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DETECTION BY THE E.P.R. METHOD OF THE TWO-PHOTON CHARACTER OF THE SENSITIZED PHOTODECOMPOSITION OF METHYL IODIDE

In 1940 West showed ([1,2]) the existence of elementary photosensitization by naphthalene of the dissociation of ethyl iodide in hexane and ethanol, which is based on resonant transfer of photoexcitation energy from naphthalene (λ = 313 nm) to an ethyl iodide molecule. (Direct photolysis most probably occurs under the action of light with $\lambda = 254$ nm.) In the development of our previous investigations of the photosensitized decomposition of various compounds at 77° K and of the mechanism of these photoreactions ([3,4]) by the e.p.r. method, we studied the sensitized photodecomposition of methyl iodide at 77° K.

Methyl iodide was first decolorized by shaking with sodium sulfate, filtered, and subjected to fractional distillation on a column packed with copper turnings. The sensitizers of the photodecomposition of methyl iodide were organic phosphorescent compounds: aromatic amines (diphenylamine, triphenylamine), aromatic hydrocarbons (biphenyl, naphthalene, phenanthrene), aromatic ketones (benzophenone), and certain organic dyes (acridine yellow, trypaflavine, fluorescein). Purified by distillation toluene (in the case of the amines) and ethanol (in the remaining cases) were used as matrix solvents. The choice of these solvents as inert matrices in which the sensitized photodecomposition of methyl iodide was carried out was made on the grounds that toluene and ethanol are relatively unreactive in the photoprocess occurring in the system sensitizer + methyl iodide, but are suitable matrices for the stabilization of the methyl radicals that arise, whereas the latter are not stabilized in sufficient quantity for detection in a matrix of methyl iodide alone at 77° K.

The solutions studied were a mixture of methyl iodide and solvent (1 : 3), to which the sensitizer was added at a concentration of $10^{-2} \div 10^{-3}$ M. Samples of the solutions were placed in quartz ampoules with an internal diameter of 3 mm. The solutions were frozen in a special Dewar vessel and irradiated with filtered light from an SVDSh-500 mercury lamp, focused with the aid of two

quartz parabolic lenses, directly in the resonator of an RE 13-01 spectrometer. It had been established beforehand in control experiments that photochemical reactions were absent in the systems sensitizer + solvent and methyl iodide + solvent.

To study the dependence of the rate of appearance of free radicals in the system sensitizer + methyl iodide + solvent on the light exciting the sensitizer, the following procedure was used. First, a range of changes in light intensity was selected that did not cause saturation of the triplet state of the sensitizer molecules. The absence of this saturation was monitored by the fulfillment of a linear dependence between the change in intensity of the light source and the magnitude of the e.p.r. signal from sensitizer molecules in the triplet state (transition $\Delta m = \pm 2$). At the maximum light intensity thus selected, the dependence of the appearance of free radicals on the

of the illumination time. Then the intensity of the light source was decreased by a factor of two with the aid of calibrated metal screens, and the time dependence was recorded again. Within the initial linear portions of these curves, either the intensities of the EPR signals of free radicals obtained for one and the same illumination time were compared, or the time required to obtain EPR signals of free radicals of equal magnitude at these two different intensities of the light source was compared. The drift of the gain coefficient of the spectrograph was corrected by means of the EPR signal from a reference standard (ZnS activated with Mn^{2+}).

Upon illumination of systems consisting of aromatic amine + methyl iodide in toluene at 77°K with light of $\lambda > 320$ nm (BS-6 filter) for 5 min, an intense EPR spectrum appears, consisting of a quartet of narrow lines with an intensity ratio of $1 : 3 : 3 : 1$ and a splitting of about 24 Oe, which is characteristic of the EPR spectrum of the methyl radical ($\dot{C}H_3$). When the light is turned off, the methyl radicals gradually disappear, apparently as a result of the reaction $\dot{C}H_3 + \dot{C}H_3 \rightarrow C_2H_6$, as evidenced by the evolution of gas bubbles upon thawing of the solutions. An analogous, but more intense, EPR spectrum is obtained under the action of light with $\lambda > 300$ nm (BS-4 filter, 4 min illumination) in the case of sensitization of the photodecomposition of methyl iodide in ethanol by naphthalene (Fig. 1). To elucidate the mechanism of this photochemical reaction, the dependence of the rate of increase in the magnitude of the EPR signals of free radicals ($\dot{C}H_3$) on the intensity of the light exciting the sensitizer was studied by the method described above. The experiments showed that the dependence of the radical yield on time obeys an exponential law, while its dependence on the light intensity is quadratic (Fig. 2), i.e., when the light intensity is increased by a factor of 2, the rate of radical yield increases by a factor of $3.7 \div 3.9$. (The error arises mainly from the different transparency of the glass formed upon freezing of the solutions, and from the dark process of disappearance of methyl radicals.) Thus, this photochemical reaction belongs to the class of two-quantum photoreactions and proceeds according to the scheme:

Fig. 1. EPR spectrum of methyl radicals in the naphthalene-photosensitized

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Figure 2

Figure 2: Figure 2

decomposition of methyl iodide (irradiation with light of $\lambda > 300$ nm for 4 min.)

$$\mathrm{Sens}_S + \mathrm{CH_3J} \xrightarrow{h\nu_1} \mathrm{Sens}_{S^* \to T} + \mathrm{CH_3J} \xrightarrow{h\nu_2} \mathrm{Sens}_{T \to T'} + \mathrm{CH_3J} \to \mathrm{Sens}_S + \dot{\mathrm{C}}\mathrm{H_3} + \dot{\mathrm{J}}$$

$$\dot{\mathrm{C}}\mathrm{H_3} \downarrow + \dot{\mathrm{C}}\mathrm{H_3} \qquad \dot{\mathrm{J}} \downarrow + \dot{\mathrm{J}}$$

$$\mathrm{C_2H_6} \qquad \mathrm{J_2}$$

To verify this assumption, the dependence of the radical yield on the spectral composition of the exciting light was investigated. It was established that, when light in the spectral region $300\,\mathrm{nm} < \lambda < 380\,\mathrm{nm}$ was used, the yield of methyl radicals was considerably smaller (by a factor of $3 \div 4$) than in the case of using light with $\lambda > 300$ nm. The illumination time in both experiments was the same. In both cases, the spectral composition and intensity of the light in the absorption region of naph-

were approximately the same. Taking into account that the solvent (ethanol), methyl iodide, and naphthalene do not absorb light in the spectral region with $\lambda > 320$ nm, it may be assumed that the band of triplet-triplet (T—T') absorption of naphthalene, located from 365 to 420 nm (5), is responsible for these changes in the yield of methyl radicals.

Fig. 2. Initial portions of the time dependences of the yield of methyl radicals when the intensity of the exciting light of the sensitizer is changed by a factor of 2 (system: naphthalene (10^{-2} M) + methyl iodide in ethanol)

To determine the role of the triplet–triplet absorption of naphthalene, the samples were irradiated outside the resonator by two sources. From the light of an SVDSh-500 mercury lamp, for excitation of sensitizer molecules with their conversion to the triplet state, the 313-nm line was isolated with a mercury filter; and from the light of an SVDSh-250 lamp, the mercury lines in the region of the triplet–triplet absorption of naphthalene were isolated with an SZS-22

filter. After irradiation for 15 min, the sample was transferred into the resonator without thawing. When irradiation was carried out with only one of the sources, free radicals were not formed, whereas with simultaneous irradiation by the two sources the EPR spectrum of the radical CH_3 appeared. Thus, it may be regarded as established that the naphthalene molecule, primarily in the triplet state, absorbs a second quantum in the spectral region $365 < \lambda < 420$ nm, passing to a higher triplet level. Apparently, the highest-lying triplet levels participate in the photochemical reaction, since with a second illumination at $\lambda > 404$ nm radicals are almost not formed.

Diphenyl, phenanthrene, and benzophenone are likewise excellent sensitizers of the photodecomposition of methyl iodide at 77°K. The sensitizing action of benzophenone proved analogous to the action of additives of aromatic hydrocarbons. To determine the role of the triplet–triplet absorption band of benzophenone, the radical yields for equal irradiation times were compared under irradiation with light of $\lambda > 340$ nm and $\lambda > 280$ nm, since the indicated band lies mainly in the spectral region with $\lambda \leq 340$ nm (5). The intensity of the EPR signal was found to be 8 times greater upon excitation with light of $\lambda > 280$ nm than upon excitation with light of $\lambda > 340$ nm. But the difference obtained in the radical yields could be explained by an increase in the population of the lowest triplet level of benzophenone due to more complete utilization of its principal absorption band. In that case, changing these filters should produce a corresponding change in the triplet EPR signal. We were unable to record the EPR signal of the triplet state of benzophenone molecules; therefore the phenomenon of triplet–triplet energy transfer was used (6, 7). Using benzophenone as the energy donor and naphthalene as the acceptor,* the triplet state of naphthalene was excited upon illumination with $\lambda > 340$ nm, absorbed only by benzophenone owing to the indicated energy transfer, and also upon illumination with $\lambda > 280$ nm, when naphthalene' s own absorption is added. However, despite these conditions, when the filters were changed the EPR signal of the triplet state of naphthalene changed only by a factor of 2. Hence it may be concluded that in the reaction of ketone-photosensitized decomposition of methyl iodide the determining role is played by the triplet–triplet absorption of benzophenone, and this reaction also has a two-photon character.

* A solution of benzophenone 10^{-3} M and naphthalene 10^{-2} M in ethanol was studied.

It proved possible to sensitize the decomposition of methyl iodide to the longest-wavelength light with the aid of acridine dyes (acridine yellow, trypaflavine) and fluorescein. The most active sensitizer among the dyes was trypaflavine, which in its efficiency is not inferior to sensitizers from the aromatic hydrocarbons. A study, by the method described above,* of the dependence of the rate of radical yield on the intensity of the light exciting the sensitizer showed that the rate depends on the square of the intensity. When the samples were irradiated with light from an SVDSh-500 mercury lamp in the spectral region with $\lambda > 340$ nm (BS-7 filter), with sensitization by any of these dyes, the yield of methyl

radicals was greater (by a factor of 3) than upon illumination in the spectral region 350–550 nm (SZS-22 filter). The irradiation time was the same in both experiments. The difference in the yields of methyl radicals when using these two filters can be understood if one takes into account the triplet–triplet absorption of the dyes employed ([8]). The band of triplet–triplet absorption of these dyes extends into a longer-wavelength region than their main absorption spectrum. Consequently, these bands are used more effectively when the BS-7 filter is employed than when the SZS-22 filter is used. It should be noted that the difference in transmission of the filters near their short-wavelength boundary is not significant, since absorption of the dyes in this spectral region is small. Indeed, no noticeable change in the magnitude of the triplet EPR signal of these dyes was found when the filters were changed.

The energies of two photons passing through the SZS-22 or BS-7 filters and successively absorbed by a dye molecule in the principal singlet and triplet states are quite sufficient for sensitized photodecomposition of methyl iodide. It is known that the height of the triplet level in these dyes is of the order of 17 000–18 000 cm^{-1}, while the energy of the second quantum is of the order of 23 000–25 000 cm^{-1} (mercury lines 404, 408, and 435–436 nm). As a result, the energy of the dye molecule will be of the order of 40 000–43 000 cm^{-1}. Upon transfer of this energy to a methyl iodide molecule, its photodecomposition may occur with the formation of methyl radicals, which was indeed observed in our experiments.

On the basis of the material presented, we come to the conclusion that the photosensitized decomposition of methyl iodide by the indicated compounds at 77°K belongs to the class of two-photon processes.

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* The use of this method is possible because the indicated dyes make it possible to obtain an intense EPR signal of their triplet state (transition with $\Delta m = \pm 2$).

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