CHEMISTRY LETTERS, pp. 1243-1247, 1972. Published by the Chemical Society of Japan

COMPLEX FORMATION IN THE GROUND AND EXCITED STATES OF THE PYRENE-N,N-DIMETHYLANILINE SYSTEM

Keitaro YOSHIHARA, Kazuyoshi FUTAMURA, and Saburo NAGAKURA
The Institute of Physical and Chemical Research, Wako, Saitama

From the measurement of absorption and fluorescence spectra, a 1:1 electron-donor-acceptor complex formation in the ground state was confirmed for the pyrene-N,N-dimethylaniline system which is a well-known exciplex formation system, the equilibrium constant being determined to be 0.2 M^{-1}.

Since the electron-donor-acceptor complex (EDA complex) in the excited state was found by Leonhardt and Weller[1)] in 1963, a number of studies have been made on the properties of exciplexes between aromatic hydrocarbons and amines. For example, Mataga et al.[2)] studied the aromatic hydrocarbons-N,N-dimethylaniline (DMA) systems and obtained a linear relationship between the energies of exciplex and the electron affinities of the lowest excited state.

There is a problem still left, however, whether or not the exciplex systems form very weak complexes in the ground states; in other words, whether or not they are really repulsive in the ground states as proposed previously. Under these circumstances, we have undertaken to study the absorption and emission spectra of the pyrene-DMA system. We succeeded in confirming the EDA-complex formation in the ground state and in determining the equilibrium constant.

Experimental

Pyrene was purified by vacuum sublimation and also by zone refining. DMA was purified by repeated vacuum distillations. The measurements were carried out as quick as possible after purification. Chlorobenzene was purified by fractional distillation. Cyclohexane of "Dotite Spectrosol" grade was used without further purification. The sample solutions were degassed by the freeze-thaw technique.

A Cary recording spectrophotometer model 14M was used for the measurements of ultraviolet absorption spectra. Fluorescence spectra were measured by the aid of an apparatus consisting of a 100W high-pressure mercury lamp as a light source, a Spex model 1700 monochromator, and an EMI photomultiplier as a detector.

Fluorescence lifetimes were measured by using a coaxial-type nitrogen gas laser as an exciting light source, which has 30kW peak intensity at 337 nm and 3 nsec duration. The fluorescence decay was detected by an RCA 1P28 photomultiplier through a Bausch and Lomb monochromator and was displayed on a Sony-Tektronix 585A oscilloscope.

Results

Absorption Spectra. We measured the ultraviolet absorption spectra of the pyrene ($\sim 10^{-2}$M)-DMA system in chlorobenzene, changing the DMA concentration in the range between 0 and 7.89M. As is shown in Fig. 1, the absorption intensity increases with the increasing concentration of DMA in the wavelength region of 350~400 nm. This increment cannot be ascribed to the solvent shift of the strong band pertinent to pyrene. This is because the spectrum of the aromatic hydrocarbon like pyrene is rather insensitive to the dielectric constant (D) and refractive index (n) of the solvent, and particularly because in this case the n and D values of chlorobenzene (n = 1.5217 and D = 5.62) used as the solvent are similar to those of DMA (n = 1.5547 and D = 5.26).

According to our opinion, the observed increment of the absorption intensity can be explained by the complex formation of pyrene with DMA in the ground state. In order to certify this opinion, the dependence of the absorbance on the concentration of DMA was analysed with the aid of the Ketelaar method.3) The actual plots of $a/(d-d_o)$ against the reciprocal of the DMA concentration fit well into a linear relationship as is seen in Fig. 2. Here, a is the concentration of pyrene and d and d_o are the absorbance values observed for the ternary solution containing pyrene and DMA in chlorobenzene and for the chlorobenzene solution of pyrene. The equilibrium constant was determined to be 0.22, 0.21, and 0.28 M^{-1}, at 385, 380, and 370 nm, respectively. These facts prove that there exists the equilibrium of the type of $D + A \rightleftarrows D{\cdot}A$. Here D, A, and D·A stand for a donor, an acceptor, and an EDA complex, respectively. The equilibrium constant is about one order of magnitude smaller compared with that for the typical bπ·aπ-type EDA-complexes,4) indicating that the CT interaction is weak in this system. This is one of the reasons why the CT band was not observed in the previous report.5) Another reason is that the CT band is covered by the absorption of pyrene.

As is seen in Fig. 1, the peak of the CT absorption may be located below ~390 nm (above ~3.18 eV). This may be justified by the following two reasons. (1) From the CT band position of the 1,3,5-trinitrobenzene (TNB)-DMA complex (475 nm (2.61 eV) in cyclohexane)6) and the electron affinities of pyrene7) and TNB8) of 0.59 and 1.4 eV, respectively, the CT band of the DMA-pyrene system may be expected to be located at ~3.4 eV (~365 nm).9) (2) From the ionization potential of DMA, 7.1 eV10) and the electron affinity of pyrene, the CT band may be expected to be located at ~3.5 eV (~355 nm)11) on the reasonable assumption that the electrostatic energy between DMA^+ and $pyrene^-$ is equal to 3.0 eV.

Fluorescence Spectra and Lifetimes. The yellow fluorescence appears at 500 nm for pyrene (10^{-5}M) in DMA at 293°K.5) This is very much different from the blue fluorescence of the exciplex observed at 440 nm for the pyrene($\sim 10^{-5}$M)-DMA($\sim 10^{-4}$M) system in cyclohexane at 293°K.

The appearance of yellow fluorescence at 500 nm may be difficult to be explained by the solvent shift of the exciplex fluorescence at 440 nm. Applying the usual theory of solvent shift12) and plotting the fluorescence maxima observed for the pyrene-DMA exciplex in various solvents13) against their $(2D-2/2D+1)-(n^2-1/2n^2+1)$ values, we obtained a straight line relation between both quantities. From this

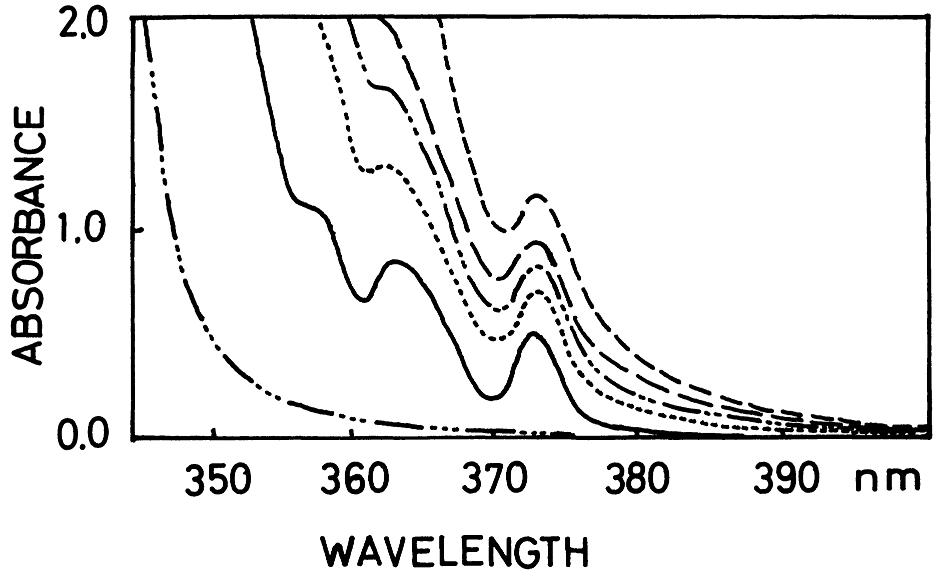

Fig. 1. Absorption spectra of the pyrene-DMA and the related systems. ----- pyrene (1.03×10^{-2}M) in pure DMA; — — pyrene(1.00×10^{-2}M)-DMA(6.30M) in chlorobenzene; ——·· pyrene(0.98×10^{-2}M)-DMA(4.80M) in chlorobenzene; ····· pyrene(0.92×10^{-2}M)-DMA (3.20M) in chlorobenzene; ——— pyrene (1.03×10^{-2}M) in chlorobenzene; ——··· pure DMA.

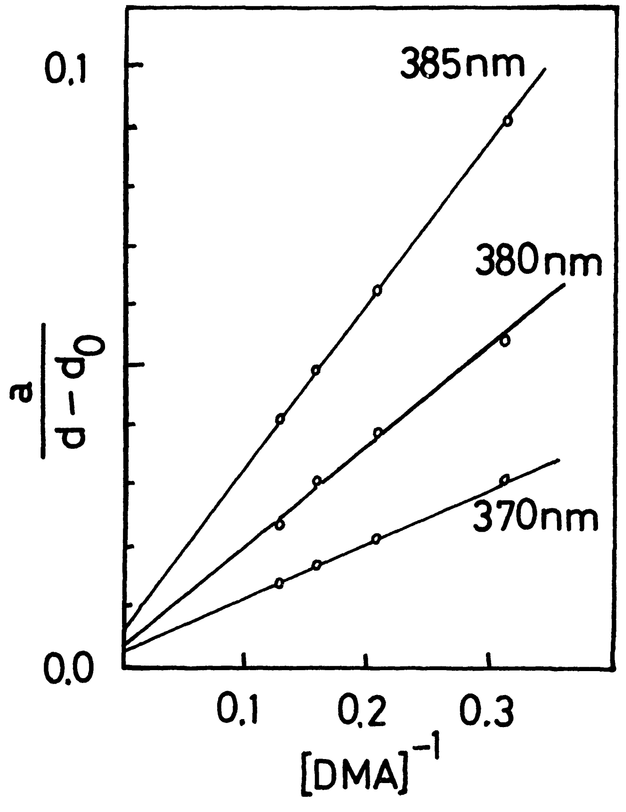

Fig. 2. The Ketelaar plots for the pyrene-DMA-chlorobenzene system at 385, 380, and 370 nm.

straight line and the $(2D-2/2D+1)-(n^2-1/2n^2+1)$ value of DMA, it is indicated that the exciplex fluorescence may appear at 470~480 nm in DMA. This value is rather different from the observed value, 500 nm.

The fluorescence lifetime of the system containing pyrene (1.0×10^{-5}M) in pure DMA was determined to be 30 nsec. This is much smaller than the value for the ternary system containing pyrene and DMA in various solvents including more polar ones than DMA.13) The latter value can be evaluated to be 180 nsec for the pyrene-DMA exciplex in cyclohexane with the aid of the kinetic data obtained by us.14,15)

From the above-mentioned facts, it may be revealed that the fluorescence at 500 nm may not be due to the usual exciplex formed between excited pyrene and DMA. The following fact may support this view. The pyrene(1.0×10^{-5}M)-DMA(2.5×10^{-3}M) in cyclohexane at 293°K shows the fluorescence peak of the exciplex at 440 nm. By using a nano-second light pulse as the excitation light source, the rise and decay times of the fluorescence at 460 nm were determined to be 22 nsec and 190 nsec, respectively. The rise time was explained by the bimolecular formation of an exciplex from the excited pyrene and DMA.14) Upon cooling the same sample to 200°K, the peak position shifts to 500 nm and the lifetime becomes 65 nsec with no rise time, even though the solvent viscosity becomes very high.

By considering the fact that the electronic absorption measurements support the weak complex formation in the ground state, the fluorescence at 500 nm which appears only in the DMA solution of pyrene or in the ternary solution at low temperatures where the equilibrium in the ground state is shifted to the complex formation may tentatively be interpreted as the emission from the excited state of the EDA complex between pyrene and DMA in the ground state.

As mentioned above, the pyrene-DMA system forms the complex, though very weak, in cyclohexane at 200°K and shows the fluorescence at 500 nm. On the other hand, the same electron-donor-acceptor system in methylcyclohexane exhibits only the exciplex fluorescence at 450 nm even at 200°K and a fluorescence rise time was observed for this system both at room temperature and at 200°K. At the lower temperature (77°K), the fluorescence of this system is only that of pyrene itself and neither fluorescence of exciplex nor EDA complex was observed. The solvent at this temperature is completely solidified like a piece of white chalk. The above-mentioned fact seems to show that the complex formation between pyrene and DMA is very sensitive to environmental conditions like solvents used. This may be reasonable in view of the fact that the complex is very weak and the formation energy is very small.

References

1) H. Leonhardt and A. Weller, Ber. Bunsenges. Phys. Chem., 67, 791 (1963).

2) N. Mataga and K. Ezumi, Bull. Chem. Soc. Japan, 40, 1355 (1967).

3) L. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit and W. Dzcubas, Rec. Trav. Chim., 71, 1104 (1952).

4) G. Briegleb, "Elektron-Donator-Acceptor-Komplexe", Springer, Berlin 1961.

5) N. Mataga, T. Okada and K. Ezumi, Mol. Phys., 10, 203 (1966).

6) R. Foster and D. L. Hammick, J. Chem. Soc. (London), 1954, 2685.

7) R. S. Becker and E. Chen, J. Chem. Phys., 45, 2403 (1966).

8) G. Briegleb, Angew. Chem., 76, 326 (1964).

9) This value was obtained by the aid of the equation presented by McConnell, Ham and Platt (H. M. McConnell, J. S. Ham and J. R. Platt, J. Chem. Phys., 21, 66 (1953)) for the CT band position of the weak complex.

10) R. Foster, Nature, 183, 1253 (1959).

11) This value was also obtained by the aid of the equation presented by McConnell, Ham and Platt.

12) E. Lippert, Z. Naturforsch., 10a, 541 (1955).

13) N. Mataga, T. Okada and N. Yamamoto, Bull. Chem. Soc. Japan, 39, 2562 (1966); Chem. Phys. Lett., 1, 119 (1967).

14) K. Yoshihara, T. Kasuya, A. Inoue and S. Nagakura, Chem. Phys. Lett., 9, 467 (1971).

15) The decay time, λ, of the exciplex is expressed by,

$$\lambda = \frac{1}{2}\left[k_1+k_2+k_3[D]+k_4+k_5+k_6-\sqrt{\{(k_1+k_2+k_3[D])-(k_4+k_5+k_6)\}^2+4k_3k_4[D]}\,\right],$$

where k_1, k_2, k_3, k_4, k_5, and k_6 are the radiative and non-radiative decay constants of the excited pyrene, the rate constant of exciplex formation, its back-reaction, the radiative, and non-radiative decay constants of exciplex, respectively and $[D]$ is the concentration of DMA. In the present case, where $[D] = 7.89$ M, $k_3[D] = 7.7 \times 10^{10}$ sec^{-1} is much faster than the other rate constants, λ is safely approximated by $\lambda = k_5+k_6 = 4.5 \times 10^6$ sec^{-1}, accordingly, $\lambda^{-1} = 180$ nsec.

(Received October 26, 1972)