BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 302—306 (1967)

An ESR Study of the Aromatic-compounds-photosensitized Decomposition of Alcohol by the Two-photon Process

Kazuo SHIMOKOSHI, Yuji MORI and Ikuzo TANAKA

Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

(Received June 15, 1966)

ESR techniques were used to examine the photosensitized decomposition of solvents in a system composed of α-naphthol and its derivatives, diphenylamine, tetraphenyl hydrazine, and diphenyl methane in methanol, EPA, and ethanol at 77°K. The effects of intermittent irradiation and incident light intensity were investigated mainly in the system composed of α-naphthol in methanol at 77°K. The lifetime of the lowest triplet state of α-naphthol was determined by the intermittent irradiation, with some kinetic considerations; it agreed reasonably well with the values obtained by the direct measurement of the phosphorescence. The rate of the radical formation was found to be nearly proportional to the square of the light intensity. From these results, it was concluded that T–T* absorption in these sensitizers played an important role in forming the radicals from alcohols. The inter-molecular triplet-triplet energy transfer process was also confirmed in a system composed of a mixed alcoholic solution of phenanthrene and naphthalene at 77°K.

The participation of molecules in the first triplet state (T_1) has been postulated for many organic photochemical reactions.[1] Also, with the development of the flash photolysis technique, the triplet-triplet absorption processes have been studied extensively for the last 10 years or so.[2] However, energy transfer to another molecule and photochemical reactions resulting from the absorption by molecules in the lowest triplet states have received little attention in spite of their important role in condensed-phase reaction. For molecules with long-lived first triplet states which are easily obtained at low temperatures in rigid media, appreciable populations in these states can achieved. Therefore, the reactions through the triplet-triplet absorption processes are of interest.[3]

Recently it has been shown, using the ESR technique[4-6] that radicals from alcohols are formed by the irradiation of light on frozen ethanol solutions of aromatic amines and naphthalene[7]; triplet-triplet absorption processes have been postulated for the mechanism of the formation of the radicals.

In this experiment, ESR techniques will be used to examine the photosensitized decomposition of solvents in a system composed of α-naphthol and its derivatives, diphenylamine, tetraphenyl hydrazine, and diphenylmethane in ethanol, EPA and methanol at 77°K. The role of T–T* absorption in forming the radicals from solvents will also be discussed. In addition, it has been known that the inter-molecular triplet-triplet energy transfer occurs in rigid media at 77°K.[8,9] The observation of delayed fluorescence caused by T–T annihilation and of the sensitized phosphorescence also confirms this fact. By using a system composed of a mixed alcoholic solution of naphthalene and phenanthrene at 77°K, where the inter-molecular triplet-triplet energy transfer would be expected, it will be shown that the naphthalene-photosensitized decomposition of alcohol through this energy transfer process forms the same radicals.

Experimental

The paramagnetic resonance spectra were observed using a JES 3110 X, X-band spectrometer with a field modulation of 100 kc/sec, and a TE_{102} mode cavity with a quartz Dewar. As the standard of the intensity and the hyperfine splitting of free radicals, Mn^{2+} in MgO was applied to the cavity. The irradiation source was SH 100 UV high-pressure mercury arc. A major fraction of the UV light from this lamp occurred at wavelengths longer than 2800 Å, though two broad, weak bands, 2540 Å and 1850 Å, were also

---

[1] For example, "Advances in Photochemistry," Vols. I—III, ed. by W. A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr., Interscience Publishers, New York (1963—1965).

[2] R. G. W. Norrish, *Proc. Chem. Soc.*, **1958**, 247; G. Porter and M. Windsor, *Proc. Roy. Soc.*, **A245**, 203 (1958).

[3] K. D. Cadogan and A. C. Albrecht, *J. Chem. Phys.*, **43**, 2550 (1965). They suggest that the photoionization of organic molecules in rigid media also proceeds *via* T–T* absorption.

[4] B. Smaller, *Nature*, **195**, 593 (1962); *Advan. Biol. Med. Phys.*, **9**, 25 (1962).

[5] V. E. Kholmogorov, E. V. Baranov and A. N. Terenin, *Dokl. Akad. Nauk SSSR*, **149**, 142 (1963).

[6] Kh. S. Bagdasaryan, V. I. Muromtsev and Z. A. Sinitsyna, *ibid.*, **152**, 349; **153**, 374 (1963).

[7] S. Siegel and K. Eisenthal, *J. Chem. Phys.*, **42**, 2494 (1965).

[8] G. Porter and F. Wilkinson, *Proc. Roy. Soc.*, **A264**, 1 (1961).

[9] C. A. Parker and C. G. Hatcherd, *J. Phys. Chem.*, **66**, 2506 (1962); *Proc. Chem. Soc.*, **1962**, 147.

emitted. To measure the dependency of the wavelength on the formation of radicals, several kinds of glass filter were applied. As will be discussed later, the irradiation of wavelengths longer than 3100 Å gave different ESR spectra of free radicals from those obtained by the irradiation at wavelengths shorter than 3100 Å. Therefore, a Halio glass was used as the filter; it transmitted 80% at 3100 Å and a few percent at 2800 Å. The effects of the light intensity were examined, varying the incident light intensity with calibrated wire screens. To investigate the effect of intermittent irradiation in these photosensitizations, a rotating sector driven by a synchronous motor was used. Methanol and ethanol were used as solvents. A special grade of methyl alcohol was used in this experiment without any special purification. The quantitative measurements were made by using α-naphthol as the sensitizer. α-Naphthol and the other solutes used were recrystallized five or more times from methanol and then sublimated. Samples consisting of 0.4 cc, (10^{-3}—10^{-5} mole/l) in a 3 mm i.d. quartz tube were degassed by multiple freezing and thawing in a high vacuum (10^{-5}—10^{-6} mmHg). The tube was then sealed off. The experiments on non-degassed systems showed that dissolved air did not have such a remarkable effect on photosensitization. However, it had a slight effect on the resolution of the spectra.

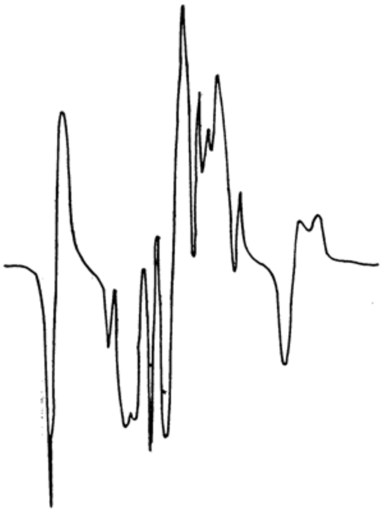

Fig. 1-A. ESR spectrum obtained by irradiation of H_2O_2 and methanol mixture at 77°K.

Fig. 1-B. ESR spectrum obtained by α-naphthol photosensitization of methanol (irradiated by <3100 Å at 77°K).

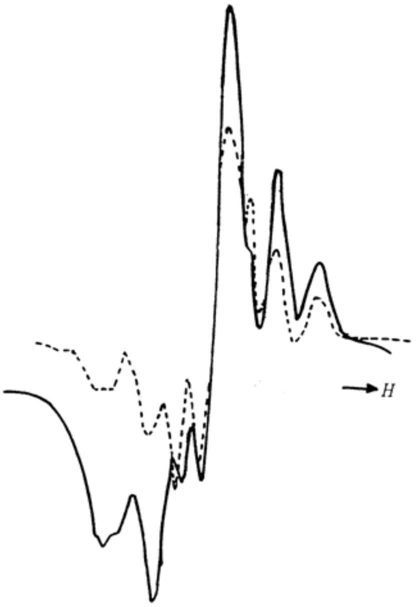

Fig. 2. ESR spectra of ethanol solution of α- (10^{-3} mol/l) irradiated by >3100 Å at 77°K (solid line) and the spectra obtained by the irradiation of H_2O_2 and ethanol mixture at 77°K (dotted line).

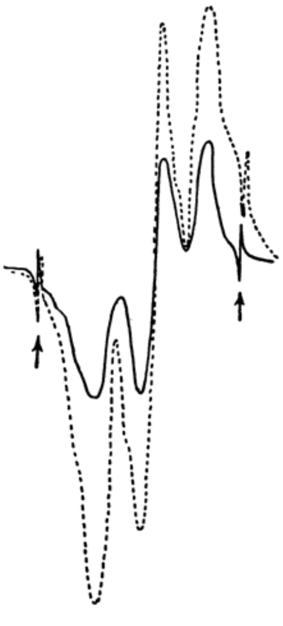

Fig. 3. ESR spectra of methanol solution (10^{-3} mol/l) of α-naphthol irradiated by >3100 Å at 77°K (solid line) and the spectra obtained by short irradiation of H_2O_2 and methanol mixture at 77°K (dotted line). Arrows show the positions of Mn^{2+} spectra with the separation of 87.5 gauss.

It has been known that methanol, ethanol and methyl acetate directly irradiated by 1849 Å[10] or by X-ray and initiated by the photolysis of H_2O_2[11] give several kinds of free radicals, such as CH_3, CH_2OH, CHO, CH_3CHOH, and CH_3CH_2. These radicals were also observed in the photosensitized decomposition of these alcohols by α-naphthol or some of the other molecules used here. The photosensitization by irradiation without a filter gave the same ESR signal pattern as that given by the peroxide-initiated radicals. Therefore, the assignment of these radicals was easily made by comparing the spectra obtained by the two methods. These spectra from methanol and ethanol obtained by the two methods are shown in Figs. 1 and 2. When the methanol solution containing α-naphthol (10^{-3} mole/l) was irradiated at 77°K by wavelengths longer than 3100 Å, the triplet spectra were observed; they were identified with those arising from the peroxide-initiation reaction upon a short irradiation (about 10 sec). A comparison of the two spectra is shown in Fig. 3.

Results and Discussion

A. General Remarks on the Photosensitized Decomposition of Alcohols. Most of the alcoholic solutions of α-naphthol and its derivatives and some other aromatic compounds irradiated by ultraviolet light at 77°K gave the ESR signals of the free radicals from alcohols. In addition, those molecules which gave the free radicals also emitted a strong phosphorescence at 77°K in rigid media. It was assumed, therefore, that there must exist a certain relationship between the formation of the free radicals and the triplet states of each solute molecule. The relationship between the phosphorescence and free radicals observed, together with the effect of the irradiation wavelength, is shown in Table 1. Diphenylamine and tetraphenyl hydrazine produced the other free radicals [Table 1, (i) and (ii)] probably as a result of their own direct photolysis, together with the free radicals from alcohols. The irradiation of alcohols alone did not give any ESR signals under the same conditions as when the solution was used.

As is shown in Fig. 1, the irradiation with light shorter than 3100 Å gave very complex spectra, so that it was difficult to examine the relative concentration of the free radicals. It could be assumed from the dependence of the radical formation on the wavelength, however, that the production of CHO required a secondary process in which the CH_2OH radicals primarily produced were photolized by the absorption of UV light shorter than 3100 Å as follows:

$$CH_2OH \xrightarrow{(<3100\ \text{Å})} CHO + H_2 \qquad (1)$$

In order to derermine, without complexity, the mechanism of photosensitization by solutes, irradiation with light longer than 3100 Å was made. In order to derermine, without complexity, the mechanism of photosensitization by solutes, irradiation with light longer than 3100 Å was made. The variations in the ESR signal intensity as a function of the irradiation time are shown in Fig. 4. All the quantitative measurements were carried out in the region where the signal intensity increased linearly.

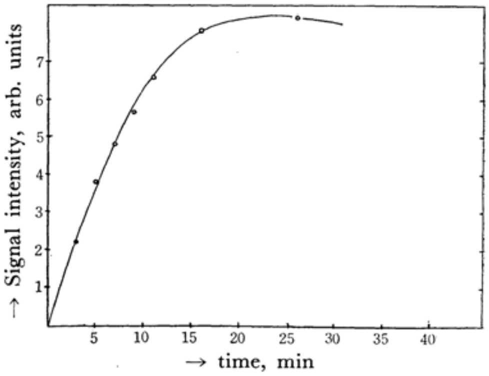

Fig. 4. Variation of the ESR signal intensity of methanol radical as a function of irradiation time.

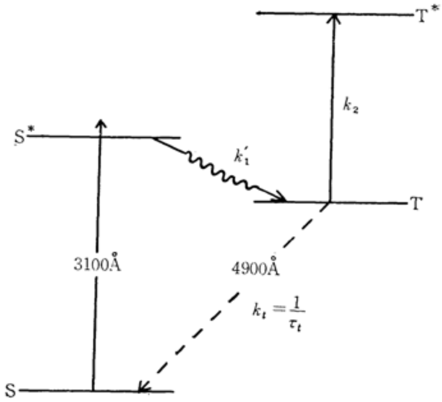

Fig. 5. Transition scheme among energy levels in α-naphthol.

The energy scheme of α-naphthol is shown in Fig. 5. As has been mentioned before, the production of the free radicals from the sensitized decomposition of the solvent required a long lifetime of the phosphorescent triplet state of the solute. However, it is energetically insufficient to rupture the C–H bonds of alcohol merely by energy-transfer from the lowest triplet state of solute to alcohol. In order to obtain a reasonable mechanism, which is connected with the lowest triplet states and satisfies the relation in energy, it may be assumed that the C–H bond rupture is caused by energy-transfer from the higher triplet states of the solutes to the alcohols, where the higher triplet states are produced by the two-photon process (T–T* absorption).

---

[10] P. J. Sullivan and W. S. Koski, *J. Am. Chem. Soc.*, **85**, 384 (1963).

[11] J. A. Brivati, N. Keen and M. C. R. Symons, *J. Chem. Soc.*, **1962**, 237.

TABLE 1. RELATION BETWEEN THE PHOSPHORESCENCE AND THE FREE RADICALS OBSERVED, AND THE EFFCT OF IRRADIATION WAVELENGTH (10^{-3} mol/l methanol solution)

	<3100 Å		>3100 Å	
	Phos.	ESR signal	Phos.	ESR signal
α-Naphthol	obs.	CHO CH_2OH CH_3	obs.	CH_2OH
1, 4-Chloronaphthol	obs.	CHO CH_2OH CH_3	obs.	CH_2OH
1-Naphthol-2-carboxylic acid	obs.	CHO CH_2OH CH_3	obs.	CH_2OH
1, 4-Bromonaphthol 2-Aceto-1-naphthol	not obs.	no signal	not obs.	no signal
Diphenylamine	obs.	CHO, CH_3 CH_2OH (i)	obs.	CH_2OH (i)
Tetraphenyl hydrazine	obs.	CHO, CH_3 CH_2OH (ii)	obs.	CH_2OH (ii)
Diphenylmethane	obs.	CHO CH_2OH CH_3	not obs.	no signal

(i) Free radicals from diphenylamine.
(ii) Free radicals from tetraphenyl hydrazine.

TABLE 2. LIFETIME OF THE LOWEST TRIPLET STATE OF α-NAPHTHOL OBTAINED BY INTERMITTENT IRRADIATION OF METHANOL SOLUTION AT 77°K

No.	Time, min	θ, sec	V	V_{int}/V	$k_t\theta$	$\tau_t=1/k_t$, sec
1	4	cont.	8.89			
	10	4	3.00	0.338	2.24	1.65
2	3	cont.	9.13			
	8	2.5	2.71	0.296	1.68	1.49
3	3	cont.	8.48			
	7	5	3.12	0.368	3.54	1.41

cont.: continuous illumination.

B. The Lifetime of the Triplet State (T_1) of α-Naphthol at 77°K as Determined by Intermittent Irradiation. In order to determine the mechanism of this photosensitized reaction, it is convenient to investigate the photochemical changes upon intermittent irradiation. If the radicals are formed by the energy-transfer from the higher excited triplet state of α-naphthol produced by the two-photon process to methanol, the rate of the production of methanol radicals will be given by the equation:

$$\mathrm{d}R/\mathrm{d}t = k_2IC \tag{2}$$

where C is the concentration of α-naphthol in the lowest triplet state (T_1). It will change periodically, corresponding to the following equations. In the light period,

$$\mathrm{d}C/\mathrm{d}t = k_1I - k_tC - k_2IC \tag{3}$$

where:

$$k_1 = k_1'[1 - \exp(-C_0d)] \tag{3a}$$

and in the dark period,

$$\mathrm{d}C/\mathrm{d}t = -k_tC \tag{4}$$

where all the rate constants correspond to those illustrated in Fig. 5, and where k_1' is the probability of intersystem crossing; C_0, the concentration of α-naphthol; d, the constant proportional to the absorption coefficient; k_t, the sum of the rate constants for radiative and non-radiative transitions from the lowest triplet state to the ground state, and k_2 the constant proportional to the optical transition from the lowest triplet state to the higher triplet state. In this experiment, it may be assumed that only a small fraction of the molecules transfer from T_1 to the higher triplet state; therefore, it is considered that $k_t \gg k_2I$. In this case, $C_{st}=k_1I/k_t$, where C_{st} is the stationary concentration of T_1 during continuous irradiation. The following equation for the ratio between the rate of formation under intermittent irradiation with equal light and dark periods and that under continuous irradiation was obtained⁵⁾:

$$(\mathrm{d}R/\mathrm{d}t)_{int}/(\mathrm{d}R/\mathrm{d}t)_{cont} = 1/2[1-\tanh(k_t\theta/2)/k_t\theta] \qquad (5)$$

where θ is the intermittent irradiation time. Using this equation, at a given value of θ the values of k_t can be obtained by measuring various $(\mathrm{d}R/\mathrm{d}t)_{int}/(\mathrm{d}R/\mathrm{d}t)_{cont}$ ratios, and the value of $1/k_t(=\tau_{\mathrm{phos}})$ can be compared with the reported values¹²⁾ ($\tau_{\mathrm{phos}}=1.9$ sec). The results are listed in Table 2. It is considered that the results show a reasonable agreement within the limits of experimental error. Therefore, they verify the assumption that the formation of the free radicals is strongly associated with the lifetime of the first triplet (T_1).

C. The Dependence of the Radical Yield on the Light Intensity. It has been assumed above, from the viewpoint of the bond energy of alcohols, that T–T* absorption actually occurs; *i. e.*, Eq. (3) implied this process. In this case, the stationary concentration of α-naphthol in the lowest triplet state is determined from Eq. (3) as follows:

$$C = \frac{k_1 I}{k_t + k_2 I} \qquad (6)$$

Therefore, the following expression for the rate of the radical formation is obtained:

$$\mathrm{d}R/\mathrm{d}t = k_2 IC = \frac{k_1 k_2 I^2}{k_t + k_2 I} \qquad (7)$$

When $k_t \gg k_2 I$, this equation (7) become:

$$\mathrm{d}R/\mathrm{d}t = (k_1 k_2/k_t) I^2 \qquad (8)$$

Therefore, an attempt was made to measure the dependence of the radical yields on the light intensity in order to confirm this equation and the T–T* absorption process. The dependence of the radical formation on the light intensity is, in general, given by the following equation:

$$\mathrm{d}R/\mathrm{d}t = kI^n \qquad (9)$$

Table 3. Dependence of the rate of radical formation on light intensity
(10^{-3} mol/*l* methanol solution)
$V=\mathrm{d}R/\mathrm{d}t$: the rate of radical formation

No.	Radical concn. arb. units	Time min	V	Transmittance %
1	53.6	3	17.8	100
2	48.6	5	9.7	70
3	37.1	10	3.7	40

$V_2/V_1 = 0.544 = (0.7)^n \quad n = 1.7$
$V_3/V_1 = 0.208 = (0.4)^n \quad n = 1.7$

By the experiments at various t and I values, n, could be obtained from the equation:

$$\log(\mathrm{d}R/\mathrm{d}t)_1/(\mathrm{d}R/\mathrm{d}t)_2 = n\log(I_1/I_2) \qquad (10)$$

The value of n, which is given in Table 3, was 1.7. Thus, the following conclusion was reached: the rate of radical formation is nearly proportional to the square of the light intensity. The results obtained in this section, together with those obtained in Section B, comfirm the T–T* absorption process.

D. Intermolecular Triplet-Triplet Energy-Transfer in Rigid Media at 77°K. It has been known that the intermolecular triplet-triplet energy transfer occurs in rigid media at 77°K.⁸,⁹⁾ In this experiment, as is shown in Fig. 6, phenanthrene acts as a triplet energy donor, because the lowest excited singlet level of naphthalene lies above that of phenanthrene, while the lowest triplet level of naphthalene lies below that of phenanthrene.

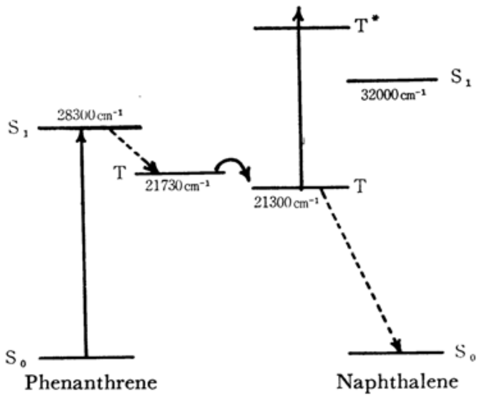

Fig. 6. Transition scheme among energy levels in phenanthrene and naphthalene including intermolecular energy transfer.

When the methanol solution of phenanthrene (10^{-3} mol/*l*) was irradiated at wavelengths longer than 3130 Å, under the same conditions as in the case of α-naphthol, no radicals were observed. Since naphthalene is almost transparent above 3130 Å, no radical was observed by the irradiation of the methanol solution, while radials from methanol were observed when using an irradiation at wavelengths shorter than 3130 Å at 77°K. However, when a 100 : 1 mixture (10^{-3} mol/*l*) of phenanthrene and naphthalene, with methanol as a solvent, was irradiated at wavelengths longer than 3130 Å at 77°K, a photosensitized decomposition of methanol, namely, the same ESR spectrum as Fig. 3, was observed. This experiment suggests the occurrence of reactions including the intermolecular triplet-triplet energy transfer process from the T of phenanthrene to the T of naphthalene and the T* state of the naphthalene-sensitized decomposition of methanol, followed by T–T* absorption in naphthalene.

---

12) *Cf.*, for example, G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944).