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Mechanism of High-energy-induced Luminescence of Solid 2,3-Dimethylbutane Containing Toluene at 77 K

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The luminescence from 2,3-dimethylbutane (23DMB) containing a small amount of toluene (To) has been observed in the solid phase at 77 K during γ-irradiation or by ns pulse irradiation with X-rays. The emission spectrum from 23DMB–To (2 mol%) during γ-irradiation at 77 K consists of the fluorescence from the singlet-excited toluene and the phosphorescence from the triplet-excited toluene. Both the singlet- and triplet-excited toluenes are formed by the energy transfer from the irradiated 23DMB to toluene. When nitrous oxide or propylene is added to the 23DMB–To mixture, the emission spectrum is changed and becomes very similar to that from the 23DMB–To mixture during illumination with UV lights at 77 K. The spectrum, which disappears upon the addition of nitrous oxide or propylene, consists mainly of phosphorescence. It is concluded that the triplet-excited toluene may be formed by the migration of a hole and an electron. The effects of electron scavengers, such as nitrous oxide and carbon dioxide, or hole scavengers, such as propylene or tetramethylethylene, on the fluorescence have been studied by nsec-pulse irradiation. Since the fluorescence is not appreciably affected by the addition of these scavengers, the singlet-excited toluene may be formed by the excitation transfer.

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. One of the most important primary processes is the migration of the short-lived entities produced by the γ-irradiation of the solid. Studies by Miyazaki *et al.* have suggested the importance of the non-ionic energy transfer in the radiolysis of solid hydrocarbons. The formation of the solvent radical and hydrogen which are formed by the fragmentation of the excited molecule is suppressed by the addition of toluene or CCl_4 in the radiolysis of solid isobutane. The phenomenon has been explained in terms of excitation transfer.[1] If toluene is an efficient acceptor of the excitation energy in the radiolysis of solid alkane, the luminescence from the excited toluene may be expected. Recently we have studied the luminescence from alkane containing a small amount of toluene during γ-irradiation at 77 K.[2] A strong emission from the excited toluene formed by the energy transfer from the irradiated alkane has been observed. The study of the luminescence gives us useful information on the energy transfer. Luminescence studies previously undertaken in radiation chemistry have been mostly concerned with the thermoluminescence or the photo-induced luminescence of γ-irradiated samples, or with the luminescence in the liquid phase during γ-irradiation.

In order to study the mechanism of the luminescence from solid 2,3-dimethylbutane containing toluene, we have here examined the effects of electron or hole scavengers on the luminescence upon irradiation with γ-rays or ns pulse X-rays.

Experimental

The 2,3-dimethylbutane(23DMB) and toluene(To) were the same as those used before.[2] They were passed through a 50 cm column packed with activated alumina and were used after distillation on a vacuum line. Nitrous oxide, carbon dioxide, and propylene, supplied by the Takachiho Shoji Co., were of a high purity and were used without further purification. The tetramethylethylene(TME), supplied by the Tokyo Kagaku Seiki Co., was more than 99.0% pure.

The errors in the measurement of the luminescence at 77 K were about 10%. Each experimental plot is an average of two or more runs.

The measurement of the luminescence during γ-irradiation was the same as that used before. The photomultiplier (Hamamatsu TV Co. R-136) can detect the light from 200 to 650 nm; its sensitivity depends upon the wavelength. It was expected that the brightness of the Shimadzu-Bausch-Lomb monochromator may depend also upon the wavelength of the lights. The sensitivity of the photomultiplier and the brightness of the monochromator were checked by using a standard tungsten lamp. The brightness of the monochromator, however, did not depend appreciably upon the wavelength of the lights. Therefore, the measured emission spectrum was corrected by considering only the sensitivity of the photomultiplier.

The pulse irradiation was done at 77 K with X-rays from Febetron 707. The maximum energy of the X-rays is 2 MeV, and the duration of a pulse is 20 ns. An apparatus for measuring the luminescence by pulse irradiation consists of a monochromator (Shimadzu GE-100), a photomultiplier (EMI-6256B), and a synchroscope (Iwatsu Electric Co., SS-112). A schematic diagram of the apparatus is given

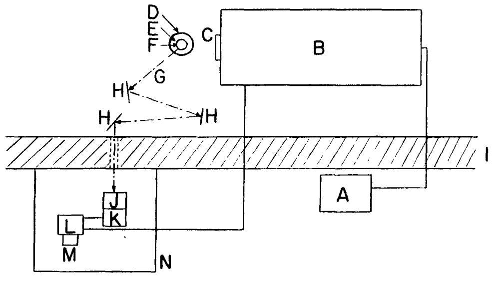

Fig. 1. Schematic diagram of the measurement of luminescence by the ns pulse irradiation at 77 K. A: Panel for operating Febetron, B: Febetron 707, C: Tungsten plate, D: Dewar flask, E: Liquid nitrogen, F: Sample, G: Emission, H: Mirror, I: Concrete wall, J: Monochrometer, K: Photomultiplier, L: Synchroscope, M: Polaroid camera, N: Dark room.

in Fig. 1. The experiment was done under condition suitable for obtaining ns time resolution.

Results

Figure 2 shows the effect of toluene on the formation of the solvent radical[2] and the luminescence from toluene in the 23DMB at 77 K. The maximum intensities of the fluorescence and the phosphorescence are normalized to 10. The fluorescence was measured at 20, 60, and 180 ns after the pulse irradiation with Febetron and during γ-irradiation. The phosphorescence was measured during γ-irradiation. The fluorescences at different times show approximately the same dependence on the concentration of toluene.

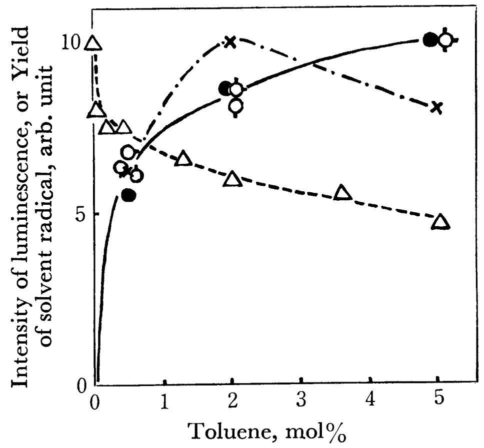

Fig. 2. Yields of solvent radical and emission from toluene in the irradiation of 23DMB at 77 K against concentration of toluene.
△: Yields of solvent radical at the dose of 9.6×10^{18} eV/g.
●: Intensity of fluorescence during γ-irradiation.
ȯ,○-,♀: Intensity of fluorescence at 20 ns, 60 ns, and 180 ns after the irradiation with ns pulse X-ray respectively.
×: Intensity of phosphorescence during γ-irradiation.

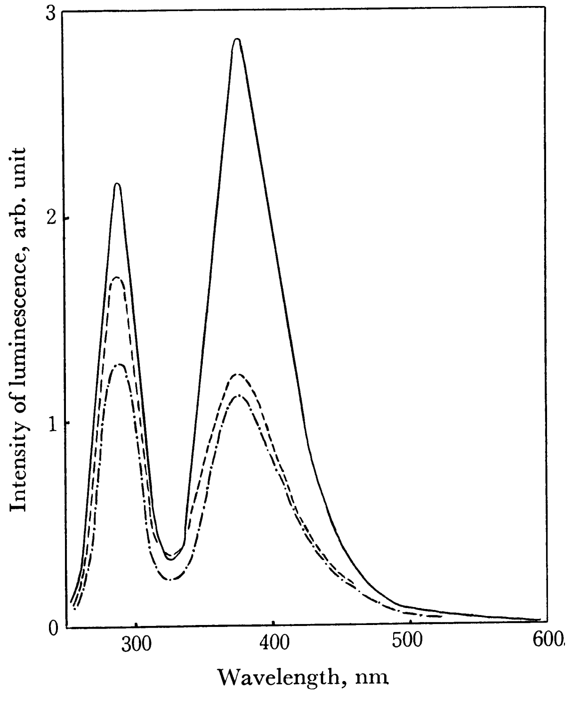

Fig. 3. Emission spectra from 23DMB-To (2 mol%) system in the solid phase during γ-irradiation at 77 K.
——: Spectrum from 23DMB–To
------: Spectrum from 23DMB–To–C_3H_6 (2 mol%)
-·-·-: Spectrum from 23DMB–To–N_2O (2 mol%)

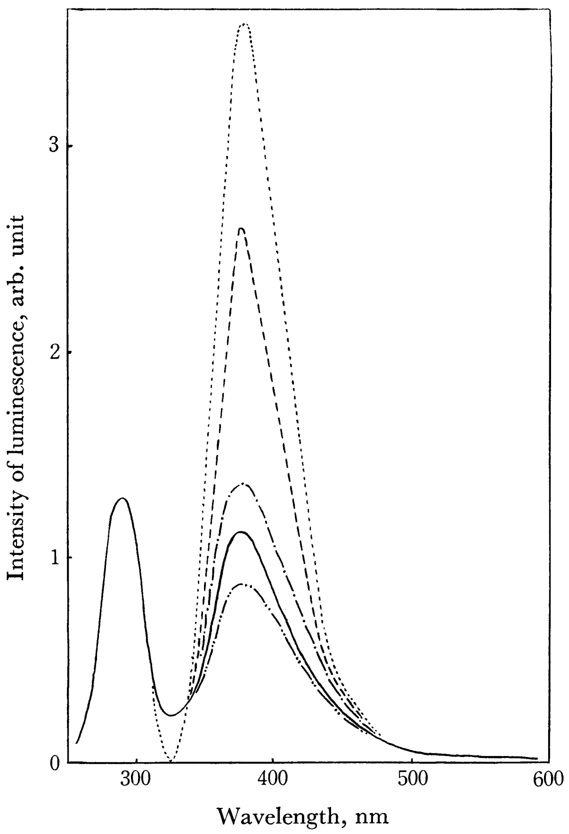

Fig. 4. Emission spectra from 23DMB–To (2 mol%) system in the solid phase at 77 K.
——: Spectrum from 23DMB–To–N_2O (2 mol%) during γ-irradiation.
-··-··: Spectrum from 23DMB–To–C_3H_6 (2 mol%) during γ-irradiation.
------: Spectrum obtained by subtracting the spectrum of 23DMB–To–N_2O (2 mol%) from that of 23DMB–To.
······: Spectrum obtained by subtracting the spectrum of 23DMB–To–C_3H_6 (2 mol%) from that of 23DMB–To.
-·-·-: Spectrum from 23DMB–To during UV illumination.[4]
The intensity of the fluorescence was normalized to the same peak intensity as that of 23DMB–To–N_2O (2 mol%).

The emission spectrum from 23DMB–To(2 mol%) during γ-irradiation at 77 K is shown in Fig. 3.[3] The spectrum consists of two peaks, with emission maxima near 280 and 390 nm. They are due to the fluorescence from the singlet-excited toluene and the phosphorescence from the triplet-excited toluene respectively. When nitrous oxide or propylene is added to the 23DMB–To(2 mol%), the emission spectrum is changed.

The spectrum which disappears upon the addition of nitrous oxide or propylene is obtained by subtracting

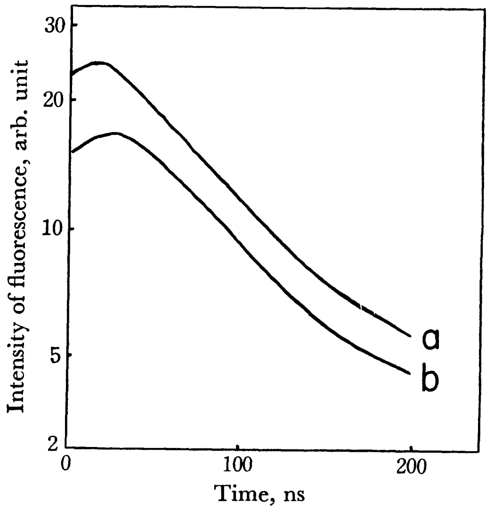

Fig. 5. Time dependence of the fluorescence intensity from toluene in the 23DMB matrix at 77 K.
a: 23DMB–To (2 mol%).
b: 23DMB–To (0.5 mol%).

the spectrum of 23DMB–To(2 mol%)–N_2O(2 mol%) or C_3H_6(2 mol%) from that of 23DMB–To(2 mol%). The intensities of the fluorescence are normalized to the same peak intensity as that of 23DMB–To(2 mol%)–N_2O(2 mol%) (Fig. 4). The emission spectrum from 23DMB–To(2 mol%) during the illumination with ultraviolet light at 77 K is also shown there.[4]

Figure 5 shows the time dependence of the fluorescence of the excited toluene formed by the ns-pulse irradiation of 23DMB containing toluene at 77 K. The rise in the fluorescence before 20 ns is due to the duration of the pulse.

Figure 6 shows the effects of electron scavengers, such as N_2O and CO_2, and hole scavengers, such as C_3H_6 and TME, on the fluorescence at 60 ns after the pulse irradiation at 77 K. Similar results are obtained also 20 and 180 ns after the pulse irradiation. The intensity of the fluorescence in the 23DMB–To(2 mol%) is taken as 10.

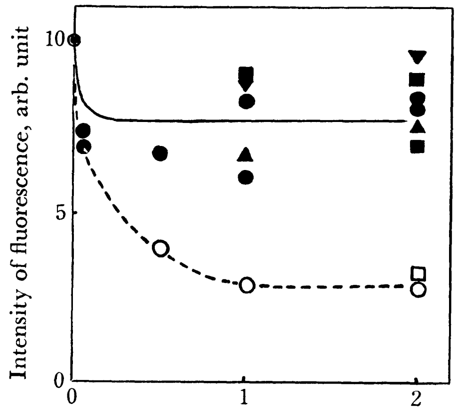

Fig. 6. Effect of additives on the fluorescence intensity from toluene at 60 ns after the ns pulse irradiation of 23DMB–To (2 mol%).
●: N_2O in the solid phase at 77 K.
■: CO_2 in the solid phase at 77 K.
▲: C_3H_6 in the solid phase at 77 K.
▼: TME in the solid phase at 77 K.
○: N_2O in the liquid phase at room temperature.
□: CO_2 in the liquid phase at room temperature.

Discussion

Energy Transfer from Irradiated 23DMB to Toluene at 77 K. There are two possibilities with regard to the formation of the excited toluene in the irradiated 23DMB matrix. One is that it results from energy transfer from the irradiated 23DMB. The other is that it results from the direct absorption of the radiation energy by the solute toluene. The following results support the former possibility: (1) As is shown in Fig. 2, the intensity of the fluorescence increases sharply with an increase in the concentration of toluene, and then gradually increases beyond 2 mol% of toluene. The intensity of the phosphorescence increases sharply and then gradually decreases beyond 2 mol% of toluene. If the luminescence is due to the direct absorption of the radiation energy by the solute toluene, the intensity should increase linearly with an increase in the concentration of toluene.

(2) The yields of the solvent radical in the radiolysis of 23DMB at 77 K decrease upon the addition of toluene; the decrease coincides complementally with the increase in the fluorescence from toluene (Fig. 2). The results suggest that the energy which ruptures the C–H bond of the irradiated 23DMB migrates to toluene to form the excited toluene.

(3) The yields of the fluorescence from toluene in the irradiated alkanes by γ-rays or pulse X-rays at 77 K depend appreciably upon the kinds of alkanes. The yield of the fluorescence in 23DMB–To(2 mol%) is about 3—4 times as large as that in *neo*-C_5H_{12}–To(2 mol%). If the fluorescence is due to the direct absorption of the radiation energy by the solute toluene, the intensity does not depend upon the kind of alkanes, but only upon the amount of toluene.

(4) The addition of CCl_4, which is an efficient energy acceptor,[1] suppresses both the fluorescence and phosphorescence from the irradiated 23DMB–To(2 mol%) at 77 K.

(5) The intensities of the fluorescence from pure solid toluene during γ-irradiation are about 4—7 times stronger than those from 23DMB–To(2 mol%). The fluorescence due to the direct absorption of the radiation energy by toluene itself may be expected to amount to, at most, 8—15% and 3—6% of the total fluorescence from 23DMB–To(2 mol%) and –To(0.5 mol%) respectively.

The time dependence of the fluorescence from 23DMB–To(2 mol%) is similar to that from 23DMB–To(0.5 mol%) (Fig. 5). Since the fluorescence of toluene appears immediately after the ns pulse irradiation,[5] the formation of the excited toluene in the irradiated 23DMB is not due to the secondary reaction of the products, such as a trapped cation, or a trapped electron, but to the rapid energy transfer in a time period less than 10 ns.

Emission Spectrum. The rapid energy transfer in the 23DMB matrix at 77 K cannot be ascribed to the molecular diffusion of active species, although this diffusion is the most important process in the liquid phase. A mobile entity in the solid phase is an exciton (DMB*),[6] a hole ($DMB^{+}{}_{m}$),[7] or an electron. For the formation of the excited toluene by energy transfer from the irradiated 23DMB, two processes are possible. One is that the exciton migrates to toluene. The other is that the hole and the electron encounter on the same toluene molecule, even if they travel freely through the matrix.

Figure 3 shows the effects of the addition of an electron scavenger (N_2O) or a hole scavenger (C_3H_6) on the emission spectrum of 23DMB–To during γ-irradiation at 77 K. It was found that propylene reacts efficiently with a hole by means of the following ion-molecule reaction at 77 K:[8]

$$DMB^{+}_{m} + C_3H_6 \longrightarrow C_6H_{12}{}^{+} + C_3H_8 \qquad (1)$$

The intensities of the phosphorescence decrease clearly upon the addition of N_2O or C_3H_6, while those of fluorescence decrease a little. The emission spectra from 23DMB–To(2 mol%)–N_2O(2 mol%) or 23DMB–To(2 mol%)–C_3H_6(2 mol%) during γ-irradiation are very similar to that from 23DMB–To(2 mol%) during the illumination with UV light (Fig. 4). The singlet-excited toluene is formed even in the presence of N_2O or C_3H_6. An excitation transfer forms a singlet-excited toluene, while an energy transfer *via* the ionic process, followed by a neutralization, favors the formation of a triplet-excited toluene. Therefore, it seems that the fluorescence may be due to the excitation transfer. This process will be discussed in more detail in connection with pulse irradiation in the next section.

On the contrary, the spectra which disappear upon the addition of N_2O or C_3H_6 are quite different from the spectrum obtained from 23DMB–To(2 mol%) during the illumination with UV light (Fig. 4). The phosphorescence is much stronger than the fluorescence in these spectra. The formation of the triplet-excited toluene is suppressed remarkably by the addition of an electron scavenger or a hole scavenger. The mechanism of the formation of the triplet-excited toluene may be represented as follows:

$$\text{23DMB} \rightsquigarrow DMB^{+}_{m} + e^{-} \qquad (2)$$

$$DMB^{+}_{m} + \text{To} \longrightarrow \text{23DMB} + \text{To}^{+} \qquad (3)$$

$$e^{-} + \text{To}^{+} \longrightarrow \text{To}^{3} \qquad (4)$$

$$e^{-} + \text{To} \longrightarrow \text{To}^{-} \qquad (5)$$

$$DMB^{+}_{m} + \text{To}^{-} \longrightarrow \text{23DMB} + \text{To}^{3} \qquad (6)$$

$$\text{To}^{3} \longrightarrow \text{To} + h\nu \text{ (phosphorescence)} \qquad (7)$$

where To^3 represents a triplet-excited toluene. The hole and the electron produced by the irradiation (Reaction (2)) migrate to toluene (Reactions (3) and (5)). Then, the neutralization reaction (Reactions (4) and (6)) produces a triplet-excited toluene. Since N_2O may capture an electron, it disturbs Reactions (4) and (5). The suppression of Reaction (5) by the addition of N_2O was demonstrated by ESR spectroscopy in the radiolysis of 23DMB–To(2 mol%)–N_2O(2 mol%) at 77 K.[2] C_3H_6 disturbs Reactions (3) and (6) by the ion-molecule reaction with $DMB^{+}{}_{m}$ (Reaction (1)). Since the amount of To^- does not correspond at all to the intensity of phosphorescence,[2] Reaction (6) may play a minor role.

Therefore, it may be concluded that the energy transfer in the 23DMB matrix consists of two processes: one forms singlet-excited toluene, and the other forms mainly triplet-excited toluene. Since the efficiencies of the emissions from the two excited states of toluene are not known in the 23DMB matrix at 77 K, the extents of the two processes cannot be determined as yet.

Effect of Scavengers on the Fluorescence. The singlet-excited toluene is formed immediately after the pulse-irradiation. Since the fluorescence in the liquid phase is suppressed by the addition of the electron scavengers (Fig. 6), ionic processes may be important in the formation of the singlet-excited toluene in the liquid phase, as has been reported previously.[9–11]

On the contrary, the fluorescence in the solid phase at 77 K is not affected appreciably by the addition of electron scavengers, such as N_2O and CO_2, or hole scavengers, such as C_3H_6 and tetramethylethylene (TME). There is a possibility that these additives may not act efficiently in the 23DMB matrix at 77 K.

In the radiolysis of 23DMB–To(2 mol%)–CO_2(2 mol%) at 77 K, CO_2 captures an electron to form $CO_2{}^-$, which is clearly detected by ESR spectroscopy, and $G(CO_2{}^-)$ is about 0.8.[12] When 23DMB–To(2 mol%) is γ-irradiated at 77 K, a toluene anion is formed in an appreciable amount. The formation of the toluene anion is completely suppressed by the addition of N_2O, while a toluene cation is clearly observed by ESR spectroscopy in the radiolysis of 23DMB–To(2 mol%)–N_2O(2 mol%) at 77 K. The amount of electrons captured by N_2O seems to be equal to the yield of the toluene cations (*i.e.*, $G\sim1.7$). Since the *G*-values of the ionization in the gas and liquid phases are about 4, there is some suspicion that the ionic reaction which is not disturbed by N_2O amounts to 2.3 *G*-unit. Although the yields of the ionization in the gas phase, in which a free electron and a cation are produced, and about 4 *G*-unit, we cannot expect that, in the crystal, the yields of holes and electrons will be 4 *G*-unit, for if a hole and an electron are bound by their mutual Coulomb force, they may be considered as an exciton.[6] It has been reported by several investigators that the yields of the electrons which can be captured by electron scavengers are 1.5—2.0 *G*-unit in the radiolysis of solid alkanes at 77 K. They used biphenyl,[13] alkyl disulfide,[14] benzene,[15] iodobenzene,[16] and nitrous oxide[16] as electron scavengers. The yields were determined by different analytical methods, such as optical or ESR spectroscopy, or gas chromatography. Therefore, the amount of electrons captured by N_2O in the 23DMB matrix ($G\sim1.7$) is near the maximum yields of electrons in the irradiated solid alkane. There is a possibility that N_2O does not directly capture a mobile electron, but that it captures an electron from a toluene anion by tunneling.[17] It can be expected from the tunneling hypothesis that the yield of the toluene cation is not affected by the addition of N_2O. The yield of the toluene cation, however, increases remarkably upon the addition of N_2O.[2] Therefore, N_2O captures a mobile electron, disturbing the neutralization reaction between the electron and the toluene cation. TME captures a hole to produce the TME^+ cation, which is observed in the irradiated 23DMB–To(2 mol%)–TME(2 mol%) by ESR spectroscopy.[12]

Therefore, it may be considered that the reactions due to electrons or holes are suppressed by the addition of the electron scavengers (N_2O or CO_2) or the hole scavengers (C_3H_6 or TME). Figure 6 shows that the fluorescence is not appreciably affected by the addition of N_2O, CO_2, C_3H_6, or TME at 77 K. It may be concluded that the formation of the fluorescence, *i.e.*, the formation of the singlet-excited toluene, is not due to the reactions of the hole and the electron, but to a non-ionic process, such as the migration of the exciton:

$$\text{23DMB} \rightsquigarrow \text{DMB}^* \tag{8}$$

$$\text{DMB}^* + \text{To} \longrightarrow \text{DMB}^* + \text{To}^1 \tag{9}$$

$$\text{To}^1 \longrightarrow \text{To} + h\nu(\text{fluorescence}) \tag{10}$$

$$\searrow \text{To}^3 \tag{11}$$

$$\text{To}^3 \longrightarrow \text{To} + h\nu\ (\text{phosphorescence}) \tag{7}$$

$$\text{DMB}^* \longrightarrow C_6H_{13} + H \tag{12}$$

where To^1 represents a singlet-excited toluene. The exciton produced by irradiation migrates to the toluene, this forming the singlet-excited toluene, which emits fluorescence and phosphorescence by intersystem crossing. DMB* indicates a Frenkel exciton, a Mott-Wannier exciton, or a mobile ion-pair. Reaction (9) implies also the possibility that toluene accepts energy directly from the excited 23DMB molecule, which itself absorbs the radiation energy. It is interesting to note that the C–H bond rupture in the radiolysis of solid isobutane, whose chemical structure is similar to 23DMB, is due to the fragmentation of the excited molecule,[1] and that the formation of the singlet-excited toluene in the 23DMB–To system at 77 K competes with the formation of the solvent radical (Fig. 2).

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3) The emission spectrum is different from the previously-reported one (Ref. 2). When the sample is irradiated, some product which absorbs the light near 280 nm may be formed, thus decreasing the emission intensity at 280 nm. Therefore, the spectra in Fig. 3 are those from a freshly-sealed sample.

4) The spectrum of 23DMB–To (2 mol%) during UV illumination with light of 250 nm at 77 K was measured by Dr. Hiroshi Masuhara.

5) The initial rise in the fluorescence before 20 ns is due to the duration of the pulse. The values at 0 ns contain larger errors than those at other times.

6) It would be useful to define the technical terms used in this paper. Such terms as "ionization", "cation", "electron", and "excited molecule" are commonly used in radiation chemistry. Though they can be clearly defined in the gas phase, where each molecule exists independently, it is difficult to do so in the crystal where the character of a molecular aggregate becomes remarkable. Since there have been very few studies of the primary process in the radiolysis of organic crystals, it is impossible to give terms suitable for the radiation chemistry in the crystal. Therefore, we adopt the terms for the mobile entities which are used in solid state physics. An electron in the conduction band and a hole can travel freely and independently through the crystal. An exciton is a neutral, excited mobile state of a crystal; an exciton can travel through the crystal, but it is electrically neutral. The exciton may be classified into two different limiting approximations. One is the Frenkel exciton, which is considered to be tightly bound, while the other is the Mott-Wannier exciton, which is weakly bound by Coulomb force, having an electron-hole interparticle distance large in comparison with the atomic radius. In this paper, we do not discriminate between the two types of excitons (*cf.* C. Kittel, "Introduction to Solid State Physics," John Wiley & Sons, New York, (1956)).

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