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Abstract

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PHYSICAL CHEMISTRY

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ENERGY TRANSFER IN THE RADIOLYSIS OF TOLUENE WITH ADDITIVES

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In the radiation action on chemical and biological systems, as has been noted repeatedly, a major role is played by processes of energy transfer that precede the rupture of a chemical bond. The study of these processes in radiation chemistry is usually based on analysis of the final products of radiolysis and therefore requires a quantitative assessment of the secondary reactions occurring in the system ([1,2]). Information on energy transfer in the early stages of radiolysis can in a number of cases be obtained by investigating the quenching and sensitization of luminescence by small additions of certain substances ([3–7]). Also of interest are direct measurements of the radiation yield of free radicals and elucidation of their nature upon irradiation of the compound under study in the presence of additives of other substances. Such measurements can make it possible not only to establish the direction of energy transfer in the mixture, but also to obtain an idea of the primary acts of chemical-bond rupture. By this method some information has already been obtained for complex compounds, where energy is transferred from some groups of the molecule to others ([8–10]). Of course, measurements of the accumulation of free radicals under irradiation are possible only in the solid phase, when the radicals are comparatively stable, but it may be thought that the results of such measurements are also of interest for understanding the mechanism of radiolysis of liquids.

In the present work, the effect of small additions of carbon tetrachloride, benzoyl peroxide, and carbon disulfide on the radiation yield of radicals and on the appearance of the spectrum upon irradiation of frozen toluene was studied by the method of electron paramagnetic resonance (e.p.r.). Scintillation-grade toluene of special purity was used, which before the experiment was degassed by pumping. From toluene containing the dissolved additive, transparent amorphous samples were obtained by rapid freezing; these were placed in a stream of cold nitrogen in the resonator of an e.p.r. spectrometer mounted under an electron beam with an energy of 1.6 MeV. Freezing and irradiation of the samples were carried out in thin-walled glass ampoules, which under irradiation give

Fig. 1

Figure 1: Fig. 1

no noticeable e.p.r. signal at values of the g-factor close to $g = 2$. The e.p.r. spectra of the sample, in the form of the first derivative, were recorded periodically directly during irradiation. At the same time the electron current on the sample was measured, which made it possible to calculate the energy absorbed in it. A description of the apparatus and of the methods for determining the concentration of free radicals and the dose received by the sample can be found in papers ([11,12]). The measurements showed that the additives indicated above strongly change the appearance of the e.p.r. spectrum and the radiation yield (G) of free radicals in frozen toluene.

Figure 1 gives the curves of radical accumulation at $-160°$ in irradiated toluene without additives and with additions of CCl_4. As is seen from Fig. 1, even a mole fraction of $CCl_4 \sim 5 \cdot 10^{-4}$ leads to an increase in the initial radiation yield of radicals by a factor of 4-5. At the same time noticeable

changes in the appearance of the EPR spectrum. Figure 2 shows the spectra of toluene (a) and carbon tetrachloride (c) without additives. The first of these coincides with the spectrum of benzene irradiated at low temperature and is due to the radical formed when a hydrogen atom is detached from the benzene ring ([13]). The asymmetric spectrum with hyperfine structure of irradiated CCl_4 apparently belongs to the CCl_3 radical. Spectrum (b) in Fig. 2 was obtained in the radiolysis of toluene with a small addition of CCl_4. It is a superposition of spectra (a) and (c), from which it follows that in the presence of the additive radicals of both types are formed in appreciable amounts. The total number of radicals formed in toluene with additives at these doses is considerably greater than would be expected in the case of independent action of the radiation on the toluene and CCl_4 molecules. Therefore, spectra (a) and (c) in Fig. 2, for ease of comparison, were recorded at higher doses than spectrum (b).

Fig. 1. Accumulation curves of radicals in toluene at $-160°$: *a*—without additive; *b*, *c*—with CCl_4 admixtures, molar fractions of CCl_4 $5 \cdot 10^{-4}$ and $7 \cdot 10^{-3}$, respectively.

Changes in the EPR spectrum and an increase in the radiation yield of radicals were also observed in experiments with toluene containing additions of benzoyl peroxide and carbon disulfide. Thus, the introduction of benzoyl peroxide, whose molar fraction was $5 \cdot 10^{-4}$, led to a threefold increase in G; a molar fraction of carbon disulfide equal to 10^{-2} increased G by 5-6 times. The radicals formed from carbon disulfide introduced into toluene have not yet been identified; the EPR spectrum of these radicals is asymmetric and rather complex. There is reason to believe that in this case radical ions are formed. Such a large influence of additives was observed only in experiments with amorphous samples of frozen toluene. Upon irradiation of crystalline samples obtained by

Fig. 2

Figure 2: Fig. 2

slow freezing of toluene, the effects were considerably weaker.

Fig. 2. EPR spectra: *a*—spectrum of toluene without additive (dose $\sim$ 50 Mrad); *b*—spectrum of toluene + CCl_4 (dose $\sim$ 5 Mrad); *c*—spectrum of pure CCl_4 (dose $\sim$ 20 Mrad).

The observed increase in the radiation yield of free radicals upon introducing additives into toluene is apparently connected with the transfer of energy to molecules of the dissolved substance or to some complexes composed of these molecules and molecules

toluene. As a result of energy transfer, a considerable fraction of the radicals is formed from the additive molecules and the toluene molecules surrounding them.

It is known (3) that carbon tetrachloride is one of the substances capable of quenching fluorescence in liquid scintillators. This is associated with the transfer of electronic excitation energy to the molecules of the quencher. Since studies of fluorescence quenching and of the formation of free radicals in the presence of additives during the radiolysis of mixtures make it possible to investigate different manifestations of the same energy-transfer processes, experiments in which identical systems are studied by both methods are of great interest. At present our results can be compared qualitatively with the data of (14), where it was shown that a mole fraction of 10^{-3} CCl_4 in a solution of terphenyl in benzene reduces the fluorescence intensity under the action of γ-rays by a factor of 2. As indicated above, approximately the same impurity in toluene in our experiments increased the yield of radicals in the solid solution by a factor of 5. Therefore it may be assumed that the quenching of fluorescence by carbon tetrachloride is associated with the expenditure of part of the energy on the rupture of chemical bonds in CCl_4.

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