of the number of carbon atoms in the fluoro-olefins from 3 to 20 does not influence the rate of epoxidation.[26] However, epoxytetrafluoroethane (ETFE) cannot be obtained by this method.[3,10–12,30]

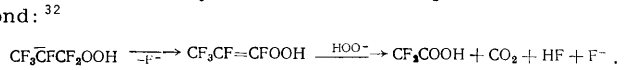
The oxidation with an alkaline solution of hydrogen peroxide is the first method of synthesis of a fluorocarbon epoxide applied on an industrial scale: the Dupont Corporation (USA) has manufactured EHFP since the middle 1960's by oxidising HFP with a 30% aqueous hydrogen peroxide in the presence of methanol and KOH at 243 K and pH of the medium above 8.[10] The yield of EHFP is then about 45%.[11,12] The EHFP obtained in this way contains only HFP and CO_2 as impurities.

The following epoxidation mechanism, incorporating a stage in which the hydroperoxide anion adds to the fluoro-olefin by a nucleophilic mechanism with subsequent elimination of a hydroxide anion, has been proposed:[10]

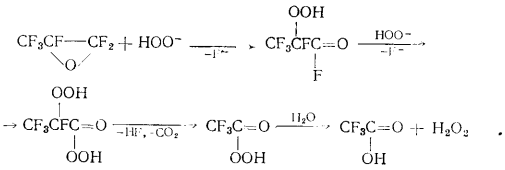


(1)

The intermediate anion (I) can also eliminate a fluoride ion, which leads ultimately to oxidation with rupture of the double bond:[32]



Under oxidation conditions, EHFP reacts relatively easily with the hydroperoxide anion to form acid products:[32]



The acid products formed neutralise the alkali which catalyses the oxidation. Because of this, the reaction is carried out with continuous supply of alkali to the solution in a far from catalytic amount.[33] When the addition of alkali is stopped, the process is rapidly arrested and the selectivity with respect to the oxide is reduced (Fig.1). The low selectivity (50–70%) even at a low conversion of the olefin (Fig.1) is striking. The selectivity in the epoxidation of other fluoro-olefins by hydrogen peroxide is within the same limits.[2,16]

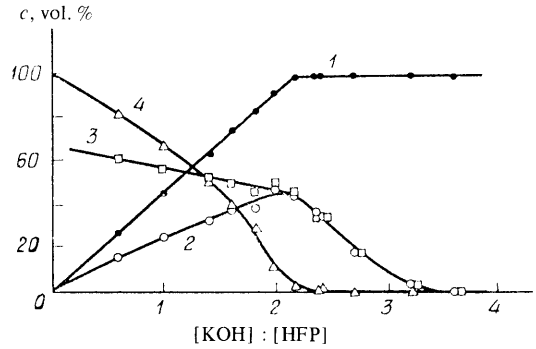


Figure 1. The influence of the molar ratio [KOH]:[HFP] on the composition of the products of the oxidation of HFP (c) with an alkaline aqueous-alcoholic solution of hydrogen peroxide at 273 K: 1) coversion of HFP; 2) yield of EHFP relative to the initial HFP; 3) yield of EHFP relative to the HFP which has reacted; 4) content of HFP in the oxidation products.[32]

A yield of the epoxide of the order of 50% is obtained also in another familiar process: the nucleophilic oxidation of fluoro-olefins by alkali and alkaline earth metal hypohalites in an aqueous alkaline medium in the presence of an aprotic

polar solvent (acetone, diglyme) at room temperature and atmospheric pressure.[34,35]

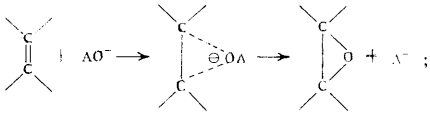
The low selectivity of the epoxidation in nucleophilic oxidation reactions of fluoro-olefins is due to the fairly high probability of the elimination of the fluoride ion from the intermediate anion (I) and the partial consumption of the epoxide in the reaction with the nucleophilic epoxidising agent.

For comparison, one may note that hydrocarbon olefins undergo epoxidation as a rule via an electrophilic mechanism and the oxidants are hydroperoxides and peracids and there is a quantitative (95–99%) yield of the epoxide and the C–H bonds are not involved.

Valuable information about the direction of attack on the double bond by the epoxidising agent and about the structure of the transition state is provided by data on the stereochemistry of the epoxidation reaction. The preferential formation of the epoxide and the stereospecificity of the epoxidation of hydrocarbon olefins by hydroperoxides and peracids are due to the specific direction of electrophilic attack on the bonding orbital of the double bond and the formation of an intermediate π-complex in the reaction[37] (see also Mathieu and Panico,[38] p.319).

The nucleophilic mechanism of the epoxidation of hydrocarbon olefins operates only in the oxidation of αβ-unsaturated carboxylic acids by alkaline hydrogen peroxide[39] and the reaction is non-stereospecific.[40,41] The latter is due to the specific direction of the nucelophilic attack on the antibonding π* orbital of the hydrocarbon olefin[38] (p.295) and the formation in the reaction of an intermediate carbanion of type (I) in which there is ready rotation about the C–C bond.[40,41]

In this connection, a report of the stereospecificity of the nucleophilic epoxidation of fluoro-olefins by hypohalites in an alkaline medium is of special interest:[34,36] since the double bond in fluoro-olefins is depleted in electron density[1] (pp.25, 30), this indicates nculeophilic attack on the bonding π orbital of the fluoro-olefin and the formation of an intermediate cyclic π-complex in the reaction:



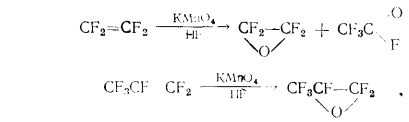
$AO^- = ClO^-$ BrO^- etc.

Thus, the fact that in the chemistry of fluoro-olefins electrophilic epoxidation via hydroperoxides and peracids has been replaced by reactions involving nucleophilic epoxidation by alkaline hydrogen peroxide and hypohalites via the opposite mechanism is a consequence of the radical alteration of the nature of the interaction of the double bond with the epoxidising agent on passing from olefins to fluoro-olefins. The mechanism of the attack on the double bond of the fluoro-olefin by the nucleophilic epoxidising agent is analogous to the mechanism of the attack on the double bond of a hydrocarbon olefin by the electrophilic epoxidising agent.

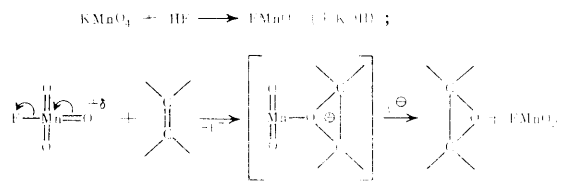
The reversal of the reaction mechanism in relation to the analogous reactions in organic chemistry is characteristic of fluorocarbons. For example, alkylation in the chemistry of hydrocarbon compounds is catalysed by acids,[38] while in the organofluorine chemistry it is catalysed by bases;[42] the catalytic role played by the proton, which is a strong acid in an aqueous medium, in organic chemistry is frequently assumed in organofluorine chemistry by the fluoride ion, which is a strong base in an aprotic medium.[1]

One example of the reversal of the mechanism is the opoxidation of fluoro-olefins by peracids discovered by Knunyants and co-workers:[43,44] methyl perfluoromethacrylate and also its derivatives are readily epoxidised by *p*-nitroperbenzoic acid in absolute ether at room temperature, but in this case the Prilezhaev reaction proceeds via a nucleophilic mechanism as a consequence of the exceptionally high electrophilicity of the perfluoromethacrylic acid ester.

The sensitivity of fluoro-olefins to electrophilic attack is low, so that their oxidation via an electrophilic mechanism is hindered. The only instance of the epoxidation of fluoro-olefins via an electrophilic mechanism is oxidation by potassium permanganate in anhydrous hydrogen fluoride at 203 K:[45]

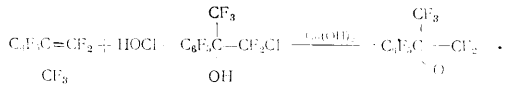


The reaction proceeds via a stage involving electrophilic attack by manganic acid fluoride on the double bond:[45]

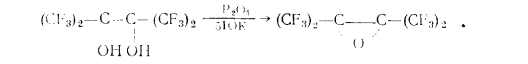


The ionic oxidation reactions of fluoro-olefins examined are characterised by a high rate and take place under mild conditions in reactive polar solvents (water, alcohols, HF, etc.) using as oxidants compounds with active oxygen (H_2O_2, $KMnO_4$, metal hypohalites, and peracids). The complete absence of polymeric products with perfluoropolyether and perfluoropolyperoxide structures, characteristic of radical oxidation reactions of fluoro-olefins, is striking. Overall, the ionic oxidation reactions of fluoro-olefins are characterised by a much lower selectivity of the epoxidation compared with the electrophilic epoxidation of hydrocarbon olefins.

The method of synthesis of fluorocarbon epoxides involving the dehydrogenation of halogenoalcohols in the presence of aqueous solutions of alkalies on brief (5–10 min) heating to 348–373 K has been developed:[119,120]



The epoxide is also formed on dehydration of perfluoropinacol:[21]



However, only the syntheses of fluorocarbon epoxides via fluoro-olefin oxidation reactions are of practical importance.

III. ELECTROCHEMICAL AND HETEROGENEOUS-CATALYTIC OXIDATION OF FLUORO-OLEFINS

In terms of their conditions, the chemical nature of the oxidants employed, and the character of the products formed, the reactions indicated occupy an intermediate position between ionic and radical oxidation reactions of fluoro-olefins. Metallic silver is known to have unique catalytic activity in relation to the epoxidation of ethylene by oxygen.[46–48]

Tetrafluoroethylene is also oxidised by oxygen in the presence of a silver catalyst with formation of epoxytetrafluoroethane (ETFE), carbonyl difluoride (CDF), and small amounts of perfluorocyclopropane and oligomers with a poly(difluoromethylene oxide) structure. Below 400 K, TFE is not oxidised in the presence of silver, but at a higher temperature virtually the only oxidation products are ETFE and CDF, i.e. the reaction proceeds via two pathways like the oxidation of ethylene:[47]

$$CF_2{=}CF_2 + \frac{1}{2}O_2 \rightarrow CF_2{-}CF_2{-}158\ \text{kJ}; \quad (2)$$

$$CF_2{=}CF_2 + O_2 \rightarrow 2COF_2 - 614\ \text{kJ}. \quad (3)$$

In the range 403–433 K, there is a virtually linear increase of the rates of formation of ETFE and CDF with increase of temperature (Fig. 2) accompanied by a constant selectivity of the epoxidation in the range 55–67 vol.%,[49] which agrees with the selectivity of the epoxidation of ethylene in the presence of silver.[45–47] The optimum temperature of the epoxidation of TFE in the presence of silver is 410–430 K,[49] i.e. appreciably below the optimum temperature of the epoxidation of ethylene, which is in the range 500–570 K;[45–47] with increase of temperature, CDF becomes the only product.

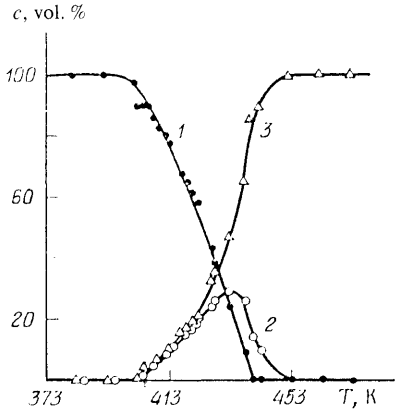


Figure 2. Temperature variation of the composition of the products of the heterogeneous-catalytic oxidation of TFE by atmospheric oxygen in the presence of a granulated silver catalyst in a flow reactor at atmospheric pressure, for the molar ratio O_2 : TFE = 1.2, and at a space velocity of the supply of TFE of 1.1 min^{-1}: 1) TFE; 2) ETFE; 3) CDF.[49]

The above data indicate a higher catalytic activity of silver in the epoxidation of TFE compared with the epoxidation of ethylene. This conclusion agrees well with the mechanism of the epoxidation in the presence of silver: TFE is much more active than ethylene in reactions with nucleophiles,[25] which facilitates its reaction with oxygen chemisorbed on the surface of silver in the form of the peroxide anion, which is the epoxidising agent.[45,46,50]

The activation energies for the epoxidation of TFE [reaction (2)] and the formation of CDF [reaction (3)] in the presence of the silver catalyst in the temperature range 408–433 K are respectively 100 ± 18 and 128 ± 35 kJ mol^{-1}, i.e. they exceed somewhat the activation energies for the analogous stages in the oxidation of ethylene:[49] and 80 and 90 kJ mol^{-1}.

The carbonyl difluoride formed in the oxidation of TFE is a highly active fluorinating agent,[1] so that the silver catalyst is poisoned as a result of the formation of surface silver fluorides.[48] The silver catalyst fully deactivated in relation to the reaction (2) behaves in reaction (3) analogously to inert quartz packing:[51] it does not initiate oxidation below 500 K; at 503 K a branched chain oxidation reaction with formation of CDF alone begins.

The heterogeneous-catalytic epoxidation of fluoro-olefins in the presence of silica gel,[52–54] which has no analogue in the chemistry of hydrocarbon compounds, is of interest. Before use as the catalyst, the silica gel is first activated at 448–673 K in a stream of air and the fluoro-olefin for 0.5 to 25 h. The oxidation is carried out in a flow reactor at atmospheric pressure, the space velocities at which the fluoro-olefin and the oxygen are supplied are 0.22 and 0.11 min^{-1}, and the optimum epoxidation temperatures are 463–498 K for HFP and 273–323 K for TFE. A yield of EHFP in excess of 80% relative to the HFP which has reacted is then attained for a conversion of 10–40%.[52–53] In the epoxidation of TFE the yield of the epoxide is more than 70% relative to the olefine which has reacted for a conversion of the latter of 40–90%.[54]

There are no data concerning the mechanism of the epoxidation of fluoro-olefins in the presence of silica gel, the process is poorly reproducible, and silica gel decomposes vigorously during activation and oxidation owing to its reaction with CDF with formation of gaseous CO_2 and SiF_4. In the activation of silica gel there is a possibility of partial conversion of surface SiOH groups into the hypofluorite groups SiOF, which can initiate radical oxidation.[54]

The electrochemical epoxidation of HFP in 80% acetic acid, acetonitrile, and an alkaline solution of sodium perchlorate using a perfluorinated ion-exchange membrane of the "nafion" type for the separation of the cathodic and anodic compartments occupies an intermediate position as regards conditions and mechanism.[55–56] At 293 K, atmospheric pressure, and a current density of 10–50 mA cm^{-2} the process is characterised by a selectivity of the epoxidation of 45–65% for a conversion of HFP of 30–50%; the current yield is 20–35% and the side products are CO_2, HF, and C_2F_5COOH.

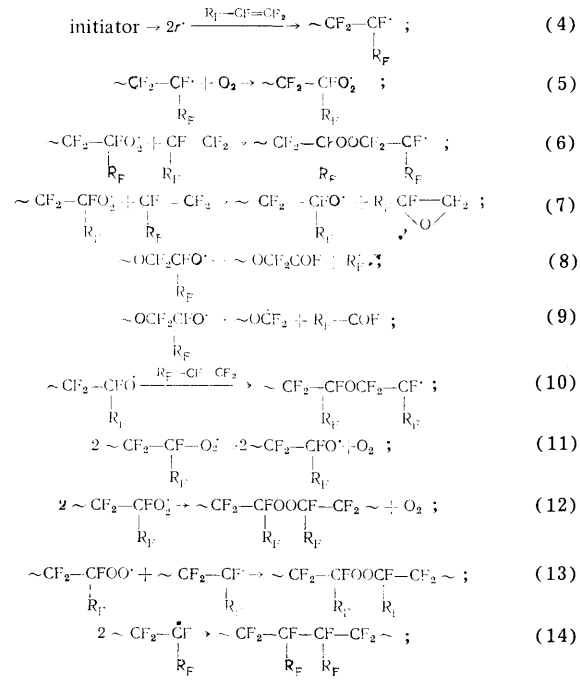
IV. OXIDATION OF FLUORO-OLEFINS VIA A RADICAL MECHANISM

Terminal fluoro-olefins are readily oxidised by molecular oxygen in both gas and liquid phases. There is at present no doubt about the fact that the oxidation of fluoro-olefins proceeds via a free-radical chain mechanism involving a large number of elementary chain propagation and termination stages and also a stage in which the free radicals decompose and which leads to the formation of non-radical products. The composition of the products and the mechanism of the oxidation of fluoro-olefins therefore vary within wide limits depending on the process conditions. For chain oxidation reactions, the selectivity is a function of the chain length, the degree of conversion, and process conditions (solvent, temperature, surface of reaction vessel) and depends on the constants for the elementary stages of the process and also on the concentrations of the substances involved in the chemical reaction.[58]

The mechanism of the oxidation of perfluoro-olefins differs little from the mechanism of the oxidation of unsaturated hydrocarbon analogues. In fluoro-olefins the C–F bond,

whose energy is 448–485 kJ mol^{-1},[1,59] is stronger than the C–H or C–C bond and the oxidation therefore proceeds directly at the double bond and not at the C–F bond. The process is more selective and proceeds with a much smaller number of side products than in the oxidation of olefins, where reaction takes place via a stage in which the hydrogen atom is abstracted preferentially from the α-position relative to the double bond of the olefin.[60,61] The oxidation of fluoro-olefins results in a formation of carbonyl-containing products with a smaller number of carbon atoms than in the initial olefin (acyl fluorides, ketones) and oligomeric products with a perfluoropolyether and perfluoropolyperoxide structures. The C–F bond is also not involved in the formation of these products.

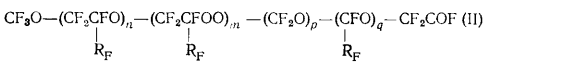
The composition of the products indicates the applicability in the oxidation of fluoro-olefins of the Mayo–Sianesi scheme, which treats oxidation as the simultaneous radical copolymerisation of the olefin and oxygen and the decomposition of the growing radicals:[62,63]



where R_F = F, perfluoroalkyl, or perfluoroalkoxy-group and $\dot{r}$ is the initiator radical.

Only terminal fluoro-olefins are oxidised via a radical mechanism.[10–13] Internal and cyclic fluoro-olefins are almost inert to radical oxidation, which agrees with their low reactivity in radical polymerisation.

The initiated oxidation of terminal fluoro-olefins proceeds already at a temperature below 273 K with the predominance of stages (5) and (6), characterised by a lower activation energy compared with the stages leading to the formation of the epoxide and acid fluorides [stages (7)–(9)]. The main products of the low-temperature oxidation are oils with the perfluoropolyether and perfluoropolyoxide structures having the general formula[13]



Perfluoroalkyl radicals combine with oxygen much faster than the fluoro-olefin molecule and for this reason blocks consisting of several fluoro-olefin fragments are absent from the polymer.[63] The low-temperature oxidation of fluoro-olefins is initiated by ozone,[64,65] oxygen difluoride,[66] etc. The low-temperature oxidative polymerisation of fluoro-olefins under the influence of ultraviolet radiation, which, apart from initiation, induces the conversion of the peroxy-groups into ether groups in the polymer formed, is technologically the most effective.

The oxidative photopolymerisation of fluoro-olefins is carried out in the temperature range from 173 to 353 K and the optimum oxidation temperature for TFE and HFP is 263 K.[67,68] Pressure is used only to keep the fluoro-olefin in the liquid state.[67]

The oxidation proceeds via a free-radical chain mechanism with degenerate chain branching. Chain branching takes place as a result of the photolysis of the perfluoroacyl fluoride and peroxides which have accumulated during the reaction as a result of photolysis. The quantum-chemical yield of the oxidative photopolymerisation of fluoro-olefins is in the range from 10 to 85.[63,69] The radiation-chemical yield in the oxidative polymerisation of HFP at 300 K under the influence of ^{60}Co γ-rays exceeds 160.[70] The effective activation energy for the oxidative photopolymerisation of perfluorinated alkyl vinyl ethers 2.1–4.2 kJ mol^{-1}.[69] In initiation by ultraviolet light, radiation with wavelengths in the range 2600–3200 Å is the most effective;[63] radiation with wavelengths below 2600 Å induces the preferential formation of peroxy-groups, while longer-wavelength radiation promotes the formation of the perfluoropolyether structure.[71]

Fluoro-olefins and oxygen hardly absorb the ultraviolet light from mercury quartz lamps; in practice sensitisers are not used in liquid-phase photochemical oxidation. The reaction begins after a short induction period during which a small amount of products having the perfluorodialkyl peroxide and perfluoroacyl fluoride structures accumulate in the system and subsequently initiation takes place as a result of the photolysis of these compounds.[63] The applicability of scheme (4)–(14) to the description of the kinetics of the oxidative photopolymerisation of fluoro-olefins has been demonstrated by Sianesi and has been discussed in two communications.[9,13]

Only the oxidative photopolymerisation of TFE [72–76] and HFP [63,67,77–79] is of practical value and the main bulk of publications have been devoted to the development of the process in relation to these two monomers. The oxidative photopolymerisation of HFP is carried out in the bulk of the olefin, the yield of the transparent viscous product having structure (II) exceeds 90%, the average degree of polymerisation is 30–40 units, the hexafluoropropylene oxide units are joined mainly "head to tail",[63] and the side products are gaseous COF_2, CF_3COF, and EHFP.[67]

The oxidative photopolymerisation of TFE is carried out in an inert solvent, the yield of the viscous polymeric product having structure (II) and a molecular weight of 10^4–10^5 is 40–50%,[63] the distribution of the difluoromethylene oxide and tetrafluoroethylene units in the chain is random, the peroxy-groups are mainly linked to the CF_2–CF_2 units, and CDF and ETFE are formed as gaseous products.[63]

Oxidative photopolymerisation of HFP is a simple and cheap method of synthesising perfluoropolyether oils.[13,80] The ratio of the peroxide and ether units in the polymer is defined by the equation[63]

$$\frac{m}{n} = \frac{k_{13}\,[\mathrm{HFP}]}{2\,(1 + k_{11}/k_{12})\,k_{12}^{1/2} I^{1/2}},$$

where k_{11}, k_{12}, and k_{13} are the rate constants for the elementary stages and I is the density of the radiation.

With increase of the temperature of the initiated oxidation of fluoro-olefins, stages (7)–(9) involving the decomposition of the growing radicals, which have higher activation energies than stages (5) and (6), become dominant. As a consequence of this, the yield of the polymeric products with structure (II) falls, the molecular weight decreases, fragments of the difluoromethylene oxide structure predominate in the polymer, and the yield of the epoxide and the carbonyl-containing products, formed as a result of oxidation with rupture of their double bond, increases.[63] In the range 370–420 K the main fluoro-olefin oxidation product is the epoxide, while at temperatures above 470 K the products resulting from the dissociation of the double bond are virtually the only ones.

By studying the kinetics of the low-temperature oxidation of HFP in the gas phase and using the principle of the quasi-stationary concentrations of free radicals, it has been shown on the basis of the scheme presented above[13] that the rate of reaction is described by the equation

$$\frac{d[O_2]}{dt} = \frac{1}{2}\left(1 + \frac{k_{11}}{k_{12}}\right) I \text{ and } \frac{d[HFP]}{dt} = \frac{1}{2}\frac{k_{11}}{k_{12}} I ,$$

while the rate of the photochemical low-temperature oxidation of HFP in the liquid phase is given by the equations

$$-\frac{d[O_2]}{dt} = \left(1 + \frac{k_{11}}{k_{12}}\right) I + k_{13}(I/k_{12})^{1/2}[HFP] ,$$

$$-\frac{d[HFP]}{dt} = 2\left(\frac{k_{11}}{k_{12}}\right) I + k_{13}(I/k_{12})^{1/2}[HFP] ,$$

The equations for the rates of formation of the epoxide (w_e) and carbonyl-containing oxidation products formed with dissociation of the double bond (w_c) from the fluoro-olefin (M) are as follows:

$$w_e = k_7[M]\left(\frac{w_i}{S}\right)^{1/2} , \quad (15)$$

$$w_c = (k_9 + k_8)\frac{k_7[M](w_i/S)^{1/2} + k_{11}(w_i/S)}{k_5 + k_9 + k_{10}[M]} , \quad (16)$$

where w_i is the rate of initiation and

$$S = k_{12} + 2k_{13}\frac{k_6 + k_7[M]}{k_5[O_2]} + k_{14}\frac{(k_5 + k_7)^2[M]^2}{k_5^2[O_2]^2} . \quad (17)$$

Compared with the rate of formation of carbonyl-containing products [Eqn.(16)] the rate of epoxidation [Eqn.(15)] depends to a greater extent on the concentration of the olefin and to a lesser extent on the rate of initiation. The selectivity of the epoxidation in the radical oxidation reactions of fluoro-olefins therefore increases with increasing olefin concentration and with decrease of the rates of initiation.

At low oxygen concentrations, chain termination takes place mainly via reaction (14), the rates of reactions (12) and (13) can be neglected, and the expression for the rate of epoxidation becomes

$$w_e = \frac{k_7 k_5[O_2]}{k_{14}^{1/2}(k_5 + k_7)} \cdot w_i^{1/2} , \quad (18)$$

i.e. the rate of epoxidation is proportional to the concentration of oxygen and is independent of the concentration of the olefin.

At high oxygen concentrations, where the main chain termination reaction is reaction (12) and the rates of reactions (13) and (14) can be neglected, the expression for the rate of epoxidation becomes

$$w_e = k_7[M]\left(\frac{w_i}{k_{12}}\right)^{1/2} , \quad (19)$$

i.e. the rate of epoxidation is independent of the oxygen concentration and is proportional to the olefin concentration. Under these conditions, the effective activation energy for epoxidation E_{eff} is defined by the expression

$$E_{eff} = \frac{1}{2}E_i + E_7 - \frac{1}{2}E_{12} , \quad (20)$$

where E_i is the activation energy for the initiation stage and E_{12} the activation energy for the recombination of the peroxy-radicals, which is zero.[81] The initiated oxidation of fluoro-olefins by oxygen at an elevated temperature is carried out in a flow regime in the gas phase at atmospheric pressure; sometimes the volume of the reactor is filled with an inert solvent.

The photoinitiated oxidation is of practical interest as the most effective method of synthesis of ETFE. Among processes of this type, the gas-phase oxidation of TFE has been most thoroughly investigated. Here too radiation at a wavelength below 3200 Å is the most effective.[82] Sensitisers are used in this reaction: mercury vapour,[83] bromine, chlorine, nitrogen oxides, hydrogen bromide,[82] etc. Bromine is the most active in this series of sensitisers.

A biradical chain mechanism is feasible for the gas-phase photochemical oxidation of fluoro-olefins sensitised by mercury vapour:[83,84,86]

$$Hg \xrightarrow{h\nu} Hg^* \xrightarrow{C_2F_4} C_2F_4^* \xrightarrow{O_2} \dot{C}F_2\dot{O}_2 + \ddot{C}F_2$$

$$\dot{C}F_2\dot{O}_2 + C_2F_4 \rightarrow C_2F_4O + COF_2 ,$$

$$\dot{C}F_2\dot{O}_2 + \ddot{C}F_2 \rightarrow 2COF_2 .$$

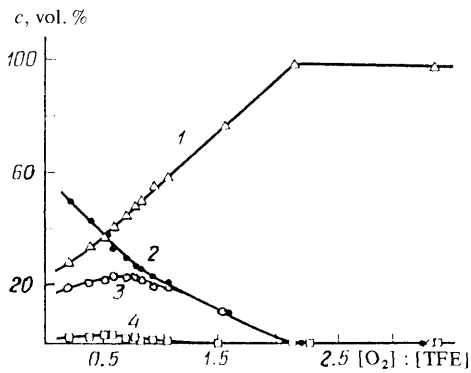


Figure 3. The influence of the molar ratio $[O_2]:[TFE]$ on the composition of the products of the gas-phase photochemical oxidation of tetrafluoroethylene by atmospheric oxygen at 365 K, at atmospheric pressure, and for a residence time in the reaction zone of 1.5 min and the molar ratio $Br_2:TFE = 2 \times 10^{-4}$: 1) CDF; 2) TFE; 3) ETFE; 4) perfluorocyclopropane.[87]

The gas-phase oxidation of TFE by oxygen in a flow reactor at atmospheric pressure, a temperature of 370–400 K, for the molar ratio $O_2:TFE = 0.8$, for a residence time of the reactants in the reaction zone of 1.5 min, and for a power of a moderate pressure mercury quartz lamp of 1395 W is characterised by yields of ETFE of 21–23% relative to the TFE which has reacted for a conversion of the latter of 65–70% (Fig.3).[82,87] CDF is a side product in the process

and the yield of oligomeric products does not exceed 5%.[82] The oligomeric products formed at an elevated temperature have the poly(difluoromethylene oxide) structures (III) and (IV) [88,89] with a low content of peroxy-groups:

$$\underset{\text{(III)}}{CF_3O-(CF_2O)_n-CF_2COF} \qquad \underset{\text{(IV)}}{CF_3O-(CF_2O)_n-COF}$$

The structure of the oligomers is determined by the lower rate of decomposition of the corresponding alkoxy-radicals ($\sim CF_2OCF_2O^{\cdot} \rightarrow \sim CF_2O^{\cdot} + COF_2$) compared with the rates of reactions (8) and (9), because the dissociation energy of the C–O bond in perfluoropolyethers (418 kJ mol^{-1}) [10] exceeds significantly the energy of the C–C bond, which is 338–376 kJ mol^{-1}.[10]

The oxidation reactions of fluoro-olefins are much more exothermic than the oxidation reactions of olefins. The exothermic effect in the oxidation of TFE to CDF is 614 kJ mol^{-1}, while in the analogous reaction involving the oxidation of ethylene to formaldehyde 286 kJ mol^{-1} is evolved.[90] The energetic stabilisation of the reaction products is therefore important in the fluoro-olefin oxidation reactions designed to obtain incomplete oxidation products, particularly expoxides. Thus, in the oxidation of TFE or HFP by atomic oxygen in the gas phase, the excited epoxide molecules formed initially do not have enough time for stabilisation and decompose with formation of CDF and difluorocarbene.[84–86]

The increase of the efficiency of the energetic stabilisation of the products resulting from the oxidation being carried out in the liquid phase leads to an increase of the yield of the epoxide. The photochemical oxidation of TFE by oxygen at 390 K in a flow regime with the reactor volume filled by an inert perfluorinated solvent makes it possible to raise the yield of TFE to 60–70% relative to the TFE which has reacted.[11,12,82] This process is one of the most effective methods of synthesis of TFE and is used as a preparative method for this purpose.[11,12] However, judging from the existing publications, there is as yet no industrial manufacture of ETFE by this procedure.

The radical oxidation of fluoro-olefins via scheme (4)–(14) is effectively initiated, apart from ultraviolet radiation, by ionising radiation, ozone, and oxygen difluoride.

The radiation-chemical oxidation of fluoro-olefins in the gas phase at an elevated temperature leads to the formation of an epoxide, carbonyl-containing products of oxidation with rupture of the double bond, and a small amount of polymers having the difluoromethylene oxide structures (III) and (IV).[82,91] An increase of the hardness of the ionising radiation reduces the yield of the epoxide and the degree of conversion of the olefin:[91] a fall of temperature entails a decrease of the degree of conversion and of the relative yield of gaseous products,[91] but the ratio of the yields of CDF and the epoxide remains constant under these conditions; an increase of the pressure entails some increase of the rate of the gas-phase radiation-chemical epoxidation of TFE,[92] the yield of the epoxide diminishing with increase of the oxygen : olefin ratio.[92] The radiation-chemical yield of the gas-phase oxidation of TFE and chlorotrifluoroethylene by molecular oxygen at room temperature and atmospheric pressure and under exposure to X-rays (50 kV) is in the range 900–3300.[74]

The gas-phase oxidation of fluoro-olefins by ozonised oxygen at room or an elevated temperature makes it possible to obtain epoxides in satisfactory yields. The oxidation of TFE by ozonised oxygen in a flow reactor at 288 K with the molar ratios $TFE:O_3 = 31.7$ and $TFE:O_2 = 1$ makes it possible to obtain ETFE in 46% yield relative to the TFE which has reacted for a conversion of the latter of 41.3%.[93] The yield of the polymeric products having structure (II) and a molecular weight of 1.5×10^3 is 19%.[93] The main structural unit of the polymer is CF_2O; the number of terminal CF_3O groups in the polymer is twice as large as the number of acid fluoride groups;[63] when the molar ratio $TFE:O_2$ is raised from 0.5 to 1.8, the number of peroxy-groups in the polymer falls from 5 to 3 per 100 CF_2O units; the content of C–C bonds in the polymer is then almost constant and is 5–6 bonds per 100 CF_2O units.[63]

It is possible to epoxidise TFE with pure ozone at 273 K, whereupon the yield of the epoxide is 50% for the molar ratio $O_3:TFE = 0.01$,[94] but, with increase of this ratio, the yield of the epoxide falls sharply and for the molar ratio $O_3:TFE = 1$ virtually the only product is CDF.[94]

Tetrafluoroethylene reacts readily with OF_2 in the dark to form an equimolar mixture of CF_4 and CDF; ETFE was not then detected.[95] Under the influence of ultraviolet radiation, the main reaction product is the epoxide.[21,95] For example, irradiation of a mixture of HFP and OF_2 with quartz ultraviolet light in the gas phase at room temperature in the course of 12 h leads to a yield of EHFP of 42% for a conversion of HFP of 57%.[95]

Catalytic epoxidation of fluoro-olefins by oxygen difluoride in the presence of silver difluoride is also known.[21,96] The reaction is carried out in a stainless steel flow reactor in the gas phase or in the presence of an inert solvent for the molar ratio OF_2 : olefin = 1 : 1 (at 333 K); the yield of the epoxide in the oxidation of HFP is 23 vol.%.[96]

In the presence of molecular oxygen OF_2 is an effective initiator of the oxidation of fluoro-olefins and the main oxidation product is the epoxide.[97]

The oxidation of fluoro-olefins initiated by oxygen difluoride proceeds at a temperature as low as 238–253 K; with increase of temperature, the rate of reaction increases and becomes technologically acceptable, starting from room temperature. The optimum epoxidation temperature depends on the chemical nature of the olefins and is in the range between room temperature and 393 K. The process is characterised by a series of kinetic features inconsistent with the Mayo–Sianesi scheme defined by Eqns.(4)–(14). Under the otpimum conditions, the yield of the epoxide exceeds 90%,[97] while according to the Mayo–Sianesi scheme the selectivity of the epoxidation should not exceed 67 vol.%.[62] The main side products are CDF, perfluoroacetyl fluoride, and small amounts of a polymeric product.[97] With increase of the amount of OF_2 introduced into the reaction mixture, the rate of oxidation and the yield of the epoxide relative to the olefin which has reacted also rise, which likewise conflicts with the Mayo–Sianesi scheme [see Eqns.(15) and (16)]. For example, in the oxidation of 6-monohydroundecafluorohex-1-ene in bulk at 393 K in the course of 4 h, an increase of the amount of OF_2 supplied to the reactor from 1.6 to 1000 ml per 1000 ml of oxygen leads to an increase of the degree of conversion of the olefin from 87.8 to 100% and to an increase of the yield of the epoxide from 59.4 to 92% relative to the olefin which has reacted.[97] The above features of the process show that, in the presence of oxygen, oxygen difluoride behaves not only as an initiator but also as a highly effective epoxidising agent.

The epoxidation with the $OF_2 + O_2$ mixture is more selective and proceeds steadily in the liquid phase, in the bulk of the olefin, or in an inert solvent.[97]

The formation of only products of oxidation with rupture of the double bond [polymeric products having structures (III) and (IV)] in the absence of epoxides is characteristic of the thermal or initiated oxidation of fluoro-olefins by oxygen in the gas phase at temperatures above 473 K.[72,98–100] The reaction of TFE with the oxygen in a shock wave results in the formation of CO_2, CF_4, C_2F_6, etc. together with CDF, but ETFE is absent.[101]

When the thermal oxidation of fluoro-olefins with oxygen is carried out in the liquid phase, the epoxide is formed as the main product; in addition, carbonyl-containing products of oxidation with rupture of the double bond and oligomeric products having structures (III) and (IV) are formed.[102-105] The oxidation is carried out at 320–520 K, the optimum temperatures for the epoxidation of different fluoro-olefins not being the same:[102] they are 348 K for chlorotrifluoroethylene, 360–380 K for TFE, and 400–420 K for HFP.

It is best to keep the molar ratio O_2:olefin below unity, since in the presence of an excess of oxygen the yield of the epoxide is reduced.[102] The solvents employed are perhalogenated compounds, for example, $CF_2ClCFCl_2$, CCl_4, etc. In order to maintain the fluoro-olefin in the liquid phase, the oxidation is carried out at an elevated pressure.

The thermal liquid-phase oxidation of fluoro-olefins is a degenerate-branched chain process, which is indicated by the S-shape of the kinetic curves (Fig.4), the complete supporession of the oxidation following the addition of inhibitors, even weak ones such as quinone or nitroxy-radicals, and the elimination of the induction period on treatment with initiators even at 50 °C (in the absence of an initiator, the oxidation becomes appreciable only at temperatures above 100 °C after a prolonged induction period).[106]

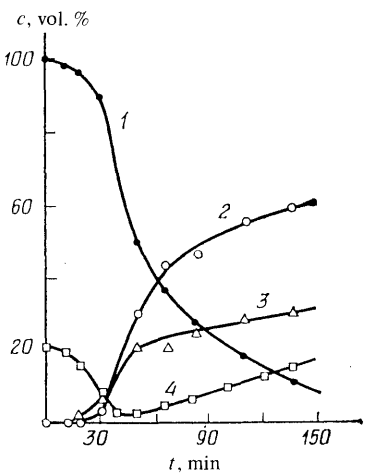


Figure 4. Kinetic curves for the thermal liquid-phase oxidation of HFP by compressed air (rate of supply 9 litre h^{-1}) in Khladon-113 at an initial HFP concentration of 0.13 M, 423 K, and a pressure of 5 MPa: 1) HFP; 2) EHFP; 3) trifluoroacetyl fluoride; 4) O_2 content in effluent gases from the reactor.[109]

The branching agents are the oligomeric peroxy-compounds with structures (III) and (IV) formed.[106,107] The chemical and nature of the solvent, the material of the reactor, and the state of the walls exert a marked inlfuence on the yield of the epoxide and other oxidation products.

The metallic surface of the reaction vessel has a catalytic effect on reactions leading to the formation of acid fluorides and oligomeric products, the selectivity with respect to the epoxide being reduced.[106] In stainless steel reactors in Freon-113, the yiled of EHFP does not exceed 40–50% relative to the HFP which has reacted, while in PTFE reactors the yield of the epoxide reaches 70–80%.[106,107] The effect of the reactor walls is reduced when the solvents employed are highly viscous liquids, consisting of mixtures of aliphatic fluorocarbons and perfluorinated ethers,[106] owing to the decrease of the rate of diffusion of the species decomposing on the wall.

In contrast to the low-temperature photoinitiated oxidation of TFE and HFP, where the rate of reaction and the selectivity are independent of the ratio of the oxygen and olefin concentrations and depend solely on the radiation intensity,[13] the ratio of the rates of accumulation of the corresponding epoxides and acyl fluorides in the thermal oxidation increases linearly with increase of the fluoro-olefin concentration[109] and diminishes with increase of the initial O_2 concentration.[110] A decrease of the selectivity with respect to the epoxide as a function of the O_2 concentration has also been observed in the oxidation of a number of olefins:[62,111]

$$\frac{w_{ox}}{w_{ol}} = \frac{1}{A + B[O_2]}, \qquad (21)$$

where w_{ox} is the rate of formation of the olefin oxide, w_{ol} the rate of consumption of the initial olefin and A and B are constants which incorporate the ratios of the rate constants for the elementary stages. In most cases this type of relation is observed only over a certain part of the O_2 concentration range.

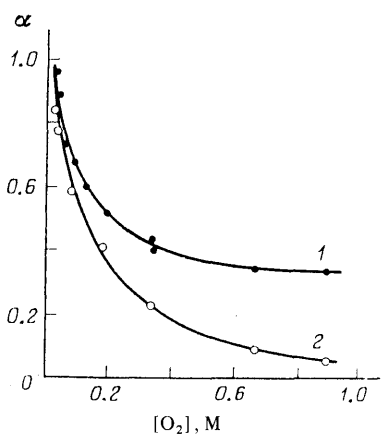


Figure 5. Dependence of the selectivity of the epoxidation α of perfluoro-octene (curve *1*) and HFP (curve *2*) on the initial O_2 concentration.[110]

At initial O_2 concentrations appreciably less than the initial fluoro-olefin concentration, the selectivity with respect to the epoxide is close to 100% and falls sharply with increase of the O_2 concentration, tending to a definite limit, which depends on the nature and length of the hydrocarbon chain of the fluoro-olefin (Fig.5). It follows from Table 1 that the oxidation of TFE in an excess of oxygen yields only COF_2 and a polymer, while in the oxidation of HFP and perfluoro-octene the yields of the corresponding epoxides reaches 20 and 36% with respect to the consumed olefin.

These data show that the mechanism of the oxidation of olefins put forward in a number of studies[4,14,62] cannot account either for the limit in the selectivity with respect to

the oxide on further increase of the O_2 concentration or for the high yields of the epoxides. It permits a theoretically feasible yield not greater than 66%, whereas in the oxidation of certain olefins and fluoro-olefins containing more than two carbon atoms their selectivity with respect to the epoxide reaches 70–100% for a conversion in an excess of 50%.[102,107,110,113] In order to explain such a high selectivity in the epoxidation of fluoro-olefins, the decrease of the process selectivity with increase of the O_2 concentration, and also the accumulation of equimolar amounts of CDF and acyl fluorides in which the number of carbon atoms is one less than in the initial olefin, the oxidation mechanism was supplemented[109] by the stage involving decomposition of the perfluoroperoxyalkyl radicals into two epoxide molecules:

$$RO_2-CF_2-\underset{R_F}{\underset{|}{CF}}OOCF_2\dot{C}F\underset{R_F}{\underset{|}{}} \rightarrow 2R_FCF\underset{O}{\diagdown\diagup}CF_2 + R\dot{O}_2 \quad , \qquad (22)$$

and also a stage involving the isomerisation and decomposition of the perfluoroalkylperoxy-radicals with rupture of the carbon skeleton:[106]

$$RO_2CF_2-\underset{R_F}{\underset{|}{CF}}-O\dot{O} \longrightarrow RO_2-CF_2-\underset{O-\underset{R_F}{\underset{|}{C}}-O}{\underset{\diagdown\diagup}{}}-CF-R_F \longrightarrow R\dot{O}_2 + R_FCOF + COF_2 \qquad (23)$$

Table 1. Dependence of the yield of the epoxide on the length of the carbon chain of the fluoro-olefin for the ratio O_2 : fluoro-olefin = 3.

Fluoro-olefin	T, K	α, %	Refs.
C_3F_4	265	0	[112]
C_5F_6	393	20	[114]
C_8F_{16}	370	36	[110]

Notation: T is the oxidation temperature and α the yield of the fluoro-olefin oxide.

This pathway, leading to the formation of acyl fluorides, is dominant for long oxidation chains. If the chains are short, then the reaction of perfluoroalkoxy-radicals, formed in a quadratic interaction of the perfluoroalkylperoxy-radicals [reactions (8) and (9)], makes a significant contribution to the overall rate of formation of acyl fluorides:

$$RO_2-CF_2-\underset{R_F}{\underset{|}{CF}}\dot{O} \xrightarrow{O_2} \begin{cases} \longrightarrow RO_2-CF_2-COF + R_F\dot{O}_2 \ , \\ \longrightarrow RO_2-CF_2O\dot{O} + R_FCOF \ , \end{cases}$$

$$R_F = CF_3, \ldots C_nF_{2n+1} \ .$$

This regime is attained at high rates of initiation comparable to the rate of oxidation (chain length ≤ 10 units). In the liquid-phase oxidation of HFE a linear dependence of the ratio of the rate of accumulation of the sum of perfluoroacetyl fluoride and CDF to the rate of formation of EHFP on the square root of the rate of initiation is observed.[114] It is known that an excess of oxygen in free radical oxidation reactions results in the predominance of the system of $R\dot{O}_2$ radicals[60] which cannot produce the epoxide if one adopts the mechanism of the epoxidation of fluoro-olefins and the formation of perfluoroacyl fluorides [reactions (22) and (23)] presented above. However, in the oxidation of perfluoro-octene even at high oxygen concentrations (Fig.5) the formation of epoxyperfluoro-octane is observed (up to 40 mole % relative to the perfluoro-octene which has reacted).

In order to account for the observed limit in the selectivity of the expoxidation of fluoro-olefins as the O_2 concentration increases, it has been suggested that, as in the oxidation of the usual olefins,[113] a molecular epoxidation mechanism as well as the radical mechanism can operate in the oxidation of fluoro-olefins.[110] One of the possible pathways in the non-radical epoxidation mechanism is apparently the interaction of the cyclic peroxide formed via a radical mechanism:[113,115]

$$RO_2-CF_2-\underset{R_F}{\underset{|}{CF}}O\dot{O} \rightarrow R\dot{O}_2 + R_F-\underset{O-O}{\underset{|\quad|}{C}}-CF_2 \quad , \qquad (24)$$

On the one hand, this peroxide can react with a second fluoro-olefin molecule to produce two epoxide molecules and, on the other, it can decompose into perfluoroacetyl fluoride and COF_2:

$$R_F-\underset{O-O}{\underset{|\quad|}{\overset{F}{\overset{|}{C}}}}-CF_2- \longrightarrow R_F-COF + COF_2 \ , \qquad (25)$$

$$\xrightarrow{R_FCF=CF_2} 2R_F-CF\underset{O}{\diagdown\diagup}CF_2 \ , \qquad (26)$$

The introduction of a molecular mechanism of the epoxidation of fluoro-olefins made it possible to explain virtually all the observed kinetic features: the high selectivity of the epoxidation, the appearance of a limit in the selectivity with respect to the epoxide as the initial O_2 concentration increases, the formation of equimolar amounts of CDF and perfluoroacyl fluoride containing a smaller number of carbon atoms than in the initial olefin, and also the influence of the reaction vessel wall, which catalyses the decomposition of the above peroxides and the peroxy-radicals with dissociation of the C–C bond.

High-temperature oxidation by molecular oxygen in order to obtain epoxides is possible only for terminal fluoro-olefins, while internal and slight fluoro-olefins do not give rise to epoxides.[102] The oxidation of TFE and chlorotrifluoroethylene by this method is difficult to achieve for technical reasons owing to the risk of explosion. Thermal liquid-phase epoxidation of HFP is a highly effective method of synthesis of EHFP;[10] the process has been carried out by the Dupont Corporation[10,103,104] in a stainless steel autoclave in a continuous regime at 430 K, at a pressure of 2.8 MPa, and for the molar ratio O_2 : HFP = 0.6. The solvent employed was Khladon-113. After 20 min, up to 70% conversion of HFP is attained and the yield of the epoxide is more than 70%.[102,104]

Apart from the fluoro-olefin oxidation reactions, fluorocarbon epoxides can be obtained by other methods, for example by the addition of difluorocarbene to ketones or acyl fluorides:[116–118]

$$CF_3COCF_3 + \ddot{C}F_2 \rightarrow (CF_3)_2CF-\underset{O}{\diagdown\diagup}CF_2 \ ,$$

$$CF_3COF + \ddot{C}F_2 \rightarrow CF_3-CF\underset{O}{\diagdown\diagup}CF_2 \ .$$

Analysis of the patent and scientific literature shows that the fluoro-olefin oxidation processes can be readily achived, have many kinetic features distinguishing them from olefin oxidation processes, and make it possible to obtain fluorocarbon epoxides and perfluoropolyethers in high yields from readily available starting materials.

V. CHARACTERISTIC FEATURES OF THE PHYSICOCHEMICAL PROPERTIES AND MAIN APPLICATIONS OF THE FLUORO-OLEFIN OXIDATION PRODUCTS

In contrast to hydrocarbon epoxides, which have significantly higher boiling points than the corresponding olefins, the boiling points of fluorocarbon epoxides are close to those

of the corresponding fluoro-olefins (Table 2), which greatly hinders their separation. ETFE, whose boiling point differs considerably from that of TFE, is an exception; their mixture can therefore be comparatively readily separated by distillation. Under industrial conditions, extractive distillation of a mixture of EHFP and HFP in the presence of substituted benzenes, carbon tetrachloride, chloroform, etc. is recommended.[126,127]

Table 2. Certain physical constants of the epoxides and the corresponding olefins.

Compound	T, K*	Absorption band, cm^{-1}	Refs.
$CF_2—CF_2$ (O)	209.5 211	— 1610	[82, 91] [121]
$CF_2=CF_2$	197	—	[122]
$CH_2—CH_2$ (O)	283.7	1270	[123]
$CH_2=CH_2$	169	—	[124]
$CF_3CF—CF_2$ (O)	245	1550	[3,9]
$CF_3CF=CF_2$	243	—	[122]
$CH_3CH—CH_2$ (O)	307	1266	[123]
$CH_3CH=CH_2$	225	—	[124]
$CF_2—CFCl$ (O)	251	1540	[121, 125]
$CF_2=CFCl$	246	—	[122]
$(CF_3)_2C—CF_2$ (O)	276	1500	[3]
$(CF_3)_2C=CF_2$	280	—	[122]
$CF_2—CF(CF_2)_4—CF—CF_2$ (O, O)	377	1500	[31]
$CF_2—CF(CF_2)_4CF=CF_2$ (O)	378	1550	[31]
$CF_2=CF(CF_2)_4—CF—CF_2$ (O)	379	—	[31]

*T = boiling point.

The fluorocarbon epoxide ring has an absorption band in the range 1460–1610 cm^{-1},[3,21,22] while the ring of the carbon epoxides absorbs in the range 1240–1260 cm^{-1}.[123]

Fluorocarbon epoxides hardly dissolve in water, diglyme, etc., but they are readily soluble in fluorocarbon solvents, Freons, etc.[10] In contrast to this, epoxyethane is miscible with water in all proportions and is readily soluble in many of the usual hydrocarbon solvents.[46]

Fluorocarbon epoxides are thermally less stable than their hydrocarbon analogues. For example, the thermal decomposition of epoxyethane begins at 620 K and is characterised by an activation energy of 209–238 kJ mol^{-1}.[46] Epoxytetrafluoroethane is stable only at a reduced temperature and it is recommended that it be stored at 195 K.[12] Even at room temperature, ETFE readily isomerises to trifluoroacetyl fluoride on the walls of the vessel.[12] Above 323 K, ETFE undergoes thermal decomposition:[30,118,128]

$$CF_2(O)CF_2 \rightarrow COF_2 + \ddot{C}F_2 .$$

The reaction is of first order with respect to ETFE and the rate constant is given by[128]

$$k = 10^{13.7}\exp(-132000/RT)\,s^{-1}\ \text{(Ref.128)}$$

With increase of pressure, the rate of decomposition of ETFE also rises and in the liquid phase there is a possibility of the explosive decomposition of ETFE, the products being CF_4, COF_2, and carbon.[10,30]

The thermal stability of fluorocarbon epoxides depends significantly on their structure. For example, epoxyperfluorocyclopentane is stable up to 573 K.[30] EHFP decomposes above 420 K:[21,30,118]

$$CF_3CF(O)CF_2—CF_3COF + \ddot{C}F_2 ,$$

$$\ddot{C}F_2—\ddot{C}F_2 \rightarrow CF_2=CF_2 + CF_2(CF_2)CF_2—(CF_2)_n— .$$

The thermal stability of fluoro-olefins is significantly greater than that of the corresponding epoxides. For example, HFP undergoes thermal decomposition above 820 K.[129]

As a consequence of the relatively high electron density at the oxygen atom of the hydrocarbon epoxide ring, its opening proceeds via a stage in which the proton attacks the oxygen atom with the intermediate formation of an oxonium cation.[123] The high electronegativity of fluorine lowers the susceptibility of the oxygen atom in the fluorocarbon epoxide ring to electrophilic attack and the opening of the latter takes place as a rule owing to nucleophilic attack on the β-carbon atom with the intermediate formation of an alkoxide anion:[3,9]

$$R_F—CF(O)CF_2 + A^- \rightarrow R_F—\underset{A}{CF}—CF_2O^- \rightarrow R_FCFCOF + F^- ;$$

A = anion.

The anionic polymerisation of fluorocarbon epoxides is of practical importance and its elementary chain propagation stage involves the opening of the epoxide ring by an alkoxide anion with formation of an addition product:[10]

$$CF_3CF(O)CF_2 \xrightarrow{F^-} CF_3CF_2CF_2O^- \xrightarrow{n\,C_3F_6O} F—(CFCF_2O)_n—CF_2CF_2O^-$$

$$C_2F_5COF + F^- \qquad F—(CFCF_2O)_n—CF_2COF + F^- .$$

The anionic polymerisation of fluorocarbon epoxides proceeds in an aprotic polar solvent in the presence of sources of fluoride ions.[10] A relatively low degree of polymerisation of the order of 70–100 is then attained,[10,130] which is due to the high probability of the stage involving chain transfer as a result of the elimination of a fluoride ion from the perfluoroalkoxy-anion.[10] There are at present no methods for the synthesis of high-molecular-weight solid polymers from perfluorinated epoxides,[10,13] which resembles the initial situation in the polymerisation of hydrocarbon epoxides.[131] After stabilisation, low-molecular-weight EHFP oligomers are used as working (functional) liquids and cooling agents.[10–12] EHFP and ETFE dimers and trimers are used to obtain highly effective surfactants[132,133] and fluorinated polyacrylates,[134] the latter being used to impart oil- and water-repellant properties to fabrics and paper and for the protection of steel, glass, etc. against corrosion.

The anionic polymerisation of EHFP has been achieved in the USA[10–12] on an industrial scale, the aim being to synthesise thermally and chemically stable perfluoropolyether

oils having the structure

$$F-(CF(CF_3)-OF_2O)_n-CF_2CF_3 \quad (n = 72)$$

and fluorocarbon solvents with the structure

$$F-(CF(CF_3)-CF_2O)_m-CFHCF_3 \quad (m = 1-9)$$

The oxidation of fluoro-olefins results in the formation of carbonyl-containing compounds; the property of these compounds of greatest practical importance is their ability to combine with EHFP via an ionic mechanism to form (after pyrolysis) perfluorinated alkyl vinyl ethers, for example:[135]

$$COF_2 + CF_3CF(O)CF_2 \xrightarrow[\text{diglyme}]{CsF} CF_3OCF(CF_3)COF \xrightarrow[ZnO]{570-600\,K} CF_3OCF=CF_2 .$$

Perfluorinated alkyl vinyl ethers readily copolymerise via a radical mechanism with a number of fluoro-olefins, for example, with TFE, to form a modified polytetrafluoroethylene of the type of PFA Teflon, capable of being worked by casting under pressure and by extrusion,[136] or fluororubbers.[14, 15,137-139]

Methods for the synthesis of perfluorinated alkyl vinyl ethers with functional groups in the ω-position have been developed on the basis of perfluorobisacyl fluorides and EHFP, for example:[140]

$$FOC-(CF_2)_n-COF + CF_3CF(O)CF_2 \xrightarrow[\text{diglyme}]{CsF} FOC-(CF_2)_n-CF_2OCF(CF_3)COF \rightarrow$$

$$\xrightarrow[470K]{Na_2CO_3} FOC-(CF_2)_{n+1}-OCF=CF_2 \xrightarrow[3)\,P_2O_5]{1)\,CH_3OH\ 2)\,NH_3} NC-(CF_2)_{n+1}-OCF=CF_2 .$$

Perfluorinated alkyl vinyl ethers with functional groups are used to synthesise vulcanisable perfluorinated rubbers.[138,140]

A method has been developed for the synthesis of perfluorinated alkyl vinyl ethers with a sulphonyl fluoride group (V) on the basis of TFE, SO_3, and EHFP:[141]

$$CF_2=CF_2 + SO_3 \xrightarrow{313K} FSO_2CF_2COF \xrightarrow[CsF,\ \text{diglyme}]{CF_2(O)CF-CF_2} \rightarrow$$

$$\rightarrow FSO_2CF_2CF_2OCF(CF_3)CF_2OCF(CF_3)COF \xrightarrow[Na_2CO_3]{500K} FSO_2CF_2CF_2OCF(CF_3)CF_2OCF=CF_2 .$$

(V)

Perfluorinated copolymers used for the preparation of thermally and chemically stable ion-exchange membranes of the type of "Nafion" for fuel cells[19] and electrolysers in the chlorine industry[142] are obtained by the copolymerisation of compound (V) with TFE.

Perfluoropolyoxa-alkylene dicyanides are obtained from perfluorobisacyl fluorides and fluoro-olefin oxides:[5,6]

$$FOC-R_F-COF + CF_2(O)CFX \xrightarrow[\text{diglyme}]{CsF} \rightarrow$$

$$\rightarrow CCFX(F)-(OCF_2CFX)_m-OCF_2R_FCF_2O-(CFXCF_2O)_n-CFXC(=O)F \rightarrow$$

$$\xrightarrow[3)\,P_2O_5]{1)\,CH_3OH\ 2)\,NH_3} NCCFX-(OCF_2CFX)_m-OCF_2R_FCF_2O-(CFXCF_2O)_n-CFXCN$$

where R_F is a perfluoroalkylene containing between 0 and 20 carbon atoms and X is usually F or CF_3.

Perfluoropolyoxa-alkylene dicyanides are used to synthesise perfluorinated triazine rubbers with improved frost resistance.[13]

Apart from the syntheses based on reactions with fluoride oxides, fluorocarbon carbonyl-containing compounds have many other applications of practical importance: CDF is used for the fluorination of the carbonyl group to CF_2 (Sheppard and Sharts [1]); surfactants and fire resistant and oil- and water-repellant substances for the impregnation of fabrics have been obtained from hexafluoroacetone;[143] CDF, hexafluoroacetone, and perfluoroaldehydes are used as monomers in radical copolymerisation,[13] etc.

Polymeric products of the oxidation of fluoro-olefins containing peroxy-groups are used for the initiation of radical polymerisation.[67,70,77]

The reduction of peroxy-groups in the above polymers (for example with hydrogen, metal hydrides, etc.[144]) leads to the formation of bifunctional linear perfluoropolyethers used as monomers in polycondensation processes and also as surfactants with high chemical and thermal stability,[70,72,91,98, 145,146] as emulsifying agents in the polymerisation of TFE,[144] and as water-repellant agents for the impregnation of fabrics.[98,145,146] Modified products of the decomposition of perfluoroperoxide polymers are also used in the last two cases.[146]

In order to stabilise them (to remove peroxy- and terminal acid fluoride groups), the polymeric products of the oxidation of fluoro-olefins are treated with fluorine at 370–620 K [147] and sulphur tetrafluoride,[98] are heated at 520 K,[70] are irradiated with ultraviolet light,[70] and are heated with alkali up to 420–620 K.[70,147]

The stabilised products with the perfluoropolyether structure obtained are employed as thermally and chemically stable oils and bases for greases, as dielectrics and heat exchangers,[70,72,98,145] and as plasticisers and solvents for fluorine-containing polymers.[91,145]

The main application of the products of the oxidation of fluoro-olefins is the introduction of oxygen-containing groups into fluorocarbon polymers. In this connection it must be emphasised that, in terms of the character of their influence on the properties of fluorocarbon polymers, the oxygen-containing groups can be divided into two categories. The first includes ether groups, whose influence is due to their chemical inertness and low potential barrier to rotation about the single C–O bond.[13-15] The introduction of ether groups into fluorocarbon polymers sharply reduces the rigidity of the polymer chains, which alters many physical properties associated with the flexibility of the macromolecules and in the first place decreases significantly the glass point, the thermal stability of the fluoropolymers remaining virtually unchanged under these conditions and lying in the range 520–570 K.[13-15] The electron-accepting properties of fluorocarbon alkyl groups and the *p*,*p*-conjugation of the unshared electron pairs of the heteroatom and the nearest fluorine atoms are responsible for the high chemical inertness of the perfluorinated ethers.[1,2,13] By virtue of this, fluorocarbon polymers with ether groups retain a high chemical stability. Thus perfluoropoly(propylene oxide) is stable in solvents such as liquid oxygen, N_2O_4, boiling concentrated nitric acid, and 90% hydrogen peroxide, in fluorinating agents such as gaseous fluorine (up to 470 K) and boiling ClF_3 and CoF_3 (up to 470 K), in strong acids such as concentrated H_2SO_4 (up to 590 K), P_2O_5 (up to 650 K), and BF_3 (up to 670 K), and in strong bases such as fused NaOH (up to 570 K), $(CH_3)_3N$ (up to 670 K), and $NaOCH_3$ (up to 650 K), in contact with metals, etc.[10,148] A consequence of the chemical inertness of perfluoropolyethers is their biological inertness and non-flammability.[11,12]

However, a certain degree of basicity of the ether groups in perfluoropolyethers remains and is manifested in reactions with Lewis acids, for example with $AlCl_3$ (even at 370 to 420 K) [2,149] and by a considerable decrease of the thermal stability of perfluoropolyethers in the presence of metals such as aluminium, titanium, and their alloys; the thermal stability

of oils of the type of "Fomblin" decreases under these conditions from 670 to 520 K,[149] while contact between fluorocarbon polymers and metal surfaces has almost no influence on their thermal stability.

Another manifestation of the residual basicity of the ether groups in perfluoropolyethers is an increase of the intermolecular interaction forces compared with fluorocarbon polymers, as a result of which perfluoropolyethers are readily soluble in fluorinated solvents while they remain insoluble in hydrocarbon solvents,[148,149] and expansion of the temperature range of their existence in the liquid phase[2] and a sharp improvement of their viscosity-temperature characteristics.[13]

When the carbon atoms in the α-position in ethers are incompletely fluorinated, a sharp impairment of the properties of the polymers is observed: the CF_2OCH_2 group is chemically less stable than the non-fluorinated ether bond, being particularly readily hydrolysed.[13]

The degree of modification of the properties of fluorocarbon polymers depends on the number of ether groups introduced into the main chain or into the side groups. The structure of the perfluoropolyether having a statistical distribution of the CF_2CF_2O and CF_2O units with the difluoromethylene oxide units predominating is optimal as regards the glass point and the viscous-temperature properties. Perfluoropolyether oils with the above structure are highly viscous and very stable at low temperatures:[13,63,150] their glass points are of the order of 120 K, their thermal stabilities are 600–630 K, and the temperature coefficients of their viscosity are low.

In terms of thermal stability, the optimum structure of perfluoropolyethers is that of perfluoropoly(ethylene oxide) $(CF_2CF_2O)_n$, whose thermal stability (770–820 K) [151] is unique for polymers with a flexible chain. The presence of difluoromethylene oxide groups in the perfluoropolyether chain lowers the thermal stability of the polymer, particularly on contact with metals.[13]

Reactive groups whose chemical reactivity is significantly higher than that of the analogous groups in hydrocarbon polymers belong to the second category of oxygen-containing groups introduced into fluorocarbon polymers by means of fluoro-olefin oxidation products. For example, the carboxy-groups are more acid and the carbonyl groups are more electrophilic,[1,152] as a result of which fluorinated polymers with functional groups in the main chain, for example, fluorine-containing polyesters, polyamides, polyurethanes, etc., have a low chemical stability, particularly in an alkaline medium.[13]

The introduction of reactive functional groups into fluorocarbon polymers as terminal or side groups imparts to the polymers a capacity for chemical vulcanisation, ion-exchange and catalytic activity, etc. These groups are introduced as a result of copolymerisation with fluoro-monomers containing a functional group in the ω-position.[5,140] The functional groups employed are COOH, COOR, $CONH_2$, CN, $CF-CF_2$ (O), SO_2F, etc.[17,139–141,153]

After vulcanisation, the reactive functional groups usually no longer affect the chemical properties of the copolymer and their influence on the physical properties of the vulcanised material is manifested only owing to the increase of the strength of the cross-links.[139] However, the introduction of a large number of reactive functional groups induces a sharp change of both chemical and physical properties of fluoro-polymers. For example, a copolymer has been obtained from TFE and the sulpho-olefin (V), which exhibits not only an ion-exchange activity but also differs significantly from polytetrafluoroethylene in its physical properties: it swells in water to the extent of 25 wt.%[19] and dissolves in polar organic solvents such as ethanol, butanol, $C_6H_5N(CF_3)_2$, etc.[154]

Examination of the main applications of the products of the oxidation of fluoro-olefins shows that this reaction leads to key monomers for the synthesis of fluorine-containing polymers.

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