Formation of free radicals in the low-temperature fluorination of polymers

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The formation of free radicals in the process of direct fluorination of natural and synthetic polymers at temperatures close to 77 K was studied by ESR. The maximum concentrations of radicals (10^{17}—$5 \cdot 10^{18}$ spin g^{-1}) and their complete oxidation were observed in the temperature interval from 77 to 250 K at a fluorine pressure of 30 Torr. The initiation of chain halogenation, which consists of homolytic breaking of chemical bonds to yield free-radical intermediates, was examined in the framework of the multi-center synchronous transitions model.

Key words: polymers, fluorination, free radicals.

Previously[1—3] we found that interaction between halogens (fluorine, chlorine) and organic polymers containing multiple bonds (polystyrene, lignin) in the range from 77 to 150 K results in the formation of free radicals. From the viewpoint of classical concepts regarding one-center transitions of reacting particles along the reaction coordinate, the spontaneous homolytic breaking of chemical bonds and formation of free radicals at low temperatures are unlikely to occur. Therefore, the phenomenon observed appears to be due to multi-center synchronous transitions in which breaking of some chemical bonds and formation of other chemical bonds occur simultaneously in one act and the endothermicity of the process is compensated for by the exothermic effect of the formation of new bonds. In this case, breaking a two-electron bond can follow a heterolytic or a homolytic mechanism, and, depending on the number of broken and newly formed bonds, molecular, ionic, and radical mechanisms of the process are distinguished.[4]

The prime objective of the present work is to study the reactions of the formation of free radicals in the low-temperature fluorination of synthetic and natural polymers containing chemical bonds of different types.

Fluorination of organic compounds by molecular fluorine is widely used to modify the physical and chemical properties of polymers as well as to obtain fluorine-containing polymeric and low-molecular-weight compounds.[5—8] However, the reactions of the formation of free radicals, particularly in low-temperature fluorination have hardly been studied, though they play a key role (as the chain initiation stage) in the radical-chain processes of halogenation of organic compounds.

Results and Discussion

1. Fluorination of synthetic polymers

The principal problem of the direct fluorination of organic compounds is to choose the necessary conditions for controling the reaction since the high exothermicity of the process often leads to ignition and charring of the products obtained.[5] Fluorination at low temperatures retards the reaction and stabilizes the intermediate short-lived particles, and, at low fluorine pressure (~30 Torr), allows one to prevent the undesirable effects of superheating of the system.

When F_2 is in contact with hydrocarbon polymers cooled to 77 K, fluorination proceeds, resulting in measurable amounts of free radicals. Thus, in synthetic polymers, the average-over-specimen concentrations of radicals were as high as 10^{17}—$5 \cdot 10^{18}$ spin g^{-1}. The efficiency and direction of the primary process of radical formation as well as the secondary reactions of oxidation and loss of radicals were significantly affected by the physical state of the specimens. In highly dispersed powders of polyethylene (PE) and polypropylene (PP), the maximum concentration of radicals, $[R^{\cdot}] = (2—5) \cdot 10^{17}$ spin g^{-1}, is recorded already at 77 K. The ESR spectra are asymmetric since they are superpositions of signals of alkyl and peroxide radicals resulting from oxidation of primary radicals by oxygen that is contained in fluorine as an impurity. The absence of broad lines or evidence of hyperfine structure indicate that the alkyl radicals are hydrocarbon radicals but are not fluorine-containing radicals (Fig. 1, *a*, spectra *1'*, *2'*). As the temperature increases radicals are lost

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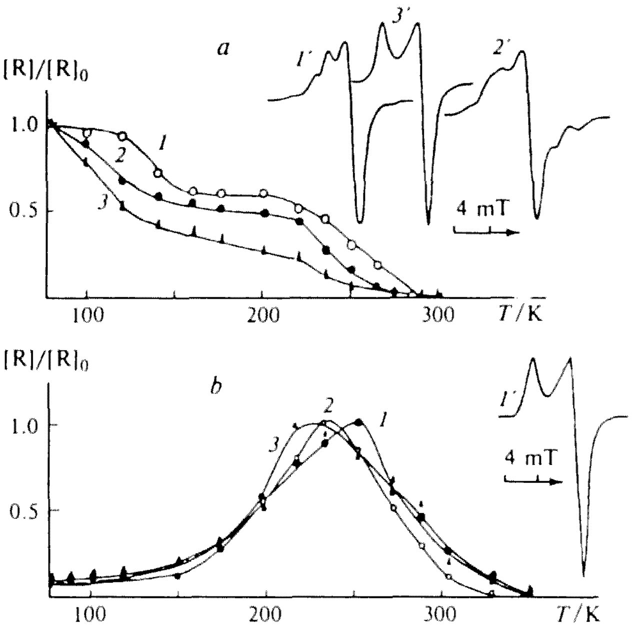


Fig. 1. Change in the concentration of free radicals in polymers fluorinated at 77 K with increasing temperature (*1—3*) and their ESR spectra at 77 K (*1'—3'*): *a*) *1,1'*, polyethylene; *2,2'*, polypropylene; *3,3'*, copolymer of ethylene and CO; *b*) *1*, poly(methyl methacrylate); *2*, poly(ethylene terephtalate); *3*, polyimide; *1'* is ESR spectrum of fluorinated poly(methylmethacrylate) after heating the specimen to 255 K.

and are completely oxidized in the range from 180 to 200 K, while further heating leads to loss of $RO_2^\cdot$ at room temperature (Fig. 1, *a*, curves *1*, *2*).

In a highly dispersed powder of the copolymer of ethylene and CO, which possesses enhanced oxidizability, all the primary radicals are transformed into $RO_2^\cdot$ at 77 K; radical concentration amounts to ~$5 \cdot 10^{18}$ spin g^{-1}. Increasing the temperature results in the progressive loss of radicals (Fig. 1, *a*, spectrum *3'*, curve *3*).

It should be noted that no free radical formation was observed in the low-temperature fluorination of commercial PE containing additives of inhibitors and antioxidants.

When poly(ethylene terephtalate) (PET) and polyimide films as well as coarse powder of poly(methyl methacrylate) (PMMA) are in contact with fluorine at 77 K a small amount of free radicals (~10^{16} spin g^{-1}) forms. It is likely that fluorination only proceeds in the thin surface layer of the polymer because of the limited diffusion of F_2. The intensity of fluorination increases with increasing temperature (due to an increase in the diffusion of F_2), and the concentration of radicals (after complete oxidation) increases by an order of magnitude and amounts to ~10^{17} spin g^{-1} in the range from 220 to 250 K. Complete loss of radicals is observed at temperatures higher than room temperature (Fig. 1, *b*).

Thus, for a group of film and coarse powder polymer specimens fluorination begins at 77 K and reaches its maximum at higher temperatures. The concentrations of radicals are nearly equal ($(0.9-1.3) \cdot 10^{17}$ spin g^{-1}) for all polymers, oxidation of $R^\cdot$ and loss of $RO_2^\cdot$ are observed in the same temperature intervals, while the efficiency of fluorination (judging from the yield of radicals) is by a factor of 2—5 lower than in the first group of polymers. Oxidation of radicals is observed in the range from 200 to 250 K, and complete loss of redicals occurs at temperatures above 300 K.

2. Fluorination of natural polymers

The ESR spectrum of lignin after fluorination at 77 K (Fig. 2, spectrum *1'*) is a broader singlet (ΔH = 0.8—0.9 mT) than the ESR spectrum of the starting lignin (ΔH = 0.5 mT, g = 2.003) with the same g-factor value. The concentration of radicals after fluorination is 20 times greater than the background concentration and amounts to ~ $1.8 \cdot 10^{18}$ spin g^{-1}. Broad structureless resonance wings reaching 20 mT in total extent, characteristic of the signals of fluorocarbon radicals, are observed in the spectrum and are retained to room temperature. Heating the fluorinated lignin does not lead to formation of $RO_2^\cdot$, and the singlet spectrum persists (with a slight decrease in ΔH) to ~373 K and above (Fig. 2, curve *1*).

The reaction of F_2 with lignin in the vicinity of 77 K can be considered to be analogous to low-temperature chlorination, resulting in the addition of a halogen to the conjugated double bonds of the olefin chains of lignin.[1] The conjugation chains are shortened during fluorination, which leads to the formation of polyene radicals with shorter chains. Therefore, the ESR spectrum (a singlet characteristic of polyene radicals) holds its shape and is merely broadened. Because of delocalization of the spin density along the conjugation system, the polyene radicals are highly thermostable and chemically inert. They do not enter oxidation reactions and remain intact in fluorinated specimens to high temperatures (~370 K). The broad line at the side wings of the lignin spectrum is probably associated with fluorocarbon radicals. This line also does not change when the lignin is heated and does not transform into the spectrum of $RO_2^\cdot$.

An asymmetric singlet characteristic of peroxide radicals (Fig. 2, spectrum *2'*) is observed in the spectra of wood cellulose and cotton cellulose after fluorination at 77 K. Peroxide radicals account for ~80 % of the total concentration of radicals, which amounts to $5 \cdot 10^{16}-10^{17}$ spin g^{-1}. Loss of radicals begins immediately after the temperature is increased in wood cellulose, and the complete disappearance of radicals is observed at 240 K (Fig. 2, curve *2*). Heating the cotton cellulose fluorinated at 77 K leads to a continuation of fluorination, followed by an increase in the concentra-

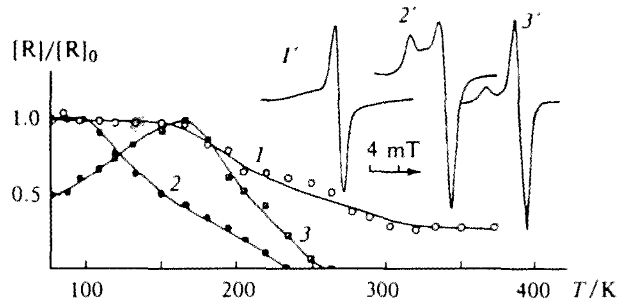


Fig. 2. Change in the concentration of free radicals in natural polymers fluorinated at 77 K with increasing temperature: lignin (*1*), wood (*2*) and cotton (*3*) cellulose and ESR spectra of fluorinated lignin (*1'*) and wood cellulose (*2'*) at 77 K; *3'* is ESR spectrum (at 77 K) of fluorinated pine wood after heating the specimen to 200 K.

tion of radicals (to ~10^{17} spin g^{-1} at 170 K), and nearly complete oxidation of the radicals, who then disappear at 260 K (Fig. 2, curve *3*).

In light of the above data, the negative result of the direct fluorination of cotton cellulose at room temperature[6] becomes clear. The action of fluorine for 20 h did not result in the appearance of free radicals (ESR-monitoring). Based on this, it was assumed that the cotton fiber is very chemically stable. As follows from the above data, cellulose as well as other polymers can be effectively fluorinated. However, unstable products of fluorination, peroxide radicals, are found to disappear at temperatures much below room temperature. On the other hand, it had been known that no spectrum of the peroxide radicals has been observed in dry specimens of γ-irradiated cellulose for a long time. The absence of $RO_2^{\cdot}$ was associated with the limited mobility of the oxygen molecules not capable of permeation through the three-dimensional network of hydrogen bonds in order to approach the radical. The $RO_2^{\cdot}$ spectrum was only detected after the matrix was moistened with water, which breaks the hydrogen bonds, and here the degree of oxidation R did not exceed 25 %.[9] In the fluorination of both cotton and wood cellulose, nearly complete oxidation of the primary radicals (by the oxygen contained in fluorine) is observed at a temperature close to that of liquid nitrogen. It is likely that the action of F_2 is accompanied by cleavage of the hydrogen bonds and replacement of the hydrogen atoms by F.

In pine wood and unbleached cellulose, where two polymers (lignin an cellulose) are present, the effect of fluorination is a combination of the two cases discussed above. Fluorination causes an increase in the content of the singlet component of the total spectrum associated with the formation of polyene radicals in lignin. Increasing the temperature results in oxidation of the radicals of the cellulose fraction. In this case, the ESR spectrum is a superposition of a singlet of width ΔH = 0.9 mT, and g = 2.003, and the asymmetric singlet of the peroxide radicals. The degree of oxidation of the radicals increases with increasing temperature and reaches its maximum (15 % for pine wood (Fig. 2, spectrum *3'*) and ~45 % for unbleached cellulose) in the temperature range from 190 to 200 K. A six-component signal from Mn^{+2} ions (which enter into the composition of the wooden complex) is observed in the starting unbleached cellulose; it is unaffected by fluorination.

Thus, the concentration of radicals for synthetic and natural polymers (except for the copolymer and lignin) are of the same order of magnitude. They are presumably determined by the fluorine pressure and amount to $(0.9-1.5)\cdot10^{17}$ spin g^{-1} at P_{F_2} = 30 Torr. The efficiency of fluorination, *i.e.*, the rate of formation of primary radicals, is determined by the diffusion of F_2, which is dependent on the physical state of the polymer. The nature of the fluorinating bonds has no effect on the efficiency of fluorination. Thus, the PMMA macromolecule contains simple C—H bonds, while PET and polyimide contain the conjugated bonds of aromatic structures. However, fluorination of those polymers proceeds in the same temperature interval. The highest concentrations of radicals ($(2-5)\cdot10^{18}$ spin g^{-1}) were obtained in two polymers quite different in their structures, lignin (which contains double olefin and aromatic bonds) and the copolymer of ethylene and carbon oxide (containing simple C—H bonds). It is likely that the high efficiency of fluorination is associated with the fact that the specimens of those polymers were highly dispersed powders. Hence, unlike chlorine, which exhibits selectivity in the chlorination of double bonds in olefin chains and aromatic rings in the temperature range from 150 to 170 K,[1] no selectivity was observed for fluorine even at 77 K.

All of the radicals obtained in the low-temperature fluorination of polymers (except for lignin) are active particles. They completely disappear in the range from 330 to 350 K, in contrast, for instance, to polystyrene, in which, up to 15 % stable fluorocarbon radicals are retained in the fluorinated layer (< 1 μm in thickness)[10] below ~500 K and they can be activated only by UV-irradiation of the fluorinated polystyrene.[11]

The initiation of the chain reactions of fluorination at room temperature is usually considered in the framework of one-center transitions and is associated with preliminary dissociation of molecular fluorine into atoms:

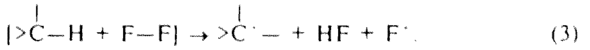
$$F_2 \rightarrow 2\,F^{\cdot}$$
(enthalpy of reaction ΔQ ~ 37 kcal mol^{-1})[5];

$$F^{\cdot} + RH \rightarrow R^{\cdot} + HF \qquad (1)$$
(ΔQ ~ −34 kcal mol^{-1}).

The dissociation of F_2 is highly improbable under cryogenic conditions, and the reaction is apparently initiated by molecular, not atomic fluorine. When the initiation stages of the processes of the interaction between molecular fluorine and organic substances are considered, the formation of free radicals is usually assumed.[5, 12] The reactions of free radical formation in the low-temperature (77 K) fluorination of polymers found in the present work can serve as experimental evidence for the correctness of these assumptions.

One should probably consider the initiation stage of the low-temperature fluorination of polymers with the formation of $R^{\cdot}$ as a synchronous multi-center reaction accompanied by homolytic dissociation of chemical bonds. One elementary act of the reaction consists of breaking the C—H and F—F bonds (the C=C bond opens in the former case) and the formation of H—F or C—F bonds, respectively:

$$[>C=C< + F-F] \rightarrow >C^{\cdot}-CF< + F^{\cdot}, \qquad (2)$$
$$(\Delta Q = -30\ \text{kcal mol}^{-1}),$$

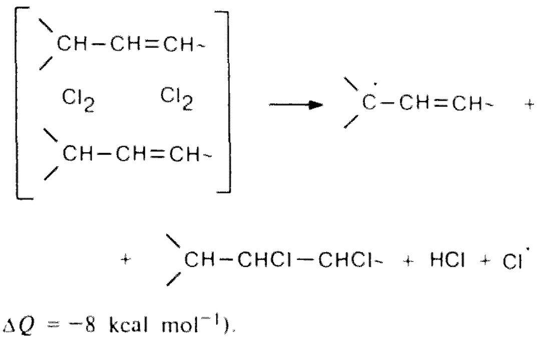


$$[>\overset{|}{C}-H + F-F] \rightarrow >\overset{|}{C}^{\cdot}- + HF + F^{\cdot}. \qquad (3)$$
$$(\Delta Q = -18\ \text{kcal mol}^{-1}).$$

The enthalpy of reaction (3) depends on the nature of the breaking bond, and lies in the interval from ~−18 kcal mol^{-1} for C—H to ~4 kcal mol^{-1} for the CH_3—H bonds in methane. Hence, the processes (2) and (3), which describe fluorination of multiple C=C bonds as well as fluorination of $>\overset{|}{C}H$—H, >CH—H, and —CH_2—H bonds, are thermodynamically permitted.[4,5]

Molecular interactions favorable for the organization of synchronous multi-center transitions in chemical reactions at low temperatures are characteristic of halogens in the condensed state. Thus, even under conditions of matrix isolation in an inert medium (neon) at 77 K, fluorine was found to exist as dimeric complexes $[F_2...F_2]$ to the point of 1 : 5000 dilution.[13] The heavier halogens are more inclined to complexation.

In the case of chlorination, reactions similar to (2) and (3) are endothermic. To explain the stages of radical formation in the low-temperature chlorination of polymers, one should assume the formation of polymolecular complexes between macromolecules and several (*n*) chlorine molecules.[4] Thus, at *n* = 2 the process already has a small exothermic effect and becomes thermodynamically permitted:



$(\Delta Q = -8\ \text{kcal mol}^{-1})$.

Similar synchronous reactions probably proceed in the case of other halogens interacting with polymers.

Although the mechanism of molecular synchronous reactions in the liquid phase has been fairly well studied,[14, 15] the theory of free-radical synchronous multi-center reactions at low temperatures has not been well developed. Additional investigations are needed here because of the fundamental importance of these phenomena in understanding the foundations of the reactivity.

Thus, the formation of free radicals at 77—150 K in the course of the direct fluorination of a large number of natural and synthetic polymers containing multiple as well as saturated bonds has been found. The initiation stage of low-temperature fluorination has been considered in the framework of the model of multi-center synchronous transitions with homolytic breaking of chemical bonds. The high reactivity and concentrations of $R^{\cdot}$ may be of practical interest as a method for generating radicals with no requirements for high-energy treatment of materials and as a method for obtaining chemically and physically modified polymeric materials.

Experimental

Commercial polymers (polyethylene (PE), polypropylene (PP), poly(methyl methacrylate) (PMMA), poly(ethylene terephtalate) (PET), polyimide) as well as the copolymer of ethylene and carbon oxide synthesized using palladium catalysts were subjected to fluorination. Hydrolysis lignin, pine wood, wood cellulose and cotton cellulose (both bleached and unbleached) were the natural polymers used. The specimens used were films (50—100 μm thick), and coarse (particles φ ~ 1 mm in size) and highly dispersed powders. Both bleached and unbleached cellulose was used as plates 1 mm thick, pine wood was used as sawdust (particles 25 μm in size), and cotton cellulose was used as a natural fibrous mass.

A weighed sample of polymer was placed into a quartz ampule which was evacuated to ~10^{-2} Torr, and F_2 was fed to 30 Torr after cooling to 77 K. The content of the impurity oxygen in the fluorine used did not exceed 1 %. After bleeding-in fluorine at 77 K, the residual fluorine was not removed, and the samples were heated to 300 K in the presence of F_2.

The ESR spectra were recorded on an EPR-21 radiospectrometer (3 cm band, UHF power of ~10^{-4} W) at 77K. The concentration of peroxide radicals in the total spectrum was calculated using the shape factor and the height of the downfield peak of the asymmetric $RO_2^{\cdot}$ singlet.

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