

QUANTITATIVE STUDIES OF BIPHOTONIC REACTIONS

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SUMMARY

A quantitative study of the biphotonic reactions of aromatic compounds in ethanol solutions at 77 K has been performed. For several aromatic compounds the triplet yields and the extinction coefficients of triplet-triplet absorption in the visible and near uv region have been determined from kinetic measurements. The triplet-triplet absorption spectra in the visible and near uv region for phenanthrene, carbazole, phenyl- β -naphthylamine and TMPD have been obtained. The quantum yield γ defined as the ratio of the number of reacting molecules to the number of photons absorbed by the molecules in the ground triplet state were measured for several aromatic compounds. In the case of carbazole the dependence of γ on the photon energy $h\nu$ (cm^{-1}) absorbed by a molecule in the ground triplet state, obeys the equation $(\log \gamma) = P(Q - h\nu)$, where $P = 2.8 \times 10^{-4} \text{ cm}$ and $Q = 42,400 \text{ cm}^{-1}$. The electron tunnelling hypothesis of biphotonic ionization is discussed.

INTRODUCTION

In 1944 Lewis and Kasha¹ proposed that triplet-triplet absorption could lead to a photochemical reaction. This reaction would be the result of the successive absorption of two photons. Only in 1963 was it proved that biphotonic reactions of this type actually proceeded in glassy solutions of aromatic compounds at low temperatures^{2,3}. Since then a large number of biphotonic reactions have been discovered. However, there are very few quantitative studies in this field of photochemistry.

Quantum yield γ , defined as the ratio of the number of reacting molecules to the number of photons absorbed by molecules in the ground triplet state, can be used as the quantitative characteristic of a biphotonic reaction. According to this definition, at low optical densities for monochromatic light, λ_{uv} , the initial rate dR/dt of a biphotonic reaction is given by:

$$\frac{dR}{dt} = 2300 J_0 \gamma \varepsilon_T^{uv} n_T \quad (1)$$

where J_0 is the incident light intensity (einstein/cm²sec), ε_T^{uv} is the extinction coefficient of triplet-triplet absorption at λ_{uv} , and n_T is the concentration of triplets. The first attempts to determine γ led to inaccurate values^{4, 5}. There seems to be only one paper⁶ in which a correct value for γ has been obtained.

In the present work the quantum yields γ , were determined for several biphotonic reactions in ethanol solutions of aromatic compounds at 77 K. To determine γ from rate measurements, values of the other quantities in eqn. (1) are required. In this work the values of ε_T^{uv} and n_T were obtained from kinetics of triplet formation⁷ by the modified method recently proposed^{8, 9}. For several compounds the triplet-triplet absorption spectra in the visible and near uv region have been obtained.

KINETICS

The rate of increase in triplet molecules during irradiation of a solution with monochromatic light λ_{uv} is given by the following equation (weak absorption):

$$\frac{dn_T}{dt} = 2300 J_0 \varepsilon_S^{uv} (n_0 - n_T) \Phi_T - \frac{n_T}{\tau} - 2300 J_0 \varepsilon_T^{uv} n_T \gamma' \quad (2)$$

where n_0 = initial concentration of solute molecules; ε_S^{uv} = extinction coefficient of singlet-singlet absorption at λ_{uv} ; Φ_T = triplet quantum yield; τ = triplet lifetime; and γ' = total probability of all the deactivation processes of excited triplet molecules except the triplet-triplet internal conversion. Evidently $\gamma' \gg \gamma$. From eqn. (2) we obtain:

$$n_T = n_T^\infty \left\{ 1 - \exp \left[- \frac{1 + B}{\tau} t \right] \right\} \quad (3)$$

where $n_T^\infty \equiv n_0 A / 1 + B$ is the stationary triplet concentration; $A = 2300 J_0 \varepsilon_S^{uv} \Phi_T \tau$ and $B \equiv 2300 J_0 \tau (\varepsilon_S^{uv} \Phi_T + \varepsilon_T^{uv} \gamma')$. Let D_T^v denote the optical density of triplet-triplet absorption in the visible part of the spectrum at wavelength λ_v which is used as monitoring light. Then,

$$D_T^v = (D_T^v)_\infty \left\{ 1 - \exp \left[- \frac{1 + B}{\tau} t \right] \right\} \quad (4)$$

$(D_T^v)_\infty$ is the stationary value of optical density at λ_v , i.e. $(D_T^v)_\infty = n_T^\infty \varepsilon_T^v l$, where ε_T^v is the extinction coefficient of triplet-triplet absorption at λ_v , and l is the thickness of the sample. Thus:

$$(D_T^y)_\infty = \frac{n_0 A \varepsilon_T^y l}{1 + B} \quad (5)$$

By plotting $\log [1 - D_T^y / (D_T^y)_\infty]$ vs. t one should obtain a straight line from which B and $A \varepsilon_T^y$ can be determined. For the majority of the systems studied $\varepsilon_S^{uv} \Phi_T \gg \varepsilon_T^{uv} \gamma'$ (see below). In this case $B = A$ and then eqn. (4) permits us to determine A and ε_T^y . Having determined A and measured J_0 in absolute units, Φ_T can be found.

If the optical density is not very small we obtain instead of eqn. (5) the expression (for the case $A = B$):

$$(D_T^y)_\infty = \frac{n_0 A \varepsilon_T^y l \left(1 - \frac{2.3}{2} D_0\right)}{1 + A} \quad (6)$$

where $D_0 = n_0 \varepsilon_S^{uv} l$ is the initial optical density (see Appendix).

The conversion of part of the singlet molecules into triplet molecules leads to an optical density change in the uv region. Let us denote this change at wavelength λ_{uv} as ΔD_∞^{uv} . If under the same excitation conditions the triplet optical density at λ_v is measured, the values $(D_T^y)_\infty$ and ΔD_∞^{uv} will be connected by the equation:

$$\frac{\Delta D_\infty^{uv}}{(D_T^y)_\infty} = \frac{\varepsilon_T^{uv} - \varepsilon_S^{uv}}{\varepsilon_T^y} \quad (7)$$

from which the value of ε_T^{uv} at wavelength λ_{uv} can be determined, having found ε_T^y as stated above. Repeating this procedure at various wavelengths, λ_{uv} , triplet-triplet absorption spectrum in the uv region can be obtained. At an isobestic point $\Delta D_\infty^{uv} = 0$ and $\varepsilon_T^{uv} = \varepsilon_S^{uv}$.

The $\varepsilon_T^{uv} \gamma'$ value can be evaluated by the following method. The stationary concentration of excited singlet molecules, n_S^* is determined by the expression (weak absorption):

$$2300 J_0 (n_0 - n_T^\infty) \varepsilon_S^{uv} = x n_S^* \quad (8)$$

where x is the sum of the rate constants of all the deactivation processes of the excited singlet state including singlet-triplet intersystem crossing. The ratio of fluorescence/phosphorescence intensity, $L_{fl.} / L_{ph.}$ is proportional to n_S^* / n_T^∞ . From eqns. (2), (3) and (8) the relation.

$$\frac{L_{fl.}}{L_{ph.}} = K (1 + 2300 J_0 \varepsilon_T^{uv} \tau \gamma^1) \quad (9)$$

can be derived, where K is the proportionality coefficient. Hence, by plotting $L_{fl.} / L_{ph.}$ vs. J_0 one should obtain $\varepsilon_T^{uv} \gamma'$. It should be noted that $L_{fl.}$ and $L_{ph.}$ can be measured in arbitrary units.

The reaction rate dR/dt (mole $l^{-1} s^{-1}$) was measured at stationary triplet concentrations. From eqn. (1) we can obtain the expression:

$$\gamma = \frac{\epsilon_T^y l dR/dt}{2300 J_0 \epsilon_T^{uv} (D_T^y)_\infty} \quad (10)$$

or

$$\gamma = \frac{\epsilon_T^y l dR/dt}{2300 J_0 \epsilon_T^{uv} (D_T^y)_\infty \left(1 - \frac{2.3}{2} D_0 - \frac{2.3}{2} \Delta D_\infty^{uv} \right)} \quad (11)$$

where the additional expression in parenthesis is a correction for the not very small optical density (see Appendix).

EXPERIMENTAL

Materials

Ethanol was treated with iodine, refluxed with zinc dust, and fractionally distilled. Phenanthrene, acenaphthene, carbazole, benzidine, phenyl- β -naphthylamine were zone refined. *N,N*-dimethyl-*p*-phenylenediamine (DMPD), *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD), diphenylamine and quinoline were sublimed *in vacuo*. Agreement of absorption and luminescence spectra with literature data served as a purity criterion.

Apparatus

A schematic diagram of the apparatus used is shown in Fig. 1. The light source was a 1000 W xenon lamp fitted to an uv ZMR-3 monochromator 1. The band with a half-width of 10 nm was used. The light was focused by a quartz lens onto a flat quartz cell, 3 \times 15 mm and 2–3 mm thick. The cell was placed in a quartz Dewar, the lower part of which had a rectangular cross-section (4 \times 4 mm). The light beam entering the cell and leaving it was limited by rectangular dia-

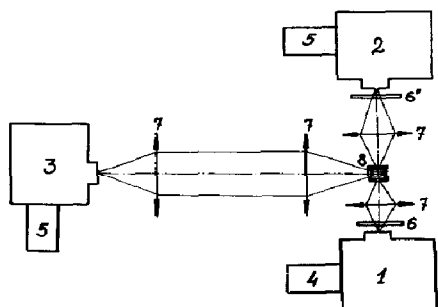


Fig. 1. Schematic diagram of apparatus. 1, 2, 3: ZMR-3 monochromators; 4: Xe lamp; 5: FEU-39 photomultiplier; 6, 6': filters; 7: quartz lens; 8: quartz Dewar and sample cell.

phragms (2×3 mm). The light transmitted through the sample was focused on the entrance slit of ZMR-3 monochromator 2, and was detected with a FEU-39 photomultiplier. The signal was recorded by an Enograph-G recorder. The exciting light was used for measuring the change of optical density in the uv range during irradiation. For measuring the optical density of triplets in the visible part of the spectrum an additional mirror was placed inside monochromator 1 so that part of the visible spectrum was reflected on the exit slit of monochromator 1 and mixed with the exciting uv light. To measure 100% transmission signal filter 6 was placed in front of the entrance slit of monochromator 1 to cut off the radiation below 350 nm. When the optical density in the visible region is measured, filter 6' similar to filter 6 was set in front of the entrance slit of monochromator 2.

In several experiments the sample was irradiated by two perpendicular beams of light. A high pressure mercury lamp equipped with filters was used as a second light source.

Absolute light intensity was measured with ferrioxalate solution¹⁰ in the sample cell at $\lambda = 310$ nm. Light intensity at a given λ_{uv} was determined by the comparison of fluorescence intensity of a solution of Rodamin B excited with light at $\lambda = 310$ nm and at λ_{uv} respectively. Fluorescence intensity was measured by a FEU-39 photomultiplier fitted to ZMR-3 monochromator 3. The constant light intensity in various experiments for a given wavelength λ_{uv} was controlled calorimetrically. One junction of a thermocouple was attached to a blackened copper plate (4×5 mm) which served as a calorimeter. The temperature rise for 3 sec irradiation with 310 nm light was recorded. This value was calibrated by the absolute light intensity at 310 nm.

Luminescence spectra for the evaluation of $\epsilon_T^{uv}\gamma'$ were detected by a photomultiplier fitted to monochromator 3 equipped with a spectrum scanning device. Luminescence spectra were recorded with an Enograph-G for various intensities of excitation light. Ratio L_{fl}/L_{ph} was expressed as fluorescence/phosphorescence intensity (in arbitrary units) at wavelengths corresponding to a fluorescence maximum or a phosphorescence maximum respectively. In experiments with high intensity of the excitation light, attention was paid to a possible reabsorption of luminescence light by the triplet molecules.

Procedure

For kinetic measurements the concentration of the aromatic compounds provided an optical density of 0.15–0.18 for the excitation light. All solutions were thoroughly degassed by the repetitive freeze–thaw technique.

Intensity of exciting light at 310 nm (band with 10 nm half-width) was 7.8×10^{-8} einstein/cm² sec and only 0.9×10^{-8} einstein/cm² sec at 270 nm.

A schematic diagram of the change in the monitoring light intensity passing through the sample during uv irradiation is shown in Fig. 2a. The initial signal h_0 corresponds to the transmission of the monitoring light through filter 6. At

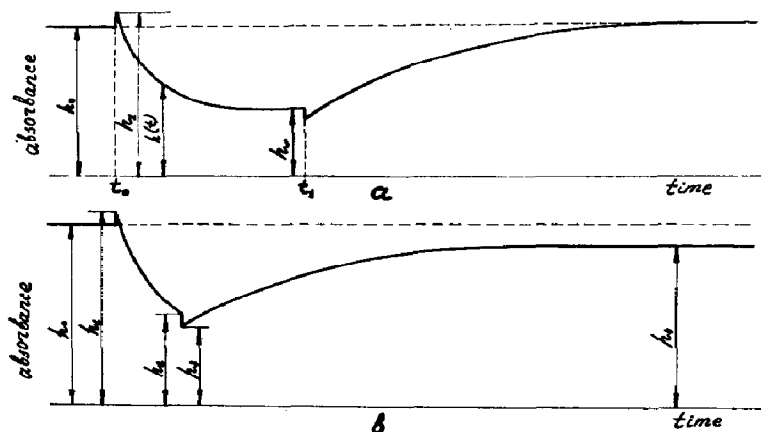


Fig. 2. A typical curve (scheme) of the change of the monitoring light intensity during an experiment. (a) No coloured products are formed; (b) coloured products are formed.

time t_0 filter 6 is removed and the monitoring light intensity is diminished owing to absorption by triplet molecules. After reaching the steady-state (signal h_∞) filter 6 is placed before monochromator 1 (uv light off) and the signal rises to its original value h_0 . Signal jumps at t_0 and t_1 are caused by the change of the light intensity due to the reflection from the filter surface. A plot of $\log \log h(t)/h_\infty$ vs. t should give a straight line which intercepts the ordinate axis at $\log (D_T^v)_\infty$. From the slope of this line B can be determined.

For comparing optical densities $(D_T^v)_\infty$ and ΔD_∞^{uv} the concentration of solute was used to provide almost complete absorption of exciting light. In the case of diphenylamine the absolute value of the difference

$$\varepsilon_S^{uv} - \varepsilon_T^v \frac{\Delta D_\infty^{uv}}{(D_T^v)_\infty}$$

was found to be too small for evaluating ε_T^{uv} with sufficient accuracy.

For measuring the reaction rate the sample was irradiated for some time with uv light at λ_{uv} for which the extinction coefficient of the triplet molecule had been determined. The photolysis of solutions containing diphenylamine, quinoline and phenyl- β -naphthylamine were performed at the isobestic point which can be easily found without quantitative measurements. During irradiation the sample was from time to time displaced vertically to provide low concentration of the products. After photolysis the sample was quickly transferred into a resonator of an electron spin resonance (e.s.r.) spectrometer.

The number of paramagnetic species was measured by comparing signals (after double integration) from samples and monocrystal of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

In some systems a gradual decrease in the triplet-triplet absorption almost immediately after reaching the stationary state was observed. Provided that this

decrease ΔD_T^v is due to photolysis of solute molecules we can write: $\Delta n_0/n_0 = \Delta D_T^v / (D_T^v)_\infty$.

Hence, we find from eqn. (1):

$$\gamma = \frac{\Delta D_T^v n_0 \varepsilon_T^v I}{2300 J_0 \varepsilon_T^{uv} (D_T^v)_\infty^2 t} \quad (12)$$

where t is the time of photolysis.

The procedure described above for determining ε_T^v , ε_T^{uv} , Φ_T and γ can not be directly applied to the system containing TMPD, DMPD and some other amines. The photolysis of these amines results in the formation of stable cation radicals in large yield. It is known that the absorption spectra of amine cation radicals are very similar to those of triplets. For these systems even after a short uv exposure (a few seconds) the intensity of monitoring light does not reach the initial value h (Fig. 2b). The difference $h_0 - h_4$ is due to absorption of monitoring light by cation radical, A^+ . Evidently: $D_T^v = \log h_4/h_3$ and $D_{A^+}^v = \log h_0/h_4$. The total optical density is equal to $\log h_1/h_2 = \log h_0/h_3$. Carrying out these mea-

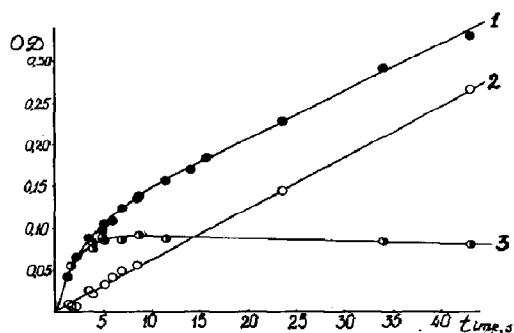


Fig. 3. Optical density at 570 nm as a function of irradiation time for a solution of $8 \times 10^{-4} M$ TMPD in ethanol at 77 K: 1, total optical density; 2, optical density of TMPD^+ ; 3, optical density of $^3\text{TMPD}$.

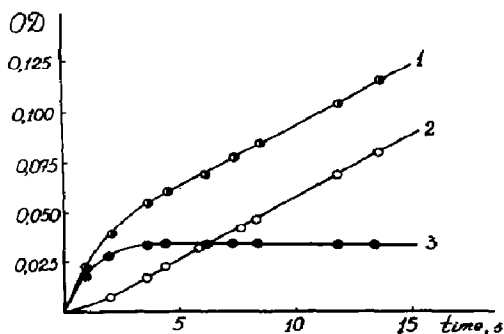


Fig. 4. Optical density at 530 nm as a function of irradiation time for a solution of $3.3 \times 10^{-4} M$ DMPD in ethanol at 77 K: 1, total optical density; 2, optical density of DMPD^+ ; 3, optical density of $^3\text{DMPD}$.

measurements for various irradiation times one can obtain kinetic curves both for D_T^v and $D_{A^+}^v$ (Fig. 3). Since for these systems γ and hence γ' are high, the term $\varepsilon_T^{uv} \gamma'$ cannot be ignored. In these cases $(D_T^v)_\infty$ and B can be found from the kinetics of triplet formation (Figs. 3 and 4) according to eqn. (4). Substituting n_T from eqn. (3) into eqn. (1), we obtain after integration the expression for the cation radical optical density:

$$D_{A^+}^v = (D_T^v)_\infty M t - \frac{(D_T^v)_\infty M \tau}{1 + B} \left\{ 1 - \exp \left[- \frac{1 + B}{\tau} t \right] \right\} \quad (13)$$

where $M \equiv 2300 J_0 \gamma \varepsilon_T^{uv} \varepsilon_{A^+}^v / \varepsilon_T^v$.

For $t > 5$ sec optical density of cation radicals (Figs. 3 and 4) increases linearly with time. From the slope of this straight line M can be evaluated from eqn. (13). If $\varepsilon_{A^+}^v$ is known then we have together with eqn. (7) four equations for determining five unknown quantities ε_T^v , ε_T^{uv} , Φ_T , γ and γ' . Assuming that $\gamma = \gamma'$, all unknown quantities can be evaluated.

It is necessary to note that under our experimental conditions only a small percentage of the amine molecules were converted into cation radicals. Therefore we may neglect the irreversible conversion of amine molecules, writing the kinetic eqn. (2).

RESULTS

For all the systems studied except TMPD and DMPD the ratio L_{fl}/L_{ph} has been found to be independent of the excitation light intensity within the limits of experimental uncertainty. The highest light intensity used amounted to $(5-10) \times 10^{-8}$ einstein/cm² sec. The evaluation of the upper limit of possible values of $\varepsilon_T^{uv} \gamma'$ in all the cases led to the conclusion that $\varepsilon_T^{uv} \gamma' \ll \varepsilon_S^{uv} \Phi_T$. Therefore $B = A$ for all these systems.

Triplet-triplet absorption

In Figs. 5, 6, 7 and 8 are shown the spectra of triplet-triplet absorption in the visible and near uv region for TMPD, carbazole, phenyl- β -naphthylamine and phenanthrene. Spectral characteristics of all the compounds studied are given in Table 1.

Quantum yield, γ

After photolysis of the frozen solution containing carbazole, TMPD, DMPD and benzidine the permanent absorption in the visible region is developed which is caused by cation radical formation. In all the other systems the formation of coloured products was not observed. A five-line e.s.r. spectrum characteristic of the CH_3CHOH radical was detected in all cases. The central part of this spectrum was usually more or less distorted by superimposing spectra of other paramagnetic

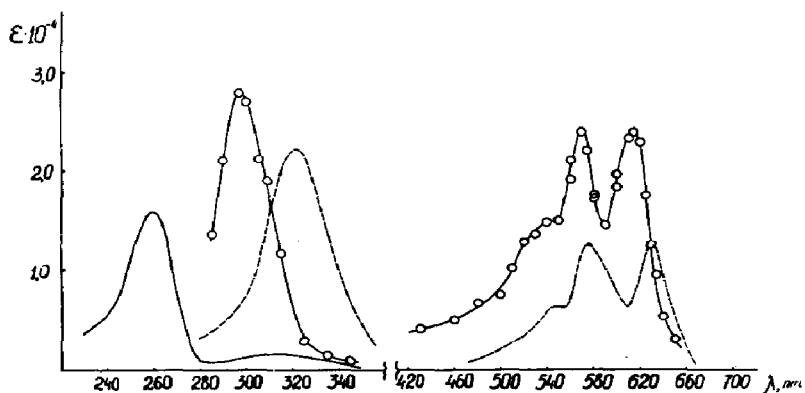


Fig. 5. Triplet-triplet absorption spectrum of TMPD in dipropyl ether at 77 K (O-O). Absorption spectrum of TMPD⁺ in ethanol at 77 K (---) singlet-singlet absorption spectrum of TMPD in ethanol at 293 K (-).

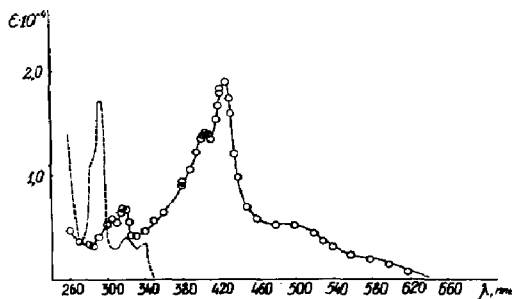


Fig. 6. Triplet-triplet absorption spectrum of carbazole in ethanol at 77 K (O-O). Singlet-singlet absorption spectrum of carbazole in ethanol at 293 K (---).

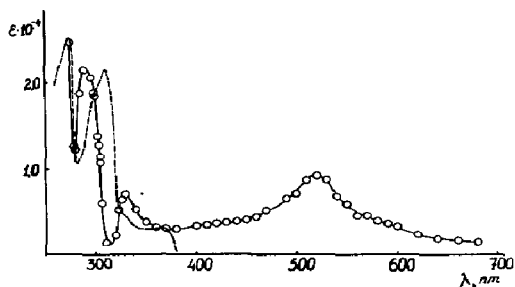


Fig. 7. Triplet-triplet absorption spectrum of phenyl-β-naphthylamine in ethanol at 77 K (O-O). Singlet-singlet absorption spectrum of phenyl-β-naphthylamine in ethanol at 293 K (---).

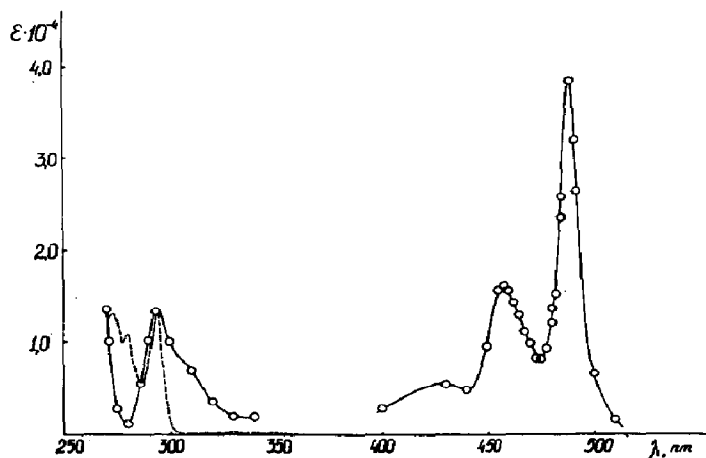


Fig. 8. Triplet-triplet absorption spectrum of phenanthrene in ethanol at 77 K (O-O). Singlet-singlet absorption spectrum of phenanthrene in ethanol at 293 K (---).

TABLE 1

SPECTRAL AND EXTINCTION DATA FOR TRIPLET-TRIPLET ABSORPTION (ethanol, 77K)

Molecule	λ max. (nm)	$\epsilon \times 10^{-3} \pm 25\%$ ($1 \text{ mole}^{-1} \text{ cm}^{-1}$)	Isobestic points (nm) and $\epsilon \times 10^{-3}$ ($1 \text{ mole}^{-1} \text{ cm}^{-1}$) in parenthesis
TMPD*	615	24	absent in the range of 345-280 nm
	570	24	
	297	28	
DMPD	530	23	not being determined
Benzidine	460	22	absent in the range 280-320 nm 298.5 (5)
Carbazole	425	19	
	406	14	
	318	7	
	305	5.7	
Diphenylamine	550	31	317 (4.7)
Phenyl- β -naphthylamine	520	9	370 (3.1), 323 (5.2),
	331	7	299 (18.8), 279.5 (11.6)
	292	21.5	
Quinoline	425	6.5	309 (1.1)
Acenaphthene	430	6	absent in the range 280-360 nm
Phenanthrene	489	38	285.5 (5.5), 271 (12.7)
	457.5	16	
	428	5.4	
	293	13	

* Data for dipropyl ether.

Notes

The following data on extinction coefficients of triplet-triplet absorption are available in the literature. They are indicated as λ max (nm); $\epsilon \times 10^{-3}$ ($1 \text{ mol}^{-1} \text{ cm}^{-1}$) in parenthesis, solvent and temperature. TMPD^a: 605 (12.2), benzene, 293 K. TMPD^b: 565 (13), 295 (17), 3-methylpentane, 77 K. Benzidine^c: 460 (49), toluene, 77 K. Carbazole^c: 425 (11), toluene, 77 K. Diphenylamine^c: 550 (28.6), toluene, 77 K. Diphenylamine^a: 530 (10.4), cyclohexane, 293 K. Quinoline^d: 400 (7.1) 30% n-butanol + 70% isopentane, 293 K. Phenanthrene^e: 489.5 (41.5), 3-methylpentane, 77 K. Phenanthrene^f: 492.5 (38), 30% n-butanol + 70% isopentane, 77 K. Phenanthrene^g: 480(24), liquid paraffin, 293 K. Phenanthrene^h: 488 (20.4), EPA, 77 K.

^a R. Bensasson and E. J. Land, *Trans. Faraday Soc.*, 67 (1971) 1904.

^b K. D. Cadogan and A. C. Albrecht, *J. Phys. Chem.*, 72 (1968) 929.

^c M. V. Alfimov, J. G. Batekha, Yu. B. Sheck and V. I. Gerko, *Spectrochim. Acta*, 27A (1971) 329

^d S. G. Hadley, *J. Phys. Chem.*, 74 (1970) 3551.

^e J. S. Brinen, *J. Chem. Phys.*, 49 (1968) 586.

^f S. G. Hadley and R. A. Keller, *J. Phys. Chem.*, 73 (1969) 4351.

^g P. G. Bowers and G. Porter, *Proc. R. Soc.*, A299 (1967) 348.

^h D. Lavalette, *J. Chim. Phys.*, 66 (1969) 1863.

species. For all the systems studied except TMPD, DMPD and benzidine the rate of photolysis was determined from e.s.r. measurements. In all cases the rate of formation of paramagnetic products was found to be proportional to the square of excitation light intensity. Thus all the reactions are biphotonic ones.

For carbazole and diphenylamine the rate of photolysis and the γ value were also determined from the decrease in the triplet stationary optical density according to eqn. (12). Both methods of the evaluation of γ agreed within the limits of experimental uncertainty.

In the photolysis of solution containing TMPD and DMPD the procedure described above for the evaluation of γ was used. Extinction coefficients of cation radicals required for these calculations were taken from the literature (for TMPD⁺ $\epsilon^{575} = 12,470^{11}$, for DMPD⁺ $\epsilon^{515} = 6500^{12}$). The extinction coefficient of the benzidine cation radical has been determined by the method recently proposed¹³; ϵ^{460} has been found to be $4.8 \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$.

Extinction coefficients, ϵ_T^{uv} , determined in the present work were used for the calculation of γ . For diphenylamine, quinoline, and phenyl- β -naphthylamine photolysis was carried out at the isobestic points.

The experimental values of γ and Φ_T , determined in the present work, are listed in Table 2.

Carbazole exhibits considerable absorption below $\lambda = 350 \text{ nm}$. This allowed us to measure γ in the wavelength range of 344 to 260 nm. In this range γ was found to rise from 2×10^{-4} to 0.066 obeying the empirical equation:

$$|\log \gamma| = P(Q - h\nu) \quad (14)$$

where $h\nu$ is the energy of photon (cm^{-1}), $Q = 42,400 \text{ cm}^{-1}$ and $P = 2.8 \times 10^{-4} \text{ cm}$. Figure 9 shows this relationship.

Some experiments with this system were performed using double source irradiation. The ground triplet level was populated with light of $\lambda = 340 \text{ nm}$.

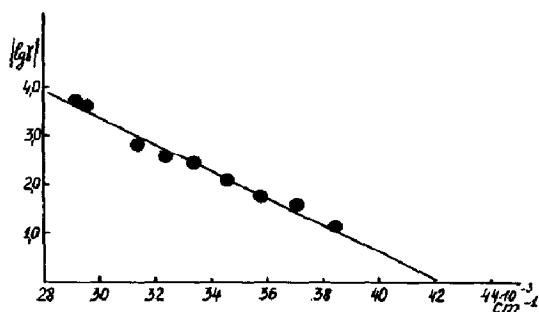
TABLE 2

QUANTUM YIELD γ AND QUANTUM YIELD OF TRIPLET FORMATION Φ_T (ethanol, 77K)

Molecule	λ^*_{uv} (nm)	γ	Φ_T
TMPD	290	0.12	0.15 ± 0.02
DMPD	300	0.16	0.09 ± 0.01
Benzidine	270	0.032	0.28 ± 0.03
Carbazole	260	0.066	$0.23 \pm 0.03^{**}$
	270	0.026	
	280	0.018	
	290	0.007	
	300	0.0036	
	310	0.0026	
	320	0.00135	
	340	0.00025	
	344	0.0002	
Diphenylamine	317	0.011	0.47 ± 0.09
Phenyl- β -naphthylamine	299	0.0009	0.30 ± 0.03
Quinoline	309	0.00045	0.25 ± 0.1
Acenaphthene	310	0.0003	0.23 ± 0.03
Phenanthrene	293	0.0004	0.46 ± 0.05

* Indicated in the centre of the band with half-width 10 nm.

** Mean value in the range 280–320 nm.

Fig. 9. The quantum yield γ as a function of photon energy of excitation light for carbazole in ethanol at 77 K.

Simultaneous irradiation with light of $\lambda = 436$ nm or $\lambda = 366$ nm (mercury lamp with appropriate filter combination) gave no additional increase in radical yield, although the intensity ratios J_{436}/J_{340} and J_{366}/J_{340} were as high as 13 and 5.6 respectively.

DISCUSSION

Photoionization of aromatic amines in solutions at 77 K is a biphotonic process^{14,15}. In ethanol the secondary photochemical reaction:



takes place¹⁶. This reaction leads to the formation of $\text{CH}_3\dot{\text{C}}\text{HOH}$ radicals and

hydrogen which can be detected chromatographically¹⁷. Detailed kinetic studies of the build-up of cation radicals, solvated electrons and $\text{CH}_3\dot{\text{C}}\text{HOH}$ radicals during uv irradiation of frozen ethanol solutions of TMPD and DMPD are in full agreement with this mechanism¹⁸⁻²⁰.

During irradiation of frozen solutions of phenyl- β -naphthylamine under our experimental conditions no permanent coloured products have been observed. In the case of diphenylamine and carbazole the sample became very slightly coloured. However, these facts cannot serve as arguments against considering the biphotonic ionization as the first step in photolysis of these amines. It has been established² that uv irradiation of frozen ethanol solutions of diphenylamine produces amine cation radicals, solvated electrons, diphenylnitrogen and $\text{CH}_3\dot{\text{C}}\text{HOH}$ radicals. The concentrations of cation radicals and solvated electrons rapidly reach the stationary values, which decrease sharply with decreasing light intensity. If the light intensity is sufficiently low no cation radicals and solvated electrons can be observed even after long irradiation. At the same time the concentrations of $\text{CH}_3\dot{\text{C}}\text{HOH}$ and diphenylnitrogen radicals grow continuously. Thus the cation radicals of diphenylamine and many other amines in contrast to TMPD and DMPD are photochemically unstable. Competition between biphotonic cation radical formation and their monophotonic decomposition results in the intensity dependence of the stationary concentration of the cation.

The mechanism of cation radical photolysis is not clear yet. The photo-recombination of cation with electron²¹ and reaction of photoexcited cation with ethanol matrix^{18, 22} were proposed as possible mechanisms.

Recently we have found^{13, 20} that the irradiation of the frozen ethanol solutions of diphenylamine in the presence of $5 \times 10^{-2}M$ benzophenone leads to a continuous increase in the amount of amine cation radicals. Simultaneously benzophenone anion radicals and ketyl radicals are produced, whereas the formation of $\text{CH}_3\dot{\text{C}}\text{HOH}$ radicals are considerably decreased and no diphenylnitrogen is observed. However, the total amount of paramagnetic species produced for the same irradiation time was equal both in the presence and in the absence of benzophenone. In both cases the formation of paramagnetic species are biphotonic processes. The formation of cation radicals of carbazole and phenyl- β -naphthylamine have also been observed in the presence of benzophenone.

On the basis of these facts we may conclude that the first step in photolysis of a frozen ethanol solution of amines is the biphotonic ionization. When photo-decomposition of cation radicals occurs the equivalent amount of paramagnetic species (free radicals) are produced. Hence, the total yield of paramagnetic species can be taken as a quantitative characteristic of biphotonic ionization.

In the case of carbazole a remarkable increase in the quantum yield γ has been found when the energy of photon of exciting light increases. It is evident that ionization occurs from vibronic states of the band ${}^3I_n \leftarrow {}^3I_1$ efficiently competing with internal conversion.

It is plausible that the biphotonic ionization occurs as a tunnelling transition of electron into matrix. For one-dimensional model the probability γ of a barrier penetration can be written in the form:

$$|\log \gamma = K d(V_0 - h\nu)^{1/2}| \quad (15)$$

where V_0 is the potential barrier above the level of the ground triplet state, $h\nu$ is the energy of photon corresponding to the triplet-triplet absorption, d is the thickness of barrier on the level of penetration, and K is a constant. The thickness of barrier is a function of the shape of the barrier and of the height of the level from which the penetration occurs. For the barrier of parabolic shape the energy of photon $h\nu$ and the thickness of barrier, d are related by the equations: $h\nu = V_0 - ax^2$ and $d = 2x$, where x is the distance from the middle of the barrier, and a is a constant. Combining these equations with eqn. (15), we obtain:

$$|\log \gamma| = b (V_0 - h\nu) \quad (16)$$

in agreement with the empirical relation (14) (b is a new constant). The quantity V_0 is the vertical ionization energy of a molecule in the ground triplet state. For V_0 the reasonable value of $42,400 \text{ cm}^{-1}$ or 5.23 eV has been found.

The dependence of γ on photon energy corresponding to the triplet-triplet absorption was also found for TMPD in 3-methylpentane solution⁶ and for benzidine in ethanol²⁸. If the vibronic relaxation from the upper triplet levels is too fast no dependence of γ on the energy $h\nu$ can be expected. Systematic investigations of this problem is in progress at our laboratory.

The mechanism of the sensitization reactions proceeded in a system containing phenanthrene, acenaphthene and quinoline is not clear yet. The quantitative studies of the dependence of γ upon photon energy and upon the chemical nature of matrix should give much useful information concerning the mechanism of these reactions.

APPENDIX

If the optical density is not very small, instead of eqn. (2) we have for the case of $\varepsilon_S^{uv}\Phi_T \gg \varepsilon_T^{uv} \gamma'$

$$\frac{dn_T}{dt} = \frac{10^3 J_0 \Phi_T (n_0 - n_T) \varepsilon_S^{uv}}{[(n_0 - n_T) \varepsilon_S^{uv} + n_T \varepsilon_T^{uv}] l} \left\{ 1 - 10^{-[(n_0 - n_T) \varepsilon_S^{uv} + n_T \varepsilon_T^{uv}] l} \right\} - \frac{n_T}{\tau}$$

Taking three terms of the series expansion, we obtain

$$\tau \frac{dn_T}{dt} = A(n_0 - n_T) \left\{ 1 - \frac{2.3}{2} \left[(n_0 - n_T) \varepsilon_S^{uv} + n_T \varepsilon_T^{uv} \right] l \right\} - n_T$$

or

$$\tau \frac{dZ}{dt} = A \left(1 - \frac{2.3}{2} D_0 \right) - (1 + A)Z \left\{ 1 - \frac{2.3 D_0 A}{2(1 + A)} \left[\left(2 - \frac{\varepsilon_T^{uv}}{\varepsilon_S^{uv}} \right) - Z \left(1 - \frac{\varepsilon_T^{uv}}{\varepsilon_S^{uv}} \right) \right] \right\}$$

where $Z = n_T/n_0$ and $D_0 \equiv n_0 \varepsilon_S^{uv} l$ is the initial optical density at λ_{uv} .

Having evaluated A and ε_T^{uv} from eqns. (4), (5) and (6) and taking $Z = A/1 + A$ we can determine the value of the last term in parenthesis. In all cases this term was found to be small in comparison with unity. Hence we obtain:

$$\tau \frac{dZ}{dt} = A \left(1 - \frac{2.3}{2} D_0 \right) - (1 + A)Z$$

which leads to eqn. (6).

It can be easily shown that in the case of $\varepsilon_T^{uv}\gamma' \gg \varepsilon_S^{uv}\Phi_T$ the correction coefficient in eqn. (5) is also

$$\left(1 - \frac{2.3}{2} D_0 \right).$$

If the optical density is not very small, instead of eqn. (1) we obtain:

$$\frac{dR}{dt} = \frac{10^3 J_0 \gamma \varepsilon_T^{uv} n_T}{I[(n_0 - n_T)\varepsilon_S^{uv} + n_T \varepsilon_T^{uv}]} \left\{ 1 - 10^{-l} [(n_0 - n_T)\varepsilon_S^{uv} + n_T \varepsilon_T^{uv}] \right\}$$

In the same approximation as above we obtain:

$$\frac{dR}{dt} = 2300 J_0 \gamma \varepsilon_T^{uv} n_T \left[1 - \frac{2.3}{2} (n_0 - n_T) \varepsilon_S^{uv} l - \frac{2.3}{2} n_T \varepsilon_T^{uv} l \right]$$

The expression in brackets can be written in the form:

$$1 - \frac{2.3}{2} D_0 - \frac{2.3}{2} (\varepsilon_T^{uv} - \varepsilon_S^{uv}) n_T l$$

The last term is the change of optical density due to conversion of part of the singlet molecules into triplet ones, ΔD_∞^{uv} . This quantity can be determined experimentally. Then

$$\frac{dR}{dt} = 2300 J_0 \gamma \varepsilon_T^{uv} n_T \left(1 - \frac{2.3}{2} D_0 - \frac{2.3}{2} \Delta D_\infty^{uv} \right)$$

and for γ we obtain relation (11).

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