Synchronous reactions of free radical formation upon low-temperature chlorination of aromatic and olefinic hydrocarbons

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The free radical formation in reactions of low-temperature (77—150 K) chlorination of monomers and phenols was studied by ESR and calorimetry. The schemes were suggested for multicentered synchronous reactions of radical formation in polymolecular complexes, whose initial composition was directly determined for the first time from the structure of the radicals formed and thermodynamic parameters of the total exothermic effect.

Key words: monomers, phenols, low-temperature halogenation, free radicals.

Previously,[1—4] we have studied the solid-state reactions of free radical formation by the direct interaction of chlorine and fluorine with polymeric materials at low temperatures. The free-radical initiation of chain chlorination was considered in terms of the model of multicentered synchronous reactions in a complex consisting of several molecules of reagents. This model has been developed for molecular processes.[5,6]

The purpose of this work is to study reactions of low-temperature chlorination of aromatic compounds (phenols) and monomers with double bonds using ESR and scanning differential microcalorimetry.

Experimental

Phenol, 4-*tert*-butylphenol, and 2,6-di-*tert*-butyl-4-methylphenol (ionol) purified by multiple distillation were used. Of olefinic monomers, ethylene, methyl acrylate, and methyl methacrylate were chlorinated. A weighed sample of phenol was placed in glass ESR-tubes, evacuated, and frozen at 77 K, and gaseous chlorine (in an amount calculated from the weight ratio of reagents of 3 : 1) was frozen above the surface of the sample.

Weighed samples of monomers were determined from the pressure, by freezing them into tubes before (or after) introduction of chlorine (the weighed ratio of reagents was 1 : 1). For the ethylene chlorination, radicals were formed when powdered polyethylene (PE) was used as the support in which chlorine was frozen, and then ethylene was slowly introduced into the PE—chlorine system cooled to 77 K.

For ESR measurements at temperatures above 77 K, samples were heated in a thermostat cooled with liquid nitrogen vapor to a specified temperature. For recording calorimetric curves of heat evolution, samples were heated in a differential scanning microcalorimeter. ESR spectra were recorded on an ERP-21 radiospectrometer with a 3-cm frequency range at a power of the ultra-high frequency field of ~10^{-4} W at 77 K.

Results and Discussion

Chlorination of phenols

The ESR spectra show that as the temperature increases stepwise from 77 to ~150 K, paramagnetic centers (PMC) appear in the phenol—Cl_2 and 4-*tert*-butylphenol—Cl_2 systems. Their concentration reaches a maximum value in the region of 180—220 K (m.p. of Cl_2 is 172 K). In 4-*tert*-butylphenol, the concentration of PMC and their thermal stability are higher than those in phenol. The efficient decay of PMC in phenol begins when the temperature is above 230 K, disappearing completely in the region of melting of the matrix (m.p. 316 K), whereas in 4-*tert*-butylphenol, up to 30% PMC are retained at temperatures up to 370 K (Fig. 1, *b*, curves *1* and *2*). According to the calorimetric data, when the phenol—Cl_2 and 4-*tert*-butylphenol—Cl_2 systems are heated, the heat evolution is observed in the region of chlorine melting (160—170 K), which indicates the chlorination reaction. The total heat effect of phenol chlorination is 15.6 kcal mol^{-1}, and that of chlorination of 4-*tert*-butylphenol is 38.9 kcal mol^{-1}. The calorimetric curve of the heat evolution for phenol chlorination is presented in Fig. 2. The length of the kinetic chain of chlorination reactions estimated from the calorimetric and ESR data is equal to ~10^4 units.

The ESR spectra recorded during chlorination of phenol and 4-*tert*-butylphenol are identical in shape, and in the 3-cm range they are symmetrical singlets with a width of 0.9—1.2 mT without HFS properties (see Fig. 1, *a*, spectra *4* and *5*). It could be assumed that they belong to phenoxyl radicals formed due to the interaction of chlorine with the OH group of phenols, and the

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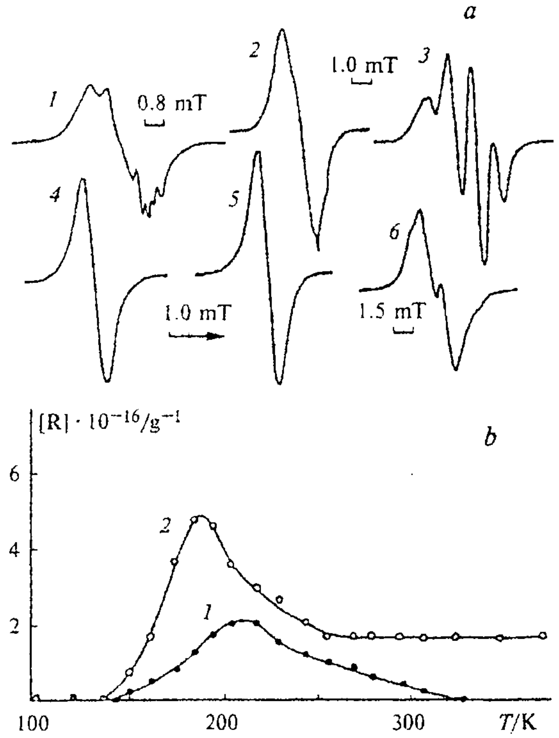


Fig. 1. *a*, ESR spectra of phenols UV-irradiated at 77 K (*1*—*3*) and chlorinated at 150—250 K (*4*—*6*); *1* and *4*, phenol; *2* and *5*, 4-*tert*-butylphenol; *3* and *6*, 2,6-di-*tert*-butyl-4-methylphenol after photolysis (*3*) and after chlorination upon irradiation with $\lambda > 360$ nm (*6*). *b*, Temperature dependence of the concentration of radicals in the phenol—chlorine (*1*) and 4-*tert*-butylphenol—chlorine (*2*) systems (the mass ratio of reagents is 1 : 1).

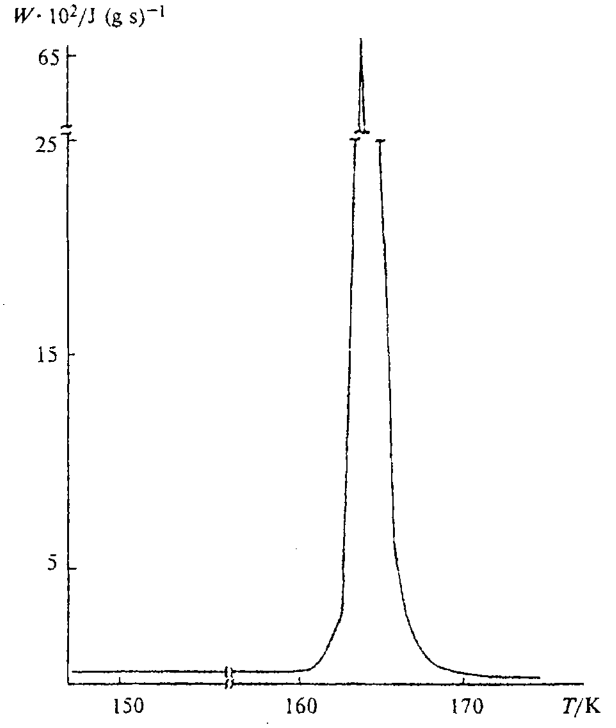
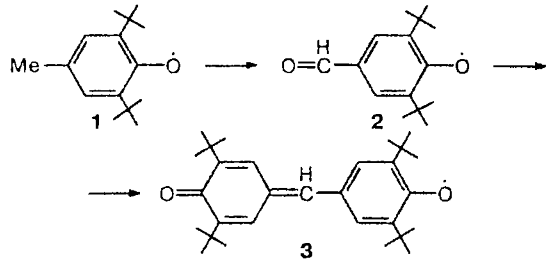


Fig. 2. Calorimetric curve of heating of the phenol—chlorine system (the mass ratio of reagents is 1 : 1).

spectra are recorded as single isotropic lines due to anisotropic broadening of the components in the solid phase. However, comparison with the phenoxyl radicals obtained upon low-temperature (77 K) photolysis of the corresponding phenols shows that PMC of the chlorinated samples differ in both the shape of the ESR spectra and thermal stability of the species. HFS appears in the spectra of phenoxyl radicals of phenol, 4-*tert*-butylphenol, and 2,6-di-*tert*-butyl-4-methylphenol (ionol, m.p. 343 K) in the solid phase. A weak quadruplet of triplets ($\Delta H_4 \cong 0.8$ mT, $\Delta H_3 \cong 0.18$ mT) and a strong quadruplet with $\Delta H = 1.1$—0.8 mT (from three protons of the CH_3 group) of phenol and ionol UV-irradiated at 77 K correspond in parameters to the spectra of phenoxyl radicals (see Fig. 1, *a*, spectra *1* and *3*).[7] HFS is virtually unnoticeable in the spectrum of the phenoxyl radical of 4-*tert*-butylphenol; however, the shape of a singlet with the width $\Delta H \cong 1.5$ mT differs from that of the singlet of the chlorinated samples with the width $\Delta H \cong 1.0$ mT (see Fig. 1, *a*, spectra *2* and *5*). In addition, PMC of chlorinated phenols disappear when the temperature increases to 220 K (in phenol) and 370 K (in 4-*tert*-butylphenol), while according to the data in Fig. 1, *b*, PMC of the chlorinated samples still persist at these temperatures. Note that no chlorination by molecular chlorine was observed for sterically hindered phenol (ionol) containing bulky substituents in the *ortho*-position. In the whole temperature range studied (77—350 K), heating of the ionol—chlorine system did not result in the appearance of ESR signals and heat release in calorimetric experiments.

It is known that phenoxyl radicals enter into reactions of oxidation and dimerization by the addition of a phenol molecule, and dimerization is accompanied by a change in the shape and HFS of ESR spectra.[7,8] The extension of the region of delocalization of a lone electron over the system of two aromatic rings results in blurring of HFS, due to which oxidized forms of phenoxyl radicals in the solid phase are detected as singlet lines with different widths. A change in the spectral shape during oxidation and dimerization is especially clear for the phenoxyl radical of ionol when solid ionol is oxidized by the air oxygen on aluminum catalysts.[8] The primary quadruplet with splitting $\Delta H = 1.1$ mT of the phenoxyl radical (**1**) (see Fig. 2, *a*, spectrum *3*), which appears in the first moments of oxidation, is transformed with a temperature increase to 353 K into a singlet with the width $\Delta H = 1.3$ mT corresponding to the aldehyde form of the phenoxyl radical (**2**), and upon heating to 373 K, the spectrum is transformed into a more narrow singlet line with $\Delta H = 0.8$ mT belonging to the galvinoxyl radical:



Oxidized forms 2 and 3 were confirmed experimentally by the chromatographic study of products of the ionol oxidation.[8]

Based on the data presented, we can conclude that PMC, which appeared due to the low-temperature chlorination of phenol and 4-*tert*-butylphenol, are oxidized dimeric forms of the corresponding phenoxyl radicals detected in the ESR spectra as single lines. Let us compare the reactions of phenol halogenation at room and low temperatures. It is known that the reaction of electrophilic substitution with the formation of a mixture of *ortho*- and *para*-chloro-derivatives of phenol is the main mechanism of phenol halogenation at standard temperatures. At low temperatures (150—250 K), there is an alternative route of phenol chlorination (distinct from the classical one) that is similar in many aspects to the oxidation process. It results in the formation of dimeric forms of phenoxyl radicals, which then are transformed into dimeric phenols and quinoid and quinonemethinoid structures.[9] According to our data,[1—4] chlorine does not react at low temperatures with aromatic rings and does not enter into reactions with polyethylene and polystyrene.

Phenoxyl radicals belong to the class of stable radicals. In addition to the conjugation effect, the stability of PhO$^\cdot$ is associated with screening of the free valence by alkyl substituents in the *ortho*- and *para*-position of the ring.[7] The phenoxyl radical of ionol, in which alkyl substituents create steric hindrances for the free valence on the O atom, is especially stable. *ortho*-Substituents also screen the OH group of the starting phenol, and this explains the absence of chlorination of 2,6-di-*tert*-butyl-4-methylphenol (ionol) at low temperatures. However, ionol is known as an inhibitor of radical reactions and, hence, it should react with atomic chlorine Cl$^\cdot$. In fact, the chlorination of ionol by atomic chlorine gave the positive result. Free radicals in the ionol—chlorine system were obtained by the irradiation of the system at 77 K with light with $\lambda > 360$ nm (indifferent to ionol, but resulting in the dissociation of Cl_2 to atoms). This results in the appearance of ESR signals, which can be presented as a superposition of a quadruplet of the primary phenoxyl radical of ionol (traces of HFS with $\Delta H = 1.1$ mT) and a singlet with the width $\Delta H = 1.2$ mT corresponding, most likely, to the oxidized form of PhO$^\cdot$ (see Fig. 1, *a*, spectrum *6*). The reaction of low-temperature chlorination of phenols is evidently initiated by molecular rather than atomic chlorine. The absence of the reaction when molecular chlorine acts upon ionol can be explained by the fact that the Cl_2 molecule cannot approach the phenol hydroxyl and detach the hydrogen atom due to steric hindrances created by the *ortho*-substituents. The chlorination starts only after the introduction of atomic chlorine capable of approaching the OH group. Phenol and 4-*tert*-butylphenol containing no *ortho*-substituents screening the OH group are chlorinated at low temperatures by molecular chlorine.

Chlorination of monomers

When ethylene is introduced into the PE—Cl_2 system cooled with liquid nitrogen, a complex signal of PMC is observed immediately at 77 K in the ESR spectra. The concentration of these PMC achieves ~10^{18} spin g^{-1}, and they disappear at the melting temperature of ethylene (~110 K). The ESR spectrum of chlorinated ethylene is presented in Fig. 3 (*1*). It contains the main quadruplet with splitting ΔH = 2.2—2.7 mT and a ratio of intensities of the lines close to 1 : 3 : 3 : 1. Each line of the quadruplet has additional HFS with ΔH =

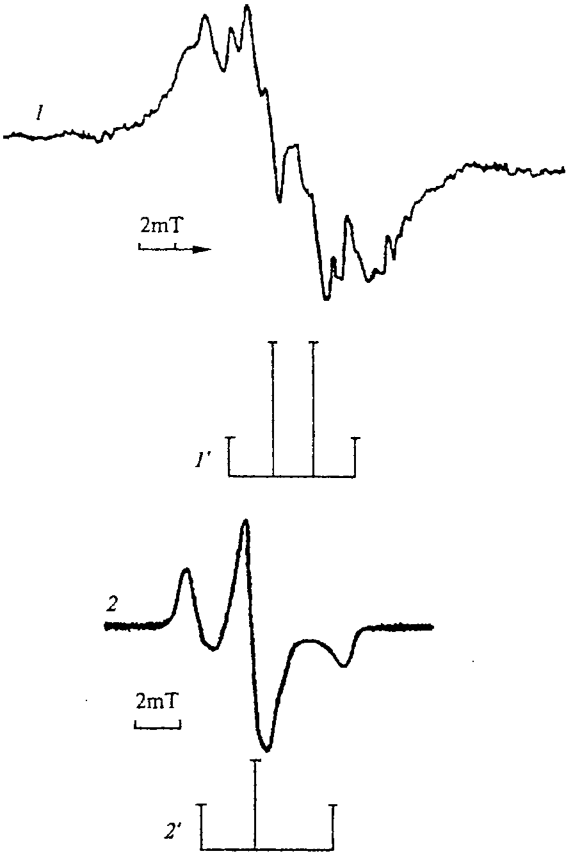
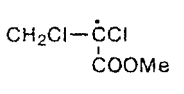


Fig. 3. ESR spectra of ethylene (*1*) and methyl methacrylate (*2*) chlorinated at 77 K; theoretical schemes of HFS lines of the corresponding spectra (*1'*, *2'*).

0.6—1.1 mT. The value of main splitting is characteristic of alkyl radicals with α- and β-hydrogens. For example, for the ethyl radical $CH_3—{}^{\cdot}CH_2$, $a_\alpha{}^H = 2.15$ mT and $a_\beta{}^H = 2.65$ mT.[10] The ratio of intensities of the lines close to binomial indicates that a lone electron interacts with three equivalent protons. Additional hyperfine splitting at 0.6—1.1 mT should be referred to the HF-interaction of the electron with the α- and β-nuclei of chlorine. The nuclear spin of Cl_2 is equal to 3/2, $a_\alpha{}^{Cl} = 0.62$ mT, and $a_\beta{}^{Cl} = 1.05$ mT.[10] Thus, according to the parameters, the spectrum obtained can be interpreted, most likely, as that belonging to the dichloroethyl radical $CH_2Cl—{}^{\cdot}CHCl$ (**4**), in which a lone electron interacts with one α-H, two β-H, and α- and β-Cl atoms. The result obtained makes it possible to refine the mechanism of olefin halogenation. It is accepted that the low-temperature chlorination of ethylene is a molecular process resulting in the formation of the dichloroethane molecule.[5] The observation of $CH_2Cl—{}^{\cdot}CHCl$ radicals indicates that the radical channel of ethylene chlorination also exists at 77 K. Under specially selected conditions where intermediate short-lived radicals could be stabilized in the polyethylene matrix, we obtained high concentrations of $R^{\cdot}$ and reliably detected their ESR spectrum. No formation of radicals was observed in the absence of polyethylene during chlorination of solid ethylene at 77 K. When the temperature of the ethylene—Cl_2 system increases, ESR signals are absent, and liquid dichloroethane is formed at 300 K. Free radicals were also obtained during chlorination of solid monomers (without a polymeric support) in the methyl acrylate—Cl_2 and methyl methacrylate—Cl_2 systems at 77 K. The concentrations of the radicals reach values $<10^{17}$ spin g^{-1}, and the radicals disappear in the region of matrix melting (180—210 K). Both signals are slightly asymmetrical triplets with the splitting value $\Delta H = 2.5—3.5$ mT, and they can be assigned, as in the case of ethylene, to the radicals formed by the addition of Cl_2 to the double bond of olefins:

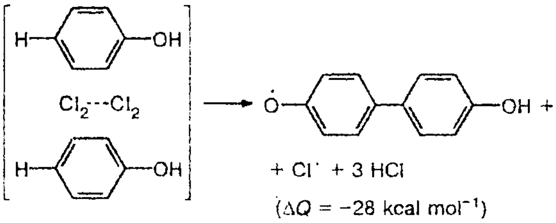


$CH_2Cl—\dot{C}Cl(COOMe)$

5

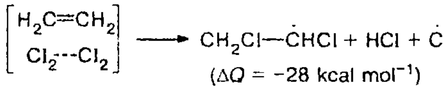
The interaction of a lone electron in radical **5** with two β-protons results in the appearance of the triplet spectrum. The triplet of chlorinated methyl methacrylate is presented in Fig. 3 (spectrum *2*). Some asymmetry of the signal is evidently due to the presence of chlorine atoms, although HFS from the interaction with Cl nuclei, unlike ethylene, is not manifested. Perhaps, this is related to a low concentration of the radicals.

For low-temperature chlorination, initiation by atomic chlorine is completely ruled out, since the temperature interval of spontaneous reactions in the gas phase for Cl_2 lies higher than 370 K.[5] Evidently, under low-temperature conditions, the reaction is initiated by molecular chlorine, which is also confirmed by experiments on the low-temperature chlorination of ionol. The direct opening of the double bond or detachment of the hydrogen atom with the formation of the corresponding radicals are strongly endothermic processes, and their occurrence is virtually impossible at such low temperatures. Therefore, to explain the stages of radical formation, we can assume the formation of polymolecular complexes between hydrocarbon molecules and several (*n*) chlorine molecules. For example, for two molecules of phenol and 4-*tert*-butylphenol at $n = 2$, an exothermic effect exists, and the process becomes thermodynamically possible upon the cleavage of the O—H, C—H, and Cl—Cl bonds to form the dimeric phenoxyl radical, HCl, and Cl.

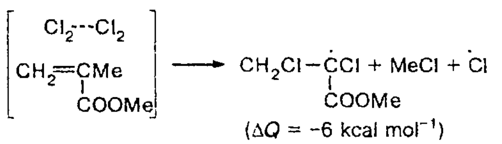


(ΔQ = −28 kcal mol⁻¹) (1)

The formation of radicals during low-temperature chlorination of monomers (ethylene, methyl acrylate, and methyl methacrylate) can initiate synchronous reactions in a molecular complex of one hydrocarbon molecule and two chlorine molecules. The simultaneous cleavage of the double bond in the >C=C< group and C—H and Cl—Cl bonds is compensated by the exothermic effect of formation of chloroalkyl radicals, the HCl (or CH_3Cl) molecule, and atomic chlorine:



$$\begin{bmatrix} H_2C{=}CH_2 \\ Cl_2\cdots Cl_2 \end{bmatrix} \longrightarrow CH_2Cl—\dot{C}HCl + HCl + \dot{C}l\ , \quad (\Delta Q = -28\ \mathrm{kcal\ mol^{-1}}) \qquad (2)$$



$$\begin{bmatrix} Cl_2\cdots Cl_2 \\ CH_2{=}\underset{\displaystyle COOMe}{\underset{|}{C}}Me \end{bmatrix} \longrightarrow CH_2Cl—\underset{\displaystyle COOMe}{\underset{|}{\dot{C}}}Cl + MeCl + \dot{C}l\ . \quad (\Delta Q = -6\ \mathrm{kcal\ mol^{-1}}) \qquad (3)$$

It should be mentioned that there are scarce experimental data that confirm the composition and properties of polymeric complexes, such as the results of studies of intermolecular bonds by IR spectroscopy and estimation of the enthalpy of self-association of molecules. A sharp increase in the electroconductivity of the systems favors the appearance of polymolecular complexes in the moment of one-time transitions.[5] The radical mechanism of solid-phase transformations of the complex is not discussed in the literature. Valuable information on the composition of radical intermediates can be obtained by ESR spectroscopy, and based on their structure, one can suggest the quantitative and qualitative compositions of the starting polymolecular complex, taking into account the total exothermic effect of the process. The results of ethylene chlorination suggest that the participation of one hydrocarbon molecule and two chlorine molecules is necessary for formation of the $CH_2Cl-{}^{\bullet}CHCl$ radical. In addition, the data on formation of radicals during low-temperature halogenation of polymers[1–4] and monomers are also evidence for the homolytic mechanism of transformations of the complex. Note that the participation of two halogen molecules can be explained by their affinity to intermolecular interactions in the condensed state, similar to that for fluorine. At low temperatures (4.2 K), fluorine exists as dimeric $F_2\cdots F_2$ complexes even in the strongly diluted state.[11] Most likely, these dimers are also possible for other halogens. Dimers of halogens should favor the organization of complexes with hydrocarbon molecules and synchronous multicentered transitions in chemical processes at low temperatures.

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