BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 70—74 (1973)

Luminescence from 2,3-Dimethylbutane Containing Toluene in the Solid Phase at 77°K during γ-Irradiation

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(Received May 12, 1972)

The luminescence from 2,3-dimethylbutane(2,3DMB) containing toluene in the solid phase has been measured at 77°K during γ-irradiation. The emission consists of fluorescence and phosphorescence from toluene. Since the emission becomes zero upon the removal of a γ-ray source, it cannot be due to a post-irradiation effect. It is concluded from the dependency of the intensity on the concentration of toluene that the luminescence is due to an intermolecular energy transfer from 2,3DMB to toluene during γ-irradiation. ESR studies of γ-irradiated 2,3DMB containing toluene have also been undertaken at 77°K in order to obtain some information on the intermolecular energy transfer. The toluene anion is formed in the γ-irradiated 2,3DMB containing toluene. The dimer cation of toluene is formed in the γ-irradiated 2,3DMB containing toluene and an electron scavenger. The luminescence from toluene in the 2,3DMB matrix decreases upon the pre-irradiation of the sample at 77°K. When the pre-irradiated sample is illuminated by the light from a tungsten lamp to photobleach the toluene anion, the luminescence during γ-irradiation is recovered. Since the intensity of the luminescence does not correspond at all to the amount of toluene anions, the luminescence from toluene in the 2,3DMB matrix during γ-irradiation must not be due to a neutralization reaction between a toluene anion and a migrating hole. It is suggested that the migration of energy from the irradiated 2,3DMB to toluene may occur *via* an excitation transfer reaction.

We have previously studied the radiolysis of hydrocarbons in the solid phase in order to elucidate the primary process and in order to obtain information about the reaction kinetics in the solid phase. In the previous studies, some phenomena peculiar to the solid-phase radiolysis have been reported.[1–3] On the basis of these results, we have proposed that two important problems must be solved in order to elucidate the mechanism of the solid-phase radiolysis. One is the species of the mobile entities produced in the solid-phase radiolysis. The other is how the condition of the solid-matrix, such as phase and defect, affects the chemical reactions.

It was found in the radiolysis of solid isobutane[1] that H_2 and C_4H_9 radicals are formed by the fragmentation of the excited isobutane molecule and that their yields decrease upon the addition of CCl_4 or toluene. These findings were interpreted as the assumption that the excitation transfer from the excited isobutane molecule to CCl_4 or toluene occurs in the solid state at 77°K.

If toluene is an efficient acceptor of excitation in the radiolysis of solid alkane, the luminescence from the excited toluene may be observed; the expected results were observed in the solid 2,3-dimethylbutane(2,3DMB) with the toluene additive during γ-irradiation at 77°K.

Those additives which are generally used as electron scavengers or charge scavengers in the liquid-phase radiolysis may react also with an excited molecule in solid-phase radiolysis.[4] Therefore, it is quite difficult to study the nature of the mobile entity in the radiolysis of solid alkane using the scavenger method. Since the ESR spectroscopy and the measurement of the luminescence reveal different aspects of the mobile entity, the radiolysis of an alkane-toluene mixture in the solid phase at 77°K was studied using both methods.

Experimental

2,3-Dimethylbutane(2,3DMB), supplied by the Tokyo Kagaku Seiki Co. with a purity of more than 99%, was passed through a 30 cm column packed with activated alumina and then distillated on a vacuum line before use. Gas-chromatographic analysis of 2,3DMB showed that the concentration of the other hydrocarbons with molecular weights smaller than 2,3DMB is less than 0.01%. The spectrograde toluene

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[1] a) T. Wakayama, T. Kimura, T. Miyazaki, K. Fueki, and Z. Kuri, This Bulletin, **43**, 1017 (1970). b) T. Miyazaki, T. Yamada, T. Wakayama, K. Fueki, and Z. Kuri, *ibid.* **44**, 934 (1971).

[2] T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, *J. Phys. Chem.*, **74**, 3584 (1970).

[3] T. Miyazaki, Y. Fujitani, T. Wakayama, K. Fueki, and, Z. Kuri, This Bulletin, **44**, 984 (1971).

[4] a) T. Miyazaki, T. Wakayama, M. Fukaya, Y. Saitake, and Z. Kuri, 14th Japanese Conference of Radiation Chemistry, Sept., 1971, Sapporo, Japan. b) Y. Saitake, T. Miyazaki, T. Wakayama, M. Fukaya, and Z. Kuri, 26th Annual Meeting of the Chemical Society of Japan, April, 1972, Tokyo, Japan.

and phenylbromide were of a high purity and were used after distillation on a vacuum line. The nitrous oxide was also of a high purity and was used without further purification.

The samples were irradiated with γ-rays from a ^{60}Co source at 77°K, and in most cases at a dose rate of 3.84×10^{19} eV/g·hr, for the ESR studies and at one of 4.83×10^{17} eV/g·hr for the measurements of the luminescence.

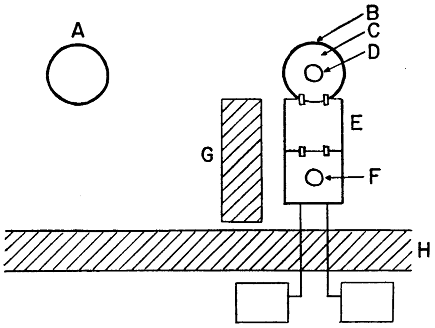

Fig. 1. Schematic diagram of the measurement of luminescence during γ-irradiation at 77°K.
A: ^{60}Co; B: Dewar flask; C: Liquid nitrogen; D: Sample; E: Monochrometer; F: Photomultiplier tube; G: Block of lead; H: Concrete wall; I: High voltage supplier; J: DC microvolt-ammeter.

The ESR spectra of irradiated samples were measured at 77°K on a JES-3BX ESR spectrometer. The luminescence was measured during γ-irradiation at 77°K. The apparatus for measuring the luminescence consisted of a high voltage supplier, a Shimadzu-Bausch-Lomb monochrometer, a photomultiplier tube (R-136) of the Hamamatsu TV Co. and a DC microvolt-ammeter. A schematic diagram of the apparatus is given in Fig. 1. When 2,3DMB containing toluene (2 mol%) was γ-irradiated at 77°K in the solid state, the photocurrent caused by the emission from toluene was about 1.2×10^{-6} ampere during γ-irradiation at a dose rate of 4.83×10^{17} eV/g·hr.

Results and Discussion

Luminescence from Toluene in the Solid 2,3DMB at 77°K during γ-Irradiation. Luminescence studies previously undertaken in radiation chemistry have mostly been concerned with the thermoluminescence or photoinduced luminescence of γ-irradiated samples, or with the luminescence in the liquid phase during γ-irradiation. There have been no studies of the limunescence from solid saturated hydrocarbons during γ-irradiation. The emission from a pure 2,3DMB is very weak during γ-irradiation at 77°K, but a small amount of toluene in 2,3DMB enhances the emission remarkably. The intensity of the luminescence is shown in Fig. 2 as a function of the concentration of toluene. The intensity increases sharply with an increase in the concentration of toluene and then gradually decreases beyond 2 mol% toluene. Since the intensity does not increase linearly with an increase in the concentration of toluene, the liminescence is not due to the direct absorption of the radiation energy by the solute toluene. The intensity of the emission from pure solid toluene during γ-irradiation is about three times stronger than that from 2,3DMB–toluene (1.3 mol%). With an electron fraction of toluene of 0.013 in the 2,3DMB–toluene, the emission due to the direct absorption of the radiation energy by the toluene itself can be expected to amount at most to 4% of the total emission from 2,3DMB–toluene (1.3 mol%).

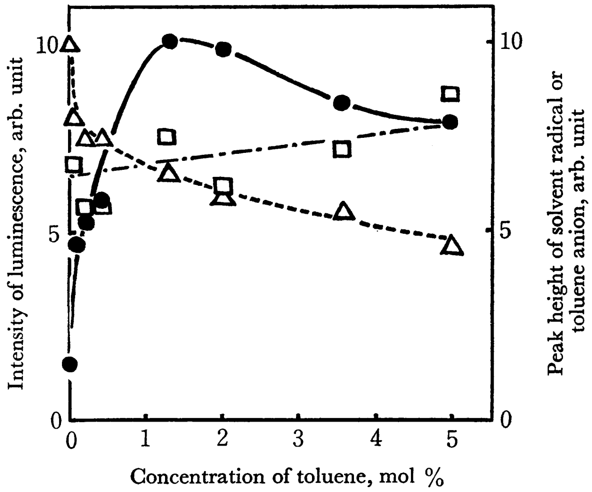

Fig. 2. Yilds of toluene anion, solvent radical, and luminescence in the γ-irradiation of 2,3 DMB at 77°K against concentration of toluene.
●—●: Intensity of luminescence during γ-irradiation.
△—△: Yields of solvent radical at the dose of 9.6×10^{18} eV/g.
□—□: Yields of toluene anion at the dose of 9.6×10^{18} eV/g.

Since the emission from toluene in 2,3DMB becomes zero upon the removal of a γ-ray source, the emission cannot be due to a post-irradiation effect. The emission from toluene in the 2,3DMB matrix may be attributable to intermolecular energy transfer from 2,3DMB to toluene.

The emission spectrum from toluene in 2,3DMB is shown in Fig. 3. The spectrum consists of two peaks, with emission maxima near 280 and 390 nm. Since the fluorescence spectrum of toluene has a band with a maximum near 280 nm,[5] the emission band near 280 nm may be due to the fluorescence from the singlet-excited toluene. Since the phosphorescence spectrum

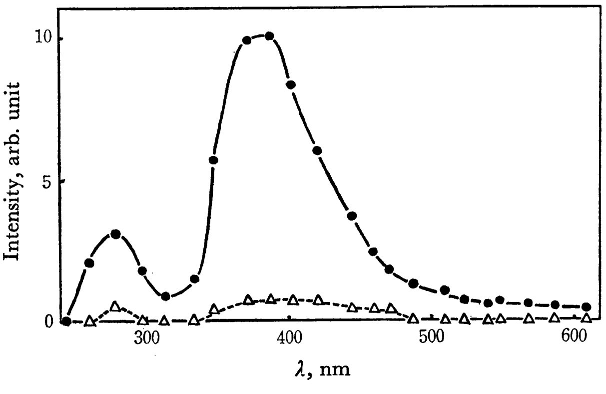

Fig. 3. Emission spectra of 2,3DMB–toluene during γ-irradiation at 77°K.
●—●: Emission from 2,3DMB–toluene (2 mol%).
△—△: Emission from 2,3DMB–toluene (2 mol%) after preirradiation of 4.73×10^{19} eV/g.

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5) F. Hirayama and S. Lipsky, *J. Chem. Phys.*, **51**, 1939 (1969).

of toluene has a band with a maximum near 390 mn,[6] the emission band observed near 390 nm may be due to the phosphorescence from the triplet-excited toluene. The vibrational structure of the emission bands could not be measured with this instrument because of the noises caused by the γ-irradiation of photomultiplier, the bubbling of liquid nitrogen in the Dewar flask, and so on.

ESR Studies of γ-Irradiated 2,3DMB Containing Toluene in the Solid Phase at 77°K. The ESR spectrum of γ-irradiated 2,3DMB at 77°K is shown in Fig. 4A. It consists of five lines, with a splitting constant of 22 G. The spectrum may be assigned to the $\cdot CH_2CH(CH_3)$-$CH(CH_3)_2$ radical.[7]

The ESR spectrum of γ-irradiated 2,3DMB–toluene (2 mol%) is shown in Fig. 4B. The new spectrum, which is obtained by subtracting the spectrum of the solvent radicals, is shown with dotted lines. The spectrum consists of five lines, with a splitting constant of 3.8 G, and it is easily photo-bleached upon illumination with light from a tungsten lamp. It coincides well with that of the toluene anion produced by the γ-irradiation of i-C_4H_{10} containing toluene.[1a] The ESR spectrum of the toluene anion produced chemically consists mainly of five lines, with a splitting constant of 4.0 G.[7] The formation of the new spectrum is suppressed completely upon the addition of an electron scavenger, such as N_2O, C_6H_5Br, SF_6, or HBr, to the system. Therefore, the new spectrum may be assigned to the toluene anion.

The ESR spectra of γ-irradiated 2,3DMB–toluene (2 mol%) containing N_2O or C_6H_5Br are shown in Figs. 4C and D respectively. The new spectrum, which is obtained by subtracting the spectrum of the solvent radicals, is shown with dotted lines. Since the spectra have the splitting constants of 6.6 G and 7.0 G in Figs. 4C and D respectively, they cannot be assigned to the toluene anion. As the splitting constants of the monomer cation and the dimer cation of toluene are 14 G and 7.0 G respectively,[9] they may be assigned to the

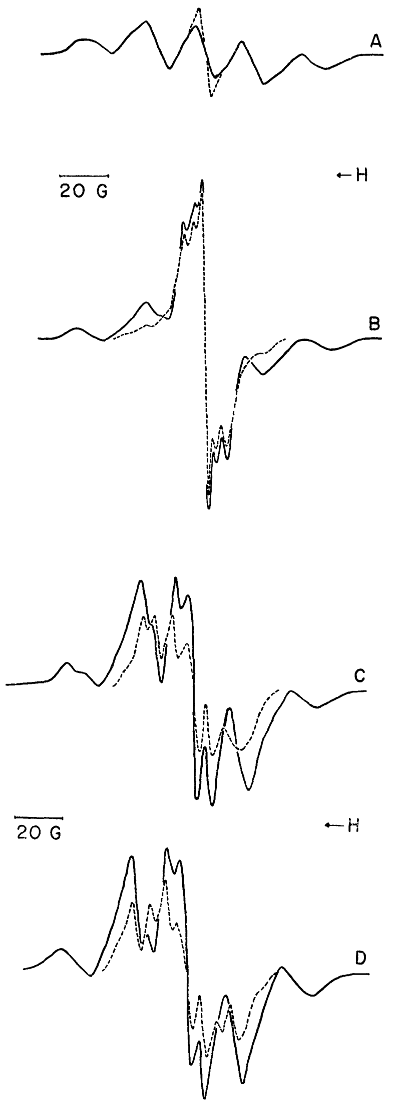

Fig. 4. A. ESR spectra of γ-irradiated 2,3DMB at 77°K. Dotted lines represent the spectrum of trapped electrons which are easily bleached by the illumination with a tungsten lamp.
B. ESR spectrum of γ-irradiated 2,3DMB–toluene (2 mol%) at 77°K. Dotted spectrum is obtained by subtracting the spectrum of solvent radical.
C. ESR spectrum of γ-irradiated 2,3DMB–toluene (2 mol%)–nitrous oxide (2 mol%) at 77°K. Dotted spectrum is obtained by subtracting the spectrum of solvent radical.
D. ESR spectrum of γ-irradiated 2,3DMB–toluene (2 mol%)–phenylbromide (2 mol%) at 77°K. Dotted spectrum is obtained by subtracting the spectrum of solvent radical.
Irradiation dose: 9.6×10^{18} eV/g. Spectrometer gain settings of A, B, C, and D are approximately the same.

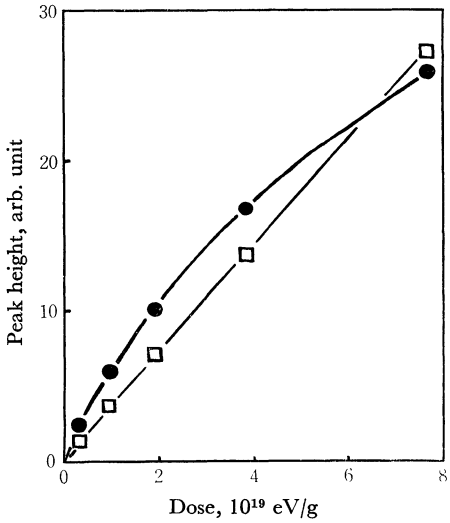

Fig. 5. Yields of toluene anion and solvent racical in the radiolysis of 2,3DMB–toluene (2 mol%) at 77°K against the total dose.
●: Toluene anion, □: Solvent radical.

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[6] Y. Kanda and H. Sponer, *J. Chem. Phys.*, **28**, 798 (1958).

[7] M. Fukaya, T. Wakayama, T. Miyazaki, Y. Saitake, and Z. Kuri, 14th Japanese Conference of Radiation Chemistry, Sept., 1971, Sapporo, Japan.

[8] S. P. Solodovnikov, *Zh. Strukt. Khim.*, **2**, 282 (1961).

[9] S. Nagai, S. Ohnishi, and I. Nitta, This Bulletin, **44**, 1230 (1971).

dimer cation of toluene. These results suggest that the toluene is not always completely dissolved, but stands sometimes in the form of a cluster, depending upon the concentration.

The yields of the toluene anion and the solvent radical are shown in Fig. 2 as a function of the concentration of toluene.

The dose dependences of the yields of toluene anion and solvent radical are shown in Fig. 5. The rate of the production of the toluene anion decreases gradually with an increases in the dose, while the yields of solvent radical increase linearly.

Pre-irradiation Effect on the Luminescence from Toluene. A quite interesting effect is found on the luminescence from toluene in the 2,3DMB matrix. When the sample is pre-irradiated at 77°K with a certain dose, the intensity of the in-source luminescence becomes much lower than that from the sample without pre-irradiation. The emission spectra from the pre-irradiated sample are shown in Fig. 3 in comparison with the emission from the sample without pre-irradiation. The intensity of the luminescence at $\lambda=390$ nm is shown in Fig. 6 as a function of the dose of pre-irradiation. The liminescence is efficiently suppressed by the pre-irradiation of 3.84×10^{19} eV/g.

Since the toluene ions produced absorb the light of 390 nm, a part of the emission may be absorbed by the toluene ions. If the optical density of the toluene anion in γ-irradiated 2,3DMB–3-methylpentane(10 mol%)–toluene(2 mol%)[10] is measured at 77°K by means of UV–VL absorption spectroscopy, the intensity of the luminescence can be corrected by considering the optical density of the toluene ions at 390 nm. The pre-irradiation effect on the luminescence from 2,3DMB–3-methylpentane-toluene is approximately the same as that of 2,3DMB–toluene, which forms a cracked transparent plastic crystal (Fig. 6). Therefore, the optical density of the toluene anion in the γ-irradiated 2,3DMB–3-methylpentane–toluene may be used for the correction of the intensity of the luminescence from 2,3DMB–toluene. Thus, the corrected intensity is shown in Fig. 6 with a dotted line.

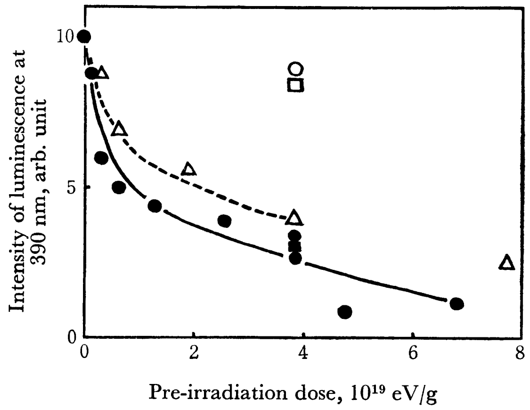

Fig. 6. Pre-irradiation effect on the luminescence from 2,3 DMB-toluene during γ-irradiation at 77°K.

●—●: Intensity of luminescence from 2,3DMB–toluene (2 mol%).

■: Intensity of luminescence from 2,3DMB-3-methylpentane (2 mol%)-toluene (2 mol%) which is pre-irradiated at the dose of 3.84×10^{19} eV/g.

---------: Corrected intensity of luminescence from 2,3-DMB–toluene (2 mol%).

△: The rate of formation of toluene anion in the γ-irradiation of 2,3DMB–toluene (2 mol%) at 77°K.

○: Intensity of luminescence from 2,3DMB–toluene (2 mol%) which is pre-irradiated at the dose of 3.84×10^{19} eV/g and then photobleached with light from a tungsten lamp for 10 min.

□: Intensity of luminescence from 2,3DMB–3-methylpentane (10 mol%)–toluene (2 mol%) which is pre-irradiated at the dose of 3.84×10^{19} eV/g and then photobleached with light from a tungsten lamp for 1 min.

The intensity of luminescence is measured at the wavelength of 390 nm. Initial rate of formation of toluene anion is nomalized to 10 for the comparison with the intensity of luminescence.

The results of Figs. 5 and 6 show that the intensity of the luminescence does not correspond at all to the yields of the toluene anions, but to their rates of formation. The luminescence diminished upon the pre-irradiation can be almost restored to the former value by the photobleaching of the toluene anion with the light from a tungsten lamp (Fig. 6). If the luminescence from toluene in the 2,3DMB matrix is due to a neutralization reaction between a toluene anion and a migrating hole, the intensity of the liminescence should be roughly proportional to the amount of the toluene anion (Reactions (1)—(4)). The experimental results, however, show that these mechanisms are not responsible for the luminescence of toluene:

$$\text{2,3DMB} \rightsquigarrow \text{2,3DMB}^{+}_{\text{m}} + e^- \quad (1)$$

$$e^- + C_6H_5CH_3 \longrightarrow C_6H_5CH_3{}^- \quad (2)$$

$$\text{2,3DMB}^{+}_{\text{m}} + C_6H_5CH_3{}^- \longrightarrow \text{2,3DMB} + C_6H_5CH_3{}^* \quad (3)$$

$$C_6H_5CH_3{}^* \longrightarrow C_6H_5CH_3 + h\nu \quad (4)$$

where 2,3DMB$^{+}{}_{\text{m}}$ represents a migrating hole.

Therefore, the energy may be transferred from the matrix to the solute by non-ionic processes until the ionization occurs partly. One plausible mechanism may be represented as follows:

$$\text{2,3DMB} \rightsquigarrow \text{2,3DMB}^* \quad (5)$$

$$\text{2,3DMB}^* + C_6H_5CH_3 \longrightarrow C_6H_5CH_3{}^+ + e^- \quad (6)$$

$$\searrow C_6H_5CH_3{}^* \quad (7)$$

$$C_6H_5CH_3{}^+ + e^- \longrightarrow C_6H_5CH_3{}^* \quad (8)$$

$$C_6H_5CH_3 + e^- \longrightarrow C_6H_5CH_3{}^- \quad (2)$$

$$C_6H_5CH_3{}^* \longrightarrow C_6H_5CH_3 + h\nu \quad (4)$$

where 2,3DMB* means an exciton. The absence of the migrating hole in the γ-irradiated 2,3DMB has also been suggested in the γ-irradiation of 2,3DMB containing carbon dioxide.[4b)]

When the excited 2,3DMB is formed by the γ-irradiation at 77°K in the solid phase, the excitation of 2,3-DMB may migrate in the solid, probably as an exciton. The exciton may be trapped at the toluene molecule to form a toluene cation, an electron, or an excited

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[10] When 3-methylpentane is added in the 2,3 DMB matrix, the matrix becomes transparent without a cracking at 77°K and is suitable for the measurement of absorption spectra.

toluene molecule (Reactions (5), (6), and (7)). A part of the toluene cations and electrons may neutralize with each other (Reaction (8)) to form an excited toluene molecule. Then, the excited toluene molecule formed in Reactions (7) and/or (8) may emit light. The formation of a solute cation by excitation transfer was also pointed out in previous studies of the radiolysis of 2,3DMB in the solid phase[4b] and in polyethylene.[11]

The decreases in the intensity of the luminescence and in the rate of the formation of the toluene anion with dose may be due to the decrease in the amount of residual toluene with the dose. When the toluene ions formed by the pre-irradiation of 3.84×10^{19} eV/g are photobleached (Reaction (9)), the intensity of the luminescence recovered by the photobleaching is about 5 arb. unit, as is shown in Fig. 6.

$$C_6H_5CH_3^- \xrightarrow{h\nu} C_6H_5CH_3 + e^- \qquad (9)$$

The concentration of toluene anions before the photobleaching is about 3.3×10^{-3} mol%, if G(toluene anions)=0.6. The amount of toluene for the intensity of luminescence of 10 arb. unit in Fig. 6 is about $3.3\times10^{-3}\times2=6.6\times10^{-3}$ mol%.

We can, then, roughly estimate the distance of the exciton migration. The real concentration of toluene in the 2,3DMB crystalline lattice is about 6.6×10^{-3} mol%, *i.e.*, 6.6×10^{-5} mol fraction. Assume that the exciton migrates to the nearest neighboring molecules of toluene to give its energy to the toluene. Supposing that the number of molecules of the nearest neighbors of toluene is twelve; the number of 2,3DMB molecules, through which the exciton migrates before encountering a toluene, can then be estimated roughly as follows;

$$\frac{1}{6.6\times10^{-5}}\times\frac{1}{12} = 1.3\times10^{3}\ \text{molecules}$$

This number of molecules is approximately equal to the calculated migration distance (10^3—10^4 molecules) of the exciton corresponding to the lowest singlet-excited state of alkane.[12]

However, the concentration of toluene anions 6.6×10^{-3} mol% is far below that of the solute, 2 mol%. This result can not yet be explained clearly, but the following assumption can be made temporarily: effective parts to receive the migrating energy are limited by the solubility or cluster formation of the additive, defect formation with the solute.

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11) R. H. Partridge, *J. Chem. Phys.*, **52**, 2491 (1970).

12) T. Miyazaki, This Bulletin, **46**, 329 (1973).