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A. T. KORITSKII, V. N. SHAMSHEV

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Abstract

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A. T. KORITSKII, V. N. SHAMSHEV

ENERGY TRANSFER IN THE RADIATION OXIDATION OF AROMATIC HYDROCARBONS

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Intermolecular energy migration is an important property of ionized and excited states, the formation of which underlies primary radiation processes. In recent years, works have appeared confirming the major role of energy-transfer mechanisms in various radiation-chemical processes, both in liquid and in solid organic substances ($^{1-3}$).

Owing to energy-transfer phenomena, the regularities of radiation-chemical reactions and their rates depend to a considerable extent on the presence, in the irradiated samples, of small admixtures of other substances. In particular, certain intermediate products formed during the radiation oxidation of hydrocarbons can have a noticeable effect on the development of radiolysis processes. Thus, S. Ya. Pshezhetskii and co-workers (^{4}) showed the active participation of hydroperoxides in the radiation oxidation of gaseous hydrocarbons. The action of radiation on intermediate reaction products in the liquid phase was observed by M. Proskurnin et al. (^{5}). The active products formed during radiation irradiation also exert an initiating effect on the development of chain thermal oxidation, as N. M. Emanuel' showed using saturated hydrocarbons as an example (^{6}).

The present work was carried out to elucidate the influence of oxidation products on the radiation yield of radicals in frozen samples. In the work an EPR setup was used under a beam of electrons with an energy of 1.6 MeV, making it possible to investigate the regularities of radical accumulation directly during irradiation of the samples (^{7}). Experiments were carried out with cumene (isopropylbenzene), which vitrifies well upon freezing. Cumene hydroperoxide (CHP), the main product of radiation chain oxidation of cumene (^{8}), was taken as an additive. The accumulation of radicals was investigated during irradiation of cumene samples with different CHP contents. The samples were irradiated in ampoules made of glass that did not give a noticeable paramagnetic signal in the region of g-factor values close to 2. Before being placed in the resonator, the cumene samples were rapidly frozen by immersion in liquid nitrogen. In this process the samples vitrified, and the introduced CHP additive remained uniformly distributed throughout the sample volume. Determination of the concentration of paramagnetic particles at a given dose value was carried out by

Fig. 1

Figure 1: Fig. 1

double integration of the EPR spectra and comparison of the obtained areas with the area of the signal from a $CuCl_2 \cdot 2H_2O$ standard with a known number of paramagnetic Cu^{2+} ions ([7]).

It was shown earlier that an admixture of CHP to cumene leads to a substantial increase in the rate of radical formation under the action of fast electrons ([9]). In the present work we obtained curves characterizing the regularities of radical accumulation in samples with different CHP concentrations. From the slopes of the initial sections of the curves, the values of the total radiation yield of radicals G_R were determined.

Fig. 1 presents the curve of the dependence of G_R on the concentration of CHP. It is seen from the figure that the increase in G_R with the concentration of the additive is nonlinear. An especially significant relative increase in G_R is observed at low CHP concentrations. Thus, an admixture of CHP $\approx 5 \cdot 10^{-3}$ mole/liter increases the rate of radical formation in cumene by approximately a factor of 2.5.

A similar regularity, characteristic of radiation processes in mixed systems, when energy migration to impurity molecules plays an essential role, was previously observed by other investigators in experiments with liquid mixtures ([1,3]). However, up to now the literature has not reported similar experimental results with samples containing hydroperoxide additives.

Fig. 1. Dependence of the radiation yield (G_R) on the concentration of cumene hydroperoxide (CHP) in cumene. Measurement temperature $-170°$. The scatter of points on the curve depends on the magnitude of the relative error of the measurements of G_R, which in these experiments is estimated at $\pm 15\%$.

The conclusion that energy is transferred to ROOH molecules in our experiments is also confirmed by the changed appearance of the EPR spectrum of irradiated cumene samples with CHP. The mere presence of a small CHP impurity already leads to the appearance of an asymmetric signal characteristic of peroxide-type radicals; moreover, this type of EPR signal was also observed in evacuated samples containing CHP. It is natural to attribute the formation of such radicals to the decomposition of ROOH ([9]).

It may be asserted that energy migration to hydroperoxides must occur at least also during the radiolysis of liquid cumene. We base this assertion on a comparison of data obtained by different methods in experiments on irradiation of liquid and frozen aromatic hydrocarbons containing small additives. Thus, energy transfer to impurities of carbon tetrachloride and benzoyl peroxide was observed both in the liquid ([1,3]) and in the solid phase ([2]). It may also be asserted that the specific phenomenon of energy transfer to various kinds of impurities and, in particular, to hydroperoxides is apparently characteristic of all aromatic hydrocarbons. We verified this by introducing cumene hydroperoxide into toluene, polystyrene, and other substances.

It is known that the thermal oxidation of condensed hydrocarbons proceeds by a chain mechanism with pronounced branching. Chain propagation occurs with the participation of radicals R and $\mathrm{RO_2}$, while pronounced branching occurs through the decomposition of hydroperoxides (ROOH) into radicals. In the radiation oxidation of cumene, as follows from the results obtained in the present work, the decomposition of (ROOH), which gives rise to chain branching, is initiated by radiation irradiation. Consequently, a chain-branched radiation process of cumene oxidation can develop at relatively low temperatures, when hydroperoxides are thermally stable. It is known from the literature that chain propagation in irradiated cumene already occurs at room temperature (8). Our data allow us to conclude that in irradiated cumene, as the concentration of hydroperoxides increases, the probability of their radiation decomposition will increase, owing to which the rate of initiation of chains will also increase substantially.

In (8), a significant increase in the rate of oxygen absorption was observed during irradiation of liquid cumene at comparatively low temperatures. This effect was not interpreted by the authors of article (8).

This can be explained by the radiolytic decomposition of hydroperoxides accumulating in the course of the oxidation of cumene. This result confirms what was said above.

The proposed mechanism of branched-chain oxidation of cumene may be represented schematically as follows:

$$(\mathrm{RH})^* \to \dot{\mathrm{R}} + \dot{\mathrm{H}} \quad \text{chain initiation;} \tag{1}$$

$$\dot{\mathrm{R}} + \mathrm{O_2} \to \mathrm{RO_2}, \quad \mathrm{R\dot{O}_2} + \mathrm{RH} \to \mathrm{ROOH} + \dot{\mathrm{R}} \quad \text{etc., chain propagation;} \tag{2}$$

$$(\mathrm{ROOH})^* \to \mathrm{R\dot{O}} + \dot{\mathrm{H}} \quad \text{chain branching;} \tag{3}$$

$$\dot{\mathrm{R}} + \dot{\mathrm{R}}, \quad \mathrm{R\dot{O}_2} + \mathrm{R\dot{O}_2}, \quad \dot{\mathrm{R}} + \mathrm{R\dot{O}_2} \quad \text{chain termination.} \tag{4}$$

Reaction (3), initiated by radiation through the migration of energy from solvent molecules to ROOH molecules, apparently leads to an increase in the rate of oxidation of cumene as the process develops and ROOH accumulates (8).

The results obtained are insufficient to make definite conclusions about the nature of the energy-transfer process. Further studies should help in choosing between the mechanism of transfer of electronic excitation and the mechanism of migration of electron–hole pairs.

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Institute of Chemical Physics
Academy of Sciences of the USSR

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