Donor–Acceptor Interactions in the Ground State of the Systems Forming Heteroexcimers in the Excited State

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Several systems which form heteroexcimers in the excited state were forced to aggregate in low temperature rigid matrices, and their absorption, fluorescence excitation and emission as well as fluorescence rise and decay curves were determined. The results indicate the existence of several kinds of donor–acceptor pairs emitting heteroexcimer fluorescence at different wavelengths. Temperature dependence of absorption spectra of those systems in liquid solutions were examined, and collisional enhancement of the absorption intensity was observed.

Numerous investigations have been carried on the heteroexcimer formation between excited singlet aromatic hydrocarbons and various ground state amines or cyano compounds. However, spectroscopic studies of the charge transfer (CT) interaction in the ground state of the heteroexcimer forming systems are scarce. Since there is no observable absorption corresponding to the excimer or heteroexcimer emission, studies on these systems have been made nearly always in a liquid state where the exciplexes are formed by diffusional encounter between the excited and ground state partners.

For a study of the electronic processes in exciplexes at low temperatures, it would be advantageous to find a matrix of a saturated hydrocarbon having adjacent sites with orientations favorable for the formation of excimer or heteroexcimer. The phenomenon of association of pyrene or anthracene molecules was found first in a cyclohexane matrix and in 3 : 1 softened glasses of isopentane and methylcyclohexane (MP) by Ferguson,[1,2] detailed spectral studies on the dimer aggregates of aromatic hydrocarbons in the rigid matrices at low temperature being carried out.[2,3] By using the same technique, we found for the first time that the solutions of pyrene and aromatic amines in cyclohexane matrix show heteroexcimer fluorescence in addition to that of pyrene monomer at various temperatures.[4]

Concerning the ground state interactions of heteroexcimer forming systems, Itoh *et al.* have recently reported their studies on dicyanoanthracene–naphthalene system at various temperatures,[5] while Yoshihara *et al.* have examined the ground state absorption spectra of concentrated solutions of pyrene–*N*,*N*-dimethylaniline (DMA) system.[6] Ishida and Tsubomura suggested the existence of the CT absorption band due to the interaction between anthracene and various aliphatic amines adsorbed on a porous glass.[7]

In order to elucidate the CT interactions in the ground state of heteroexcimer forming systems, we have made detailed studies on the absorption, excitation, and emission spectra as well as fluorescence rise and decay curves of some systems in low temperature matrices. We have also measured the absorption spectra at various temperatures in liquid solution in order to examine the collisional CT interactions in these systems. The results are given in the following.

Experimental

Absorption spectra of rigid solutions at low temperature were measured with a Shimadzu MPS-50L spectrophotometer and those of liquid solutions with a Cary 15 spectrophotometer. Fluorescence spectra were measured with an Aminco-Bowman spectrophotofluorometer calibrated by means of a standard tungsten lamp. Excitation spectra were measured with a Nalumi RM 20-G spectrometer equipped with a 600 grooves/mm grating and a 500 W xenon lamp as a light source. Fluorescence was passed through a Bausch & Lomb high intensity monochromator and detected with a 1P28 photomultiplier. The fluorescence rise and decay curves were determined on an apparatus composed of a Bausch & Lomb high intensity monochromator, 1P28 or HTV-R213 photomultiplier, Tektronix 661 sampling oscilloscope, and a pulsed nitrogen gas laser.

Pyrene, anthracene, perylene, DMA, *N*,*N*-diethylaniline (DEA) and *N*,*N*-dimethyl-*p*-toluidine (*p*-DMT) were purified by the same method as reported.[8] Tributylamine[9] and 1,2,4,5-tetracyanobenzene (TCNB)[10] were also the same as before. 1-(2-or 9-anthryl)-3-(*p*-*N*,*N*-dimethylaminophenyl)-propane(2-or 9-A–$(CH_2)_3$–DMA) was supplied by Professor S. Misumi of this University. Spectrograde hexane, cyclohexane, methylcyclohexane, toluene and tetrahydrofuran (THF) were used without further purification. Isopentane and chlorobenzene were purified by the usual method.[11] All the solutions were carefully deareated by freeze-pump-thaw cycles.

The temperature of the sample was measured with a thermocouple placed on the sample tube. A thin quartz cell with 1 mm optical path was used for measuring the absorption spectra in cyclohexane matrix.

Results and Discussion

Interactions between Electron Donor and Acceptor in Low Temperature Matrices. The temperature dependence of the absorption spectrum of perylene (5×10^{-5} M)–DMA (2×10^{-3} M) system in cyclohexane is shown in Fig. 1. The dotted curve gives the absorption spectrum of perylene dimer observed in the cyclohexane matrix at 173 K, agreeing with that reported by Ferguson.[2] The absorption spectrum shows a gradual red shift and broadening with the lowering in temperature. A similar temperature dependence of the absorption spectrum was observed in the system of pyrene (2×10^{-5} M)–DEA (1×10^{-4} M) in cyclohexane (Fig. 2).

On the other hand, the absorption spectra of pyrene–aliphatic amine (triethylamine or tributylamine) systems in cyclohexane matrix were essentially the same as those of solution at room temperature, *i.e.* of pyrene. In the case of anthracene–DMA and DEA systems, no appreciable change of absorption band arising from the interaction between donor and acceptor was observed but the absorption spectra of stable dimer and higher aggregates of anthracene[3] were detected.

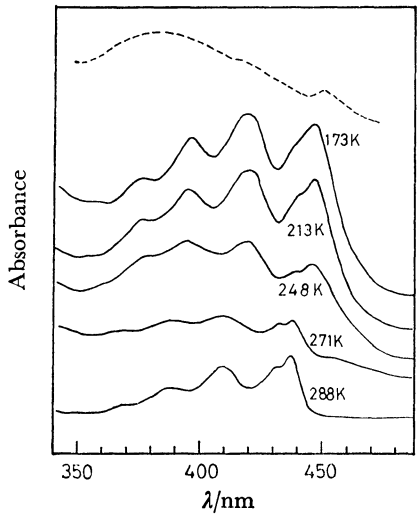

Fig. 1. Temperature dependence of the absorption spectrum of perylene (5×10^{-5} M) – DMA (2×10^{-3} M) system in cyclohexane. The dotted spectrum represents the absorption spectrum of perylene dimer observed at 173 K.

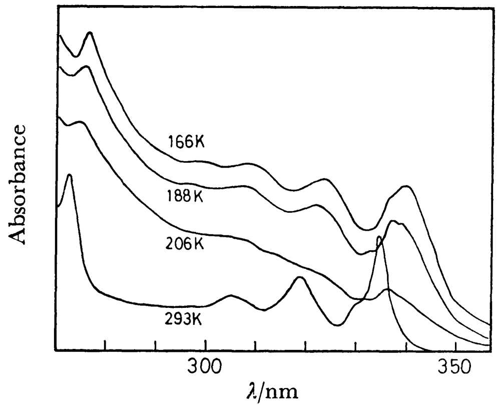

Fig. 2. Temperature dependence of the absorption spectrum of pyrene (2×10^{-5} M)-DEA (1×10^{-4} M) system in cyclohexane.

It was found that the dimer formation was a dominant process even in the case of pyrene or perylene solution with concentrations greater than 10^{-4} M in cyclohexane.

The excitation spectrum of the heteroexcimer fluorescence of the pyrene–DEA system monitored at 460 nm and that of the pyrene fluorescence monitored at 400 nm are shown in Fig. 3. The former is broadened and shifted to red as compared with the latter, similar to the absorption spectrum at low temperatures. The excitation spectrum of pyrene fluorescence is essentially the same as the absorption spectrum in solution at room temperature. In the system of high concentration of DEA (1×10^{-2} M), only the heteroexcimer fluorescence was observed throughout from room temperature to 77 K, the maximum of the excitation spectrum being observed at 342 nm in low temperature matrix as shown in Fig. 3. The same result was obtained in the case of the pyrene–DMA system. The broad excitation spectrum cannot be ascribed to the pyrene dimer since it differs notably from that of the pyrene excimer in low temperature cyclohexane matrix.[12]

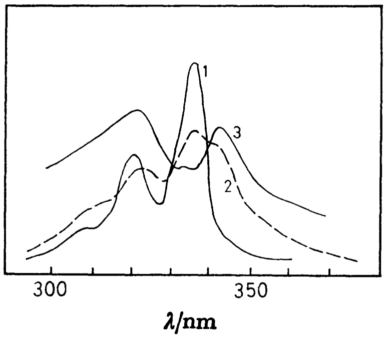

Fig. 3. Excitation spectra of pyrene-DEA system in cyclohexane matrix.
(1): [Pyrene] = 2×10^{-5} M, [DEA] = 10^{-4} M, monitored at 400 nm.
(2): [Pyrene] = 2×10^{-5} M, [DEA] = 10^{-4} M, monitored at 460 nm.
(3): [Pyrene] = 2×10^{-5} M, [DEA] = 10^{-2} M, monitored at 460 nm.

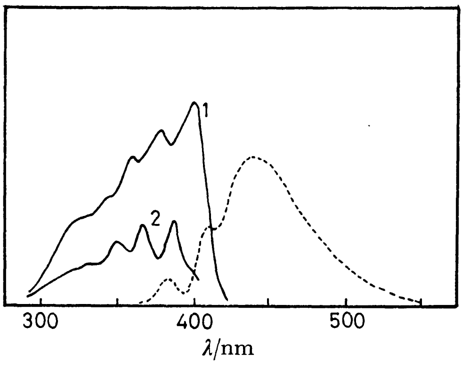

Fig. 4. Fluorescence (dotted) and excitation spectra of 2-A-$(CH_2)_3$-DMA in MP at 77 K monitored at 470 nm (1) and 400 nm (2).

Another clear-cut example of the ground state donor–acceptor interaction is the system of 2-A–$(CH_2)_3$–DMA in MP solution. The fluorescence and excitation spectra at 77 K are shown in Fig. 4. The excitation spectrum of the heteroexcimer fluorescence and that of the fluorescence from the anthracene part showed good correspondence with the absorption spectra at 77 K and room temperature, respectively.

The nature of the electronic transition responsibe for the excitation spectrum of the heteroexcimer fluorescence is not very clear at the present stage of the investigation. However, it seems that a loosely bound pair of donor and acceptor is formed in the low temperature matrix, the red shift of the absorption spectrum of which might be ascribed to the interaction between the locally excited state of the acceptor and the CT state which is situated higher than the former. When this donor–acceptor pair is excited by light absorption there occur some displacements of molecules in the pair leading to the heteroexcimer (CT state) formation.

Rise and Decay Curves of Heteroexcimer Fluorescence. In the systems described above, the rise curve of the heteroexcimer fluorescence in low temperature matrix was the same as the time-integrated function of exciting ns light pulse. This suggests that some stable

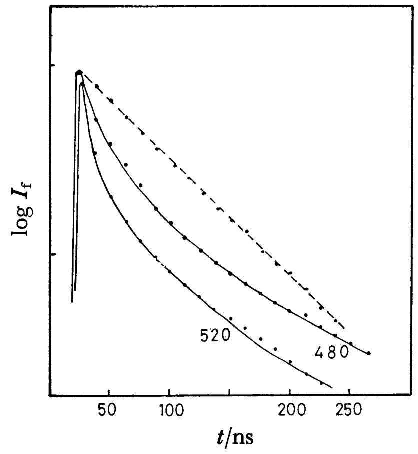

Fig. 5. Fluorescence decay curves of pyrene (1×10^{-5} M)−DEA (1×10^{-4} M) system in cyclohexane matrix at 196 K. See text.

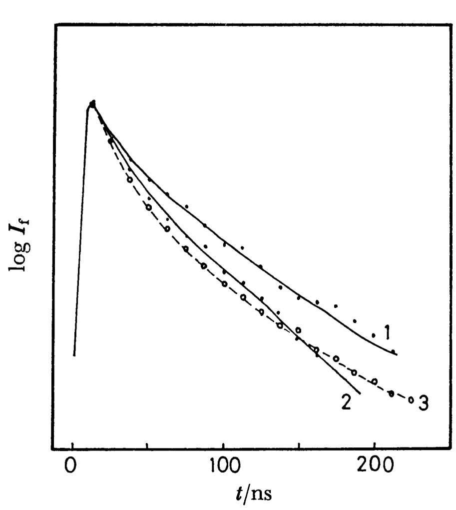

Fig. 6. Fluorescence decay curves of 9-A-$(CH_2)_3$-DMA in cyclohexane matrix at 196 K.
(1) Observed at 450 nm, (2) observed at 520 nm, (3) observed by detecting the whole emission band of heteroexcimer using a Toshiba VY-42 filter.

complex is already formed in the ground state, which agrees with the above results of absorption and excitation spectral measurements. However, it has been confirmed that the decay curve of the heteroexcimer fluorescence depends on the wavelength at which it is observed and shows a deviation from the simple exponential decay. The degree of deviation from exponential decay changes to some extent with temperature, depending also on the rate of heating or cooling. Roughly speaking, the longer the wavelength of observation, the greater the amount of the shorter decay component. This might be ascribed to the fact that there are several kinds of associated pairs emitting at different wavelengths. This phenomenon was observed in all the systems we studied but not in the case of excimer fluorescence band. As an example, the decay curves of some heteroexcimer systems are shown in Figs. 5 and 6. In the case of the pyrene–DMA or DEA system, the decay curve observed by detecting the whole emission band of heteroexcimer using an appropriate filter was accidentally single exponential (dotted line, Fig. 5). The apparent single exponential decay might represent the mean lifetime $\bar{\tau}_f$ if various kinds of heteroexcimers of the pyrene–DMA or DEA system. In the case of the pyrene (1×10^{-5} M)–DMA (1×10^{-2} M)–cyclohexane system, when the temperature is lowered, the band maximum of the heteroexcimer fluorescence shifts to red accompanied by a decrease both in the relative fluorescence intensity I_f and the mean lifetime at first, and then makes a blue shift, accompanied by increase in I_f and $\bar{\tau}_f$, to approximately the same position as it has at 300 K. The results of the temperature effects on the heteroexcimer fluoroscence are summarized in Table 1. It seems that some distribution of the associated donor–acceptor states differing with temperature might be forced to arise in the cyclohexane matrix. When the DMA concentration is small (1×10^{-4} M), the heteroexcimer fluorescence can be observed only in the wavelength region of 440—450 nm. One of the possible mechanisms for the appearance of the long wavelength fluorescence might be the formation of a more highly aggregated state than the 1 : 1 donor–aceptor pair.

TABLE 1. TEMPERATURE DEPENDENCE OF HETEROEXCIMER FLUORESCENCE OF PYRENE (1×10^{-5} M)-DMA (1×10^{-2} M)-CYCLOHEXANE SYSTEM

T/K	300	273	240	230—210	190-100
λ_{max}/nm	440	450	465	480	440
I_f	100	85	15	≈6	90
$\bar{\tau}_f$/ns	140	120	85	80	≈110

Absorption Spectra in Liquid Solutions. Yoshihara *et al.* studied the absorption spectra of the pyrene–DMA system in chlorobenzene, changing the DMA concentration in the range 0—7.89 M.[6] The absorption intensity in the wavelength region of 350—400 nm increases with an increase in concentration of DMA, the equilibrium constant of complex formation in the ground state being determined to be 0.2 M^{-1} with the aid of the Ketelaar plot. We also examined the anthracene–DMA system and obtained similar results.

In order to elucidate the electron donor–acceptor interactions in solution, it is worthwhile to measure the temperature dependence of the ultraviolet absorption spectra of donor–acceptor systems. The observed values of absorbance d for the THF solution of TCNB are plotted against the reciprocal of the temperature in Fig. 7. The value of d decreased at first with a rise in temperature from 298 K to 313 K, increasing with a further rise in temperature. A similar result was obtained for the system of perylene in p-DMT. The temperature dependence of ($d-d_0$) of the pyrene (1×10^{-2} M)-DMA (1×10^{-2} M) system in hexane is shown in Fig. 8, where d and d_0 are the absorbance values observed for the ternary solution containing pyrene and DMA in hexane and for the equimolar hexane solution of pyrene, respectively. All of the d values are corrected for the volume change caused by temperature variation.

The observed increment of the absorption intensity at low temperatures can be explained by the very

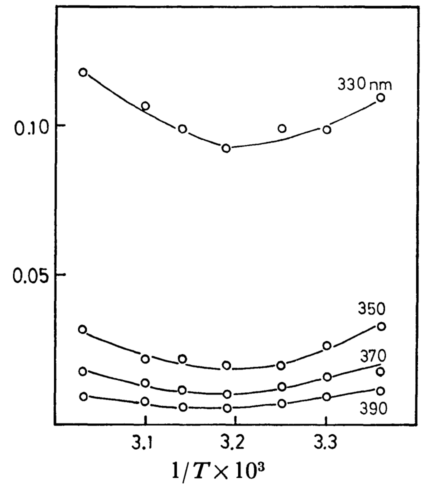

Fig. 7. Temperature dependence of d at various wavelengths in the TCNB-THF system.

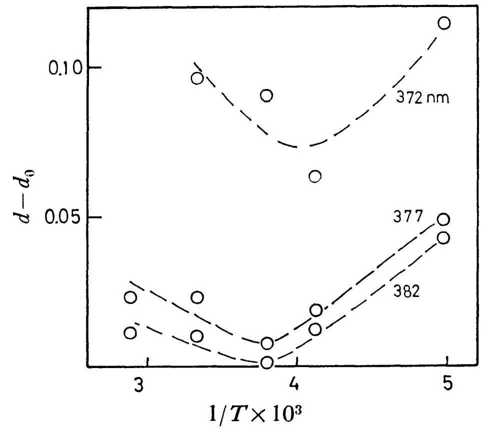

Fig. 8. Temperature dependence of $(d-d_0)$ at various wavelengths in the pyrene $(1\times10^{-2}$ M)-DMA $(1\times10^2$ M)-hexane system.

weak complex formation between donor and acceptor in the ground state which leads to the broadening and red shift of absorption band.

A collision induced CT interaction may arise at a high temperature leading to the enhancement of the absorption intensity, as it is actually observed in pyrene–DMA as well as TCNB–THF systems. Measurements of the collision induced absorption band would be difficult in the stable CT complex systems as compared with the heteroexcimer systems. Actually, in the case of the TCNB–toluene system, the intensity of the CT absorption band decreases monotonically with an increase in temperature up to 348 K (Fig. 9).

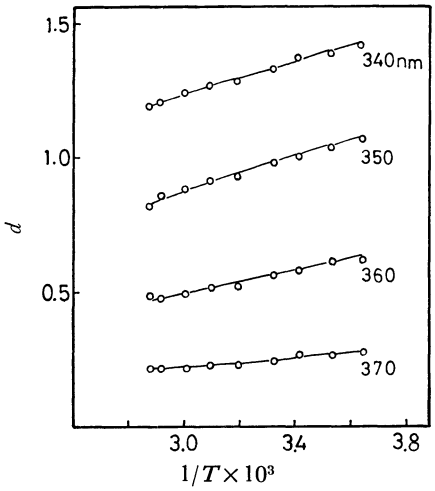

Fig. 9. Temperature dependence of d at various wavelengths in the TCNB-toluene system.

References

1) J. Ferguson, *J. Chem. Phys.*, **43**, 306 (1965).

2) J. Ferguson, *J. Chem. Phys.*, **44**, 2677 (1966).

3) E. A. Chandross, J. Ferguson, and E. G. McRae, *J. Chem. Phys.*, **45**, 3546 (1966); E. A. Chandross and J. Ferguson, *ibid.*, **45**, 3554 (1966).

4) N. Mataga, T. Okada, and H. Oohari, *Bull. Chem. Soc. Jpn.*, **39**, 2563 (1966).

5) M. Itoh, T. Mimura, H. Usui, and T. Okamoto, *J. Am. Chem. Soc.*, **95**, 4388 (1973); M. Itoh and T. Mimura, *Chem. Phys. Lett.*, **24**, 551 (1974); M. Itoh, *ibid.*, **26**, 505 (1974).

6) K. Yoshihara, K. Futamura, and S. Nagakura, *Chem, Lett.*, **1972**, 1243.

7) H. Ishida and T. Tsubomura, *Chem. Phys. Lett.*, **9**. 296 (1971).

8) N. Mataga and K. Ezumi, *Bull. Chem. Soc. Jpn.*, **40**, 1355 (1967).

9) N. Nakashima, N. Mataga, F. Ushio, and C. Yamanaka, *Z. Phys. Chem. N. F.*, **79**, 150 (1972).

10) N. Mataga and Y. Murata, *J. Am. Chem. Soc.*, **91**, 3144 (1969).

11) A. Weissberger, Ed., "Technique of Organic Chemistry," Vol. III, Interscience, New York (1955).

12) N. Mataga, Y. Torihashi, and Y. Ota, *Chem. Phys. Lett.*, **1**, 385 (1967).