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Abstract

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A Two-Quantum Photochemical Reaction. Photolysis of a Frozen Solution of Diphenylamine in Ethyl Alcohol

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It has recently been established (^{1}, ^{2}) that, when light acts on solutions of aromatic amines or nitrogen-containing heterocycles in alcohols (or in an alcohol-ether mixture) frozen at 77° K, alcohol radicals are formed. By studying triplet-triplet energy transfer (^{3}), it was established in these works that the formation of alcohol radicals is associated with the transition of the amines to the triplet state. Smoller (^{1}) suggested that the formation of alcohol radicals is associated with a two-quantum process. However, he did not obtain definite data in favor of this mechanism. In order to study the mechanism of this reaction in greater detail, we investigated the effect of light intensity on the rate of radical formation during irradiation of the diphenylamine-ethanol system.

A solution of diphenylamine ($5 \cdot 10^{-5}$–$5 \cdot 10^{-3}$ mole/l) in absolute ethyl alcohol was introduced into a quartz tube (2.5 mm internal diameter) sealed at one end. The other end of the tube was connected through a vacuum rubber tube to a vacuum system. The solution was freed from dissolved air by repeated freezing and thawing under high vacuum, after which the tube was sealed off. The light source was an SVDSh-250 lamp equipped with a system of lenses and a UFS-1 light filter. The intensity of the incident light was varied by means of metal screens. The transmittance of the screens was measured on an SF-4 spectrophotometer. The solution was irradiated in a quartz Dewar vessel in liquid nitrogen.

The concentration of radicals, in relative units, was measured on an EPR spectrometer at the temperature of liquid nitrogen. As the irradiation time was increased, the intensity of the EPR signal at first increased proportionally to time, and at longer irradiation times tended toward a constant value, apparently corresponding to complete consumption of diphenylamine. All quantitative measurements were made in the region of linear increase of the signal.

The observed shape of the spectra corresponds to the superposition of at least two spectra, one of which is due to the radical $CH_3\dot{C}H—OH$, and the other to an unidentified radical, apparently formed from diphenylamine. The latter spectrum is a singlet with a width of ~ 17 Oe, or an unresolved triplet which, being superposed on the spectrum of the $CH_3\dot{C}HOH$ radical, distorts its central components. The radical having a singlet structure is characterized by long spin-lattice relaxation times, which makes it possible to separate it from the $CH_3\dot{C}HOH$ radical on the basis of differences in their recombination temperatures, as well as differences in relaxation times. As can be seen from Fig. 1 (experiment No. 1), at low power levels the $CH_3\dot{C}HOH$ radical has a lower relative intensity, which is explained by saturation of the radical having the singlet structure at an SVC power of ~ 10 mW. The height of the peak of the central component of the spectrum was taken as a measure of the total yield of radicals. The magnitude of the outer components of the spectrum was also measured. It should be noted that pure ethanol, in the absence of diphenylamine, under the same irradiation conditions gives practically no EPR signals.

Experiments to study the dependence of the yield of radicals on the intensity of light were carried out as follows. Two quartz ampoules containing the same concentration of diphenylamine were irradiated under identical conditions for different times at different light intensities. After this, the EPR spectra were recorded under identical conditions. Fig. 1 shows the EPR spectra obtained for three experiments. Table 1 gives the conditions under which these experiments were carried out and the results obtained.

Table 1

Dependence of the number of radicals formed on the intensity of light

Experiment No.	Irradiation intensity, relative units	Irradiation time, min	Height of the peak of the central component, in relative units	n	Amine concentration, mol/l
1	$I_1 = 1 I_2 = 0.445$	413	12085	1.88	$5 \cdot 10^{-3}$
2	$I_1 = 1 I_2 = 0.445$	4.522.5	148156	1.92	$5 \cdot 10^{-5}$
3	$I_1 = 1 I_2 = 0.282$	112.5	111109	1.97	$5 \cdot 10^{-4}$

The number of radicals formed ΔR, the irradiation time t, and the light intensity I are in the general case related by the equation:

Fig. 1

Figure 1: Fig. 1

$$\Delta R = kI^n t \tag{1}$$

Experiments performed at different I and t make it possible to calculate n from the equation

$$\lg \frac{t_2 \Delta R_1}{t_1 \Delta R_2} = n \lg \frac{I_1}{I_2} \tag{2}$$

Table 1 gives the values of n calculated from this equation. Calculation from the peak of the central component in all cases gives values of n close to two. Calculation from the peaks of the outer components gives a wide scatter of values from 1.72 to 2.50.

Fig. 1

Thus, we arrive at an important conclusion: the rate of radical formation is proportional to the square of the light intensity. In works (^{1,2}) it has been demonstrated beyond doubt that the formation of alcohol radicals occurs through the intermediate formation of amine molecules in the triplet state. The result obtained by us gives reason to think that the amine molecule in the lowest triplet state secondarily absorbs a quantum of light and passes into an excited triplet state, which leads to the formation of radicals by one mechanism or another. In this case the stationary concentration of amine molecules in the lowest triplet state $[A_T]$ is determined by the following equation:

$$I\alpha_{ST} = k_{TS}[A_T] + kI[A_T], \tag{3}$$

where α_{ST} is the probability of transition from the excited singlet state to the lowest triplet level, k_{TS} is the sum of the constants of radiative and nonradiative transitions from the lowest triplet state to the lowest singlet state, and k is the proportionality coefficient for the process of transition from the lowest triplet level to an excited triplet level. For the rate of radical formation we obtain the following expression:

$$\frac{dR}{dt} = \frac{kI^2 \alpha_{ST}}{k_{TS} + kI} \tag{4}$$

If

$$k_{TS} \gg kI. \tag{5}$$

then $dR/dt = ka_{\mathrm{ST}} I^2/k_{\mathrm{TS}}$. Hence equation (1) follows with $n = 2$. From condition (4) there follows a small value for the quantum yield of radical formation (not more than 0.1).

In the liquid phase, the lifetime in the triplet state is of the order of 10^{-3}–10^{-5} sec. Therefore two-quantum photochemical processes in the liquid phase can in practice be detected only at very high energy absorption densities (flash photolysis). In frozen media at 77° K the lifetime in the triplet state for many organic molecules increases to several seconds. The following calculation, approximately corresponding to the conditions of our experiments, shows that at 77° K high stationary concentrations of molecules in the lowest triplet state can be reached with ordinary irradiation sources. If the light source gives 10^{-7} einstein/cm$^2 \cdot$ sec, the amine concentration is 10^{-3} mole/liter, the absorption in a 1 cm layer is 0.5 (i.e., $\varepsilon = 300$), and the lifetime in the triplet state is 2 sec, then the stationary concentration of molecules in the triplet state is

$$10^{-7} \cdot 0.5 \cdot 1000/0.5 = 1 \cdot 10^{-4} \text{ mole/liter.}$$

This amounts to 10% of the diphenylamine concentration. At larger absorption coefficients an anti-Boltzmann population of the lower triplet and ground singlet levels can easily be achieved. Thus, in frozen systems the processes $^3T \to {}^3T^*$ should be a common phenomenon.

Two-quantum photochemical processes should lead to an intermittent-illumination effect. The scheme of processes given above leads to the following expression for the ratio of reaction rates under intermittent V_{inter} and continuous V irradiation (under the condition $k_{\mathrm{TS}} \gg kI$):

$$\frac{V_{\mathrm{inter}}}{V} = \frac{1}{m+1}\left\{1 - \frac{1}{k_{\mathrm{TS}}\theta}\frac{(1-e^{-k_{\mathrm{TS}}\theta})(1-e^{-k_{\mathrm{TS}}m\theta})}{\{1-e^{-k_{\mathrm{TS}}\theta(m+1)}\}}\right\}, \tag{6}$$

where θ is the time interval of illumination, and $m\theta$ is the interval of darkness. For small θ this expression tends to $1/(m+1)^2$, and for large θ to $1/(m+1)$. The ratio V_{inter}/V can be found by the rotating-sector method. Thus, equation (6) makes it possible to determine

$$k_{\mathrm{TS}} = \frac{1}{\tau_{\mathrm{phosph}}}.$$

Comparison of the value τ_{phosph} thus found from equation (6) with the value obtained from spectroscopic measurements can serve as a quantitative check of the correctness of the proposed explanation of the I^2 law. This investigation is presently being carried out in our laboratory.

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