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Abstract

Full Text

PHYSICAL CHEMISTRY

M. V. ALFIMOV, N. Ya. BUBEN, A. I. PRISTUPA, V. N. SHAMSHEV

EXCITATION OF TRIPLET STATES OF NAPHTHALENE MOLECULES IN SOLID SOLUTIONS BY FAST ELECTRONS

(Presented by Academician V. N. Kondrat' ev, January 16, 1964)

When γ-radiation or fast electrons pass through organic systems containing aromatic molecules, one may expect that, along with other primary radiolysis products, molecules in the triplet state will be present in appreciable concentrations. The relatively long lifetimes and "biradical" character of such molecules, as is known from photochemical studies, lead to their increased chemical activity ([1],[2]). Considerations have often been expressed concerning the substantial role of excited molecules also in the mechanism of radiolysis of solid organic systems; however, until the present time there have been no experimental works devoted to the study of molecules excited to the triplet state during irradiation of such systems by ionizing radiation. This is connected mainly with the fact that observation of phosphorescence is greatly hindered by the superposition of intense recombination luminescence ([3]).

In recent years it has been shown that the method of electron paramagnetic resonance (EPR) makes it possible to register molecules located at the phosphorescent level ([4],[5]). With the use of this method a number of interesting photochemical studies have been carried out ([6],[7]). The aim of the present work was to determine the possibility of observing and measuring the concentration of molecules in the triplet state upon irradiation of solid solutions of naphthalene by fast electrons.

Mixtures of reagent-grade naphthalene with polymethyl methacrylate (PMMA) and with polystyrene were used. Naphthalene was introduced into PMMA by dissolution in the monomer followed by thermal polymerization in the absence of a catalyst. To obtain samples based on polystyrene, the latter was dissolved together with naphthalene in cumene, after which the solvent was removed. The initial monomers (methyl methacrylate and styrene) were carefully purified of stabilizers. The work was carried out with the following mixtures: naphthalene + PMMA (10^{-2} g/g) (I); naphthalene + polystyrene ($2 \cdot 10^{-2}$ g/g) (II); naphthalene + polystyrene ($2 \cdot 10^{-3}$ g/g) (III). A sample weighing about 0.1 g was fixed at the end of a thin thermocouple and introduced into the resonator (os-

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Fig. 1

Figure 1: Fig. 1

cillations of type H_{011}) of an EPR spectrometer installed under a beam of fast electrons with an energy of 1.6 MeV ([8]). Measurements were carried out at a temperature of 100° K, for which purpose the sample was blown with a stream of cold nitrogen. Methods for determining the radical concentration and the dose received by the sample have been described earlier ([8]). The measurement of the concentration of molecules in the triplet state is discussed below.

Upon irradiation by fast electrons of solid solutions of naphthalene in PMMA and polystyrene, in the EPR spectrum, along with the formation of radicals (at a g-factor value of about 2), a single asymmetric line of paramagnetic absorption is observed near $g = 4$ (Fig. 1a) ([9]). The width of the line, measured between the points of maximum slope of the absorption curve, is $\Delta H = 10 \pm 1$ Oe. After irradiation is stopped, the intensity of this line decreases according to an exponential law with a time $\tau_e = 2.5 \pm 0.5$ sec, which was determined from the curve of change in signal amplitude. For this purpose, during irradiation, at the time of passage through the line po-

the magnetic-field sweep of the spectrometer was switched off and the signal amplitude h_0 was recorded; then irradiation was stopped and the dependence of h on t was recorded.

When the samples under study were illuminated with unfiltered light from a DRSh-250 lamp, we observed EPR signals near g-factor 4, of the same width and with the same time τ_e as in the case of irradiation by fast electrons. Similar signals had previously been found upon ultraviolet irradiation of naphthalene in other solvents and had been attributed to paramagnetic absorption of molecules in the triplet state in the transition with $\Delta m = \pm 2$ ([5,6]). On this basis it may be assumed that, upon irradiation by fast electrons of solid solutions of naphthalene in PMMA and polystyrene, naphthalene molecules are formed in the triplet state.

Fig. 1. *a*—first derivative of the paramagnetic absorption line at $g = 4$; *b*—dependence of $[N_T]_{\text{st}}$ on the irradiation dose. Curves 1, 2, and 3 correspond to solid solutions of naphthalene I, II, and III.

To determine the stationary concentration of molecules in the triplet state by the EPR method, it is necessary to take into account that the probability of the magnetic transition with $\Delta m = \pm 2$ is considerably smaller than the probability of the transition with $\Delta m = \pm 1$, which is observed when radicals and paramagnetic ions with spin 1/2 are recorded. Therefore the area under the absorption curve (S_T) is related to the stationary concentration of molecules in the triplet state $(N_T)_{\text{st}}$ in the following way:

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$$[N_T]_{\text{st}} = \alpha \frac{S_T}{S_{\text{e}}} [N_{\text{e}}],$$

where α is the ratio of the probability of the transition with $\Delta m = \pm 2$ to the probability of the transition for $\Delta m = \pm 1$, S_{e} is the area under the absorption curve of the standard, and $[N_{\text{e}}]$ is the concentration of paramagnetic particles in the standard. According to calculations by I. V. Aleksandrov and K. K. Pukhov* the value of α can be determined from the parameters of the absorption line and for the naphthalene molecule is equal to 10.

Figure 1b gives the dependence of $[N_T]_{\text{st}}$ on the irradiation dose for mixtures I, II, and III, calculated for $\alpha = 10$. It is seen that in the course of irradiation the value of $[N_T]_{\text{st}}$ decreases rather rapidly with increasing dose. However, this is not connected with completely irreversible changes in the irradiated substance. Thus, in a sample of mixture I, after heating to 500° K, upon repeated irradiation the initial concentration $[N_T]_{\text{st}}$ was restored to 70% of the original. "Bleaching" of the irradiated sample with ultraviolet light did not lead to an increase in $[N_T]_{\text{st}}$ upon subsequent irradiation.

Figure 2 gives the dependence of the initial concentration $[N_T]_{\text{st}}$ on the dose-rate power (j) for the same naphthalene solutions. At higher dose-rate powers, the values of $[N_T]_{\text{st}}$ in Fig. 2 include a correction for the dose received by the sample during the measurement. It is seen from Fig. 2 that the dependence of $[N_T]_{\text{st}}$ on j is linear in the measured dose-rate interval $2 \div 50$ mrad/min. Since at small doses the stationary concentration $[N_T]_{\text{st}}$ is determined by the equation

$$\frac{d[N_T]_{\text{st}}}{dt} = 10^{-2} G_T j - \frac{[N_T]}{\tau_e} = 0,$$

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* Submitted for publication to the journal *Optics and Spectroscopy*.

the angular coefficients of the straight lines in Fig. 2 make it possible to determine the radiation yields G_τ of naphthalene molecules in the triplet state. For mixtures I, II, and III the values of G_τ, calculated per 100 eV of energy absorbed by the whole solution, were found to be, respectively, 1.1, 0.8, and 0.4; the accuracy of the determination of G_τ (without taking into account the error in the value of α, calculated theoretically) is $\sim 50\%$. Since the electron fractions of naphthalene in solutions I, II, and III are only $8.5 \cdot 10^{-3}$, $1.3 \cdot 10^{-2}$, and $1.3 \cdot 10^{-3}$, the above values of G_τ cannot be explained without invoking energy transfer from the polymer to naphthalene molecules. Indeed, for solutions I and II, when 100 eV of energy is absorbed, about 1 eV falls on naphthalene, and for solution III about 0.1 eV, whereas even without allowing for losses to ionization, not less than 2.5 eV is required to excite a naphthalene molecule to the triplet state. The small difference in the value of G_τ for mixtures II and III, in which

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Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

Fig. 2

Fig. 3

Fig. 2. Dependence of $[N_\tau]_{\text{st}}$ on the dose-rate power of irradiation. 1, 2, and 3 as in Fig. 1

Fig. 3. Dependence of $1/[N_\tau]_{\text{st}}$ on the concentration of radicals upon irradiation of solid solutions of naphthalene. 1, 2, and 3 as in Fig. 1

the concentrations of naphthalene differ by a factor of 10, may be associated with overlap of the "spheres of action" of the naphthalene molecules.

The decrease in the stationary concentration of naphthalene molecules in the triplet state as the mixtures under study are irradiated can be connected with the accumulation in the system of radicals, which recombine when the specimen is warmed.* If it is assumed that energy transfer from the solvent to the radicals that are formed also occurs, then there will be competition between naphthalene molecules and radicals. A kinetic consideration of such a scheme leads to the following relation between $[N_\tau]_{\text{st}}$ and $[N_R]$

$$[N_\tau]_{\text{st}} = \frac{a}{b + c[N_R]},$$

where $[N_R]$ is the concentration of radicals, and a, b, c are constants depending on the choice of specimen and on the magnitude of the dose-rate power. We recorded curves of radical accumulation during irradiation of mixtures I, II, III and compared the concentrations $[N_\tau]_{\text{st}}$ and $[N_R]$.

It is seen from Fig. 3 that

$$\frac{1}{[N_\tau]_{\text{st}}}$$

is satisfactorily described by a linear dependence on $[N_R]$, in accordance with the assumption of competition in the capture of excitation energy. Competition of this kind may play

* In work (7), upon excitation of triplet states by UV light, a decrease in $[N_\tau]_{\text{st}}$ with increasing concentration of radicals in the system was also noted.

play a significant role in two cases: 1) a considerable part of the excitation energy present in the medium is transferred to aromatic molecules and radicals; 2) radicals are formed in the immediate vicinity of naphthalene molecules. It

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should be noted that the literature contains indications of the predominant formation of radicals near impurity molecules or other radicals ([10–12]). Systematic studies are now being carried out of the dependence of $[N_T]_{st}$ on the concentration of aromatic molecules in the mixture and on temperature; these studies, we hope, will provide additional information on the excitation of triplet states of molecules by fast electrons.

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