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Thermoluminescence from the UV-Irradiated Solution of Triphenylmethane at Low Temperature

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Triphenylmethane, irradiated in the near ultraviolet region in a non-polar rigid medium at 77 K, showed thermoluminescence consisting of three bands, fluorescence and phosphorescence of triphenylmethane and fluorescence of triphenylmethyl radical. With the increase of solute concentration the yield of the emissions from triphenylmethane decreased while that of the emission from the radical increased. It was concluded that the emissions from triphenylmethane were due to the recombination between triphenylmethane cation and the photoejected electron, and that the fluorescence from the radical was mainly due to the electron transfer reaction between triphenylmethane cation and triphenylmethyl anion. Detailed emission processes inlcuding electron transfer and energy transfer processes were discussed.

Thermoluminescence from low temperature UV-irradiated solution of aromatics has been investigated by many authors.[1-4] It has been recognized that the luminescence in many cases is caused by recombination of the charged species generated by the photo-ionization of aromatic molecules. Gibbons *et al.*[3] found that the thermoluminescence from an irradiated solution of toluene comprises the fluorescence and the phosphorescence of toluene together with the fluorescence of the benzyl radical. The former two emissions were concluded to be caused by the recombination of the solvated electron with the toluene cation, while the mechanism for the last one was left untouched.

In this paper, we have investigated the thermoluminescences from triphenylmethane irradiated in non-polar organic rigid solutions and give an explanation for the emission mechanism.

Experimental

Commercial triphenylmethane was sublimed in vacuum. Purification of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine

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[1] W. Meyer and A. C. Albrecht, *J. Phys. Chem.*, **66**, 1168 (1962).

[2] M. Gauthier-Bodard and J. Bullot, *Ber. Bunsen. Phys. Chem.*, **72**, 348 (1968).

[3] W. A. Gibbons, G. Porter, and M. I. Savadatti, *Nature*, **206**, 1355 (1965).

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

(TMPD) was described previously.[5] Isopentane and methylcyclohexane were purified by passing through 1 m silica gel columns. Solutions of triphehylmethane in a 2 : 1 mixture of isopentane and methylcyclohexane (hereafter called MP) were deaerated by purging with nitrogen. Irradiation of the solution in the UV region was carried out at 77 K with a high pressure mercury lamp (250 W) through a Toshiba UV-D25 glass filter and an aqueous solution of 2.0 M nickel sulfate. Infrared light was obtained from the same lamp using a Toshiba VR-67 glass filter. The thermoluminescence from the irradiated solution was measured with a Shimadzu GF 16 monochromator and an RCA 1P28 photomultiplier. Details of the measurement are described elsewhere.[6] The absorption spectra were measured with a Cary Model 15 spectrophotometer.

Results

Change of the absorption spectrum of an MP solution of triphenylmethane by UV-irradiation is shown in Fig. 1. The bands lying in the range 25—35 kK and around 20 kK were in fairly good agreement with those of triphenylmethyl radical assigned by Adam and Weissman.[7] Formation of the triphenylmethyl radical was found to be proportional to the square of the intensity of UV-light from the absorption intensity measurement. It is therefore concluded that the radical is produced by a bi-photonic mechanism.[4,8] The irradiated solution showed weak luminescence on warming. A thermoluminescence spectrum is shown in Fig. 2. The band with maximum at 34.5 kK corresponds to the fluorescence of triphenylmethane, and that at 24.4 kK to the phosphorescence of the same molecule. The band at 19.4 kK agrees well in shape and position with the normal fluorescence of triphenylmethyl radical ($^2E \leftarrow {}^2A_2$ transition).[9]

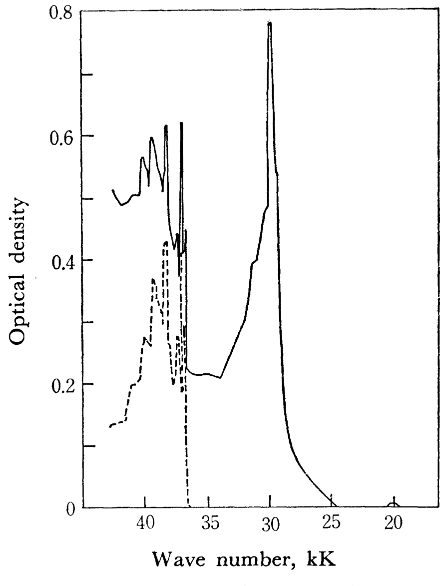

Fig. 1. Absorption Spectra of a 1.5×10^{-4} M MP solution of triphenylmethane at 77 K.
---- before irradiation
—— after irradiation for 10 min

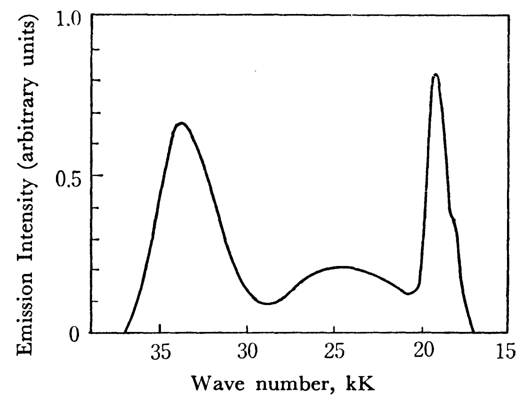

Fig. 2. Thermoluminescence spectrum from a 5×10^{-4} M solution of triphenylmethane irradiated for 10 min at 77 K.

The intensity of thermoluminescence was measured for each emission band as functions of time after the irradiated solution was taken out from the Dewar (Fig. 3). Curves (a) for fluorescence and (b) for phosphorescence of triphenylmethane are similar in shape, while curve (c) for fluorescence of the triphenylmethyl radical differs considerably, suggesting that the latter appears by a different mechanism from that for the emission of triphenylmethane. It was also found from simultaneous observation of the glow curves and the change of absorption with warming that the radical survives after the emission from the radical already fades out.

The emission intensities change markedly with experimental conditions such as concentration of the solution and UV-irradiation time. Figure 4 shows the emission yield (obtained by integrating the thermal

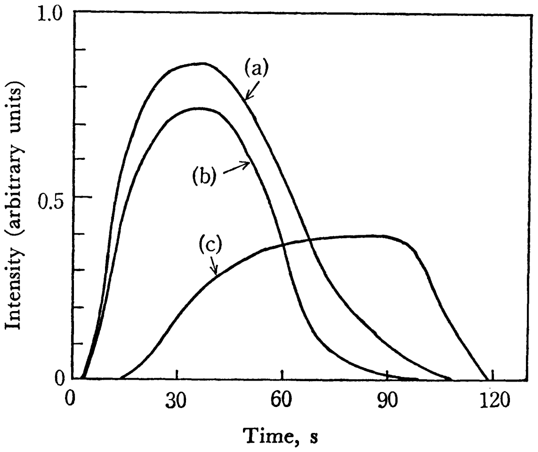

Fig. 3. Thermal glow curves for the irradiated 2.5×10^{-4} M solution of triphenylmethane. The irradiateon time was 5 min. The curves were obtained for the three bands corresponding to the fluorescence (a) and phosphorescence (b) of triphenylmethane and the fluorescence of triphenylmethyl radical (c), respectively.

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[5] T. Imura, N. Yamamoto, and H. Tsubomura, This Bulletin, **43**, 1607 (1970).

[6] K. Yoshinaga, N. Yamamoto, and H. Tsubomura, *J. Luminescence*, **4**, 417 (1971); **6**, 179 (1973).

[7] F. C. Adam and S. I. Weissman, *J. Amer. Chem. Soc.*, **80**, 2057 (1958).

[8] H. Yamada, N. Nakashima, and H. Tsubomura, *J. Phys. Chem.*, **74**, 2897 (1970).

[9] G. N. Lewis, D. Lipkin, and T. T. Magel, *J. Amer. Chem. Soc.*, **66**, 1579 (1944).

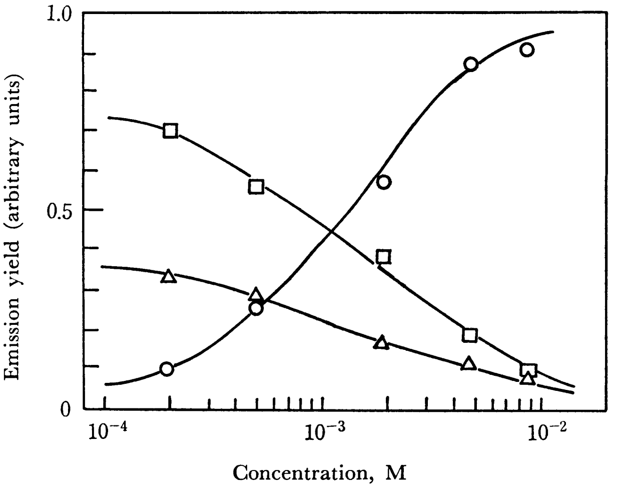

Fig. 4. Emission yields (see text) for the thermoluminescence from the irradiated MP solutions of triphenylmethane as a function of the triphenylmethane concentration. The yields were measured at the maxima for the fluorescence (-□-□-) and phosphorescence (-△-△-) of triphenylmethane and for the fluorescence of triphenylmethyl radical (-○-○-), respectively.

glow curve with time) for the three bands of the thermoluminescence against the concentration of the solute. Concentrated solutions (10^{-3}—10^{-2} M) absorbed almost all the UV-lights (the cell used was 13 mm thick) and therefore gave nearly constant amounts of triphenylmethyl radical in the media for the irradiation time of 10 min. For solutions with concentrations below 10^{-3} M, part of the light passes through the solution. Such solutions were irradiated until the yield of the radical became equal to that of the concentrated solutions. As is obvious from Fig. 4, the emission from triphenylmethane were strong at lower concentration and weak at higher concentration. On the other hand, the fluorescence from the radical, hardly observable at concentration of 2×10^{-4} M, became strong at concentration above 10^{-3} M.

No absorption band of triphenylmethane cation was found for the irradiated solution in the visible and near infrared region.10)

We also measured the thermoluminescence for the MP rigid solution containing TMPD (1.5×10^{-5} M) and triphenylmethane (7×10^{-3} M). Strong thermoluminescence was observed and its spectrum was found to consist of three bands, *i.e.*, the fluorescence and phosphorescence of TMPD and the fluorescence of triphenylmethyl radical (Fig. 5, curve a). The fluorescence of triphenylmethyl radical was 11 times stronger in intensity than that obtained for an MP solution containing only 7×10^{-3} M triphenylmethane where the irradiation time was 5 min for both cases. For the irradiated TMPD-triphenylmethane solution, the TMPD cation and triphenylmethyl radical were proved to be present by absorption measurement, but no absorption band was found in the visible region ascribable to triphenylmethyl anion.11)

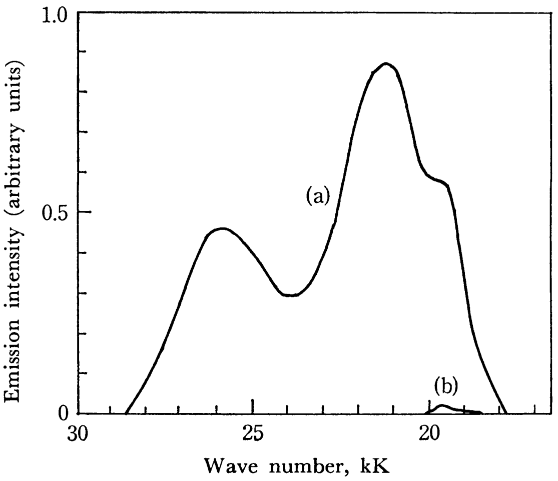

Fig. 5. Emission spectra for the thermoluminescence from the irradiated MP solutions.
(a), for a solution containing $1,5\times10^{-5}$ M TMPD and 7×10^{-3} M triphenylmethane;
(b), for a solution of 7×10^{-3} M triphenylmethane.

TABLE 1. INFLUENCE OF IR-IRRADIATION ON THE YIELD OF THERMOLUMINESCENCE

Concentration of triphenylmethane 2.25×10^{-4} M
UV-irradiation time 10 min.
IR-irradiadiation time 30 sec.

	Emission yield (arbitrary units)		
	Fluorescene band of triphenylmethane	Phosphorescence band of triphenylmethane	Fluorescence band of triphenylmethyl radical
Without IR-irradiation	337	184	106
With IR-irradiation	45	22	87

The thermoluminescence was also studied for a UV-irradiated solution of triphenylmethane after being exposed to infrared light. The emissions from triphenylmethane became weak but the fluorescence from the radical was only slightly affected (Table 1).

Discussion

Emission Mechanism. It is evident from UV absorption spectra studies that the triphenylmethyl radical is formed in the UV-irradiated solution of triphenylmethane at 77 K. The radical is presumably formed by the following bi-photonic excitation.4,8)

$$\phi_3CH \xrightarrow{h\nu_1} {}^3[\phi_3CH] \xrightarrow{h\nu_2} \phi_3C\cdot + H\cdot \tag{1}$$

The ionization potential of triphenylmethane is 8.80 eV in the gas phase,12) and its triplet state energy is 3.58 eV higher than that of the ground state. Therefore, if it is photo-ionized by the bi-photonic process as are many aromatics in the low temperature matrices,

$$\phi_3CH \xrightarrow{h\nu} {}^3[\phi_3CH] \xrightarrow{h\nu'} [\phi_3CH]^+ + e \tag{2}$$

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10) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2375 (1966).

11) K. K. Brandes, R. Suhrmann, and R. J. Gerdes, *J. Org. Chem.*, **32**, 741 (1967).

12) V. V. Sorokin, *Zh. Fiz. Khim.*, **40**, 2332 (1966).

the second step needs a photon energy equal to or higher than 5.2 eV in the gas phase. Due to polarization energy, the necessary energy for the second step in the matrix may be smaller. As the light source used in the present work has an energy distribution in the range 5.2—3.4 eV, such a photo-ionization is assumed to take place to a small extent, though we could not observe the absorption bands for the triphenylmethane cation.

The triphenylmethyl radical formed is expected to capture the electron ejected in the medium because of its large electron affinity.

$$e + \phi_3C\cdot \longrightarrow \phi_3C^- \qquad (3)$$

The anion and other charged species frozen at 77 K become mobile when the solution is warmed. The triphenylmethane cation and the solvated electron will recombine causing emissions from triphenylmethane as follows:

$$\phi_3CH^+ + e_{solv} \longrightarrow {}^1\phi_3CH^* \text{ or } \phi_3CH^* \qquad (4)$$

$$^1\phi_3CH^* \longrightarrow \phi_3CH + h\nu_F \qquad (5)$$

$$^3\phi_3CH^* \longrightarrow \phi_3CH + h\nu_P \qquad (6)$$

On the other hand, the triphenylmethyl anion will react with the triphenylmethyl cation and emit fluorescence of the triphenylmethyl radical as follows:

$$\phi_3CH^+ + \phi_3C^- \longrightarrow \phi_3CH + {}^2\phi_3C\cdot^* \qquad (7)$$

$$^2\phi_3C\cdot^* \longrightarrow \phi_3C\cdot + h\nu_F' \qquad (8)$$

As the first excited doublet state of the radical is energetically the lowest of all the excited states of triphenylmethane and the radical formed, the fluorescence from it will prevail as the result of the electron transfer and energy transfer processes.

Variations in the intensities of the emission bands with concentration (Fig. 4) can be explained as follows. In dilute solutions, reactions (1) and (2) by irradiation occur uniformly in the cell, while in concentrated solutions they take place mostly near the surface of the irradiated side of the cell, the concentration of the triphenylmethyl radical thus becoming much higher at that part of the solution. As the concentration of the radical becomes higher, the ratio of the photo-ejected electrons captured by the radical compared with those trapped in the matrix become higher.[6,13] Consequently, as reactions (4), (5) and (6) are dominant so are the emissions from triphenylmethane at low concentrations, while as reactions (7) and (8) become dominant so do the emissions from the radical at high concentrations. This fits the trends of curves in Fig. 4.

For the case of TMPD-triphenylmethane solution, it is most probable that the electrons generated mainly by the photo-ejection from TMPD are captured by triphenylmethyl radicals, and the electron transfer reaction between TMPD cation and triphenylmethyl anion leads to the fluorescence from the radical. That the emissions from triphenylmethane were weakened by illumination in the infrared to a greater extent than the emission from the radical seems to result from the fact that the electron is bound by the radical more tightly than in the matrix (Table 1).

The emission from benzyl radical observed for the irradiated solution of toluene might be due to the reaction between benzyl anion and toluene cation.[3,14]

Electron transfer and energy transfer on recombination. We have concluded that the combination of triphenylmethane cation with triphenylmethyl anion leads to emission from the triphenylmethyl radical.

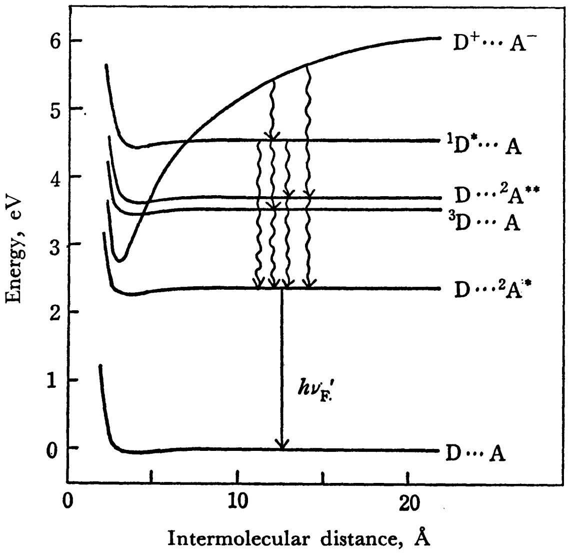

Fig. 6. The potential energy curves for the various states of a system made of triphenylmethane cation (D^+) and trimethyl radical anion (A^-).

The triphenylmethyl anions are expected to be distributed at fairly large distances (~100 Å)[13,15] from the triphenylmethane cations at 77 K. As the matrix is warmed, the anion is mobilized and is drawn near the cation by the Coulombic force along the $D^+\cdots A^-$ curve in Fig. 6. The velocity of the anion should be determined by the Coulombic force $e^2/\varepsilon r^2$, and the resisting force by $6\pi\eta bv$ according to the Stokes' law, where ε and η are respectively the dielectric constant and viscosity of the medium, and b and v the radius and velocity of the anion, respectively. Thus we have

$$v = e^2/6\pi\eta b\varepsilon r^2 \qquad (9)$$

In order to estimate the distance between the ions at which the electron transfer reaction occurs at the maximum rate, it is necessary to derive the absolute value of the reaction rate as a function of the distance. The probability of the electron transfer from the anion to the cation P_{CT} is proportional to the amount of charge transfer interaction V_{CT}.

$$P_{CT} = 2\,|V_{CT}|/h \qquad (10)$$

$$V_{CT} = \langle \Phi_f | H | \Phi_i \rangle \qquad (11)$$

where Φ_i and Φ_f are, respectively, the wave functions for the initial and final states of the system and H is

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[13] N. Yamamoto, Y. Nakato, and H. Tsubomura, This Bulletin, **40**, 451 (1967).

[14] B. Brocklehurst, R. D. Russell, and M. I. Savadatti, *Trans. Faraday Soc.*, **62**, 1129 (1966).

[15] W. M. McClain and A. C. Albrecht, *J. Chem. Phys.*, **44**, 1594 (1966).

the total Hamiltonian. We roughly estimate the value of the right side of Eq. (11), using a simple model consisting of two carbon monocations C_A^+ and C_B^+ fixed at a distance of r and an electron. Assuming that the electron is initially localized on C_A^+ and transferred to C_B^+, the initial and the final electronic wave functions are the atomic orbitals of the each atom represented by Φ_A and Φ_B, respectively. In this case, the matrix element in Eq. (11) can be simply written as follows.

$$\langle \Phi_f | H | \Phi_i \rangle = \langle \Phi_B | H | \Phi_A \rangle \tag{12}$$

Assuming that it is proportional to the overlap integral of the orbitals, approximated to be proportional to $\exp(-3.07 \times 10^8 r)$, and taking the value of 2.4 eV for the element at $r = 1.40$ Å, as suitable for the usual MO calculation of π-electron systems, we obtain

$$P_{CT} = 8.48 \times 10^{16} \exp(-3.07 \times 10^8 r) \tag{13}$$

By taking the probability of existence of unreacted ion-pair to be p, and assuming the initial distance between the cation and the anion to be very much greater than the distance at which the electron transfer reaction takes place predominantly, the extermination of the ion-pairs due to the electron transfer can be represented as a function of distance:

$$\begin{aligned} \mathrm{d}p/\mathrm{d}r &= -(P_{CT}/v)p \\ &= -6.94 \times 10^{36}\, \eta b \varepsilon r^2 \exp(-3.07 \times 10^8 r)p \end{aligned} \tag{14}$$

The most probable distance for the reaction corresponds to the distance making $\mathrm{d}p/\mathrm{d}r$ the maximum. Hence, the following equation is obtained, taking $\mathrm{d}^2p/\mathrm{d}r^2 = 0$

$$\begin{aligned} &-(2 - 3.07 \times 10^8 r_{\max})/r_{\max}^3 \\ &= 6.94 \times 10^{36} \eta b \varepsilon \exp(-3.07 \times 10^8 r_{\max}) \end{aligned} \tag{15}$$

It is found that the $r_{\max}$ determined from Eq. (15) is rather insensitive to η, b and ε. Saturated hydrocarbons at 77 K have viscosities of the order of 10^{12} P.[16] At the temperature of maximum thermoluminescence, the viscosity is definitely higher than 10^3 P. We calculated $r_{\max}$ using the values of 10^{12} and 10^3 P for the viscosity of the solvent. Taking 4.0 Å for b and 2.5 for ε, the distances obtained are 7.6 Å for $\eta = 10^3$ P and 14.8 Å for $\eta = 10^{12}$ P.

The primary electronic state thus formed by the electron transfer reaction, which should have a total energy equal to the CT state at that distance, may be such as D**···A, D···A** etc., where D** and A** are higher excited states of triphenylmethane and triphenylmethyl radical. The energy relaxation due to intra-molecular radiationless transitions is thought to be very quick. The inter-molecular energy transfer, such as transition from either ^{1}D* or ^{3}D* to ^{2}A*, depends strongly on the inter-molecular distance. Since the dipole-dipole transition from ^{1}D* to ^{2}A* is spin-allowed, this process should take place very effectively at the distances considered.[17] The transition from ^{3}D* to ^{2}A*, although it is spin-forbidden, seems also to be effective because the triplet state of D is long-lived at low temperatures. These radiationless processes are represented in Fig. 6 by the wave lines. The fluorescence from the radical observed is understandable as due to the electron transfer followed by energy transfer reactions (Fig. 6).

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16) J. R. Lombardi, J. W. Raymonda, and A. C. Albrecht, *J. Chem. Phys.*, **40**, 1148 (1964).

17) D. L. Dexter, *ibid.*, **21**, 836 (1953).