The Radiophoto-luminescence of γ-Irradiated Hydrocarbon Glasses at 77 K

Hideo Yamazaki, Koichi Oka, Masabumi Sato, and Shoji Shida
Laboratory Physical Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo 152

(Received March 9, 1973)

The radiophoto-luminescence (RPL) from γ-irradiated hydrocarbon glasses, *i.e.*, 3-methylhexane, methylcyclohexane, and ethylcyclohexane, containing small amounts of various aromatics (1,3,5-trimethylbenzene, biphenyl, naphthalene, and 1,4-diazine) is investigated at 77 K by infrared-light irradiation. The spectra of the RPL consist of the fluorescence and phosphorescence of the guest aromatic molecule, and the ratio of the phosphorescence to the fluorescence intensity is larger than that in the photoexcitation, indicating the existence of another path to the triplet state. The RPL is quenched by the addition of N_2O, but it is not much affected by that of NH_3. A possible mechanism for the RPL is considered, and its analysis is given.

In the primary process of the radiation chemistry of hydrocarbons, the mechanism of neutralization is not quite understood because of the rapidity of the process. The rigid-solvent method has been used to slow down the reaction rate and to facilitate the measurements. The radiation energy stored in a rigid matrix can be liberated by means of several methods; elevation of temperature[1,2] (radiothermo-luminescence), irradiation by infrared light[3-6] (radiophoto-luminescence, RPL), and application of an electric field.[7-10] The control of the luminescence intensity is easiest in RPL, and the relaxation time of emission can be measured from the response time of the luminescence by intermittent irradiation of infrared light, so the RPL is used in this study. Hamill *et al.*[3,4] have measured the RPL from biphenyl in a 3-methylpentane solution and obtained a rather diffused spectrum of the phosphorescence of biphenyl by rapid scanning with an oscilloscope. Magat *et al.*[5,6] studied the RPL spectrum of biphenyl and its excitation spectrum in a methylcyclohexane solution. In their measurement of the excitation spectrum, a filter was used to pass through the whole wavelength of the phosphorescence. A more precise experiment is necessary, however, to obtain detailed information.

Experimental

Hydrocarbon samples purchased from Merck, Aldrich Chemical, and the Phillips Co. were passed through an activated silica gel column and then outgassed by the freeze-pump method and stored with a sodium mirror. The biphenyl and naphthalene were purified by the zone-melting method. The 1,4-diazine and 1,3,5-trimethylbenzene (Merck and Tokyo Kasei Co.) were used without further purification. The sample tubes used were made of high-purity quartz or of molybdenum glass; the dimension of diameters are 5 and 10 mm. After degassing *in vacuo*, the samples were irradiated by γ-rays from ^{60}Co with total doses of 10^4—10^5 r at 77 K in darkness. The spectra of RPL were measured with a Hitachi MPF-2A fluorometer, the intensity of emission was standardized by using the data of emission from β-naphthol in photoexcitation.[11] The sample was irradiated by diffracting infrared light of the zeroth order through a grating from a light source of a 150 W Xe-lamp equipped with Toshiba IR-D1A and VB-46 filters. The average intensity of emission was used to obtain a spectrum by repeating the forward and backward scanning, since the intensity of emission decreased slowly as the concentration of trapped electrons decreased.

Results and Discussion

The RPL spectra of 3-methylhexane, methylcyclohexane, and ethylcyclohexane (3-MHX, MCHX, and ECHX) showed a weak and broad spectrum with a maximum at about 420 nm; the response time of the emission by the infrared light was several seconds, so it is likely that the emission is due to the transition of a different spin multiplicity. Such a diffuse emission spectrum was also observed in the RTL and RPL of 3-methylpentane.[12,13] The low-lying electronic states of saturated hydrocarbons have been observed by Hamill in a solid matrix with the energy-loss spectrum[14] of electrons and with the emission spectrum upon electron impact.[15,16] When small amounts of aromatic hydrocarbons (10—100 ppm) were added to these solvents, distinct fluorescence and phosphorescence of aromatic hydrocarbons were observed. Figure 1 shows the relaxation of the phosphorescence at 465 nm from biphenyl in 3-MHX due to the intermittent irradiation of infrared light. The relaxation time is determined by the lifetime of the phosphorescence, and the intensity of the emission decreases slowly as the concentration of trapped electrons in the matrix decreases. Figures 2—4 show the emission (solid curves) of fluorescence and phosphorescence with reference to those (dotted curves) of the photoexcitation in the ultraviolet region. In these figures the maximum values of the intensities of the fluorescence for both cases were standardized as unity. No appreciable difference in the spectrum was observed with the change

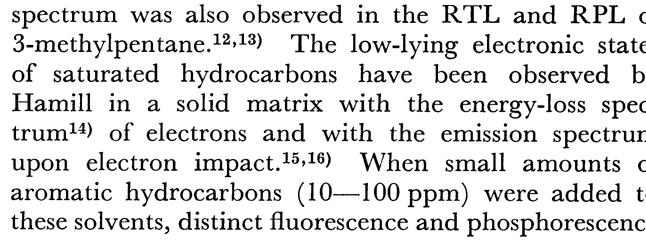

Fig. 1. Response of the emission at 465 nm from biphenyl in 3-MHX at 77 K by the intermittent irradiation of infrared light. The interval between "on" and "off" is 30 s in the time scale.

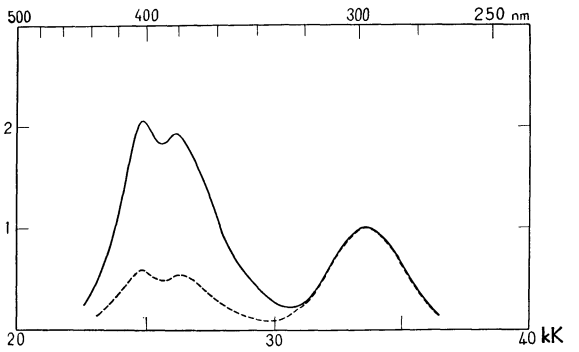

Fig. 2. RPL (full curve) and photoexcited emission (dotted curve) from 1,3,5-trimethylbenzene in 3-MHX at 77 K.

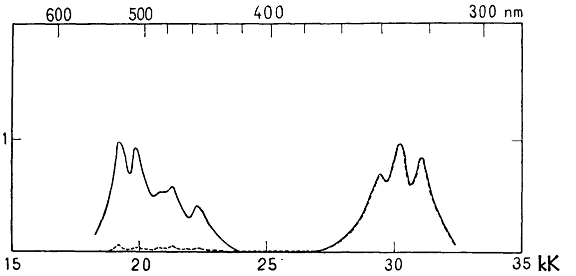

Fig. 3. RPL (full curve) and photoexcited emission (dotted curve) from naphthalene in 3-MHX at 77 K.

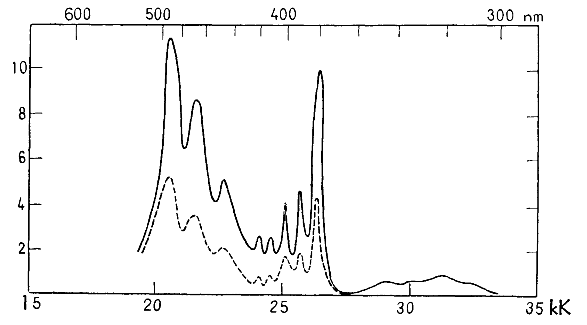

Fig. 4. RPL (full curve) and photoexcited emission (dotted curve) from the one-to-one mixture of 1,4-diazine and biphenyl in 3-MHX at 77 K.

in the solvents (3-MHX, MCHX, and ECHX). The ratio of the intensity of the phosphorescence to the fluorescence was larger in the case of RPL than in that of photoexcitation as observed by a number of authors.[12,17,18] The ratio of the phosphorescence and fluorescence depends on the sample. A very large relative intensity of phosphorescence was observed in a naphthalene solution, as is shown in Fig. 3. The proportion of phosphorescence in the total emission gradually changed upon prolonged irradiation by infrared light. The dilute solution of a one-to-one mixture of two aromatic compounds generally showed the phosphorescence of each component with a certain ratio of intensity; *e.g.*, the ratio of the intensity of the phosphorescence of a one-to-one mixture of 1,4-diazine and biphenyl in 3-MHX was about 1 : 4 (Fig. 4). The ratio of the intensities of the component fluorescences from such a solution depended on the concentration, since the ratio was much perturbed by the energy-transfer process. The RPL was quenched by the addition of an electron scavenger such as N_2O, as was observed in the emission due to a recombination process after photoionization,[19—21] but it was not much affected by the addition of NH_3, which was used as a positive-charge scavenger in the liquid phase.

The emission process must be followed by the excitation of aromatic compounds. The production of the excited states of aromatic compounds is expressed by the following scheme:

$$e_t^- \xrightarrow{h\nu} e_m^- \qquad (1)$$

$$RH^+ + e_m^- \longrightarrow RH^* \qquad (2)$$

$$RH^* + RH \longrightarrow RH + RH^* \qquad (3)$$

$$RH^* \longrightarrow RH + h\nu \qquad (4)$$

$$RH^* + A \longrightarrow RH + A^* \qquad (5)$$

where e_t^- and e_m^- are the trapped and mobilized electrons and where RH and A refer to the hydrocarbon and aromatic molecules. By the absorption of infrared light, the trapped electrons are mobilized by means of Reaction (1).

$$RH^+ + A^- \longrightarrow RH + A^* \qquad (6)$$

$$A^+ + A^- \longrightarrow A^* + A \qquad (7)$$

$$A^+ + e_m^- \longrightarrow A^* \qquad (8)$$

$$A^* \longrightarrow A + h\nu' \qquad (9)$$

The geminate and random recombination can produce RH* by means of Reaction (2), and the energy migration may take place in solid hydrocarbon, as is expressed by Reaction (3). In the absence of an aromatic compound, a weak emission at 420 nm was detectable; this may be attributed to Reaction (4). In the presence of aromatic additives, the excited states of the aromatic molecule, A*, can be produced by the energy-transfer reaction (5), the ionic neutralizations (6) and (7), and the recombination of A^+ with an electron by means of Reaction (8).

Three types of direct excitations of aromatic molecule are considered, namely, the excitation by the reaction between A^+ and an electron (8), that by A^- and RH^+ (6), and that by A^+ and A^- (7). From the experimental results that the mobilities of A^-, A^+, and RH^+ are not large and that the excitation spectrum of the RPL is similar to the absorption spectrum of a trapped electron,[5] the process involving the transport of these species (A^-, A^+, and RH^+) can be ignored. The neutralization between A^+ and an electron is not important under the present condition of a low concentration (10—100 ppm) of A, because A^+ can be detected only at high concentrations of aromatic additives in hydrocarbon matrices. Therefore, the indirect excitation by the energy transfer from RH* produced by the neutralization between RH^+ and electron is most probable in forming A*. Such an energy transfer from the excited states of paraffins to additives was observed by the measurement of the emission[16] and by the method of product analysis[22,23] in the vacuum ultraviolet photolysis of liquid paraffins. This explanation is consistent with the experimental result that the RPL is quenched by the addition of an electron scavenger and not much affected by the addition of a positive-charge scavenger.

Apart from the detailed mechanism of the excitation, the aromatic molecule can be excited to the singlet- or triplet-excited state by the liberation of a trapped electron. The process can be symbolically written by Reactions (10) and (11). Therefore, the emission process from the transition of these excited states is described by the following reactions:

$$\begin{array}{llll}
\mathrm{A} \longrightarrow \mathrm{A}^*(\text{singlet}) & & k_\mathrm{s} & (10)\\
\mathrm{A} \longrightarrow \mathrm{A}^*(\text{triplet}) & & k_\mathrm{t} & (11)\\
\mathrm{A}^*(\text{singlet}) \longrightarrow & \mathrm{A} + h\nu_\mathrm{f} & k_\mathrm{f} & (9')\\
\mathrm{A}^*(\text{triplet}) \longrightarrow & \mathrm{A} + h\nu_\mathrm{p} & k_\mathrm{p} & (9'')\\
\mathrm{A}^*(\text{singlet}) \longrightarrow & \mathrm{A}^*(\text{triplet}) & k_\mathrm{isc} & (12)\\
\mathrm{A}^*(\text{singlet}) \longrightarrow & \text{A or products} & \sum k_\mathrm{x} & (13)\\
\mathrm{A}^*(\text{triplet}) \longrightarrow & \text{A or products} & \sum k_\mathrm{y} & (14)
\end{array}$$

where k_s, k_t, k_f, k_p, k_isc, $\sum k_\mathrm{x}$, and $\sum k_\mathrm{y}$ are the rate constants for the production of the singlet state and for the triplet state, for the emission of fluorescence and of phosphorescence for the intersystem crossing, for reactions from the singlet state and for reactions from the triplet state respectively.

From Reactions (9′), (9″), (10)—(14), the intensity ratio between the fluorescence and the phosphorescence (*F*/*P* value) in the electron-recombination process can be evaluated by:

$$\sigma_\mathrm{e} \equiv (F/P)_\mathrm{e} = \frac{k_\mathrm{f}k_\mathrm{s}(k_\mathrm{p}+\sum k_\mathrm{y})}{(k_\mathrm{s}k_\mathrm{isc}+k_\mathrm{t}k_\mathrm{f}+k_\mathrm{t}k_\mathrm{isc}+k_\mathrm{t}\sum k_\mathrm{x})k_\mathrm{p}} \qquad [1]$$

In the photoexcitation by the first singlet-excited state, the *F*/*P* value is given by:

$$\sigma_\mathrm{h} \equiv (F/P)_\mathrm{h} = \frac{k_\mathrm{f}(k_\mathrm{p}+\sum k_\mathrm{y})}{k_\mathrm{isc}k_\mathrm{p}} \qquad [2]$$

The ratio of the initial distribution of the singlet state to the triplet state of the aromatic molecule is given by:

$$\rho = (k_\mathrm{s}/k_\mathrm{t}) = \frac{\sigma_\mathrm{e}\sigma_\mathrm{h}k_\mathrm{p}/(k_\mathrm{p}+\sum k_\mathrm{y})+\sigma_\mathrm{e}+\sigma_\mathrm{e}\sum k_\mathrm{x}/k_\mathrm{isc}}{\sigma_\mathrm{h}-\sigma_\mathrm{e}} \qquad [3]$$

Under the conditions of $\sum k_\mathrm{x}=0$ and $\sum k_\mathrm{y}=0$, the *F*/*P* values, σ_e and σ_h, are reduced to:

$$\sigma_\mathrm{e} = \frac{k_\mathrm{f}(k_\mathrm{s}/k_\mathrm{t})}{k_\mathrm{isc}(k_\mathrm{s}/k_\mathrm{t})+k_\mathrm{f}+k_\mathrm{isc}} \qquad [4]$$

and:

$$\sigma_\mathrm{h} = k_\mathrm{f}/k_\mathrm{isc} \qquad [5]$$

Then, the singlet-triplet ratio is expressed by:

$$\rho = k_\mathrm{s}/k_\mathrm{t} = (\sigma_\mathrm{h}\sigma_\mathrm{e}+\sigma_\mathrm{e})/(\sigma_\mathrm{h}-\sigma_\mathrm{e}) \qquad [6]$$

In Eq. [3] the increase in $\sum k_\mathrm{x}$ may cause the increase in ρ, but the increase in $\sum k_\mathrm{y}$ may cause the decrease in ρ. If both the values $\sum k_\mathrm{x}$ and $\sum k_\mathrm{y}$ increase from zero in Eq. [3], the value of ρ will not change much from the value of ρ given by Eq. [6]. Thus, Eq. [6] is still a plausible approximation for the small values of $\sum k_\mathrm{x}$ and $\sum k_\mathrm{y}$. For example, the values of ρ calculated from the spectra (Figs. 2 and 3) and assuming Eq. [6] are 0.93 and 1.0 for 1,3,5-trimethylbenzene and naphthalene respectively in 3-MHX. These results indicate that the values of k_t and k_s are almost equal. However, the value of k_t would be expected to be three times larger than that of k_s if the triplet and singlet states are produced by random recombination with the spin conservation. The departure from the statistical value in the ρ value may be another evidence of indirect excitation. Recently Tsubomura *et al.*[24] found that the *F*/*P* value was 0.7—0.8 for the photothermoluminescence of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylene diamine in various matrices and that the *F*/*P* value was approximately equal to the ratio of the production of singlet and triplet states, therefore, the simple spin conservation rule does not hold in their case, either.

The authors wish to thank Professor Hiroshi Tsubomura, Drs. Naoto Yamamoto and Yoshihiro Nakato of Osaka University for reading the preliminary manuscript of this paper and for their helpfull discussions.

References

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

2) M. Burton, M. Dillon, and R. Rein, *J. Chem. Phys.*, **41**, 2228 (1964).

3) D. W. Skelly and W. H. Hamill, *ibid.*, **43**, 3497 (1965); **44**, 2891 (1966).

4) W. H. Hamill, "Ion Radicals," E. T. Kaiser, and L. Keran, ed., John Wiley, New York (1968), p. 383.

5) A. Deroulede, F. Keiffer, and M. Magat, *Advan. Chem. Ser.*, **82**, 401 (1968).

6) M. Magat, "Progress and Problems in Contemporary Radiation Chemistry," Prague (1971), p. 423.

7) A. C. Albrecht, *ibid.*, p. 331.

8) G. H. Johnson, W. M. McCain, and A. C. Albrecht, *J. Chem. Phys.*, **43**, 2911 (1965).

9) J. Bullot and A. C. Albrecht, *Acta Phys. Polon.*, **34**, 691 (1968).

10) J. Bullot and A. C. Albrecht, *J. Chem. Phys.*, **51**, 2220 (1969).

11) E. Lippert, W. Nägele, I. Seibold-Blankenstein, V. Staiger, and W. Voss, *Z. Anal. Chem.*, **170**, 1 (1959).

12) K. Funabashi, C. Hebert, and J. L. Magee, *J. Phys. Chem.*, **75**, 3221 (1971).

13) P. B. Merkel and W. H. Hamill, *J. Chem. Phys.*, **53**, 3414 (1970).

14) L. M. Hunter, D. Lewis, and W. H. Hamill, *ibid.*, **52**, 1733 (1970).

15) P. B. Merkel and W. H. Hamill, *ibid.*, **54**, 1695 (1971).

16) F. Hirayama and S. Lipsky, *ibid.*, **51**, 3616 (1969).

17) D. S. Klinger, J. D. Laposa, and A. C. Albrecht, *ibid.*, **48**, 4326 (1968).

18) N. Yamamoto, Y. Nakato, and H. Tsubomura, This Bulletin, **39**, 2603 (1966).

19) K. Yoshinaga, N. Yamamoto, M. Ozaki, and H. Tsubomura, *Nippon Kagaku Zasshi*, **92**, 124 (1971).

20) K. Yoshinaga, N. Yamamoto, and H. Tsubomura, *J. Luminescence*, **4**, 417 (1971).

21) K. D. Cadogan and A. C. Albrecht, *J. Phys. Chem.*, **72**, 929 (1968).

22) H. A. Holroyd, *Adv. Chem. Ser.*, **82**, 488 (1968).

23) V. I. Pitchoozhkin, H. Yamazaki, and S. Shida, This Bulletin, **46**, 67 (1973).

24) K. Yoshinaga, N. Yamamoto, and H. Tsubomura, *J. Luminescence*, **6**, 179 (1973).