BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2002—2007 (1970)

The Photosensitized Decomposition of Methyl Acetate at 77°K. A Kinetic Analysis of the Biphotonic Process

Shigeru MIZUTANI, Yukihiko NAKAJIMA, Kazuo SHIMOKOSHI and Shin SATO

Department of Applied Physics, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

(Received January 26, 1970)

The photosensitized decomposition of methyl acetate at 77°K has been investigated using an ESR technique. Naphthalene, α-naphthol, phenanthrene, anthracene, and benzophenone were used as sensitizers. When wavelengths longer than 2700Å were used, the formation of methyl radicals was observed except in the cases of anthracene and benzophenone. For the systems containing naphthalene, phenanthrene, and α-naphthol, the rate of the formation of methyl radicals was studied in detail and was found to obey the following relation:

$$R=\alpha I^{3/2}C^{1/2}$$

Here, α is a proportional constant, I is the light intensity, and C is the solute concentration, which ranged from 5×10^{-5} to 2×10^{-3} mol l^{-1}. Possible reaction mechanisms to explain the above relation were discussed; they include the biphotonic excitation of sensitizers, the triplet-triplet annihilation for the decay of the solute triplet, and the photolysis of the radicals produced in the photosensitization.

The lowest triplet states of some aromatic compounds have very long lifetimes at 77°K.[1,2] The subsequent absorption of another photon by the triplet molecule, therefore, often occurs, even with a conventional ultraviolet light source, and produces a higher triplet state. When the ionization potential of the solute molecule is close to the energy of the higher triplet state, the charge separation takes place. Such is the case when tetramethyl-*p*-phenylenediamine (TMPD) is photolyzed in a rigid matrix.[3,4] The formation of benzyl radicals in the 2537 Å photolysis of toluene at 77°K has also been attributed to the biphotonic process.[2] The rate of the formation of this radical is reported to be proportional to $I^{3/2}$. Here, I denotes the light intensity. When an aromatic compound is dispersed in a rigid matrix solvent, the decomposition of the solvent by the biphotonic process is frequently observed.[5] Recently, one of the present authors investigated the photosensitized decomposition of methanol at 77°K using several aromatic compounds as sensitizers and concluded that the formation of CH_2OH radicals is due to the biphotonic process described above.[6]

In this paper, methyl acetate has been used as

1) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).
2) B. Brocklehurst, W. A. Gibbons, F. T. Lang, G. Porter and M. I. Savadatti, *Trans. Faraday Soc.*, **62**, 1793 (1966).
3) K. D. Cadogan and A. C. Albrecht, *J. Chem. Phys.*, **43**, 2550 (1965).
4) Y. Nakato, N. Yamamoto and H. Tsubomura, This Bulletin, **40**, 2480 (1967).
5) S. Siegel and K. Eisenthal, *J. Chem. Phys.*, **42**, 2494 (1965).
6) K. Shimokoshi, Y. Mori and I. Tanaka, This Bulletin, **40**, 302 (1967).

the matrix solvent, because the methyl radicals produced in the photosensitization show a clear and comparatively stable ESR spectrum. Therefore, we expected that a detailed kinetic analysis of the biphotonic process would be feasible.

Experimental

The methyl acetate (Tokyo Kasei Co.) was distilled at 57.5°C before use. The α-naphthol, phenanthrene, and benzophenone were used as supplied by the Wako Pure Chemical Co. The naphthalene and anthracene purified by the zone-melting method were kindly supplied by Professor Hayakawa of this Institute.

About 0.4 m*l* of a methyl acetate solution containing a known amount of a sensitizer was sealed in a Spectrosil quartz tube (2.5 mm in diameter) and they immersed in liquid nitrogen in an unsilvered quartz Dewar flask. The solution in the flask was irradiated with a high-pressure mercury arc (Toshiba SHL 100 UV-2) through a combination of two quartz lenzes, a glass filter, and a calibrated wire net to control the light intensity. The glass filters used were Toshiba UV-27, Corning CS-054, and Toshiba UV-33 filters; they were used to cut off the wavelengths shorter than 2700, 3000, and 3300 Å respectively.

After the irradiation, the radicals produced were examined by means of a JEP-1 X-band ESR spectrometer with a field modulation of 100 kc/sec. The concentrations of the radicals were measured by comparing the signal heights from the solutions and a Mn marker (Mn^{2+} in MgO).

In order to ascertain the kind of products formed in photolysis, prolonged irradiation was made on a rigid solution. After warming the irradiated sample up to room temperature, the gas non-condensable at −120°C was analyzed by gaschromatography.

Results

The ESR spectrum obtained with an irradiated methyl acetate solution of naphthalene is shown in Fig. 1, along with the assignment of the peaks. With other sensitizer solutions almost the same spectra were obtained, although the relative peak heights due to the different radicals were a little changed.

Table 1 summarizes the general features of the experimental results. Pure methyl acetate gave an ESR signal only when irradiated for a long period with light and through no filter. In the presence of naphthalene, it was necessary to use wavelengths shorter than 3000 Å to obtain the ESR spectrum. The strong absorption band of naphthalene has its onset at 3000 Å. When anthracene and benzophenone were used as sensitizers, no ESR signals were obtained. When a mixture of benzophenone and naphthalene was used, an ESR spectrum similar to that in Fig. 1 was obtained even by the irradiation of the light at wavelengths longer than 3300 Å. The luminescence observed from this solution was the same as that from a naphthalene solution. These results suggest an energy transfer from triplet benzophenone to naphthalene in the rigid matrix of methyl acetate. A similar observation has already been made in the matrix of methanol.[6]

Decay of Methyl Radicals in the Rigid Matrix. During the measurement of the ESR

Table 1. Radicals produced by photosensitization

Solute	Filter	Luminescence	ESR signal	τ[2]
Solvent only		violet	CH_3, CH_3O, CHO CH_2COOCH_3 or CH_3COOCH_2	
	>2700 Å			
Naphthalene	>2700 Å	yellow green	CH_3, CH_3O, CHO CH_2COOCH_3 or CH_3COOCH_2	2.5
	>3000 Å			
α-Naphthol	>2700 Å	green	CH_3, CH_3O, CHO CH_2COOCH_3 or CH_3COOCH_2	1.9
	>3000 Å	green	CH_3, CH_3O CH_2COOCH_3 or CH_3COOCH_2	
Phenanthrene	>2700 Å	yellow green	CH_3, CH_3O, CHO CH_2COOCH_3 or CH_3COOCH_2	3.3
	>3000 Å	yellow green	CH_3, CH_3O CH_2COOCH_3 or CH_3COOCH_2	
Anthracene	>2700 Å			
Benzophenone	>2700 Å			
Naphthalene + Benzophenone	>3300 Å	yellow green	CH_3, CH_3O CH_2COOCH_3 or CH_3COOCH_2	

τ: triplet lifetime (sec).

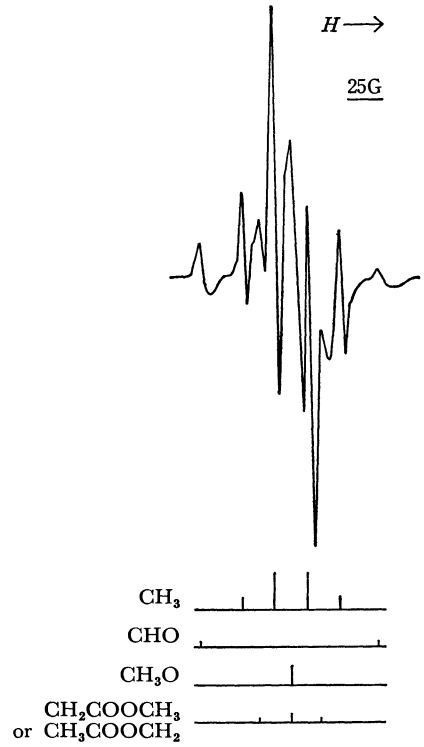

Fig. 1. ESR spectrum obtained by naphthalene photosensitized decomposition of methyl acetate (irradiated by >2700 Å at 77°K).

spectrum of the rigid matrix, the peak height due to methyl radicals gradually decreased. The rate of the decrease was dependent upon the initial peak height. The results obtained with a naphthalene solution are shown in Fig. 2. When the reciprocal of the peak height is plotted as a function of the time of measurement, a linear relationship is always obtained. This suggests that the initial decay of methyl radicals is of a second order. For the sake of simplicity, the peak heights shown in the following data are those obtained by extrapolating the linear relation to zero time, that is, the time when the irradiation was terminated.

Dependence on the Light Intensity. Using two calibrated wire nets, three light intensities were examined, one of them without a net. Figure 3 shows the irradiation-time dependence obtained with a naphthalene solution. Initially, the peak height increased linearly with the irradiation time, but on further irradiation the peak height reached a maximum and then gradually decreased. This decrease is probably due to the screening of light by decomposition products. In Fig. 4, the initial slopes obtained with three sensitizer solutions are plotted as a function of the light intensity. In every case, the rate of increase in peak height, *i.e.*, the rate of the formation of methyl radicals, was found to be proportional to $I^{1.5\pm0.1}$. Here,

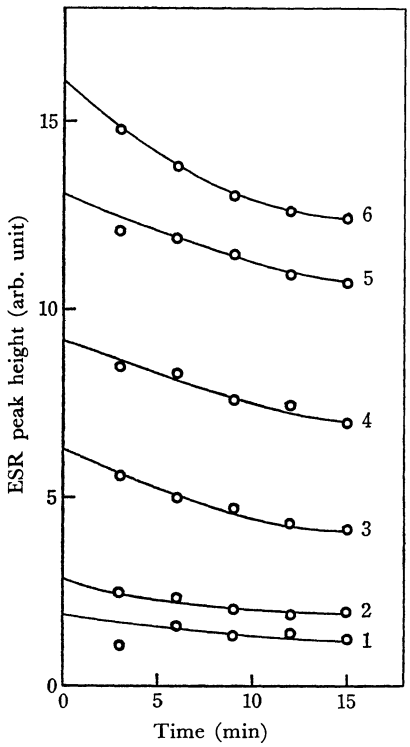

Fig. 2. Decay of methyl radicals after UV-irradiation of methyl acetate solution of naphthalene at 77°K.

1. 5×10^{-5} mol l^{-1}
2. 2×10^{-4} mol l^{-1}
3. 5×10^{-4} mol l^{-1}
4. 2×10^{-3} mol l^{-1}
5. 5×10^{-5} mol l^{-1}
6. 2×10^{-2} mol l^{-1}

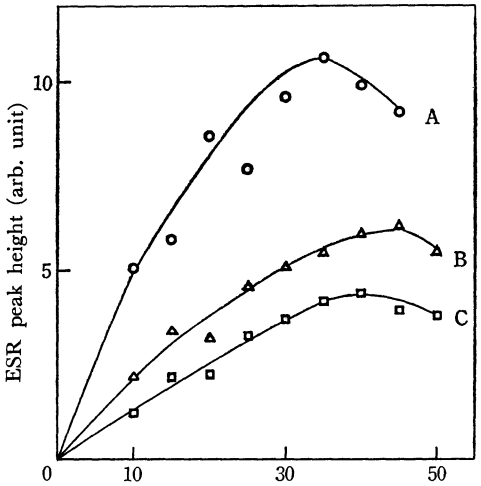

Fig. 3. ESR signal intensity of methyl radicals of naphthalene solution as a function of irradiation time.

A(○), relative light intensity=100
B(△), relative light intensity= 60
C(□), relative light intensity= 45

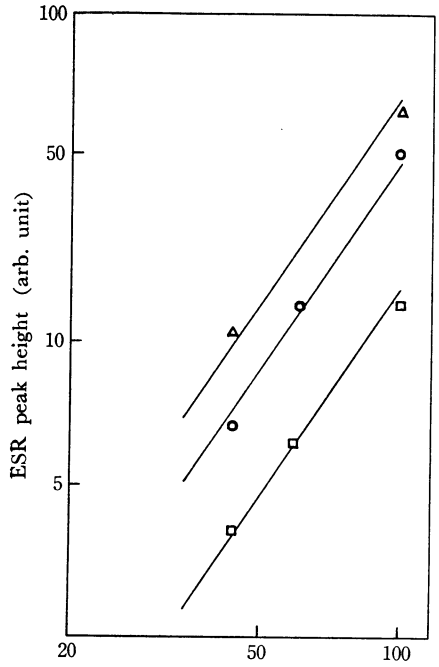

Fig. 4. ESR signal intensity of methyl radicals as a function of the light intensity. Sensitizer concentration is 2×10^{-3} mol l^{-1}. Solid curves are drawn proportionally to $I^{1.5}$.
A(○), naphthalene
B(△), α-naphthol
C(□), phenanthrene

I denotes the light intensity.

Dependence on the Concentrations of Solutes. Two series of experiments were made for each sensitizer solution. The results are shown in Fig. 5. Where the logarithm of the rate of the formation of methyl radicals is plotted as a function of the logarithm of the concentration. An approximately linear relationship was obtained over a wide range of concentrations from 5×10^{-5} to 2×10^{-3} moll^{-1} for each solution. All the slopes were nearly equal to 0.5. At concentrations higher than 10^{-2} moll^{-1}, the slope decreased with an increase in the concentration.

Reaction Products. To identify gaseous products in photolysis, a long irradiation was made on a rigid methyl-acetate solution. The products non-condensable at −120°C were analyzed by gaschromatography. The product consisted of methane and a small amount of ethane, although no quantitative measurement could be made because of their small amounts. To check whether these gases are produced during the photolysis or when the sample is warmed up for analysis, a sample kept for a long period at 77°K after irradiation, during which period most of the methyl radicals decayed, was analyzed; the amounts of methane and ethane obtained were, however, almost the same as those obtained immediately after irradiation.

Discussion

The following mechanism is usually assumed for the interpretation of the kinetics of biphotonic

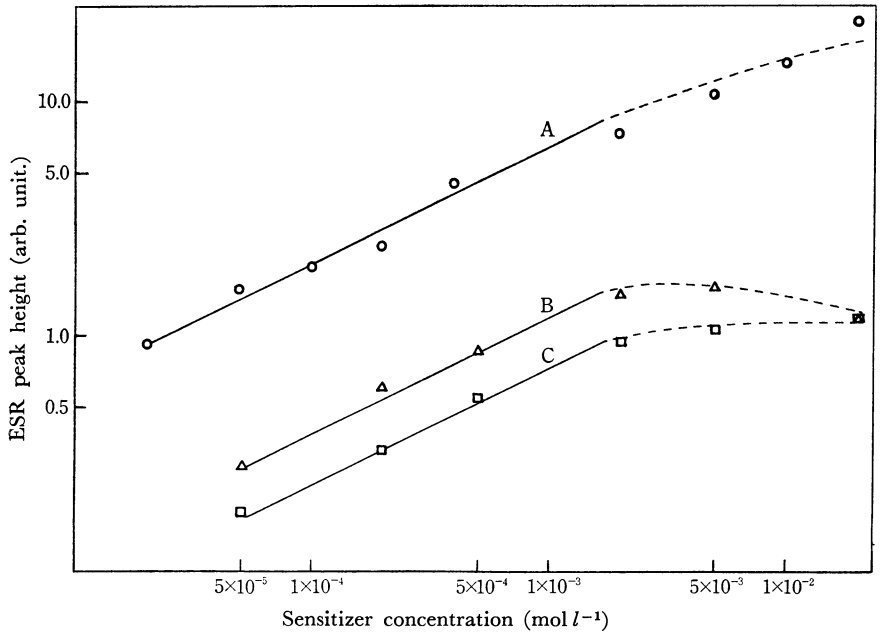

Fig. 5. ESR signal intensity of methyl radicals as a function of the sensitizer concentration.
A(○), naphthalene B(△), α-naphthol C(□), phenanthrene

processes:[2]

$S + h\nu \rightarrow S^*$ rate$=I\varepsilon_S C_S l$

$S^* \rightarrow S(+h\nu)$, $S^* \rightarrow T$ } quantum yield of $T=\phi_T$

$T \rightarrow S(+h\nu)$ rate$=(1/\tau)C_T$

$T + h\nu \rightarrow T^*$ rate$=I\varepsilon_T C_T l$

$T^* \rightarrow T$, $T^* + M \rightarrow S +$ radical } quantum yield of radical $=\phi_P$

Here, S and T represent the lowest singlet and triplet states; S^* and T^* represent the higher excited states; τ is the lifetime of the triplet state with respect to decay, $T \rightarrow S$, by phosphorescence or a radiationless process; ε_S and ε_T are the extinction coefficients; C_S and C_T are the concentrations of the ground-state and triplet molecules, and $C_S + C_T = C$ is the initial concentration. I is the light flux in the sample, and M represents the matrix solvent molecule, while l is the path of the impinging light in the matrix.

Using this mechanism, however, the experimentally-obtained relation:

$$R = \alpha I^{3/2} C^{1/2} \qquad \text{(I)}$$

cannot be easily derived. We have tried various assumptions regarding ε_S, ε_T, ϕ_T, ϕ_P and τ, but were not successful in deriving the relation (I) in the frame of the mechanism proposed above. The most stubborn difficulty was the concentration dependence.

As far as we have found in the literature, the solute concentration dependence in biphotonic processes have not been measured extensively. Brocklehurst *et al.* reported, in a study of the biphotonic photolysis of 3-methyl pentane sensitized by benzene, that the rate of the formation of radicals was not proportional to the solute concentration, but, rather increased with an increase in the concentration more slowly than the first order.[2] They tentatively attributed this to the participation of impurities.

If the triplet-triplet annihilation:

$$2T \rightarrow S^* + S \qquad \text{rate}=k_d C_T^2$$

is the most important among the decay processes of T (although this is not likely to occur in a very dilute solution such as 5×10^{-5} moll^{-1}),[7,8] the relation (I) can easily be derived as follows:

$$R = \varepsilon_T l \phi_P [\varepsilon_S l \phi_T / k_d (2-\phi_T)]^{1/2} I^{3/2} C^{1/2} \qquad \text{(II)}$$

This mechanism is very tempting, but, obviously, it needs more consideration and more extensive experiments on it before it can be adopted.

Another possible mechanism we have considered includes the participation of the produced radicals in the following manner:

$$T^* + M \rightarrow S + CH_3O + CH_3CO \qquad (1)$$

$$CH_3O + CH_3CO \rightarrow M \qquad (2)$$

$$CH_3CO + h\nu \rightarrow CH_3^* + CO \qquad (3)$$

$$CH_3^* + M \rightarrow CH_4 + CH_2COOCH_3 \text{ or } CH_3COOCH_2 \qquad (4)$$

$$CH_3^* \rightarrow CH_3 \qquad (5)$$

$$CH_2COOCH_3 \text{ or } CH_3COOCH_2 + h\nu \rightarrow CH_3^* + 2CHO \qquad (6)$$

In this mechanism, a solvent molecule excited by the interaction with T^* is assumed to decompose into CH_3O and CH_3CO radicals. Moreover, the subsequent absorption of a photon by a CH_3CO radical is assumed to occur and to lead to the formation of CH_3^* and CO. Here, CH_3^* denotes an activated methyl radical; it is considered to be a precursor of methane. The absorption of a hydrogen atom by a thermal methyl radical is not probable in the matrix at the temperature of liquid nitrogen, but, as is shown in the Results section, much more methane than ethane was produced during the photolysis.

To explain the light-intensity dependence of the methyl radical formation, we did not adopt the following reactions in the above mechanism:

$$T^* + M \rightarrow CH_3 + CH_3COO + S \qquad (7)$$

$$CH_3COO + h\nu \rightarrow CH_3 + CO_2 \qquad (8)$$

This discrimination seems to correspond to the following observations. First, as is shown in Fig. 1, the ESR spectrum we obtained has a rather large singlet at the center; this we assigned to CH_3O radicals. The formation of this radical can easily be explained by the above mechanism, but not by the mechanism consisting of the formation of methyl radicals by the reactions (7) and (8). Second, although we could not detect the formations of CO and CO_2 in photolysis because of their small amounts, the radiolysis of methyl acetate at 77°K is known to produce a large amount of CO compared with CO_2, as has been stated in a previous paper.[9] This fact seems to support the occurrence of the reaction (3) rather than the reaction (8).

Judging from the peak height of the ESR spectra of methyl radicals and the amounts of CH_4 and C_2H_6 observed, the quantum yields of these products are estimated to be very small. In other words, the reaction (2) is probably very fast in the matrix. If so, the steady-state treatment gives the following equation:

$$R = \varepsilon l I [\varepsilon_S \varepsilon_T l^2 \phi_T \phi_P \tau I^2 C / k_2 [1 + (\varepsilon_T \phi_P + \varepsilon_S \phi_T) l \tau I]]^{1/2} \qquad \text{(III)}$$

Here, ε is the extinction coefficient of the CH_3CO radical, while k_2 is the rate constant of the re-

7) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **39**, 1186 (1963).

8) C. A. Parker, *Trans. Faraday Soc.*, **60**, 1998 (1964).

9) Y. Nakajima, S. Sato and S. Shida, This Bulletin, **42**, 2132 (1969).

action (2). Then, by assuming a tentative relation, $1 \ll (\varepsilon_T \phi_P + \varepsilon_S \phi_T) l \tau I$, we can derive an equation which has the experimentally-observed dependences of the light intensity and the solute concentration.

At higher concentrations of solutes, the rate of the formation of methyl radicals showed a tendency toward saturation. This cannot be explained by the relation (III), which has been derived on the basis of inadequate relations: the rate of light absorption by $C_S = I\varepsilon_S C_S l$ at high concentrations. If a more proper relation is used, the tendency toward saturation can easily be explained. This point has already been discussed by other investigators.[2)]