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Abstract

Full Text

Physical Chemistry

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Two-Quantum Photochemistry. Evidence for the Participation in the Reaction of Molecules at the Second Triplet Level

(Presented by Academician S. S. Medvedev, June 3, 1963)

The photochemical reaction of aromatic amines or nitrogen-containing heterocycles with alcohols at 77° K leads to the formation of alcohol radicals (^{1,2}). Recently we established that the rate of formation of radicals is proportional to the square of the light intensity (^{3}). In that work the suggestion was made that the formation of radicals is the result of reaction of an alcohol molecule with an amine molecule located at the second triplet level. In frozen media at 77° K, the stationary concentration of molecules at the lower triplet level is appreciable even with ordinary irradiation sources, and the optical transition $^3\Gamma \to {}^3\Gamma^*$ can have a real significance for photochemistry.

Fig. 1. Theoretical curve of the dependence of V_{pr}/V on $k_{TS}\theta$ for $m = 1$.

To test the correctness of the proposed assumption, we investigated the photochemical effect of intermittent illumination for the systems diphenylamine + ethanol and triphenylamine + ethanol.

The theory of the photochemical effect of intermittent illumination has been well developed for the case when the reaction rate is proportional to $I^{1/2}$; this case is often encountered in the photoinitiation of chain reactions (see, for example, (^{4})). For the case of interest to us, the dependence of the reaction rate on the frequency of intermittent illumination can be obtained in an analogous manner. Let θ and $m\theta$ be the durations of the intervals of illumination and darkness. Then, after some time from the beginning of illumination, the concentration n of amine molecules in the ground triplet state will vary periodically within the limits from n_1 to n_2, where $n_1 \geq 0$, and $n_2 \leq n_{\text{st}}$, n_{st} being the stationary concentration under continuous illumination. During illumination,

Fig. 2. EPR spectra of the amine + ethanol system after irradiation with light at 77°K: a—diphenylamine, experiment No. 2 (Table 1), b—triphenylamine, experiment No. 2 (Table 1)

Figure 2: Fig. 2. EPR spectra of the amine + ethanol system after irradiation with light at 77°K: a—diphenylamine, experiment No. 2 (Table 1), b—triphenylamine, experiment No. 2 (Table 1)

$$\frac{dn}{dt} = \alpha_{ST} I - k_{TS} n - kIn; \tag{1}$$

in darkness,

$$\frac{dn}{dt} = -k_{TS} n, \tag{2}$$

Fig. 2. EPR spectra of the amine + ethanol system after irradiation with light at 77°K:
a—diphenylamine, experiment No. 2 (Table 1); *b*—triphenylamine, experiment No. 2 (Table 1).

where α_{ST} is the probability of a radiationless singlet-triplet transition; k_{TS} is the sum of the rate constants of radiative and radiationless transitions from the first triplet level to the ground singlet level; evidently, $k_{TS} = 1/\tau_{\text{phosph}}$, and k is the proportionality constant for the optical transition from the first triplet level to the second. The rate of formation of alcohol radicals obeys the equation

$$\frac{dR}{dt} = kIn, \tag{3}$$

where n is determined by equation (1).

It is obvious that $n_{\text{st}} = \alpha_{ST} I/(k_{TS} + kI)$. Let us introduce a new variable $z = n/n_{\text{st}}$. Integration of equation (1) (under the conditions $t = 0,\ z = z_1$ and $t = \theta,\ z = z_2$) and of equation (2) (under the conditions $t = \theta,\ z = z_2$ and $t = \theta + m\theta,\ z = z_1$) leads to the following system of equations for z_1 and z_2:

$$\ln \frac{1 - z_2}{1 - z_1} = -(k_{TS} + kI)\theta,$$

$$\ln \frac{z_1}{z_2} = -k_{TS} m\theta. \tag{4}$$

If the upper limits are not fixed when integrating equation (1), we obtain an expression for the dependence of z on t during illumination:

$$z = 1 - (1 - z_1)e^{-(k_{TS}+kI)t}. \tag{5}$$

Table 1

Effect of intermittent illumination in the photolysis of amine + ethanol systems at 77°K

No. of experiment	Irradiation time, min	θ, sec	Peak height, rel. units	V_{inter}/V	$k_{TS}\theta$	τ_{phosph}, sec
Diphenylamine, $5 \cdot 10^{-4}$ **mol/l**	**Diphenylamine,** $5 \cdot 10^{-4}$ **mol/l**	**Diphenylamine,** $5 \cdot 10^{-4}$ **mol/l**	**Diphenylamine,** $5 \cdot 10^{-4}$ **mol/l**	**Diphenylamine,** $5 \cdot 10^{-4}$ **mol/l**	**Diphenylamine,** $5 \cdot 10^{-4}$ **mol/l**	**Diphenylamine,** $5 \cdot 10^{-4}$ **mol/l**
1	3	Continuous illum.1.875	12398	0.265	0.90	2.08
2	2	Continuous illum.7.5	119134	0.375	3.83	1.95
3	2	Continuous illum.3.75	92110	0.30	1.75	2.14
4	2	Continuous illum.3.75	156189	0.305	1.82	2.06
Triphenylamine, $5 \cdot 10^{-4}$ **mol/l**	**Triphenylamine,** $5 \cdot 10^{-4}$ **mol/l**	**Triphenylamine,** $5 \cdot 10^{-4}$ **mol/l**	**Triphenylamine,** $5 \cdot 10^{-4}$ **mol/l**	**Triphenylamine,** $5 \cdot 10^{-4}$ **mol/l**	**Triphenylamine,** $5 \cdot 10^{-4}$ **mol/l**	**Triphenylamine,** $5 \cdot 10^{-4}$ **mol/l**
1	2	Continuous illum.0.50	8074	0.265	0.90	0.56
2	2	Continuous illum.1.875	8099	0.355	3.12	0.60
3	2	Continuous illum.3.75	78108	0.395	4.65	0.81

Substituting this expression into equation (3) and integrating over the limits from 0 to θ, we obtain:

$$\Delta R = kIn_{\text{st}}\theta \left\{ 1 - \frac{1 - z_1}{\theta(k_{TS} + kI)} \left[1 - e^{-(k_{TS}+kI)\theta} \right] \right\}. \tag{6}$$

The average rate V_{inter} of radical formation (the experimental quantity) is equal to

$$V_{\text{inter}} = \frac{\Delta R}{\theta + m\theta}. \tag{7}$$

Under continuous illumination the rate V of radical formation is

$$V = kIn_{\text{st}}. \tag{8}$$

Eliminating z_1 from equation (6) with the aid of equations (4) and dividing (7) by (8), we obtain a general expression for the ratio V_{inter}/V.

Let us consider the case in which $k_{TS} \gg kI$, i.e., when only a small fraction of the molecules pass from the first triplet level to the second. In this case $n_{\text{st}} = \alpha_{ST} I/k_{TS}$, $V = kI^2/k_{TS}$, and

$$\frac{V_{\text{inter}}}{V} = \frac{1}{m+1}\left[1 - \frac{1}{k_{TS}\theta}\frac{\left(1 - e^{-k_{TS}\theta}\right)\left(1 - e^{-k_{TS}m\theta}\right)}{\left(1 - e^{-k_{TS}\theta(m+1)}\right)}\right]. \tag{9}$$

Equation (9) makes it possible to determine k_{TS} by measuring V_{inter}/V for given values of m and θ. Since $k_{TS} = 1/\tau_{\text{phosph}}$, comparison of the value of τ_{phosph} found from equation (9) with the value obtained by direct determination permits a quantitative check of the explanation proposed earlier for the I^2 law.

For $m = 1$ (equal intervals of illumination and darkening), equation (9) assumes the simple form

$$\frac{V_{\text{inter}}}{V} = \frac{1}{2}\left[1 - \frac{1}{k_{TS}\theta}\,\text{th}\,\frac{k_{TS}\theta}{2}\right]. \tag{10}$$

Figure 1 presents the dependence of V_{inter}/V on $k_{TS}\theta$, which makes it possible to determine k_{TS} from the experimental value of V_{inter}/V at a given value of θ.

Air-free solutions of the amine in ethanol were irradiated with filtered light from an SVDSh lamp ($\lambda 313$ mμ) at 77°K in quartz tubes 2.5 mm in diameter. The concentration of free radicals, in relative units, was determined by the EPR method from the height of the central peak (Fig. 2). Intermittent illumination was carried out with the aid of a rotating sector. The results obtained are given in Table 1.

In the last column of the table are given the obtained values of τ_{phosph}: diphenylamine 2.04 ± 0.1 sec, triphenylamine 0.66 ± 0.1 sec. Within the accuracy of the measurements, these values agree with the direct measurements of V. L. Ermolaev[5]: diphenylamine 1.90 ± 0.1, triphenylamine 0.70 ± 0.05. This agreement should be regarded as quantitative confirmation of the supposition expressed by us[3] that the formation of alcohol radicals in the systems considered occurs as a result of an optical triplet-triplet transition $^3\Gamma \rightarrow {}^3\Gamma^*$ of the amine molecule and its subsequent reaction with an alcohol molecule.

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