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There is no one opinion on the mechanism of oxidation of halogen-containing olefins. Based on the example of oxidation of tetrafluoroethylene and hexafluoropropylene, it has been established [1, 2] that the selectivity of their oxidation with respect to the olefin oxide decreases with an increase in the concentration of  $O_2$ , while it increases with respect to perfluorocarboxylic acid fluorides, CF<sub>2</sub>COF and COF<sub>2</sub>. A decrease in the selectivity with respect to the oxide with an increase in the concentration of oxygen has also been observed in oxidation of styrene [3].

The kinetics of the oxidation of 1-perfluorooctene and the effect of the starting concentrations of  $O_2$  on the formation of the end products Tof the reaction were investigated in the present article to extend the concepts of the mechanism of oxidation of perfluorinated olefins.

## EXPERIMENTAL

1-Perfluorooctene (PFO) was prepared by the method in [4] by pyrolysis of the sodium salt of perfluoropelargonic acid at 320°C. PFO was purified of impurities by bromination of the olefin with subsequent separation of the dibromide, which was debrominated in diglyme at 140°C, while simultaneously distilling the PFO (bp 105°C, specific gravity 1.7 g/ml); the degree of purity was  $\geq$  99% according to the IR and GLC findings.

Perfluoropolyester containing peroxide units in its chain  $(0.68 \cdot 10^{-3} \text{ mole active } 0_2/\text{g})$  was used as the oxidation initiator. The constant of decomposition of perfluoropolyesterpolyperoxide (PP) into free radicals at 97°C, measured by the method in [5], was  $2.3 \cdot 10^{-5}$  sec<sup>-1</sup>.

The experiments on oxidation were conducted at  $97^{\circ}$ C in a circulation setup (Fig. 1) connected with a gasometric system used to study the kinetics of oxidation of hydrocarbons based on absorption of  $O_2$  [6]. The glass piston of pump 3, with a ferromagnetic core sealed inside, was set in motion by an induction coil to which variable voltage of the required frequency was delivered. The oxygen for oxidation entered from the buret of the gasometric installation. Technical-grade oxygen from a tank was used for the reaction. Intense mixing of the reaction mixture with a magnetic mixer ensured that the process would take place in the kinetic region.

The concentration of peroxide compounds was determined colorimetrically using Variamine Blue [5] and measuring the intensity of the color of the solution on a Specord UV VIS spectrophotometer at 610 nm.

GLC analysis of the PFO and 1-perfluorooctene oxide (OPFO) was performed on a LKhM-8MD chromatograph with a thermal conductivity detector at 95°C, column length of 8 m, diameter of 3mm, Celite-545, 5% hexafluoropropylene oxide polymer (of the weight of the carrier), He carrier gas. A standard (n-perfluoroctane) whose concentration was not varied during oxidation was introduced in the reaction mixture in quantitative GLC analysis of consumption of PFO and accumulation of the products of the reaction with small degrees of transformation.

In addition to GLC, IR spectroscopy in the 1550 cm<sup>-1</sup> (epoxy ring in OPFO), 1990 (COF group), 1930-1940 (COF<sub>2</sub>), 2340 (CO<sub>2</sub>), and 1650 cm<sup>-1</sup> (PFO) frequency region was used for identification of the products of the reaction and observation of the kinetics of accumulation of perfluoroenanthic acid fluoride and carbonyl fluoride. The GLC data satisfactorily coincided with the results of the spectral analysis.

The solubility of  $O_2$  at 97°C at 3-52 atm in the balanced liquid (BL) used as the solvent for oxidation of PFO was measured for studying the dependence of the rate of oxidation of PFO

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Fig. 1. Diagram of the oxidation circulation setup: 1) reaction vessel; 2) sampler; 3) pump; 4) induction coil; 5) trap containing Ascarite; 6) cooler; 7) magnetic mixer.

Fig. 2. Dependence of the solubility of the oxygen in a balanced liquid on pressure, 97°C.

on the concentration of  $0_2$ . The solubility of  $0_2$  at 1 atm, found by extrapolation of the line (Fig. 2), was 0.005 mole/liter at 97°C and was in good agreement with the value for the solubility in 1,2-dichloroethylene at 100°C, equal to 0.003 mole/liter [7].

The kinetics of oxidation of PFO was studied at 1-52 psig in a glass cell of the bubbling type equipped with a reflux condenser in a metal beaker. The  $O_2$  pressure in the cell was followed with a standard pressure gauge at the inlet into the reactor, and the flow rate of the  $O_2$  through the reactor was determined with a flow meter at the outlet of the condenser. Helium was used as the diluent for attaining concentrations of  $O_2$  in solution of less than O.005mole/liter at 1 atm.

## DISCUSSION OF THE RESULTS

In the absence of an initiator, oxidation of PFO was not observed. After addition of PP to the reaction mixture (the time of addition is indicated by the arrow, Fig. 3b), the reaction did not begin immediately but after a short induction period. The basic products of oxidation were OPFO (cf. Fig. 3b, curve 3), and the yield at 1 atm attained 80% and higher on conversion to unconsumed PFO, perfluoroenanthic acid fluoride (curve 4),  $CO_2$  and  $COF_2$ . It was found that both acid fluorides (AF) were formed in equimolar amounts. However, carbonyl fluoride easily reacted with the glass surface of the reaction cell in the atmosphere of  $O_2$ , yielding  $CO_2$ .

The acid fluorides and perfluorooctene oxide were formed in two parallel, but independent reactions, as indicated by the approximate constancy of the ratio of the rates of formation of OPFO and AF  $(w_{OM}/w_{AF})$  during the entire experiment (cf. Fig. 3a).

The analysis of the kinetic curves shows that the amount of absorbed  $O_2$  (cf. Fig. 3b, curve 2) and PFO consumed (curve 1) was 10-12 mole % higher than the amount of reagents required for formation of OPFO and AF. The deficiency in the balance of the olefin and  $O_2$  was apparently due to the fact that compounds with ether and peroxide bonds, which were not determined in these experiments, were also formed together with OPFO and AF.

The kinetic curves of the consumption of PFO and accumulation of the products of the reaction after removal of the initiator were S-shaped. In contrast to this, oxidation of olefins containing no fluorine, for example, 1-nonene [8], 2-methyl-2-pentene [9], or styrene [10], initiated by azodiisobutyronitrile (AIBN) or benzoyl peroxide, takes place at



Fig. 3. a) Dependence of the ratio of the rate of accumulation of perfluorooctene oxide to the rate of accumulation of perfluoroenanthic acid fluoride in oxidation of 1-perfluorooctene; 1 atm, 97°C; b) kinetic curves of consumption of 1-perfluorooctene (1), oxygen (2), accumulation of perfluorooctene oxide (3), and perfluoroenanthic acid fluoride (4).

Fig. 4. Dependence of the selectivity based on perfluorooctene oxide (1), the rate of accumulation of perfluorooctene oxide (2), and the rate of consumption of 1-perfluorooctene (3) on the starting concentration of oxygen,  $97^{\circ}C$ .

a constant rate immediately after addition of the initiator to the reaction mixture. The S-shaped kinetic curves observed in the case of perfluoroalkenes are characteristic of chain free-radical reactions with degenerate branching of the chains, autocatalytic reactions, or a set of sequential stages, a minimum of two of which take place at comparable rates.

It is possible to hypothesize that perfluoropolyesters can participate in a chain propagation reaction as a catalyst. In this case, the induction period should have decreased with an increase in the concentration of  $O_2$  and with a constant concentration of PP. However, as the experiments showed, the concentrations of  $O_2$  did not affect the duration of the induction period.

One explanation of the autoacceleration of the process of oxidation of PFO could be the fact that PP initiates oxidation less actively than the peroxides formed during the reaction of PFO with  $O_2$ . Use of AIBN, benzoyl peroxide, lauryl, and a number of other peroxides which efficiently initiate oxidation of hydrocarbons did not produce positive results in oxidation of perfluoroolefins, apparently due to the extremely low solubility of these initiators in organoflucrine solvents.

It is also possible that the presence of an induction period is due to the fact that PP forms an intermediate complex with the olefin. Since a perfluorinated olefin, which has such strong electrophiles as fluorine atoms and perfluoroalkyl groups at the double bond, easily undergoes nucleophilc attack, and the peroxide group can be polarized in the presence of such an olefin with formation of RO<sup>-</sup> and RO<sup>+</sup> ions, attack of the RO<sup>-</sup> ion on the double bond in the olefin could result in its addition to the olefin and formation of a RO<sup>+</sup>...ROM<sup>-</sup> ion pair (M is a molecule of PFO) which could exist for a relatively long time in the conditions of a viscous and nonpolar solvent. Electron transfer into such a pair would result in formation of a radical from the ROM<sup>-</sup> ion which is capable of further carrying out the chain of oxidation, and a RO<sup>+</sup> radical from RO<sup>+</sup>. This mechanism of the reaction of PP with an olefin which includes several slow stages could explain the S-shape of the kinetic curves.

The maximum rates of consumption of PFO and accumulation of OPFO with low concentrations of  $O_2$  (0-0.1 mole/liter) is linearly dependent on the concentration of  $O_2$  (Fig. 4). With a further increase in the concentration of  $O_2$ , the rates increase more slowly, approaching some limit. The selectivity of the process with respect to OPFO (S) with small concentrations of  $O_2$  is close to unity, but decreases sharply with an increase in its concentration, attaining

TABLE 1. Effect of the Length of the Carbon Chain in the Perfluoroolefin Oxide  $w_{OM}$  and Perfluorocarboxylic Acid Fluorides  $w_{AF}$  in a Threefold Excess of Oxygen with Respect to the Olefin

Perfluoro- lefin	Oxidation tempera- ture, °C	w <sub>OM</sub> / <sup>W</sup> AF	Reference
C <sub>2</sub> F <sub>4</sub>	92	0	[1]
C <sub>3</sub> F <sub>6</sub>	120	0,2	[2]
C <sub>8</sub> F <sub>16</sub>	97	0,36	Our data

the maximum value with  $[0_2] = 0.15$  mole/liter (cf. Fig. 4, curve 1). This type of dependence of S, of the rates of consumption of the olefin and accumulation of OPFO on  $[0_2]$  is in agreement with the mechanism of epoxidation of olefins [8], where an oxide is formed as a result of monomolecular decomposition of intermediate radical complexes of the olefin with perfluoroperoxide radicals into two molecules of a perfluoroolefin oxide

$$ROMO_2 + M \rightleftharpoons ROMO_2 M \to 20M + RO.$$
(1)

$$| \xrightarrow{O_3} \operatorname{ROMO}_2 \operatorname{MO}_2'$$
 (1')

while  $CF_3(CF_2)_5COF$  and  $COF_2$  are formed as a result of decomposition of perfluoroalkylperoxide radicals,  $ROM_2 \cdot$ ,  $ROMO_2MO_2 \cdot$ , etc., regardless of the number of peroxide units in the radical

$$\begin{array}{c} \operatorname{RO-CF_2-CFOO} \to \operatorname{RO} \to \operatorname{RO} \to \operatorname{CF_3(CF_2)_5COF} + \operatorname{COF_2} \\ ( \stackrel{|}{\operatorname{CF_2)_5}} \\ \stackrel{|}{\operatorname{CF_3}} \end{array} \tag{2}$$

This pathway of formation of AF predominates in long oxidation chains. If the chains are short, the reaction of perfluoroalkoxy radicals formed in breaking of the chains makes an important contribution to the total rate of accumulation of AF

$$2RO-CF_{2}-CFOO^{\bullet} \rightarrow 2RO-CF_{2}-CFO^{\bullet} + O_{2}$$

$$(CF_{2})_{5} \qquad (CF_{2})_{5}CF_{3}$$

$$(F_{2})_{5} \qquad (CF_{2})_{5}CF_{3}$$

$$(F_{2})_{5}CF_{3}$$

$$(F_{2})_{5}CF_{3}$$

$$(F_{2})_{5}CF_{3}$$

$$RO - CF_2 - CFO' \xrightarrow{O_2} RO - CF_2COF + CF_3(CF_2)_5OO'$$
(4)  
$$RO - CF_2 - CFO' \xrightarrow{O_2} RO - CF_2OO' + CF_3(CF_2)_5OO'$$
(4)

$$\begin{array}{c} & \xrightarrow{} & \operatorname{KO} - \operatorname{CF}_2 \operatorname{OO}^+ + \operatorname{CF}_3 \operatorname{COF} \\ (\operatorname{CF}_2)_5 \\ & \downarrow \\ & \operatorname{CF}_3 \end{array}$$

$$(4')$$

The intermediate complex radicals react with  $O_2$  with an activation energy of  $E \approx 2$  kcal/mole and a constant rate on the order of  $10^6$  mole<sup>-1</sup> · liter · sec<sup>-1</sup>, while decomposition of these radicals requires energy of 8-10 kcal/mole [9]. As a consequence, the stability of the intermediate complex radical ROMO<sub>2</sub>M · should affect the competition of reactions (1) and (1'), i.e., the ratio of the rates of accumulation of OPFO and AF, together with the temperature and the starting concentration of  $O_2$ : The higher the stability, the higher the probability of its reacting with  $O_2$ , and the higher the yield of AF.

The length of the carbon chain in the perfluorolefin strongly affects the ratio of the rates of formation of the perfluoroolefin oxide and AF. With all other conditions being equal (ratio of the concentrations of  $0_2$  and the olefin, temperature), oxidation of tetra-fluoroethylene only results in formation of COF<sub>2</sub> and a polymer, while the yield of OPFO attains 36% (Table 1).

Since no products other than OPFO and AF are found in important amounts as a result of the reaction of PFO with  $O_2$ , it is possible to assume that the process of oxidation takes place with long chains. It follows from the proposed scheme of oxidation of perfluoroole-fins in [2], on the assumption that the concentration of intermediate free radicals is quasi-stationary, that the yield of the olefin oxide for the unreacted olefin is subordinate to the ratio

$$S = \frac{d[OM]}{d[M]} = \frac{2}{2 + \frac{k_{AF}}{k_{OM}}[O_2]}$$

However, this dependence of the selectivity on the starting concentration of  $O_2$  only describes the starting segment of the curve (cf. Fig. 4) and does not explain the limits with respect to the rate of accumulation of OPFO and the selectivity with  $[O_2] > 0.1$  mole/liter. Following the well-known [6] scheme for free-radical oxidation reactions, it could be expected that  $RO_2MO_2$ ' radicals, which cannot yield an epoxide within the framework of the mechanism of oxidation cited above, should predominate in the system with an excess of  $O_2$ . However, in oxidation of PFO, even when  $[O_2] > 0.1$  mole/liter, formation of OPFO is observed (cf. Fig. 4) with a yield of up to 40% for the unreacted PFO. For this reason, it is possible to assume that there is another, nonradical pathway of formation of an olefin oxide in addition to decomposition of ROMO\_2M<sup>+</sup>. One of these pathways of epoxidation of an olefin could be the formation of two molecules of the olefin oxide [11]. Decomposition of ROMO\_2 • radicals apparently takes place according to a more complex mechanism than indicated in the scheme reported in [2] and includes a stage of formation of an intermediate cyclic peroxide

$$ROMO_2 \rightarrow RO' + MO_2 \tag{5}$$

Such cyclic peroxides could react with a second molecule of the olefin, yielding two molecules of oxide on one hand, and could be decomposed into AF on the other hand

$$CF_{4}(CF_{2})_{*}CF_{--}CF_{--} \longrightarrow CF_{3}(CF_{2})_{*}COF + COF_{2}$$
(6)

$$\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \end{array} \xrightarrow{} 0 \end{array} \xrightarrow{} 2 CF_2(CF_2)_5 CF \\ 0 \\ 0 \\ 0 \end{array} \xrightarrow{} 0 \end{array}$$

$$(6')$$

The composition of the products of oxidation in an excess of  $0_2$  will thus only be determined by the ratio of the rates of reactions (6) and (6').

## CONCLUSIONS

1. Oxidation of perfluorooctene by molecular oxygen results in the parallel formation of perfluoroctene oxide and perfluorocarboxylic acid fluorides.

2. An induction period was found in oxidation of perfluoroctene in the presence of perfluoropolyesterpolyperoxide, which is presumably related to the formation of an intermediate complex of perfluoropolyesterpolyperoxide with perfluoroctene, and the mechanism of formation of this complex includes slow stages.

3. The selectivity with respect to perfluorooctene oxide and the rate of its accumulation decrease to some limiting value with an increase in the concentration of oxygen. Their independence with respect to the concentration of oxygen in conditions of an excess of oxygen is due to the nonradical stage of epoxidation of the perfluorooctene.

## LITERATURE CITED

1. P. I. Valov and L. F. Sokolov, Azerb. Khim. Zh., No. 4, 78 (1981).

- 2. P. I. Valov and L. F. Sokolov, Neftekhimiya, 27, 247 (1982).
- 3. D. E. Van Sickle, F. R. Mayo, E. S. Gould, and R. M. Arluck, J. Am. Chem. Soc., <u>89</u>, 977 (1967).
- 4. M. Gudlitskii, Chemistry of Organic Fluorine Compounds [in Russian], Goskhimizdat, Moscow (1961).
- 5. I. M. Korenman, Methods of Determination of Organic Compounds. Photometric Analysis [in Russian], Khimiya, Moscow (1970).

- 6. N. M. Émanuél', E. T. Denisov, and Z. K. Maizus, Chain Reactions of Oxidation of Hydrocarbons in the Liquid Phase [in Russian], Nauka, Moscow (1965).
- 7. A. I. Chernyavskii, Dissertation, Moscow (1982).
- 8. L. G. Privalova, L. D. Tyutchenkova, S. P. Kirichenko, and Z. K. Maizus, Izv. Akad. SSSR, Ser. Khim., 1042 (1972).
- 9. V. M. Parfenov and Z. K. Maizus, Neftekhimiya, 11, 416 (1971).
- 10. N. A. Shipunova, T. V. Filippova, and E. A. Blyumberg, Neftekhimiya, 22, 551 (1982).
- 11. T. V. Filippova and É. A. Blyumberg, Usp. Khim., 51, 1017 (1982).

REACTION OF ELEMENTAL SULFUR WITH 1,1-DIMETHYLSILA-3-

CYCLOPENTENE IN THE PRESENCE OF Fe3(CO)12

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The insertion of elemental sulfur into olefinic double bonds in the presence of iron carbonyls was described in our earlier work for the case of 1-hexene [1] and cyclohexene [2]. In the present work, we showed that elemental sulfur reacts with 1,1-dimethylsila-3-cyclopentene in the presence of Fe<sub>3</sub>(CO)<sub>12</sub> to form the following products: diethiodiironhexacarbonyl (I), dithiotriironnonacarbonyl (II), 1-dimethylsila-4,5,6,7-tetrathiabicyclo[4.3.0]nonane (III), 1,8-bis(dimethylsila)-4,5,11,12-tetrathiatricyclo[9.3.0.0<sup>6</sup>,<sup>10</sup>]tetradecane (IV),1,9-bis(dimethylsila)-4,5,6,12,13-pentathiatricyclo[10.3.0.0<sup>7</sup>,<sup>11</sup>]pentadecane (V), and diironhexacarbonyl dithiolane complex (VI)

Me<sub>2</sub>Si 
$$-S_{s} + Fe_{3}(CO_{12}) \rightarrow S_{2}Fe_{2}(CO)_{6} + S_{2}Fe_{3}(CO)_{9} + (1)$$



The yield relative to the sulfur taken for the reaction is 5-10% for (I) + (II), 5% (III), 1-2% (IV) and (V), and 2% (VI).

Thin-layer chromatographic analysis shows that the initial reaction products are (I), (II), and (III). Special experiments in benzene at  $60^{\circ}$ C for 4 h showed that the generation of complex (VI) proceeds by the action of Fe<sub>3</sub>(CO)<sub>12</sub> on (III)

$$Me_2Si \underbrace{S_4 + Fe_3(CO)_{12} \rightarrow (VI) + (I) + (II) + CO}_{S_4}$$

A mixture of polysulfides (IV) and (V) upon treatment with  $Fe_3(CO)_{12}$  also gives complex (VI) but the rate of these reactions is lower than for the reaction of (III) with  $Fe_3(CO)_{12}$ . No other iron carbonyl complexes could be isolated in this case

$$\underbrace{\operatorname{Me}_{a}\operatorname{Si}}_{= 2(IV), 3(V).} \underbrace{\operatorname{Si}}_{S_{a}} \underbrace{\operatorname{Si}}_{S_{a}} \operatorname{Si}_{Me_{2}} + \operatorname{Fe}_{3}(\operatorname{CO})_{1_{2}} \rightarrow \operatorname{S}_{2}\operatorname{Fe}_{2}(\operatorname{CO})_{6} + \operatorname{S}_{2}\operatorname{Fe}_{3}(\operatorname{CO})_{9} + (VI)_{1_{1}} + (VI)_{1_{$$

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