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Abstract

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ON THE BENZENE-PHOTOSENSITIZED BREAKDOWN OF HYDROCARBONS AT LOW TEMPERATURES

Upon irradiation with ultraviolet light (λ2537 Å) of benzene frozen to the temperature of liquid nitrogen in transparent organic glasses, along with fluorescence and phosphorescence processes, its decomposition also occurs with rupture of the C–C bond of the benzene ring ($^{1-8}$). Using ultraviolet spectroscopy and gas chromatography it was shown that the product of photochemical decomposition of benzene at 77° K is a substituted hexatriene,

$$\mathrm{H_2C{=}CH{-}CH{=}CH{-}CH{=}CH{-}R}$$

(the molecule of the hydrocarbon medium in which the photolysis is carried out will be denoted by the symbol RH). It has been shown that hexatriene is formed directly during irradiation of benzene solutions at 77° K. It is assumed that its formation occurs by a four-center reaction (^{3}):

$$\mathrm{C_6H_6 + RH \xrightarrow{h} H_2C{=}CH{-}CH{=}CH{-}CH{=}CH{-}R}$$

or through the intermediate stage of formation of a biradical (^{8}):

$$\mathrm{C_6H_6 \xrightarrow{h} \dot{H}C{=}CH{-}CH{=}CH{-}CH{=}\dot{C}H \xrightarrow{+RH} H_2C{=}CH{-}CH{=}CH{-}CH{=}CH{-}R}$$

The quantum yield of hexatriene depends on the concentration of benzene; its maximum value in an ether–isopentane–ethanol (EPA) medium is 0.023^*. The quantum yields of fluorescence and phosphorescence for benzene in EPA are approximately the same (^{9}) and are 10 times greater than the quantum yield of hexatriene formation ($\varphi_{\text{fluor}} = \varphi_{\text{phosph}} = 0.25$). In (^{10}) it was shown that, upon irradiation of benzene solutions in saturated hydrocarbons at 77° K, alkyl radicals are formed together with hexatriene, the formation of which during benzene photolysis cannot be explained by any of the schemes proposed to account for the formation of substituted hexatriene. Therefore it must be assumed that other processes are present, responsible for the formation of alkyl radicals.

Fig. 1. Diagram of the apparatus for irradiation with ultraviolet light at 77° K

Figure 1: Fig. 1. Diagram of the apparatus for irradiation with ultraviolet light at 77° K

To obtain additional information on these photochemical processes, we used the EPR method to study the radicals formed and investigated the final gaseous products of the reaction.

Photolysis was carried out on transparent solid solutions of benzene in methylcyclohexane and 3-methylpentane at the temperature of liquid nitrogen. The concentration of the solutions was varied from $1.8 \cdot 10^{-3}$ to $2.1 \cdot 10^{-1}$ mole/liter. Irradiation was performed with a PRK-7 mercury lamp in a quartz vessel cooled with liquid nitrogen (Fig. 1). The thickness of the layer of benzene solutions was ~ 5 mm. Before irradiation the solutions were thoroughly evacuated. After irradiation the solution was thawed, again frozen to 77° K, and the pressure of the evolved gas was measured with a membrane manometer, after which the gas was collected for mass-spectrometric analysis. Then the irradiated solution was diluted with carefully purified *n*-heptane and the amount of hexatriene formed as a result of irradiation was determined by light absorption at $\lambda = 275$ mμ on an SF-4 spectrophotometer. The molar extinction coefficient for this wavelength was taken, according to work (^{5}), to be $6.8 \cdot 10^4$.

For investigation of the radicals formed by the EPR method, the degassed benzene solution was irradiated in a quartz Dewar vessel at 77° K in quartz ampoules with an internal diameter of 2.5 mm, which were then transferred without thawing into a Dewar vessel with liquid nitrogen placed in the resonator of an EPR-2 instrument. The amount of radicals was determined relative to standard coal samples calibrated with diphenylpicrylhydrazyl. The solution was then thawed and quantitatively transferred from the ampoule into a cuvette, diluted with *n*-heptane, and the amount of hexatriene was determined on an SF-4. Analysis of the gaseous reaction products was not carried out in this case.

Fig. 1. Diagram of the apparatus for irradiation with ultraviolet light at 77° K

When benzene solutions in methylcyclohexane were irradiated, an EPR spectrum was obtained (Fig. 2a) which, in the number of components, their relative intensity, and hyperfine splitting, coincides with the spectrum of the methylcyclohexyl radical obtained upon irradiation of frozen methylcyclohexane with fast electrons (^{11}) (Fig. 2b). When benzene solutions in 3-methylpentane were irradiated, the spectrum shown in Fig. 3 was obtained. It consists of 6 well-resolved components of hyperfine structure with equal splitting between the components,

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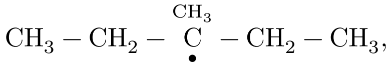
* This value of the quantum yield is approximate, since the absorption coefficient of the substituted hexatriene is not precisely known.

Fig. 2. EPR spectra of radicals formed: a —upon irradiation of benzene in methylcyclohexane and b —upon irradiation of methylcyclohexane with fast electrons

Figure 2: Fig. 2. EPR spectra of radicals formed: a —upon irradiation of benzene in methylcyclohexane and b —upon irradiation of methylcyclohexane with fast electrons

equal to ~ 24 oersted. This spectrum can be assigned to the radical



$$CH_3 - CH_2 - \overset{CH_3}{\underset{\bullet}{C}} - CH_2 - CH_3,$$

formed as a result of abstraction of a hydrogen atom from the tertiary carbon atom in the 3-methylpentane molecule. In this radical the EPR spectrum is evidently due to only 5 of the 7 β-protons, since two of them (one in each of the methylene groups), owing to purely geometrical conditions, cannot interact appreciably with the unpaired electron (^{12}). The spectra of Figs. 2a and 3 were also obtained in the case of irradiation of hexadeuterobenzene, C_6D_6, in methylcyclohexane and 3-methylpentane. A very significant fact proved to be that, upon irradiation of C_6H_6 in 3-methylpentane, hydrogen is formed together with the R-substituted hexatriene, whereas upon irradiation of C_6D_6 in the same hydrocarbon—H_2 and small amounts of HD.

Fig. 2. EPR spectra of radicals formed: a —upon irradiation of benzene in methylcyclohexane and b —upon irradiation of methylcyclohexane with fast electrons

Conc. C_6D_6, mol/l	$1.8 \cdot 10^{-3}$;	$1.6 \cdot 10^{-2}$;	$6.0 \cdot 10^{-2}$
H_2/HD	9.5;	8.2;	8.1

The process leading to the simultaneous formation of alkyl radicals and hydrogen may apparently be the reaction of photosensibiliza-

benzene-sensitized decomposition of hydrocarbons:

$$C_6H_6\,(C_6D_6) \xrightarrow{h\nu} C_6H_6^*\,(C_6D_6^*), \qquad C_6H_6^*\,(C_6D_6^*) + RH \rightarrow C_6H_6\,(C_6D_6) + R\cdot + H\cdot . \tag{1}$$

The most essential feature of this reaction is that the energy of the light quantum absorbed by benzene (112 kcal/mole) is transferred (partly or completely) to the hydrocarbon molecule and causes the rupture of one of the C—H bonds (the energy of rupture of the weakest of them is 86 kcal/mole) (^{13}).

Fig. 3. E.p.r. spectrum of radicals formed upon irradiation of benzene in 3-methylpentane

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Figure 3: Fig. 3. E.p.r. spectrum of radicals formed upon irradiation of benzene in 3-methylpentane

The benzene molecule thereby returns from the excited state to the ground, unexcited state. The hydrogen atoms formed in this process (probably "hot" ones) may enter into the following reactions:

$$H\cdot + RH \rightarrow H_2 + R\cdot, \tag{2}$$

$$H\cdot + C_6H_6\,(C_6D_6) \rightarrow H_2\,(HD) + C_6H_5\cdot\,(C_6D_5\cdot) \tag{3}$$

with the subsequent process

$$C_6H_5\cdot\,(C_6D_5\cdot) + RH \rightarrow C_6H_6\,(C_6D_5H) + R\cdot \tag{4}$$

Since we do not observe $C_6H_5\cdot\,(C_6D_5\cdot)$ in the e.p.r. spectra at 77° K, and since there is no diphenyl among the reaction products, reaction (4) probably occurs very rapidly in the solid phase. The very slight change in the H_2/HD ratio upon a considerable change in the benzene concentration (by a factor of 33) in the case of deuterated benzene indicates that reactions (2) and (3) probably occur in the immediate vicinity of the benzene molecule causing rupture of the C–H bond according to reaction (1).

The proposed scheme thus assumes that, upon irradiation with u.v. light of frozen benzene solutions at 77° K, two parallel processes occur: the reaction of formation of a substituted hexatriene and the benzene-photosensitized decomposition of hydrocarbons with the formation of hydrocarbon radicals and hydrogen. In order to test the hypothesis that these two processes proceed independently, the present work investigated the quantitative relation between the yield of hexatriene, on the one hand, and the yield of radicals and hydrogen, on the other. The corresponding data are given in Table 1. As is seen from the data of this table, the ratios N_{hex}/R and

$$\frac{N_{\mathrm{hex}}}{H_2}\left(\frac{N_{\mathrm{hex}}}{H_2 + HD}\right)$$

depend on the benzene concentration both for C_6H_6 and for C_6D_6. This confirms our assumption of the existence of two independent photochemical reactions. The ratio

$$\frac{\mathrm{H_2}}{2R}\left(\frac{\mathrm{H_2+HD}}{2R}\right)$$

proved to be greater than unity for all benzene concentrations; this shows that only some part of the total amount of hydrocarbon radicals formed in the primary act is stabilized. It should be noted that the ratios

$$\frac{\mathrm{H_2}}{2R}\left(\frac{\mathrm{H_2+HD}}{2R}\right)$$

given in the table are very approximate, since the experiments to determine the amounts of $\mathrm{H_2}$ and R· were carried out under nonidentical conditions.

The yields of hexatriene and radicals per unit time depend on the benzene concentration and pass through a maximum at a concentration approximately equal to $1.6 \cdot 10^{-1}$ mole/liter for $\mathrm{C_6H_6}$ and $6.0 \cdot 10^{-2}$ mole/liter for $\mathrm{C_6D_6}$. The yield of hexatriene depends on the benzene concentration much more strongly than the yield of radicals. Thus, the yield of hexatriene in the case of $\mathrm{C_6H_6}$ in the concentration interval $1.8 \cdot 10^{-3}$–$1.6 \cdot 10^{-1}$ mole/liter increases by a factor of 4.2, while the yield of radicals increases only by a factor of 1.2. The corresponding increase in the yields in the case of $\mathrm{C_6D_6}$ in the interval concentrations $1.8 \cdot 10^{-3}$–$6 \cdot 10^{-2}$ mol/l is 2.3-fold and 1.1-fold. The yield of hexatriene is approximately 2–3.5 times greater for C_6D_6 than for C_6H_6 for all

Table 1

Benzene concentration, mol/l	C_6H_6 $N_{\text{hex}}/R\cdot$	C_6H_6 N_{hex}/H_2	C_6H_6 $H_2/2R\cdot$	$C_6D_6^*$ $N_{\text{hex}}/R\cdot$	$C_6D_6^*$ N_{hex}/H_2+HD	$C_6D_6^*$ $H_2+HD/2R\cdot$
$1.8 \cdot 10^{-3}$	0.77	0.20	1.9	2.2	0.34	3.2
$1.6 \cdot 10^{-2}$	0.92	0.29	1.6	3.4	0.44	3.9
$6.0 \cdot 10^{-2}$	–	–	–	3.7	0.80	2.3
$1.6 \cdot 10^{-1}$	2.9	0.54	2.7	5.2	–	–
$2.1 \cdot 10^{-1}$	3.6	–	–	–	–	–

* It is assumed that the molar quenching coefficients for $H - C_6H_6 - R$ and $H - C_6D_6 - R$ are identical.

concentrations studied, whereas the yield of radicals remains approximately the same in both cases. The dependence of the yield on the benzene concentration can be explained as follows. Let us suppose that, for the reaction of benzene decomposition with formation of hexatriene to proceed, some definite, rather rarely realized mutual arrangement of C_6H_6 and RH is required, and that reaction (1) depends little on geometrical conditions. Let τ_1 be the lifetime of the excited state of benzene, and τ_2 the time of excitation transfer between benzene molecules, with τ_2 decreasing as the distance between benzene molecules decreases. Then the ratio τ_1/τ_2 characterizes the number of benzene molecules to which the excitation can be transferred. With increasing benzene concentration the average distance between benzene molecules decreases, τ_1/τ_2 increases, and, consequently, the probability increases that the excitation will fall on such benzene molecules for which the reaction

$$C_6H_6 + RH \rightarrow H_2C = CH - CH = CH - CH = CH - R$$

is facilitated by virtue of geometrical conditions. This explains the increase in the yield of hexatriene with increasing benzene concentration. The decrease in the yield of hexatriene upon further increase in the benzene concentration is apparently associated with the formation of benzene dimers in frozen solutions ([14]).

To explain the increase in the yield of hexatriene in the case of deuterated benzene, one must assume that, for a given concentration of C_6D_6, the ratio τ_1/τ_2 is greater than in the case of C_6H_6. It is known ([15]) that $\tau_1(C_6D_6)$ is greater than $\tau_1(C_6H_6)$; it follows from this that, on going from C_6H_6 to C_6D_6, τ_2 either does not change or, if it increases, then more weakly than τ_1. Then the maximum yield of hexatriene in C_6D_6 should be observed at a lower concentration than in C_6H_6, which is confirmed experimentally.

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