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Abstract

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Kh. S. Bagdasaryan, N. S. Izrailevich, and V. A. Krongauz

INTRAMOLECULAR MIGRATION OF ENERGY IN THE RADIOLYSIS OF ALKYLBENZENES

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The idea of intramolecular migration of energy in molecules that do not contain a conjugated system of bonds has repeatedly been invoked to explain many phenomena observed under the action of light and ionizing radiation on polymers and biological objects. At the same time, studies performed on simple molecules, and moreover under conditions permitting an unambiguous conclusion as to the existence of this phenomenon, are almost entirely lacking. In discussing data relevant here, it must be borne in mind that intramolecular migration of energy, even in one-component systems, may be masked or suppressed by intermolecular transfer of energy from some groups to others. For solving the problem posed, polymers are rather inconvenient objects of study, since the phenomena observed under the action of radiation on polymers usually do not permit an unambiguous interpretation.

Arylalkyls, as well as mixtures of aromatic and aliphatic hydrocarbons, are very convenient for studying intra- and intermolecular energy transfer. Since the radiation stability of aromatic hydrocarbons is considerably greater than that of aliphatic hydrocarbons, the processes of energy transfer in these systems can be studied by the method of deviations from the rule of radiation-chemical additivity. By this method Barton and co-workers (^1) established that the yield of gaseous products in the radiolysis of alkylbenzenes is considerably smaller than follows from the additivity rule if an alkylbenzene is regarded as a mixture of benzene and the corresponding alkane. It remains unclear, however, whether the protection of the aliphatic chain by phenyl rings is explained by intramolecular or intermolecular transfer of energy from the aliphatic chain of one molecule to the phenyl ring of another alkylbenzene molecule, analogous to the intermolecular transfer of energy from cyclohexane to benzene (^2).

A more unambiguous conclusion concerning intramolecular migration of energy can be drawn from the data of Alexander and Charlesby (^3), who established that, for cross-linking naphthyldodecane into an insoluble network, a substantially larger dose is required than for cross-linking decalyldodecane, and that a naphthyl group attached to the middle of the dodecane chain exerts a stronger protective effect than one attached to the end of the chain. For a final conclusion it would be desirable to investigate the influence of a naphthyl group on the probability of rupture of the dodecane chain. Voevodskii and co-workers (⌒4), by the EPR method, investigated "frozen" radicals formed in the radiolysis of 1,1-substituted dodecanes at −196°. The substituents were phenyl and cyclohexyl rings. The authors convincingly showed that, under the conditions of their experiments, effective transfer of energy from aliphatic groups to phenyl rings occurs, leading to a considerable decrease in the total yield of radicals. A less clear conclusion can be drawn from these experiments concerning the mechanism of energy transfer. The smaller yield

radicals found by the authors for the mixed phenylcyclohexyl derivative in comparison with an equimolecular mixture of the diphenyl and dicyclohexyl derivatives, although it may serve as an indication of a greater efficiency of intramolecular energy migration compared with intermolecular transfer, nevertheless, as the authors point out, may possibly be explained by macroinhomogeneity of the mixture of dodecanes.

The most direct data on the question of interest to us can be provided by a study of the yield of primary radicals in the radiolysis of alkylbenzenes and mixtures of benzene with the corresponding alkanes. Schuler and co-workers (^{5}) measured the yield of radicals in the radiolysis by X-rays of benzene, certain alkanes, and alkylbenzenes. Some of their data are given in Table 1. In the same table we give the values calculated by us from these data, according to the rule of additivity of radicals yields, for toluene and ethylbenzene. The calculation was carried out according to the formula:

Table 1

Substance	Schuler's data	Schuler's data	Our data	Our data	Substance	Schuler's data	Schuler's data	Our data	Our data
	G	G_{ad}	G	G_{ad}		G	G_{ad}	G	G_{ad}
Benzene	0.6	(0.6)	0.6	(0.6)	Octylbenzene	–	–	0.9	3.9
Toluene	2.4	2.0	0.8	1.0	Octane + benzene (1 : 1)	–	–	2.1	3.9
Ethylbenzene	2.8	2.6	0.85	2.3	Hexane	7.4	(7.5)	5.8	(6.0)
Cumene	–	–	0.7	2.8	Octane	7.6	(7.5)	6.4	(6.0)
Butylbenzene	–	–	0.9	3.1					

Note. Mean values of G are given.

$$G_{\mathrm{ad}} = \varepsilon_{\mathrm{A}} G_{\mathrm{A}} + \varepsilon_{\mathrm{Ph}} G_{\mathrm{Ph}}, \tag{1}$$

where ε_{A} and $\varepsilon_{\mathrm{Ph}}$ are the electron fractions of the aliphatic chain and the aromatic ring, and G_{A} and G_{Ph} are the radical yields for alkanes and benzene. As is seen from Table 1, the values of G found in the present work for toluene and ethylbenzene are close to the calculated additive values, which clearly does not agree with the results of the works considered above.

We studied the yield of radicals in the γ-radiolysis of toluene, ethylbenzene, cumene, n-butylbenzene, and n-octylbenzene, and also in an equimolecular mixture of benzene with n-octane. For comparison, the radical yields from benzene, n-hexane, and n-octane were also determined. Iodine was used as the radical acceptor. Benzene, toluene, ethylbenzene, and cumene were purified by repeated shaking with concentrated sulfuric acid. After drying over metallic sodium, the substances were distilled on a column with an efficiency of 25–30 theoretical plates; fractions boiling within 0.1° were collected. Butylbenzene and octylbenzene were obtained by Wurtz' s method from bromobenzene and the corresponding alkyl bromides. Butylbenzene was fractionated on a column; octylbenzene was distilled several times with a dephlegmator.

Iodine was used at concentrations of $5 \cdot 10^{-4}$–$5 \cdot 10^{-3}$ M. It was shown that changing the iodine concentration within these limits does not affect the determined value of the radical yield. The iodine concentration was determined spectrophotometrically at the absorption maxima of the corresponding solutions (490–520 mμ). Radiolysis was carried out in the absence of air. Air was removed by repeated freezing and thawing of the liquid in vacuum.*

* After freezing iodine solutions in octane or octylbenzene that were free from air and subsequently thawing them, a considerable weakening of the iodine color occurs. After illuminating such a solution with the light of a bright lamp or irradiating it with γ-rays, the original color of the solution is completely restored. This, apparently, is due to the formation, during freezing, of molecular compounds of iodine with hydrocarbons, which are destroyed upon irradiation.

The radiation source was Co^{60}; dosimetry was carried out using a ferrous sulfate dosimeter. The dose rate was $1.8 \cdot 10^{18}$ eV/l • sec.

The radical yields measured by us are given in Table 1. Our data for alkanes are somewhat lower than the values obtained in Ref. (^{5}), but coincide with the value obtained in the later work (^{6}). The value of G found by us for toluene and ethylbenzene is considerably lower than the values found by Schuler. In order to make sure that the low value of G for toluene was not due to the presence of any impurities capable of accepting radicals, we investigated various samples of toluene and subjected them to various purification methods. In all cases, values close to that given in Table 1 were obtained. Measurement of the radical yield from toluene with diphenylpicrylhydrazyl gave 1.1, which agrees with the value

Fig. 1

Figure 1: Fig. 1

obtained by Shapiro (^{7}). Finally, the fact that for all alkylbenzenes we obtained practically the same value of G, equal to 0.8-0.9, gives grounds for assuming that precisely this value of G is correct, and not the high values obtained in Ref. (^{5}).

Fig. 1

As is seen from Table 1, for all alkylbenzenes the experimental value of G is considerably smaller than the additive value. Thus, the phenyl ring protects the aliphatic chain from decomposition, which agrees with data obtained by other methods. A very interesting fact is that the radical yield from octylbenzene is considerably smaller than from an equimolecular mixture of octane and benzene. From this one may conclude that intramolecular energy migration in octylbenzene is more effective than intermolecular energy transfer from the aliphatic chain of one molecule to the phenyl ring of another molecule. The relative probabilities of these two processes can be estimated. Consideration of the processes occurring during radiolysis of alkylbenzenes leads to the following two steady-state equations for excited aliphatic chains A^* and excited phenyl groups Ph^*:

$$a_A J \varepsilon_A = k_{\dot{A}}[A^*] + k_A[A^*] + k_{A\mathrm{Ph}}[A^*][\mathrm{Ph}] + k_M[A^*]; \tag{2}$$

$$a_{\mathrm{Ph}} J \varepsilon_{\mathrm{Ph}} = k_{\dot{\mathrm{Ph}}}[\mathrm{Ph}^*] + k_{\mathrm{Ph}}[\mathrm{Ph}] - k_{A\mathrm{Ph}}[A^*][\mathrm{Ph}] - k_M[A^*], \tag{3}$$

where J is the dose rate, ε_A and $\varepsilon_{\mathrm{Ph}}$ are the electron fractions of the aliphatic chain and phenyl ring, $k_{\dot{A}}$ and $k_{\dot{\mathrm{Ph}}}$ are the rate constants for the formation of radicals from the corresponding excited molecules or groups, k_A and k_{Ph} are deactivation constants, $k_{A\mathrm{Ph}}$ is the rate constant of intermolecular energy transfer from the aliphatic chain to the phenyl ring, [Ph] is the concentration of phenyl rings, k_M is the rate constant of intramolecular energy migration from the aliphatic chain to the phenyl ring, and a_A and a_{Ph} are proportionality coefficients, i.e., the yields of excited molecules A^* and Ph^* per unit of absorbed energy.

From equations (2) and (3) one can obtain the following expression for the radical yield G:

$$G_{\mathrm{ad}} - G = \varepsilon_A \frac{\theta}{1+\theta} \left(G_A - \frac{a_A}{a_{\mathrm{Ph}}} G_{\mathrm{Ph}} \right), \tag{4}$$

where

$$\theta = \frac{k_M + k_{A\mathrm{Ph}}[\mathrm{Ph}]}{k_{\dot{A}} + k_A}. \tag{5}$$

In Fig. 1 the dependence of $(G_{\mathrm{ad}} - G)$ on the electron fraction ε_A of the aliphatic chain is plotted; the straight line passes through the origin, whence it follows that $\theta/1+\theta$ is approximately constant.

To determine θ from equation (4), it is necessary to know a_A/a_{Ph}. Since the lowest excitation level for the aliphatic chain lies above the lowest excitation level of the phenyl ring, the ratio a_A/a_{Ph} cannot be greater than 1. Taking for a_A/a_{Ph} the values 1 and 0.5, we obtain for θ the values 12.5 and 7.1. An analogous calculation for an equimolecular mixture of octane and benzene at the same values of a_A/a_{Ph} gives for θ' (octane + benzene) the values 1.2 and 1.08

$$\left(\theta' = \frac{k_{A\mathrm{Ph}}[\mathrm{Ph}]}{k^{\cdot}_{A} + k_A}, \quad \text{since for the mixture } k_M = 0\right)^{*}.$$

For the difference $\theta - \theta'$, equal to $k_M/(k^{\cdot}_{A} + k_A)$, we obtain 11.3 and 6.0. Finally, for the ratio

$$\frac{\theta - \theta'}{\theta'} = \frac{k_M}{k_{A\mathrm{Ph}}[\mathrm{Ph}]}$$

we obtain the values 9.5 and 5.5 (for octylbenzene). Thus, intramolecular energy migration in octylbenzene occurs with much greater probability than intermolecular energy transfer from the aliphatic chain to phenyl rings.

Studying the efficiency of luminescence under the action of radiation, Avivi and Weinreb (^{8}) established that the efficiency of energy transfer from polystyrene to 2,5-diphenyloxazole and anthracene does not depend on whether the luminophore molecule is chemically bonded to the chain of the polystyrene molecule or not. This result does not contradict the fact established by us of efficient intramolecular energy migration along an aliphatic chain. In the polystyrene molecule, the energy absorbed by the aliphatic chain migrates to neighboring phenyl rings, and not to luminophore molecules attached to the ends of polystyrene molecules. Luminescence occurs as a result of intermolecular energy transfer from the phenyl rings to the luminophore molecule.

Physicochemical Institute
named after L. Ya. Karpov

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* Note that since [Ph] = 4 mol/l, it follows from the value found for θ' that:

$$\frac{k_{\mathrm{APh}}}{k^{\cdot}_{A} + k_{A}} = 0.25.$$