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The Mechanism of the Scintillation from a Benzene Solution of *p*-Terphenyl

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The luminescence from a benzene solution containing *p*-terphenyl induced by γ-ray irradiation has been compared with that induced by UV irradiation at 2500 Å in the presence of various quenchers. The quenching efficiencies of electron and positive ion scavengers (SF_6, N_2O, CO_2 and NH_3) were found to be greater for the γ-ray excitation than for the UV excitation, while 1,3-butadiene, which is known as a quencher for excited benzene, ($^1B_{2u}$), showed almost the same efficiency for both modes of excitation. These results suggest that, even in a benzene solution, a series of ionic reactions is partly responsible for the formation of the scintillating state of *p*-terphenyl, and that the apparent quenching effect of ion scavengers is mainly due to their interference in the formation of the excited state of the benzene which is produced by the recombination reaction between the benzene cation and an electron. It was estimated that more than 30% of the excited state of benzene is formed by the recombination reaction.

In previous papers[1] we have shown that the luminescence from a cyclohexane solution containing *p*-terphenyl (*p*TP) irradiated with γ-rays is quenched by electron and positive ion scavengers and have suggested that the following ionic processes occur in this scintillator solution:

$$C \rightsquigarrow C^+ + e \qquad (1)$$

$$C \rightsquigarrow C^* \qquad (2)$$

$$T + e \rightarrow T^- \qquad (3)$$

$$T + C^+ \rightarrow T^+ + C \qquad (4)$$

$$T^- + C^+ \rightarrow T^* + C \qquad (5)$$

$$T^+ + e \rightarrow T^* \qquad (6)$$

$$T^+ + T^- \rightarrow T^* + T \qquad (7)$$

Here, C, T, and T* denote cyclohexane, *p*TP, and a scintillating state of *p*TP respectively. The conclusions obtained in the previous papers are that the reaction (2) does not much contribute to the luminescence, and that the scintillating state of *p*TP is mainly formed by the neutralization reactions of the anions or cations of *p*TP. A similar conclusion has recently been reached by several groups of investigators. Thomas *et al.* used a pulse technique to elucidate the origin of the triplet state of scintillator molecules,[2] Ludwig analyzed the decay curve of the γ-ray induced luminescence in terms of ionic reactions,[3] and Hentz and Knight[4] used an electron-scavenging method similar to ours.

The present paper will show the results obtained by using a benzene solution containing *p*-terphenyl as a scintillator solution and will discuss the role of charged species in the γ-ray induced luminescence. Hitherto, many investigations have been carried out on this scintillator solution, but most of the investigations have not paid any attention to the participation of charged species in the mechanism of the scintillation.

Experimental

Dotite Spectrosol benzene and scintillation-grade *p*TP supplied by the Nakai Chemical Co. were used without purification. Nitrous oxide, ammonia, sulfur hexafluoride, 1,3-butadiene, and carbon dioxide purchased from the Takachiho Trading Co. were used after bulb-to-bulb distillation. The cyclohexane was purified in a manner described previously.[1]

Figure 1 shows the arrangement of the apparatus for measuring the intensity of the luminescence from a solution. A Toshiba UV-31 filter was inserted between the solution vessel and a photomultiplier (Toshiba SY-99) in order to cut off the luminescence from benzene itself. The source of γ-rays was 1.3 mCi-^{60}Co sealed in a glass tube. As the UV light sources at 3100 Å and 2400—2600 Å, a Hitachi hydrogen discharge lamp and a Beckman monochromator were used. When we

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[1] Yoshida and S. Sato, This Bulletin, **40**, 2216 (1967). T. Saito, K. Takahashi and S. Sato, *ibid.*, **41**, 2603 (1968).

[2] J. W. Hunt and J. K. Thomas, *J. Chem. Phys.*, **46**, 2954 (1967); J. K. Thomas, K. Johnson, T. Klippert and R. Lowers, *ibid.*, **48**, 1608 (1968); R. Cooper and J. K. Thomas, *ibid.*, **48**, 5097 (1968).

[3] P. K. Ludwig, *Mol. Cryst.*, **4**, 147 (1968); P. K. Ludwig and M. M. Huque, *J. Chem. Phys.*, **49**, 805 (1968).

[4] R. R. Hentz and R. J. Knight, *J. Phys. Chem.*, **72**, 1783 (1968).

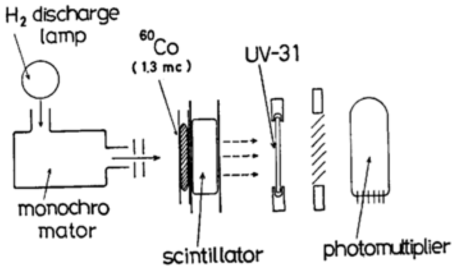

Fig. 1. Arrangement of the apparatus.

used the lights at 3100 Å, which excite only *p*TP molecules in a solution, the arrangement of the apparatus was changed so that the excitation beam could not directly enter the photomultiplier. When the UV lights used were in the 2400—2600 Å range and the apparatus was arranged as is shown in Fig. 1, essentially all the light impinging into the vessel was absorbed by benzene, since the concentration of *p*TP used in this experiment did not exceed 4.0×10^{-4} moll^{-1}, while the ratio of the optical density of benzene to that of *p*TP at 2400 Å was 250 : 1. In preparing the solutions, benzene containing a certain amount of *p*TP was degassed by freeze-and-thaw cycles in a mercury-free high-vacuum manifold. The concentration of an added gas in a solution was calculated by using the Ostwald absorption coefficient separately measured. The method of the measurement has already been described.[1] The Ostwald absorption coefficients in benzene obtained at 30°C were as follows: 2.7 for nitrous oxide, 0.67 for sulfur hexafluoride, 2.4 for carbon dioxide, and 7.5 for ammonia. 1,3-Butadiene was assumed to be completely soluble.

In order to ascertain the reactivity of electrons to nitrous oxide and sulfur hexafluoride in benzene, the *G*-value of the nitrogen from a benzene solution of nitrous oxide in the presence of sulfur hexafluoride was measured by using a method previously described.[5,6]

Results

Direct Excitation of *p*-Terphenyl. Figure 2 summarizes the effects of electron and positive ion scavengers and 1,3-butadiene on the luminescence from a cyclohexane solution of *p*-terphenyl when excited by light at 3100 Å. These experiments were carried out in order to establish whether or not any direct interaction between excited *p*TP and quenchers exists. Obviously, all the ion scavengers do not interact with the scintillating state of *p*TP, but 1,3-butadiene does a little, as was expected. The data obtained with 1,3-butadiene were well in accord with the Stern-Volmer relation (I):

$$I_0/I = 1 + \gamma[Q] \qquad \text{(I)}$$

The constant, γ, was obtained to be 0.68 $l\,\text{mol}^{-1}$. Here, [Q] denotes the concentration of the quencher.

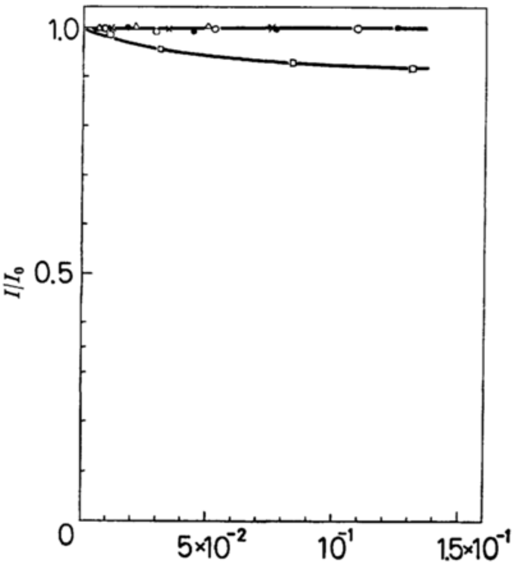

Fig. 2. Quenching curves obtained with a cyclohexane solution.
[*p*TP]$=10^{-5}$ mol l^{-1}, excited by 3100Å;
□, 1,3-butadiene; ●, NH_3; ×, CO_2; Δ, SF_6; ○, N_2O

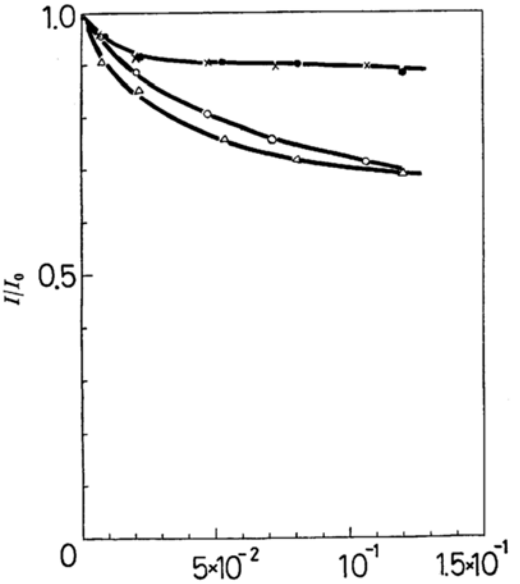

Fig. 3. Quenching by nitrous oxide.
[*p*TP]$=4.4\times10^{-3}$ mol l^{-1}, ○, excited by γ-rays; ×, excited by UV; [*p*TP]$=4.0\times10^{-4}$ mol l^{-1}; Δ, γ-rays; ●, UV

I and I_0 are the intensities of the luminescence in the presence and in the absence of the quencher respectively.

Quenching Efficiencies of Electron and Positive Ion Scavengers. In Fig. 3, the relative emission intensities from *p*TP-benzene solutions

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[5] S. Sato, R. Yugeta, K. Shinsaka and T. Terao, This Bulletin, **39**, 156 (1966).

[6] S. Sato, T. Terao, M. Kono and S. Shida, *ibid.*, **40**, 1818 (1967).

excited by light at 2500 Å and by γ-rays are plotted as a function of the nitrous oxide concentration. The concentrations of pTP used were 4.4×10^{-3} and 4.0×10^{-4} moll^{-1}. Here, two points should be noticed. First, the quenching ability of nitrous oxide under γ-rays is much greater than that under the UV lights. Second, the quenching ability does not depend much on the concentration of pTP.

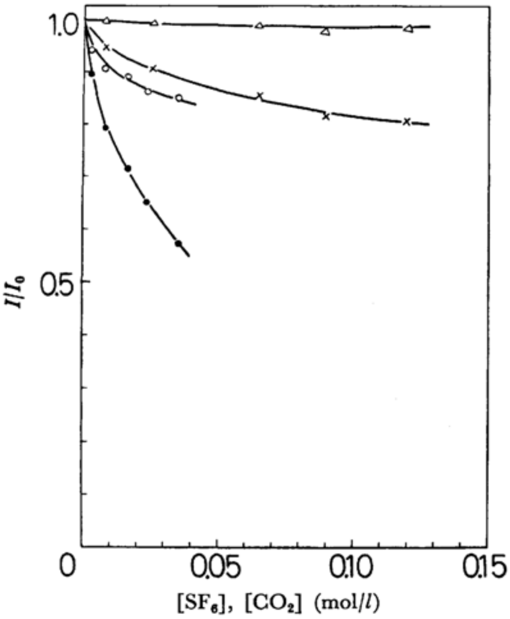

Fig. 4. Quenching by electron scavengers. [pTP]=4.0×10^{-4} mol l^{-1}; △, CO$_2$(UV); ×, CO$_2$(γ-rays); ○, SF$_6$(UV); ●, SF$_6$(γ-rays)

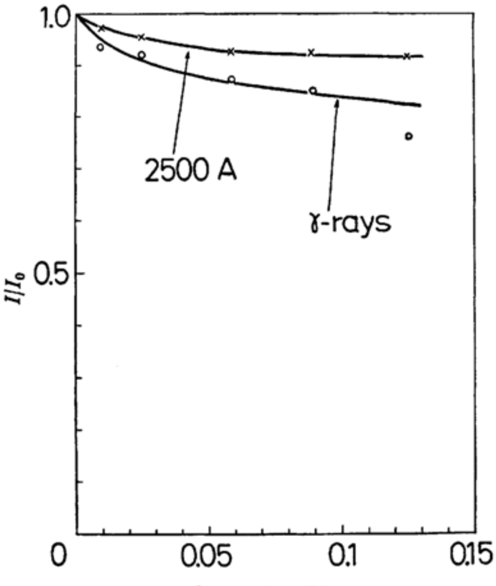

Fig. 5. Quenching by ammonia. [pTP]=4.0×10^{-4} mol l^{-1}, ×, UV, ○, γ-rays

Similar experiments were also carried out using sulfur hexafluoride, carbon dioxide, and ammonia in place of nitrous oxide. The results are shown in Figs. 4 and 5. Obviously, the quenching abilities are in the following order: sulfur hexafluoride, nitrous oxide, carbon dioxide, and ammonia. All these quenchers are more effective under γ-rays than under UV light. Although the only UV lights used here were at 2500 Å, exactly the same quenching curves for each quencher were obtained by using the wavelengths of 2400 and 2600 Å.

Quenching by 1,3-Butadiene. Figure 6 shows the relative emission intensity as a function of the concentration of 1,3-butadiene. The quenching curves obtained under UV light and under γ-rays practically coincide with each other. This coincidence contrasts with the results obtained by using ion scavengers as the quencher.

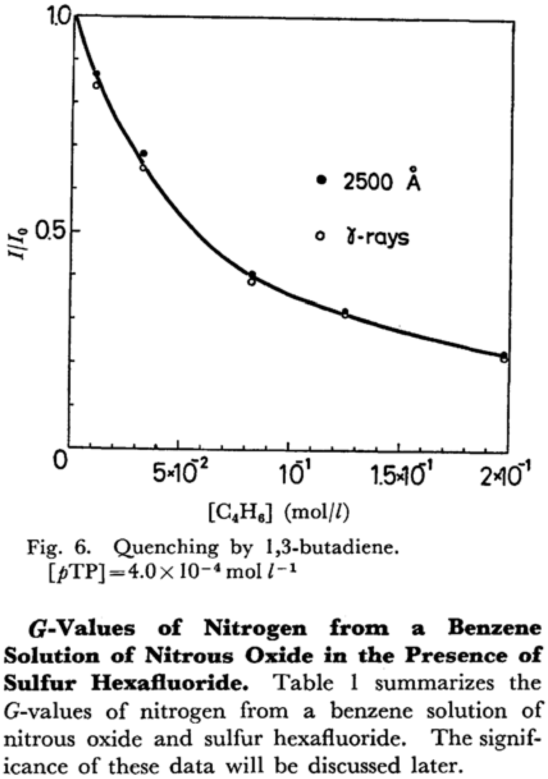

Fig. 6. Quenching by 1,3-butadiene. [pTP]=4.0×10^{-4} mol l^{-1}

G-Values of Nitrogen from a Benzene Solution of Nitrous Oxide in the Presence of Sulfur Hexafluoride. Table 1 summarizes the G-values of nitrogen from a benzene solution of nitrous oxide and sulfur hexafluoride. The significance of these data will be discussed later.

TABLE 1. EFFECT OF SULFUR HEXAFLUORIDE ON $G(N_2)$ FROM A BENZENE SOLUTION OF NITROUS OXIDE

N$_2$O mol l^{-1}	SF$_6$	$G(N_2)$
0.34	0	2.5
0.33	0.011	2.3
0.35	0.027	2.0
0.37	0.15	1.1
0.36	0.35	0.84
0.37	0.59	0.57

Discussion

As is shown in Fig. 2, ion scavengers did not interact with the scintillating state of *p*TP in the range of the concentrations of *p*TP and scavengers studied. On the other hand, these scavengers did quench the luminescence induced by UV at 2500 Å, although they were not strong. The quenching by carbon dioxide was practically negligible. Since the excitation energies of these scavenger molecules are not smaller than that of the $^1B_{2u}$ state of benzene, the simple energy-transfer mechanism cannot be used in the interpretation. One possible mechanism is that involving the formation of a charge-transfer complex between an excited benzene molecule and an ion scavenger molecule in the process. Since the quenching effects were not strong, the participation of impurities cannot be excluded.

When the excitation was made by γ-rays, the quenching effects of ion scavengers became prominent, as is shown in Figs. 3, 4, and 5. Even carbon dioxide showed the effect. This compound is now known as an electron scavenger in radiation chemistry.⁶⁾ These quenching effects may, therefore, be attributed to the interference of ion scavengers in the ionic process by which the scintillating state of *p*TP is formed. There are two possible mechanisms for such interference. One (Mechanism 1) is the competition between *p*TP and ion scavengers for the charged species produced in the system. This mechanism satisfactorily explains the quenching effect of ion scavengers in a *p*TP-cyclohexane scintillator.¹⁾ If this mechanism plays a major role in the quenching, a strong dependence on the concentration of *p*TP should be observed, as has actually been observed in a *p*TP-cyclohexane scintillator. The other mechanism (Mechanism 2) is the interference of ion scavengers in the ionic process by which excited benzene is formed. This reaction scheme may be described as follows:

$$B \rightsquigarrow B^+ + e_B \qquad (8)$$

$$B \rightsquigarrow B^* \qquad (9)$$

$$B^+ + e_B \rightarrow B^* \qquad (10)$$

$$e_B + S \rightarrow S^- \qquad (11)$$

$$B^+ + S \rightarrow B + S^+ \qquad (12)$$

$$B^+ + S^- \rightarrow B + S \qquad (13)$$

$$B^* + T \rightarrow B + T^* \qquad (14)$$

Here, B, S, and T denote, respectively, benzene, scavenger, and *p*-terphenyl molecules. The suffix B is attached to the electron e, in order to indicate that the electron is in benzene. If this mechanism is operative, the quenching curves should not depend strongly on the concentration of *p*TP, but this was actually observed. This discrimination, however, is not conclusive. Another support for Mechanism 2 will be given later.

Regardless of the mechanism of the interference of ion scavengers in the ionic processes occurring in the system, the quenching curves obtained under γ-ray irradiation suggest that a large part of the luminescence results from the ionic reactions. Since the luminescence from UV-irradiated benzene solutions was quenched by ion scavengers, as is shown in Figs. 3 and 4, the following tentative correction was made in an attempt to visualize the purely ionic effects of ion scavengers:

$$(I/I_0)_{\text{corr}} = (I/I_0)_\gamma / (I/I_0)_{\text{UV}} \qquad \text{(II)}$$

Here, the subscripts γ and UV denote γ-ray and UV irradiations respectively. The results are plotted in Fig. 7. If sulfur hexafluoride behaves only as an electron scavenger, the corrected curve indicates that more than 30% of the excited benzene, which is the precursor of the scintillation, is formed by an ionic reaction, probably the recombination reaction between benzene cations and electrons.

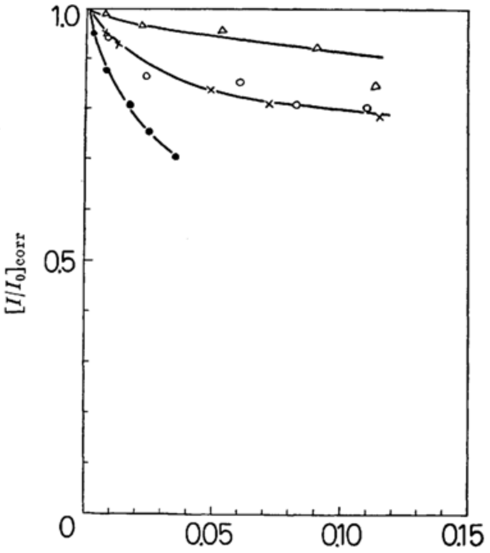

Fig. 7. $[I/I_0]_{\text{corr}}$ as a function of the concentrations of ion scavengers.
△, NH_3; ×, N_2O; ○, CO_2; ●, SF_6

According to Fig. 7, the electron-scavenging ability of sulfur hexafluoride is stronger than those of nitrous oxide and carbon dioxide. In cyclohexane solutions, however, the abilities were estimated to be almost the same for these three scavengers.⁶⁾ In order to interpret this discrepancy, we have measured the *G*-values of nitrogen from a benzene solution of nitrous oxide in the presence of various amounts of sulfur hexafluoride. The results are shown in Table 1. If a simple relation (III) is applicable to these data:⁶⁾

$$\frac{1}{G(N_2)} = \frac{1}{G_0(N_2)}\left(1 + k\frac{[SF_6]}{[N_2O]}\right) \qquad \text{(III)}$$

the slope k should show the ratio of the rate constant of the reaction of electrons with sulfur hexafluoride to that with nitrous oxide. As is shown in Fig. 8,

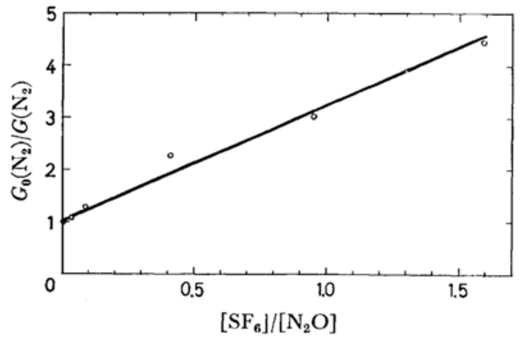

Fig. 8. Dependence of $G(N_2)$ on the concentration of sulfur hexafluoride.

a linear relationship has been obtained and the slope k has been calculated to be 2.2; this value should be compared with that of 1.0 obtained in a cyclohexane solution.⁶⁾ This difference qualitatively explains the difference between the two quenching curves obtained with sulfur hexafluoride and nitrous oxide. Electrons in benzene may be solvated more strongly than those in cyclohexane. This is not unreasonable, since aromatic hydrocarbons larger than benzene, such as naphthalene and biphenyl, are known to capture electrons to form anions.⁷⁾ Therefore, the reaction between electrons and electron scavengers in benzene may not be diffusion-controlled.

The quenching curves obtained with 1,3-butadiene are shown in Fig. 6. In the case of UV excitation, the species being quenched must be the $^1B_{2u}$ state of benzene.⁸⁾ If the ion-molecule reaction between the benzene cation and 1,3-butadiene is important in the present system, the quenching curve obtained by γ-ray irradiation should deviate from the curve obtained by UV irradiation, because the benzene cation must be the precursor of the $^1B_{2u}$ state of benzene and both the cation and the excited state of benzene are subject to the interference of 1,3-butadiene. The coincidence of the two quenching curves strongly suggests, therefore, that most of the benzene cations produced in the system are neutralized before the ion-molecule reaction with 1,3-butadiene occurs. In other words, Mechanism 2 is at least predominant in this system over Mechanism 1. However, a detailed inspection reveals that the quenching ability of 1,3-butadiene under γ-rays is a little stronger than that under UV light. This suggests that the participation of Mechanism 1 cannot be excluded conclusively. Recently, the G-value of "free electrons" in benzene has been measured as 0.053 by the conductivity method.⁹⁾ These electrons must contribute to the scintillation by the formation of p-terphenyl anions (Mechanism 1).

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7) S. Arai and L. M. Dorfman, *J. Chem. Phys.*, **41**, 2190 (1964).

8) A. Morikawa and R. J. Cvetanović, *ibid.*, **49**, 1214 (1968).

9) W. F. Schmidt and A. O. Allen, *J. Phys. Chem.*, **72**, 3730 (1968).