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Abstract

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PHOTOSENSITIZED DECOMPOSITION OF HYDROCARBONS BY CERTAIN BENZENE DERIVATIVES AT LOW TEMPERATURES

Earlier we found (1) that, upon irradiation with ultraviolet light ($\lambda > 2300$ Å) of frozen dilute solutions of benzene in saturated hydrocarbons at 77° K, a benzene-photosensitized decomposition of hydrocarbons occurs,

$$C_6H_6^* + RH \rightarrow C_6H_6 + R\cdot + H\cdot,$$

proceeding in parallel with the previously established (2,3) process of formation of substituted hexatriene

$$C_6H_6 + RH \xrightarrow{h} CH_2{=}CH{-}CH{=}CH{-}CH{=}CH{-}R)^*.$$

It seemed to us very interesting to determine whether the photosensitization process also takes place in solutions of benzene derivatives. From work carried out using the method of ultraviolet spectroscopy, it is known (4–6) that upon irradiation with ultraviolet light of solutions of certain aromatic compounds (for example, alkyl-substituted benzenes, dibenzyl, triphenylmethane, etc.) under conditions analogous to those described above, radicals are formed from the aromatic molecules themselves. As the authors of the cited works assume, in this case photodissociation of the C—H bond in the side chain occurs:

$$Ph{-}MH \rightarrow Ph{-}M\cdot + H\cdot.$$

In the present work the following compounds were investigated: toluene, ethylbenzene, *iso*-propylbenzene, *o*-, *m*- and *p*-xylenes, diphenylmethane, triphenylmethane, fluorobenzene, chlorobenzene, and acetophenone. Dilute solutions of the above-listed compounds in 3-methylpentane and in deuterium-containing 3-methylpentane at 77° K were irradiated with ultraviolet light. The procedure for carrying out the experiments, for analysis of the evolved gases, and for recording the e.p.r. spectra of the radicals formed was analogous to that used earlier (1).

Upon irradiation of solutions of the above-listed aromatic compounds, evolution of hydrogen and formation of 3-methylpentyl radicals were found in all cases except solutions of C_6H_5F, C_6H_5Cl, and $C_6H_5COCH_3$. The 3-methylpentyl radicals were identified by us from their e.p.r. spectra (see (^{1})).

In carrying out experiments using partially deuterated 3-methylpentane as solvent, evolution of H_2, HD, and D_2 was observed. The results obtained allow one to conclude that, for this group of compounds, a process of photosensitized decomposition of hydrocarbons takes place, proceeding according to the following scheme:

$$\mathrm{Ph{-}MH} \xrightarrow{\mathrm{h}} \mathrm{Ph{-}MH}^*.$$

$$\mathrm{Ph{-}MH}^* + \mathrm{RH}\ (\mathrm{RD}) \rightarrow \mathrm{Ph{-}MH} + \mathrm{R}\cdot + \mathrm{H}\cdot\ (\mathrm{D}\cdot). \tag{1}$$

$$\mathrm{H}\cdot\ (\mathrm{D}\cdot) + \mathrm{RH}\ (\mathrm{RD}) \rightarrow \mathrm{H}_2\ (\mathrm{HD}, \mathrm{D}_2) + \mathrm{R}\cdot. \tag{2}$$

$$\mathrm{H}\cdot\ (\mathrm{D}\cdot) + \mathrm{Ph{-}MH} \rightarrow \mathrm{H}_2\ (\mathrm{HD}) + \mathrm{Ph{-}M}\cdot. \tag{3}$$

Experiments carried out by us on irradiation of solutions of $C_6H_5CD_3$ (D content in the methyl group 79%) in undeuterated 3-methylpentane showed that the hydrogen evolved in this case contains 94% H_2 and only 6% HD. These data show that the assumption that the primary photochemical act consists in cleavage of the C–H bond in the side chain of the aromatic molecule, at least for solutions of toluene, is incorrect.

* By the symbol RH we shall denote a hydrocarbon molecule, and by the symbol Ph–MH, molecules of aromatic hydrocarbons that are benzene derivatives.

There is every reason to believe that, in the other aromatic compounds we investigated, such photodissociation is likewise not the predominant primary process. This also follows from the fact that we do not observe EPR spectra corresponding to aromatic radicals (i.e., $[\mathrm{Ph}-\mathrm{M}\cdot] \ll [\mathrm{R}\cdot]$), whereas the assumption of photodissociation would imply that $[\mathrm{Ph}-\mathrm{M}\cdot] \gg [\mathrm{R}\cdot]$. The formation, by reaction (3), of aromatic radicals evidently occurs to a much smaller extent than the formation of alkyl radicals by reaction (2).

The absence of hydrogen and radicals in irradiated solutions of C_6H_5F, C_6H_5Cl, and $C_6H_5COCH_3$ shows that these compounds are not photosensitizers.

The second task of the present work was to clarify the question of which energy level of the aromatic molecule (singlet or triplet) is associated with the photochemical transformations we observed. For this purpose we measured the initial rates of hydrogen evolution $(w_{H_2})^*$ and compared them with the concentration of triplet states of the aromatic molecules [T]. To determine [T], the relative values of the initial intensity I_0 and the decay time τ of the phosphorescence of a series of aromatic compounds in solutions in 3-methylpentane at 77° K were measured. The concentration [T] was calculated from the formula: $[T] = I_0\tau$. The afterglow of the solutions under study was recorded with an FEU-19M photomultiplier, with the phosphorescence decay curves recorded on an EPP-09 electronic potentiometer.

The data we obtained are presented in Table 1. As is evident from the table, the rate of hydrogen evolution changes in parallel with the value $I_0\tau = [T]$, i.e., a larger value of w_{H_2} corresponds to a larger value of $I_0\tau$. For the compounds listed in the table for which w_{H_2}, I_0, and τ were measured, the value of τ does not vary greatly (from 5.8 to 7.7 sec.); the situation is different for solutions of acetophenone and chlorobenzene, for which w_{H_2} lies below the limit of measurement (< 0.04 μmol/hour), while the value of τ is very small ($\tau = 8 \cdot 10^{-3}$ sec. for acetophenone and $\tau = 4 \cdot 10^{-3}$ sec. for chlorobenzene (7)). Although acetophenone has a high phosphorescence quantum yield (0.6) (7), and hence also a high I_0, the product $I_0\tau$ in this case proves to be at least 200 times smaller than the corresponding value for benzene**, which, apparently, is the reason for the very small value of w_{H_2}. The same reasoning can be applied to chlorobenzene, for which, in addition to the small value of τ, the phosphorescence quantum yield is also very small (0.04) (7). Thus, the data obtained are consistent with the assumption that aromatic-compound molecules in the triplet state participate in the photosensitization reaction.*** Against the alternative hypothesis—the possibility of participation by molecules excited to the singlet state—stands the absence of photosensitization in the case of fluorobenzene solutions. Indeed, this compound has no phosphorescence, while its fluorescence quantum yield is close to the corresponding value for benzene (7). However, despite the relatively high concentration of C_6H_5F molecules excited to the singlet state, the photosensitization process does not occur. In our opinion, there is no reason to suppose that, in the case of other aromatic molecules, excited singlet states can be responsible for sensitization.

The question arises as to how triplet states can participate in the sensitization process: as is known, the energy of the triplet levels of the aromatic compounds considered does not exceed 78-85 kcal/mol (9, 10), whereas the energy of rupture of the $C-H$ bond at a tertiary carbon atom in a hydrocarbon molecule is estimated at 86 kcal/mol

* The initial rate is proportional to the quantum yield.
** On conversion to the arbitrary units of Table 1, for acetophenone $I_0\tau \cong 90$.
*** Recently the suggestion that triplet-excited molecules of triphenylamine and carbazole participate in photochemical reactions at 77° K was put forward in work (8).

(11). A possible explanation of this discrepancy is the assumption that the photosensitization reaction proceeds with the participation of a second quantum.

It is known, for example (12), that the process of formation of alcohol radicals upon irradiation with ultraviolet light of alcoholic solutions of diphenylamine under analogous conditions is a two-quantum process.

We have studied the dependence of the rates of formation of hydrogen and alkyl radicals for solutions of toluene and benzene on the light intensity I^*. It was found that $w_{\mathrm{H2}} \sim I^{1.8}$ and $w_{\mathrm{R}\cdot} \sim I^{2.2}$ (for toluene); $w_{\mathrm{R}\cdot} \sim I^{1.7}$ (for benzene). This dependence indicates that the photosensitization process is indeed a two-quantum process. The long lifetime of the aromatic molecule in the excited triplet state permits the possibility of its absorbing one more quantum of light, with transition to a higher triplet level**, in which state the molecule possesses a large excess of energy compared with the energy required to break the C–H bond in the hydrocarbon, and can cause the sensitized decomposition of solvent molecules. It should be noted that the rate of formation of substituted hexatriene upon irradiation of benzene solutions depends linearly on the light intensity (13), i.e., this reaction is a one-quantum process.

Table 1

Aromatic compound	Conc. of solutions in 3-methylpentane (mol/l)	w_{H2} (µmol/hour)	I_0 (relative units)	τ (sec.)	$I_0\tau$
Benzene	$2 \cdot 10^{-2}$	0.9	38	5.9	224
iso-Propylbenzene	$2 \cdot 10^{-2}$	1.6	72	5.8	418
o-Xylene	$2 \cdot 10^{-2}$	1.8	106	7.3	780
Ethylbenzene	$2 \cdot 10^{-2}$	1.8	115	7.7	890
Toluene	$2 \cdot 10^{-2}$	1.95	138	7.4	1020
p-Xylene	$2 \cdot 10^{-2}$	2.3	125	7.6	955
m-Xylene	$2 \cdot 10^{-2}$	2.8	130	7.75	1010
Triphenylmethane	$5 \cdot 10^{-3}$	0.64	76	6.9	530
Diphenylmethane	$5 \cdot 10^{-3}$	0.82	99	7.3	720

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* The light intensity was varied by means of previously calibrated screens.

** According to theoretical calculations (14), such levels exist in benzene molecules and in a number of its derivatives; however, the corresponding triplet-triplet transitions have not been detected experimentally.

Note: Figure translations are in progress. See original paper for figures.

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