Radical Formation Initiated by the Biphotonic Excitation of Acridone

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(Received March 20, 1973)

The photochemical formation of alcohol radical has been found to occur in the rigid solvent of ethanol (77 K) and in the polyvinyl alcohol (PVA) film (77 K and at room temperature), when acridone is dissolved as a sensitizer. It has been established that by absorbing two photons stepwise acridone gives rise to radicals which abstract hydrogen atoms from alcohol molecules, this being called the radical reaction mechanism and abbreviated as R-R mechanism. The energies necessary for the radical formation were estimated by determining energy levels of acridone and examining the wavelength dependence of the reaction. They differed for ethanol (77 K), PVA (77 K) and PVA (room temp.), perhaps due to the cage effect. The feature of the R-R mechanism has been compared with that of the energy transfer type (E-T mechanism) in which the energy is transferred from the higher triplet of solute to solvent molecules. When methyl iodide with a lower dissociation energy is added to an ethanol solution of acridone (77 K) and is then irradiated by an exciting light ineffective for R-R mechanism, methyl radical is formed by E-T mechanism. When the two types of reaction were energetically possible, E-T mechanism occurred more easily than R-R mechanism.

Photochemical reactions initiated by the absorption of two photons *via* the lowest triplet state are fully established.[1-7] Studies on the biphotonic sensitized solvent decomposition so far reported have led to the conclusion that the mechanism is the energy transfer from higher triplet states of solute to solvent molecule.[2-5] Siegel *et al.*[2,3] chose the ethanol solution of naphthalene and extensively studied the formation of solvent radicals from the excited solvent molecules produced by the energy transfer from the higher excited triplet states of naphthalene. In these cases the electronic states of the solvent molecules susceptible to dissociation should be located somewhat lower than the higher triplet states of solute molecules. It was found that only the T-levels above the fourth T-level of naphthalene lying 60 kK above the ground state are effective for the solvent radical formation. In the case of ethanol the direct radical formation also occurs upon irradiating the solvent alone with a light of about 50 kK.[8] This state is possibly responsible for the sensitized reaction.

It is expected that the formation of solvent radicals occurs also *via* the biphotonic formation of solute radicals which subsequently abstract hydrogen atoms from solvent molecules. This radical reaction mechanism (R-R mechanism) is thought to be common in view of the fact that alcohols act as a H-donor to many reducible substances; for instance, the ethanol radical is formed by one photon reduction of acridine in ethanol at room temperature and also by one photon decomposition of acridan in ethanol at liquid nitrogen temperature.[9]

However, no such example has been found in literature, although the unimolecular biphotonic solute radical formation was reported for *p*-xylene.[7] We have found the occurrence of such a biphotonic solvent radical formation *via* R-R mechanism when acridone dissolved in rigid organic solvents is irradiated with the light of a lower energy than in the case of energy transfer mechanism (E-T mechanism). We have also found that radical formation by E-T mechanism also occurs when the substance with a lower dissociation energy such as CH_3I is added to the ethanol solution of acridone at 77 K.

Experimental

The decomposition of solute and solvent was examined by measuring the ESR signals and the electronic absorption spectra. A JEOL P-10 type ESR spectrometer was used.

Light from a superhigh pressure mercury arc (Ushio USH-500D) was used with or without filters (Toshiba UV-39, UV-35, Hoya-crystal U-2). The intensity distribution of the radiation output from the mercury arc and transmittances of

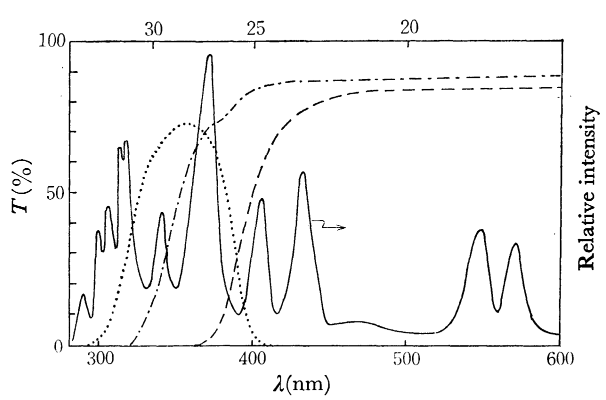

Fig. 1. Transmittances of filters and the intensity distribution of the radiation output from the mercury arc.
----: UV-39, —·—·—: UV-35, ······U-2

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[1] K. D. Cadogan and A. C. Albrecht, *J. Chem. Phys.*, **43**, 2550 (1965).

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

[3] S. Siegel and H. S. Judeikis, "The Triplet State," ed. by A. B. Zahlan, Cambridge University Press, (1967), p. 195.

[4] B. Brocklehurst, W. A. Gibbons, F. T. Lang, G. Porter, and M. I. Savadatti, *Trans. Faraday Soc.*, **62**, 1793 (1966).

[5] A. Terenin, V. Rylkov, and V. Kholmogorov, *Photochem. Photobiol.*, **5**, 543 (1966).

[6] V. G. Vinogradova, B. N. Shelimov, N. F. Fok ,and V. V. Voevodskii, *Doklady Akad. Nauk. S. S. S. R.*, **154**, 188 (1964).

[7] P. M. Johnson and S. A. Rice, *Chem. Phys. Lett*, **1**, 709 (1968).

[8] P. J. Sullivan and W. S. Koski, *J. Amer. Chem. Soc.*, **85**, 384 (1963); **86**, 159 (1964). A. J. Harrison and J. S. Lake, *J. Phys. Chem.*, **63**, 1489 (1959).

[9] S. Niizuma and M. Koizumi, This Bulletin, **41**, 1090 (1968).

filters are shown in Fig. 1.

Materials. Polyvinyl alcohol (PVA) (Koso-Kagaku) and ethanol (Wako-Junyaku, G.R.) were used without further purification. Methyl iodide (Wako-Junyaku, E.P.) was purified by the standard method. Acridone (Tokyo-Kasei, G.R.) was recrystallized from ethanol. The concentration of acridone was usually $10^{-3} \sim 10^{-4}$ M. PVA films were about 200 μ in thickness.

Results

Triplet State of Acridone. For the present investigation it is desirable to know the triplet levels of acridone. A stepwise biphotonic process *via* the lowest triplet states requires that the triplet state concentration is appreciable and this in turn requires a long lifetime of the triplet state. These data were therefore determined.

Phosphorescence was observed near 20 kK in glassy ethanol and PVA at 77 K. The triplet lifetimes evaluated from the decay of phosphorescence are as follows.

Solvent	Temp.	τ(s)
EtOH	77K	2.0
PVA	77K	2.0
	R.T.	1.2

Acridone in PVA at room temperature showed phosphorescence, the lifetime of which was not much shorter than that at 77 K. T-T absorption of acridone in PVA was observed by flash technique at room temperature. The triplet lifetime was approximately the same as that of phosphorescence. T-T absorption spectrum in ethanol at room temperature is shown in Fig. 2.[10] There are two absorption bands, one near 17.5 kK and the other above *ca.* 28 kK. The energy diagram of acridone obtained from these data is given in Fig. 3.

The steady state concentration of the lowest triplet state, $\phi_{ST} I_{ab} \tau$ (ϕ_{ST}, S*-T transition probability; τ, the lifetime of the lowest triplet state) was estimated to be of the order 10^{-5} M under the present experimental conditions. It is expected that a considerable amount of the lowest triplet molecules is excited to higher triplet states. A $\Delta m = \pm 2$ signal from acridone in the lowest triplet state was observed. The value of the zero-field splitting parameter D* was 0.065 cm^{-1}, which is comparable with that of acridine, 0.0688 cm^{-1}.[11]

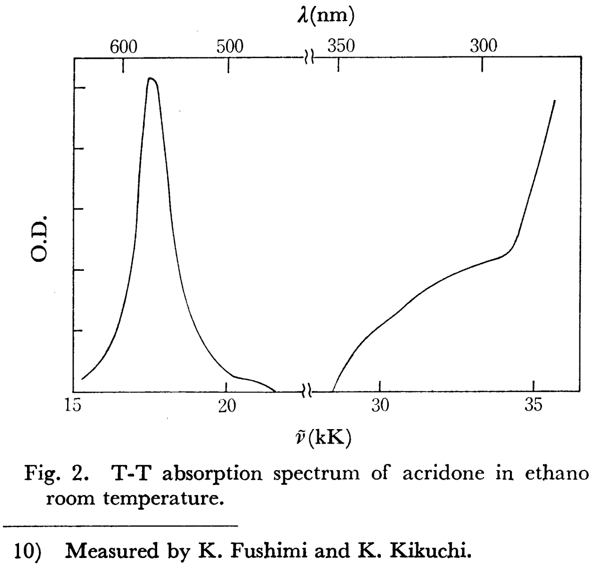

Fig. 2. T-T absorption spectrum of acridone in ethanol at room temperature.

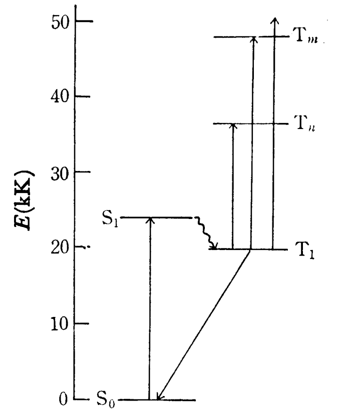

Fig. 3. Energy diagram of acridone.

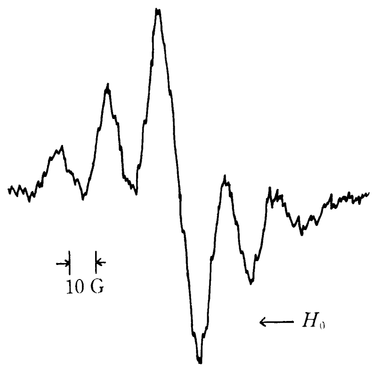

Fig. 4. ESR spectrum of photoproducts in deaerated ethanol solution irradiated with a UV-35 filter at 77 K.

Reaction in Ethanol Solution at 77 K. Deaerated ethanol solutions of acridone were irradiated with a UV-35 filter. The ESR spectrum of radicals is shown in Fig. 4. Broadly speaking, the spectrum consists of five lines, which can be safely attributed to ethanol radical ($CH_3\dot{C}HOH$), but a very high central line suggests the contamination of some other species. Irradiation with a UV-39 filter, on the other hand, did not give any signals.

The effect of light intensity on the rate of radical formation was examined by assuming the following relation between the two quantities,

$$d[R]/dt = kI_0^n \qquad (1)$$

where [R] is radical concentration, I_0 light intensity, and n and k are constants characteristic for the reaction.

The value of n was found to be 1.7. Thus the rate of radical formation is nearly proportional to the square of light intensity.

Radical formation was accompanied by a purple coloration, which disappeared upon warming the ir-

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[10] Measured by K. Fushimi and K. Kikuchi.

[11] Y. Kubota and M. Miura, This Bulletin, **42**, 2763 (1969). *Cf.* J.-Ph. Grivet, *Chem. Phys. Lett.*, **11**, 267 (1971).

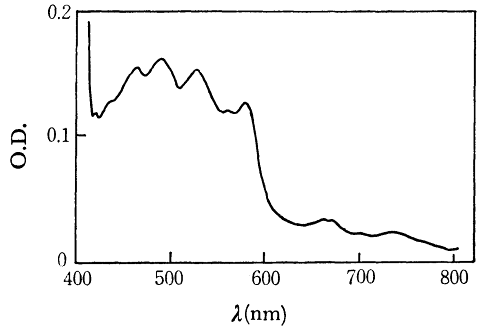


Fig. 5. Absorption spectrum of intermediates in ethanol upon irradiation with a UV-35 filter at 77 K.

radiated sample to room temperature. The absorption spectrum of the irradiated sample at 77 K is shown in Fig. 5. Since the ethanol radical does not absorb the visible light,[12] it is ovbious that some other intermediates are produced from acridone. Hence an abnormally high central line in the ESR spectrum is safely attributed to the intermediates originating from acridone.

The irradiated sample, when warmed to room temperature, showed a prominent decrease of the main absorption bands of acridone. The decrease was very slight in the case of irradiation with a UV-39 filter, the irradiated sample not being colored.

We can conclude that in ethanol at 77 K, formation of the ethanol radical is accompanied with the decomposition of acridone, as shown in Table 1.

TABLE 1. SUMMARY OF THE RESULTS

Solvent	Temp.	Filter	ESR	Abs.
EtOH	77K	UV-39	×	×
		UV-35	○	○
PVA	77K	UV-35	×	
		U-2	×	×
		No	○	○
	R.T.	UV-39		○
		UV-35		○
		U-2	○	○
EtOH (20% CH_3I)	77K	UV-39	○	×
		UV-35	○	×

× : ESR, no signal
Abs., Acridone not decomposed
○ : ESR, signal appearance
Abs., Acridone decomposed

The effect of the dissolved oxygen on the reaction was examined. Irradiation with a UV-35 filter of the aerated solutions gave the ESR signal of an ethanol radical. But the signal was unsymmetric from the initial stage of irradiation and gradually truned into a peroxide-like signal (Fig. 6). It can be said that oxygen participates in the reaction mainly after a biphotonic process has been completed.

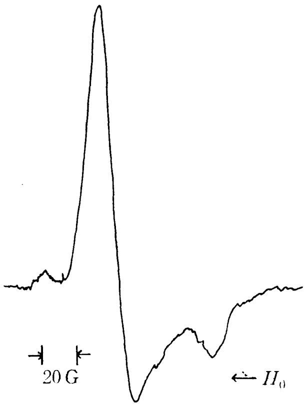


Fig. 6. ESR spectrum of photoproducts in aerated ethanol solution, 15 min. after irradiation with a UV-35 filter at 77 K.

Reaction in Polyvinylalcohol Films. Polyvinylalcohol is a solvent which is glassy at room temperature. When PVA films containing 10^{-3} M acridone were irradiated at 77 K with a UV-35 filter and a U-2 filter whose limit of transmission is 10 nm shorter than for UV-35, they did not give any ESR signal. Irradiation with a total output from the mercury arc at 77 K gave a three line ESR spectrum (Fig. 7), no signal being detected in the case of PVA alone.

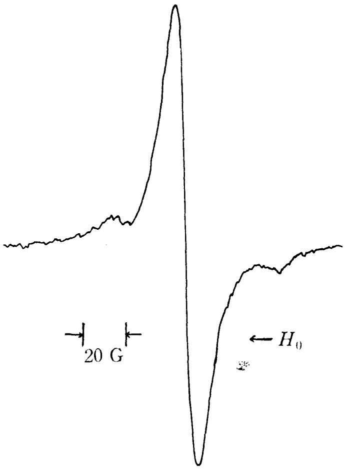
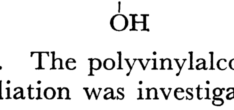


Fig. 7. ESR spectrum of photoproducts in PVA irradiated with a total output from mercury arc at 77 K.

These radical species were stable at 77 K. When irradiated samples were warmed up to room temperature, the ESR signals were still observed although the intensities were somewhat decreased and decayed slowly. When an irradiated sample was warmed to the glass transition temperature (70—80 °C), the signal disappeared completely.

Since a coupling constant of the radical is about 35 Gauss[13] there is no doubt that a polyvinylalcohol



$$(\sim\mathrm{CH_2}\text{-}\underset{\mathrm{OH}}{\underset{|}{\dot{\mathrm{C}}}}\text{-}\mathrm{CH_2}\sim)$$

radical is formed. The polyvinylalcohol radical formed by γ-ray irradiation was investigated by Ogawa.[13] He reported that a crystalline region gives an ESR signal of three lines and an amorphous region, a broad line, the resulting spectrum consisting of the two com-

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[12] S. Fuji and J. E. Willard, *J. Phys. Chem.*, **74**, 4313 (1970).

[13] S. Ogwa, *J. Phys. Soc. Japan*, **16**, 1488 (1960).

ponents. The present result reconfirms this conclusion. The radical species not being attacked by oxygen was found to be stable in the presence of oxygen at 77 K.

The effect of light intensity on the rate of radical formation was examined by means of Eq. (1). The value of n was found to be 1.8, supporting a biphotonic nature of the main reaction. As in the ethanol solution at 77 K, irradiation with a U-2 filter which gave no ESR signal did not cause any change in the main absorption bands of acridone. Irradiation by a total output from the mercury arc caused a decrease in the main absorption bands of acridone with the appearance of a new absorption in the visible region at *ca.* 100 K.

It is remarkable that the irradiation of samples at room temperature with a U-2 filter which caused no reaction at 77 K gave the ESR signal accompanied with a change of absorption spectrum in the visible and ultraviolet regions. The results obtained are listed in Table 1, which leads to the conclusion that the formation of a solvent radical is always accompanied by the decomposition of acridone.

Reaction in Ethanol Containing Methyl Iodide at 77 K. Since the irradiation with UV-39 (total energy $\leq$46 kK) does not decompose acridone in ethanol at 77 K, a possible mechanism for biphotonic radical formation in the wavelength region below 46 kK is only energy transfer. According to Terenin *et al.*[5] the minimum energy required for the direct photodissociation of methyl iodide is 5.0 eV (40 kK). It is therefore expected that the irradiation of acridone in ethanol containing methyl iodide gives rise to methyl radical by the biphotonic E-T mechanism.

The deaerated ethanol solutions of acridone containing methyl iodide (20%) which were glassy at 77 K were irradiated with the use of UV-39. ESR spectra due to a methyl radical (1 : 3 : 3 : 1 intensity ratio and a 24 Gauss hyperfine splitting) and an ethanol radical were detected. The height of the central line could be interpreted as originating only from the ethanol radical. The effect of light intensity on the rate of radical formation was examined by Eq. (1) and a value of 1.8 was obtained for n supporting a biphotonic process. Irradiation with UV-35 also produced the two kinds of radical. In both cases the ESR spectra in the initial stage mainly consisted of methyl radicals. The methyl radical disappeared with the life-time of 13 min, which agrees with the value in literature,[8] only the ethanol radical remaining in the later stage. Figure 8 gives an example of the variation of ESR spectra with time after irradiation. When the irradiated sample was kept in the dark, the ethanol radical increased with a decrease of the methyl radical. This implies that the methyl radical abstracts a hydrogen atom from ethanol according to $\dot{\mathrm{C}}\mathrm{H}_3+\mathrm{C}_2\mathrm{H}_5\mathrm{OH}\longrightarrow\mathrm{CH}_4+\mathrm{CH}_3\dot{\mathrm{C}}\mathrm{HOH}$.

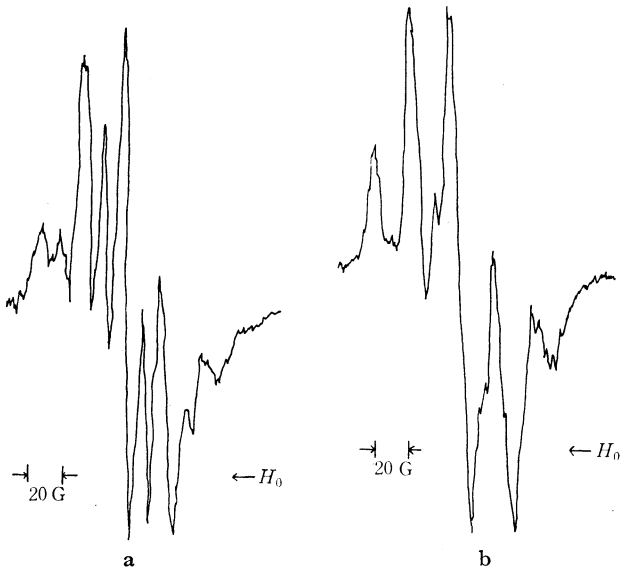


Fig. 8. ESR spectrum of photoproducts in deaerated ethanol solution containing 20% methyl iodide, a) 2 min, b) 20 min after irradiation with a UV-35 filter at 77 K.

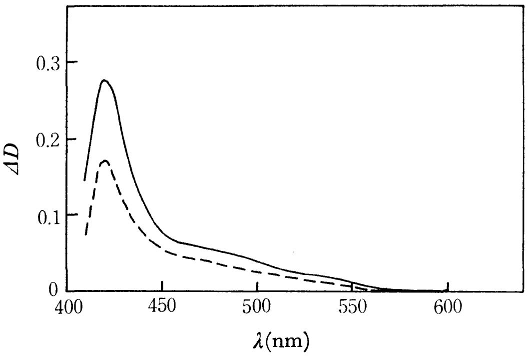


Fig. 9. The difference spectra between the irradiated (with a UV-35 filter) and non-irradiated deaerated ethanol solution containing 20% methyl iodide at 77 K.
----: 10 min irradiation, ——: 40 min irradiation.

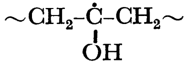
The irradiation imparted an yellow color to the solution. The difference spectrum between the irradiated (with UV-35) and non-irradiated solution is shown in Fig. 9. The band located at 420 nm is safely assigned to iodine, the spectrum with no band near 500 nm supports an E-T mechanism, acridone not being decomposed. Irradiation with UV-35 is certainly energetically capable of bringing about R-R mechanism in addition to E-T mechanism. However, it is judged from the above results that E-T mechanism predominates, giving a larger quantity of methyl radicals in the initial stage.

It was established experimentally that the excitation in the T-T absorption band corresponding to 17.5 kK (the total excess energy, 37.5 kK) is not effective. Therefore the total energy required in the present case is 46 kK. This is consistent with the statement of Terenin *et al.*[5]

Discussion

The energy of the second photon required for the decomposition of acridone is obtained from Figs. 1 and 3. In both ethanol and PVA, irradiation with a UV-39 filter which excites the T-T absorption around 17.5 kK did not induce reaction. Thus 37.5 kK (17.5 kK plus the energy of the lowest triplet state) is not effective for the formation of an ethanol radical *via*

TABLE 2. TOTAL ENERGIES REQUIRED FOR RADICAL FORMATION

Sensitizer	Solvent	Temp.	Energy (kK)	Radicals
Acridone	EtOH	77 K	$E \geq 50$	$CH_3\dot{C}HOH$
	PVA	77 K	$E \geq 53$	 $\sim CH_2-\underset{OH}{\dot{C}}-CH_2\sim$
		R.T.	$E \geq 46$	
	EtOH (20% CH_3I)			
		77 K	$E \geq 46$	$\dot{C}H_3$, $CH_3\dot{C}HOH$
Naphthalene	EtOH	77 K	$E \geq 60$	$CH_3\dot{C}H_2$, $CH_3\dot{C}HOH$

R-R mechanism. The total energies required for the radical formation in the present systems are listed in Table 2. The results of Siegel *et al.*[2,3] on the naphthalene–ethanol system are given for the sake of comparison. Naphthalene as a sensitizer is not decomposed in ethanol at 77 K; the mechanism of radical formation is E-T. On the other hand the present mechanism is R-R.

It is interesting to compare the general features of the two mechanisms. First, the energy required for E-T mechanism is remarkably higher than that for R-R. This is natural, because ethanol does not absorb the light below *ca.* 50 kK. Sullivan and Koski,[8] using the light in this region, investigated the radicals produced by the direct photochemical decomposition of ethanol. Several radicals were detected but the main one was $C_2H_5\cdot$. The total energy of 60 kK required for radical formation which Siegel *et al.*[2,3] obtained is consistent with the result of direct photodecomposition. The energies of the four lowest triplet levels of naphthalene being about 45.6, 47, 48, and 60 kK, the lowest three are deficient in energy for exciting ethanol. On the other hand, the energy required for R-R mechanism naturally depends upon the solute employed. Once a solute radical is produced, the formation of an ethanol radical usually occurs very easily, *e.g.*, it is produced by one photon decomposition of acridan in ethanol at 77 K.[9]

Secondly, various types of radicals are produced by E-T mechanism while only the ethanol radical is produced by R-R mechanism. This is also reasonable since various types of radicals are expected to be formed with a high excitation energy followed by the secondary photochemical and thermal reactions between them and their mother substances. However, Judeikis and Siegel[14] proposed the sequence

$$^3S^* + CH_3CH_2OH \longrightarrow S + CH_3CH_2OH^* \tag{0}$$

$$CH_3CH_2OH^* \longrightarrow CH_3\dot{C}HOH + H\cdot \tag{1}$$

$$CH_3\dot{C}HOH + h\nu \longrightarrow CH_3\dot{C}HOH^* \tag{2}$$

$$CH_3\dot{C}HOH^* + CH_3CH_2OH \longrightarrow CH_3CHO + CH_3\dot{C}H_2 + H_2O \tag{3}$$

where $^3S^*$ is a highly excited triplet state solute molecule. Their finding that the $CH_3\dot{C}HOH$ radical is the only species observed during the early part of photolysis in ethanol strongly suggests that reaction (1) is the first step of dissociation. It is likely[12] that the ethanol radical has an absorption increasing from 300 to 200 nm which gives the ethyl radical according to (2) and (3).

In the case of R-R mechanism, the exciting light is so low in energy that (2) and (3) do not occur. In fact we could establish the occurrence of (2) and (3) when the deaerated solutions of acridone in ethanol were irradiated with a total output from the mercury arc. Thus the initial spectrum consisted mainly of ethanol radicals while at a later stage of continuous irradiation, the quantity of ethyl radicals gradually increased. It is not yet certain whether the decomposition of acridone is unimolecular, but this is most likely the case in view of the fact that acridone is not easily reduced by ethanol.

The cage effect is important for the formation of separate radicals. Rigidity of the medium, relative orientation of solute and solvent molecules as well as the microscopic structure around the solute molecules are important factors in addition to the excitation energy. The difference in the required energy for ethanol and PVA at 77 K may be due to the cage effect. In PVA, a rather hard medium as compared with ethanol, the diffusion of two radicals apart from each other may require a little higher energy than for ethanol. This is supported by the fact that at room temperature the required energy for PVA decreases to a smaller value than for ethanol. Another evidence is the occurrence of P-type delayed fluorescence at room temperature but not at 77 K.

It is intersting that acridone acts as a sensitizer for the biphotonic decomposition of methyl iodide. It has been established by Terenin *et al.*[5] that this compound dissociates when the energy 5.1—5.6 eV is supplied from various sensitizers raised *via* biphotonic process to higher triplet levels. Further, it is known that the absorption of light around 40 kK causes the direct dissociation of this compound. The continuous band located in this region is a n-σ^* transition.[15] Therefore there is no doubt that the triplet acridone with the excess energy of $\geq$46 kK gives rise to dissociation of methyl iodide by E-T mechanism. The ethanol radical is formed by the secondary radical reaction which is quite reasonable in view of similar reactions already reported. It is thus strange that Terenin *et al.*, without observing the formation of ethanol radical, proposed the combination of two methyl radicals into ethane.

It is very suggestive that E-T mechanism overwhelms R-R mechanism when they are both energetically possible. Perhaps this indicates that energy transfer occurs far more quickly than the dissociation of a molecule for which rearrangement of atoms is usually required. It is not yet clear what kinds of intermediate are produced from acridone.

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[14] H. S. Judeikis and S. Siegel, *J. Chem. Phys.*, **43**, 3625 (1965).

[15] K. Kimura and S. Nagakura, *Spectrochim. Acta*, **17**, 166 (1961).