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Abstract

Full Text

PHYSICAL CHEMISTRY

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TRIPLET MOLECULES IN LIQUID BENZENE. PHOTOCHEMICAL PROCESSES IN A THIN ABSORBING LAYER

(Presented by Academician S. S. Medvedev, November 16, 1963)

Despite the fact that the detection and investigation of triplet molecules of benzene in the liquid phase is of exceptional interest, this question has until recently been practically unstudied. Apparently this is explained by the fact that benzene does not phosphoresce in the liquid phase and does not exhibit noticeable triplet-triplet absorption (1,2).

Recently Dubois and Wilkinson (3) and Lipsky (4) attempted to detect triplet molecules of benzene by studying the sensitized phosphorescence of biacetyl in dilute three-component solutions of benzene and biacetyl in hexane and cyclohexane. The data of papers (3,4) contradict one another, which led the authors of these studies to opposite conclusions. Whereas in paper (3) the conclusion was drawn that there is no triplet-triplet energy transfer from benzene to biacetyl, in paper (4) the presence of such energy transfer is regarded as proven. The lower limit of the lifetime of triplet benzene molecules, estimated by Lipsky, is 10^{-6} sec. There are no indications of the reasons for the discrepancy between the data of (3) and (4).

Table 1

Wavelength, mμ	Solvent	Quantum yield
253.7	Cyclohexane	0.79
300–313	Cyclohexane	0.32
303–313	Benzene	0.36

In the present work, to detect triplet molecules in liquid benzene, the photosensitized reaction of trans-cis isomerization of stilbene in benzene solutions was used. The photoisomerization of stilbene apparently proceeds through triplet states (5–7), which makes it possible to use it for studying triplet-triplet transfer in solutions (6,7).

The reaction was carried out in solutions carefully freed from air in a high vacuum. The light source was a PRK-2 mercury lamp. To isolate the 253.7 mμ line, a chlorine-bromine filter and UFS-1 were used. To isolate the 303–313 mµ line, a solution of potassium chromate in water and a UFS-2 filter were used. Actinometry was carried out with a uranyl oxalate solution. The concentration of stilbene isomers was determined spectrophotometrically. Absorption spectra of cis- and trans-stilbene in benzene (in the region 300–340 mµ) and in cyclohexane (220–340 mµ) were recorded beforehand. The photoluminescence of the solutions was measured by the method described earlier ([8]).

Table 1 gives the quantum yields of trans-cis isomerization of stilbene under the direct action of light on stilbene in cyclohexane and benzene. The errors in determining the absolute values of the quantum yields were ±10%.

Figure 1 shows curves of the dependence of the quantum yields of sensitized trans-cis isomerization of stilbene in benzene on the concentration of stilbene under the action of light of 253.7 mµ. The three curves correspond to different intensities of the incident light. As can be seen from the figure, the quantum

yields rapidly increase with increasing concentration up to $\sim 1 \cdot 10^{-4}$ M, after which they reach a limiting value and remain practically constant over the range of concentrations studied ($< 10^{-3}$ M).

The fluorescence intensity of pure benzene and of benzene solutions of stilbene under the action of light at 253.7 $\mathrm{m}\mu$ was also measured. In the concentration range 10^{-5}–10^{-3} M, the luminescence intensity of the solutions is the same as that of pure benzene.

Since practically all the incident light is absorbed only by benzene, the isomerization of stilbene is evidently caused by energy transfer from excited benzene molecules to stilbene molecules. The fact that additions of stilbene do not affect the fluorescence intensity of benzene apparently indicates that energy transfer occurs not from the singlet excited level of benzene, which is responsible for the fluorescence, but from the triplet level.

Obviously, at stilbene concentrations $< 1 \cdot 10^{-5}$ M, energy transfer competes with spontaneous deactivation of the triplet molecules of the solvent. The attainment of limiting quantum yields at stilbene concentrations greater than $1 \cdot 10^{-4}$ M is probably connected with the fact that all the benzene triplet molecules participating in energy transfer have time to transfer energy to stilbene before their spontaneous deactivation.

The quantum yields of isomerization, as can be seen from Fig. 1, increase when the light intensity is decreased. This unusual fact can be explained if one takes into account that 99% of the incident light is absorbed in a very thin benzene layer, $\sim 10^{-3}$ cm. Consequently, all triplet benzene molecules are formed in this layer. Energy transfer to stilbene also occurs in this layer, since diffusion of triplet molecules out of the layer during their lifetime is negligibly small. At high light-absorption densities in a thin layer, a high stationary concentration may be obtained of triplet stilbene molecules formed upon energy transfer from benzene*. One may suppose that two triplet stilbene molecules can interact with one another, giving, for example, excited and unexcited singlet molecules (for some luminescent substances similar reactions have been observed (^{10})). Since isomerization proceeds from the triplet level, an increase in light intensity should lead to a decrease in the quantum yields of isomerization. Thus, in the layer absorbing the light, the following reactions should be considered:

	Rate of elementary step
Formation of benzene triplets	
$\mathrm{A} + h\nu \rightarrow (\mathrm{A}_S^*) \rightarrow \mathrm{A}_T$	$\gamma_T I$
Energy transfer to stilbene	
$\mathrm{A}_T + \mathrm{B} \rightarrow \mathrm{A} + \mathrm{B}_T$	$k_{\mathrm{AB}}[\mathrm{A}_T][\mathrm{B}]$
Spontaneous deactivation of benzene triplets	
$\mathrm{A}_T \rightarrow \mathrm{A}$	$\frac{1}{\tau_{\mathrm{A}}}[\mathrm{A}_T]$
Isomerization of stilbene	
$\mathrm{B}_T \rightarrow$ isomer B	$k_{\mathrm{i}}[\mathrm{B}_T]$
Deactivation of stilbene triplets without isomerization	
$\mathrm{B}_T \rightarrow \mathrm{B}$	$k_{\mathrm{d}}[\mathrm{B}_T]$
Bimolecular disappearance of stilbene triplets	
$\mathrm{B}_T + \mathrm{B}_T \rightarrow \mathrm{B}_S^* + \mathrm{B}$	$k_{\mathrm{BB}}[\mathrm{B}_T]^2$

* The possibility of the formation of high stationary concentrations of triplet molecules upon absorption of light in thin layers (at high absorption coefficients) was pointed out by Kh. S. Bagdasar' yan in his lectures at the L. Ya. Karpov Physicochemical Institute in April 1963. See also (^{9}).

I is the intensity of the light absorbed in the layer. For simplicity we assume that the light is absorbed uniformly in the thin layer. γ_T is the quantum yield of formation of benzene triplets. The meaning of the remaining notation is clear from the scheme. In the steady state

$$\gamma_T I = \frac{1}{\tau_A}[A_T] + k_{AB}[A_T][B],$$

$$k_{AB}[A_T][B] = k_{\mathrm{i}}[B_T] + k_{\mathrm{d}}[B_T] + k_{BB}[B_T]^2. \tag{1}$$

Hence the quantum yield of sensitized isomerization (γ) is expressed as:

$$\gamma = \frac{k_{\mathrm{i}}[B_T]}{I} = \frac{k_{\mathrm{i}}^2}{2k_{BB}\nu I}\left[\left(1 + \frac{4k_{BB}\nu^2\gamma_T I k_{AB}\tau_A[B]}{k_{\mathrm{i}}^2(1 + k_{AB}\tau_A[B])}\right)^{1/2} - 1\right], \tag{2}$$

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Figure 1

Figure 1: Figure 1

Fig. 1. Dependence of the quantum yields of sensitized trans-cis isomerization of stilbene in benzene on the concentration of stilbene. $\lambda = 253.7$ mµ. Intensity of light incident on 1 cm^2 of the cuvette surface:
1 $-I_0 = 3.5 \cdot 10^{-11}$,
2 $-I_0 = 11.7 \cdot 10^{-11}$,
3 $-I_0 = 38 \cdot 10^{-11}$ $\mathrm{einstein/cm^2 \cdot sec}$

where

$$\nu = \frac{k_\mathrm{i}}{k_\mathrm{i} + k_\mathrm{d}}$$

is the fraction of triplet stilbene molecules passing into the other isomeric form.

a) At $I = \mathrm{const}$ and at small $[B]$, expression (2) can be expanded in a series in powers of $[B]$. Restricting ourselves to the first two terms of the series, we obtain an expression of the Stern–Volmer type:

$$\gamma = \frac{\gamma_T \nu k_{AB} \tau_A [B]}{(1 + k_{AB} \tau_A [B])}. \tag{3}$$

Expression (3) describes the curves in Fig. 1 obtained at constant light intensities. With the aid of this equation, from the course of the curves in Fig. 1 the product of the energy-transfer rate constant and the lifetime of the triplet benzene molecules, $k_{AB}\tau_A$, was calculated; it characterizes the efficiency of energy transfer, $k_{AB}\tau_A \simeq 10^4$ l/mol. The obtained value of $k_{AB}\tau_A$ exceeds by approximately two orders of magnitude the values of $k_{AB}\tau_A$ in the case of singlet–singlet energy transfer from solvent to dissolved substance (8). In triplet-triplet interaction, energy transfer apparently occurs upon diffusional approach of the molecules to distances of kinetic radii (^{11}); therefore the maximum value is $k_{AB} \simeq 10^{10}$ l/mol · sec, whence $\tau_A \gtrsim 10^{-6}$ sec. This value of τ_A agrees well with Lipsky' s estimate (^{4}).

b) At sufficiently high concentrations of stilbene ($> 10^{-4}$ M), γ does not depend on $[B]$:

$$\gamma = \frac{k_\mathrm{i}^2}{2 k_{BB} \nu I} \left[\left(1 + \frac{4 k_{BB} \nu^2 \gamma_T I}{k_\mathrm{i}^2} \right)^{1/2} - 1 \right]. \tag{4}$$

In this case, at large I, the quantity γ is inversely proportional to $\sqrt{I}$:

Fig. 2

Figure 2: Fig. 2

$$\gamma = \left(\frac{k_{\mathrm{i}}^2 \gamma_T}{k_{BB} I} \right)^{1/2}. \tag{5}$$

At small I

$$\gamma \to \gamma_T \nu.$$

In Fig. 2 the reciprocals of the quantum yields of isomerization at a stilbene concentration of $2 \cdot 10^{-4}\, M$ are plotted against $\sqrt{I}$. For I the values were taken corresponding to a layer of half absorption of light, equal for benzene to $2.7 \cdot 10^{-3}$ cm (the extinction coefficient of benzene for $\lambda = 253.7$ mμ is ~ 230). As is seen from the figure, over a rather broad range of intensities the quantum yields are inversely proportional to $\sqrt{I}$, which confirms the proposed mechanism of photolysis.

Fig. 2. Dependence of $1/\gamma$ on the square root of the intensity of light absorbed in a layer of half absorption. The shaded points correspond to a lowering of the intensity by dilution of benzene with cyclohexane.

When benzene is diluted with an optically transparent solvent—cyclohexane—the intensity of the light absorbed in the layer decreases in proportion to the dilution, and the quantum yields correspondingly increase (Fig. 2).

From the graph in Fig. 2 it is seen that at $I \to 0$ the limiting quantum yield γ_T^ν is ~ 0.25. Consequently, the minimum quantum yield of triplet benzene molecules (at $\nu = 1$) is 0.25. In reality, it is obviously higher.

The value calculated from the slope of the curve in Fig. 2 is

$$\frac{k_{BB}}{k_i^2 \gamma_T} = 5 \cdot 10^5.$$

Taking $k_{BB} \simeq 10^{10}$ liter/mole • sec and $0.25 \leqslant \gamma_T \leqslant 1$, we obtain $1.4 \cdot 10^2 \leqslant k_i \leqslant 2.8 \cdot 10^2$ sec^{-1}. Since

$$\gamma_T^\nu = \frac{\gamma_T k_i}{k_i + k_d} \simeq 0.25,$$

the lifetime of triplet stilbene molecules,

$$\tau_B = \frac{1}{k_i + k_d},$$

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will lie in the interval $1.8 \cdot 10^{-3} \leqslant \tau_B \leqslant 3.6 \cdot 10^{-3}$ sec. The stationary concentration of stilbene triplets in the layer at intensities $\sim 10^{-4}$ einstein/l • sec is $\sim 10^{-7}$ mole/l.

Thus, by using the effect of energy transfer, it is possible to create fairly high stationary concentrations of triplet molecules in liquids with comparatively small extinction coefficients. This is evidently explained by the fact that, at low concentrations of the energy acceptor, concentration deactivation of its triplet molecules is absent, which leads to an increase in the lifetime in the triplet state.

The data obtained show that the study of photochemical processes in a thin layer opens new possibilities for investigating the properties of excited molecules.

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