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The Formation and Electronic Relaxation of Intermolecular Exciplex in the Vapor Phase

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The intermolecular exciplex formation and electronic relaxation of 1,4-dicyanonaphthalene (DCN) with pentamethylbenzene (PMB) in the vapor phase have been studied by means of nanosecond fluorescence spectroscopy. The exciplex formation and decay-rate constants were independent of the excitation energy, while the decay-rate constants of DCN fluorescence was dependent on the excitation energy. The rate constants of the exciplex formation and decay kinetics were discussed in comparison with the collisional relaxation rate of the upper vibrational states.

The observation of the exciplex formation in the vapor phase provides valuable information concerning the electronic interaction between the electron donor and acceptor in the absence of solvent. It also provides information concerning vibrational effects on the radiative and nonradiative deactivation of the exciplex. Exciplex formation in the vapor phase has been reported on 9-cyanoanthracene and alkylamine systems.[1,2] Prochorow *et al.*[3] and Okajima and Lim[4] have reported on exciplex formation and electronic relaxation in the 1,2,4,5-tetracyanobenzene (TCNB) and *p*-xylene system in the vapor phase. Very recently, Itoh *et al.*[5,6] reported the intramolecular exciplex formation of 1-(9,10-dicyano-2-anthryl)-3-(1- or 2-naphthyl)propane (DCAN) in the vapor phase. In the collision-free vapor of DCAN, the excitation wavelength dependence in the $S_1 \leftarrow S_0$ spectral region of exciplex formation and the lifetimes was observed. A considerable blue shift of the exciplex fluorescence of the collision-free vapor on the excitation of the upper vibrational state was also observed in comparison with the excitation of the lower vibrational state. They suggested that the fluorescent relaxation from the upper vibrational state of the exciplex was significant.

This paper will describe the intermolecular exciplex formation and electronic relaxation of 1,4-dicaynonaphthalene (DCN) and also 1,4-dicyanonaphthalene-d_6 with pentamethylbenzene (PMB) in the vapor phase. The rate constants of the exciplex formation and decay kinetics were measured in the excitations at 337 and 293 nm. The lifetime of the exciplex fluorescence is independent of the excitation wavelength, while that of the DCN fluorescence is dependent. The reaction rates and the vibrational relaxation suggest that PMB may act not only as an electron donor, but also as a vibrational relaxer of the upper vibrational states of the S_1 state.

Experimental

The 1,4-dicyanonaphthalene was prepared and purified by known procedures.[7] 1,4-Dicyanonaphthalene-d_6 was prepared from naphthalene-d_8 (Merck, $C_{10}D_8$, 99%) by bromination in bromine vapor and by cyanogenation in a pyridine-d_5 (merck, C_5D_5N, 99%) solution, and was purified two times by means of silica-gel chromatography and recrystallization. Proton NMR gave an isotope purity of approximately 95%. The H-D exchange reaction was examined by the following method: after a mixture of DCN-d_6 and PMB (1:1) has been heated for 3 h at ≈523 K, the proton NMR signal shows that no H-D exchange reaction has occured between the two compounds. The spectral determinations in the vapor phase were made as follows: a rectangular quartz cell (1 cm) with graded seals containing solid DCN and PMB was degassed by means of a vacuum line and then sealed off. By using hexane as a buffer gas, a cell containing crystalline compounds and a trace of hexane corresponding to ≈500 Torr (1 Torr=133.32 Pa) at ≈503 K was degassed by the freeze-pump-thaw method. The absorption and fluorescence spectra and lifetimes were measured in a quartz Dewar vessel at a controlled temperature by means of a heated air flow. The absorption and fluorescence spectra were measured by means of Hitachi 220 and MPF-4 spectrophotometer, respectively. The fluorescence lifetimes were determined by excitation with a nitrogen laser and a dye laser (Molectron DL-14) with a frequency doubler (Rhamda Physik KDP unit). The fluorescence decays were measured by the use of a HTV R666 photomultiplier and by means of Tektronix 7904 (7A19 and 7B85) oscilloscope, and were analyzed by the deconvolution method.

Results and Discussion

The exciplex fluorescence at room temperature and also the excited-state complex fluorescence at low temperatures have been reported in a solution of 1,4-dicyanonaphthalene (DCN) and alkylbenzenes.[7] On the other hand, the fluorescence polarization of DCN in a rigid solution of 3-methylpentane at 77 K suggests that the absorption spectrum of DCN at 280—340 nm is attributable to the L_a ($S_1 \leftarrow S_0$) and L_b ($S_2 \leftarrow S_0$) bands. The absorption spectrum of DCN in the vapor phase shown in Fig. 1 may be ascribed to the L_a and L_b bands, though the spectral feature is quite different from that in solution. Figure 1 shows the fluorescence and excitation spectra of DCN and PMB vapor. The excitation spectra monitored at several wavelengths are identical with that of the DCN fluorescence determined in the vapor phase, which is attributable to the $S_1 \leftarrow S_0$ absorption band of DCN. The fluorescence spectrum exhibits the exciplex fluorescence ($\lambda_{max} \approx 395$ nm) in addition to the DCN fluorescence ($\lambda_{max} \approx 343$ nm). In the presence of a buffer gas (hexane, ≈500 Torr$=6.65 \times 10^4$ Pa) which may act as a vibrational relaxer, both exciplex and DCN fluorescence increase in intensity in comparison with those in the absence of a buffer gas, as shown in Fig. 1. The fluorescence maximum of the vapor-phase exciplex exhibits a considerable blue shift from that

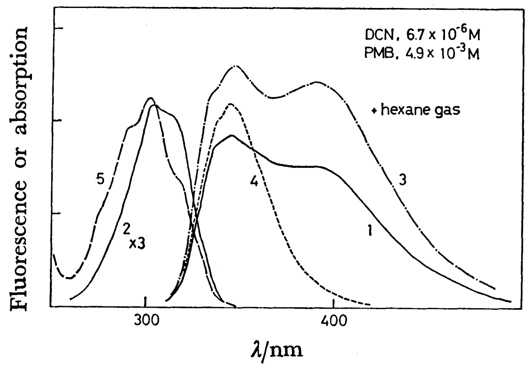

Fig. 1. (1) Fluorescence (excited at 300 nm) and (2) excitation (monitored at 450 nm) spectra of 1,4-dicyanonaphthalene and pentamenthylbenzene in the vapor phase at ≈503 K. (3) fluorescence spectrum determined in the identical condition with (1) except addition of hexane gas (≈500 Torr=6.6×10^4 Pa) as a vibrational relaxer (1 M=1 mol dm^{-3}). (4) Fluorescence (excited at 300 nm) and (5) absorption spectra of 1,4-dicyanonaphthalene vapor at ≈503 K.

in the nonpolar solution ($\lambda_{max}\approx416$ nm in 3-methylpentane) at room temperature,[7] while that of the DCN fluorescence shows no significant spectral shift.

The well-known photochemical reaction scheme and decay kinetics of DCN and exciplex are as follows;[8]

$$\begin{tikzcd}
 & A^* + D \arrow[dl, "k_1"'] \arrow[dr, "k_2"] \arrow[rrr, shift left, "k_3"] & & & (DA)^* \arrow[lll, shift left, "k_4"] \arrow[dl, "k_5"'] \arrow[dr, "k_6"] & \\
A + h\nu & & A & D + A + h\nu', & & D + A
\end{tikzcd}$$

$$[A^*] = c_1 \exp(-\lambda_1 t) + c_2 \exp(-\lambda_2 t)$$

$$[(DA)^*] = c_3 \exp(-\lambda_1 t) - c_3 \exp(-\lambda_2 t)$$

$$\lambda_1, \lambda_2 = \frac{1}{2}[k_1+k_2+k_3[D]+k_4+k_5+k_6 \mp (\{k_1+k_2+k_3[D]-(k_4+k_5+k_6)\}^2+4k_3k_4)^{1/2}],$$

where A and D are DCN and PMB, respectively. The time constants, λ_1 and λ_2 were determined in several concentrations of PMB in the excitation at 337 nm at ≈503 K. Figure 2 shows a plot of $\lambda_1+\lambda_2$ ($=k_1+k_2+k_3[D]+k_4+k_5+k_6$) *vs.* [D], the slope of which yields the rate constant of $k_3=1.2\times10^{11}$ dm^3 mol s^{-1}. Further, the fluorescence intensity ratio of DCN (excited at 337 nm) in the absence (I_0) and presence (I) of the electron donor (PMB) is expressed by the following equation:[8]

$$(I_0/I) - 1 = k_3[D](k_5+k_6)/(k_4+k_5+k_6)(k_1+k_2).$$

From k_3, the lifetimes of the exciplex and DCN, and the slope of the plot of I_0/I *vs.* [D], the dissociation rate constant (k_4) of the exciplex was determined to be 3.56×10^7 s^{-1}, as is summarized in Table 1.

The exciplex formation can be expressed by the following scheme:

$$\begin{tikzcd}
A^*(\nu_h) + D \arrow[r] \arrow[d, squiggly, "+R"] & (DA)^*(\nu_h) \arrow[d, squiggly, "+R"] \\
A^*(\nu_l) + D \arrow[r] & (DA)^*(\nu_l),
\end{tikzcd}$$

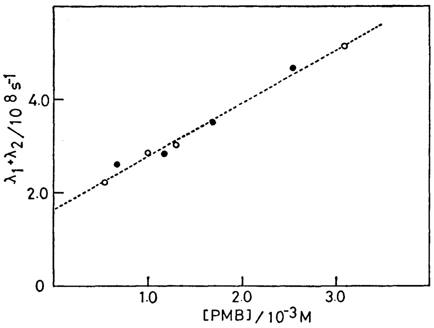

Fig. 2. Plots of ($\lambda_1+\lambda_2$) *vs.* concentration of pentamethylbenzene in the vapor phase at 503 K; λ_1 and λ_2 were obtained from double exponential decay curves determined at 370 nm in the excitation at 337 nm.

TABLE 1. THE DECAY-RATE CONSTANTS AND THE FORMATION AND DISSOCIATION RATE CONSTANTS OF THE EXCIPLEX IN THE VAPOR PHASE AT 503 K IN THE EXCITATION AT 337 nm

Rate constant	DCN-PMB	DCN-d_6-PMB
(k_1+k_2)/s^{-1} [a)]	1.25×10^8	1.05×10^8
k_3/dm^3 mol^{-1} s^{-1}	1.2×10^{11}	1.2×10^{11}
$(k_4+k_5+k_6)$/s^{-1}	4.9×10^7 [b)]	5.2×10^7 [c)]
k_4/s^{-1}	3.56×10^7	4.1×10^7
k_q/dm^3 mol^{-1}	2.6×10^2	2.4×10^2

a) Determined in DCN and DCN-d_6 vapors. b) Determined in the DCN (6.7×10^{-6} mol dm^{-3}) and PMB (1.2×10^{-3} mol dm^{-3}) vapor. c) Determined in the DCN-d_6 (6.7×10^{-3} mol dm^{-3}) and PMB (1×10^{-3} mol dm^{-3}) vapor.

where ν_h and ν_l denote high and low levels of the vibrational state, respectively. R is a vibrational relaxer. In the excitation of the $S_1\leftarrow S_0$ absorption band at 337 nm, the fluorescence lifetimes of DCN vapor is 8.0 ns, while it is 3.6 ns for the $S_2\leftarrow S_0$ excitation at 292 nm. Since the energy level of the S_2 state may be very close to that of the S_1 state, and since the isoenergetic internal conversion from the S_2 state to the vibrationally hot S_1 state proceeds very rapidly, the short lifetime of DCN (3.6 ns) for the excitation of S_2 is attributable to decay from the upper vibrational state of S_1. However, the fluorescence lifetime of the exciplex in the DCN–PMB vapor does not exhibit any of the excitation-wavelength dependence mentioned above. Okajima and Lim[4] suggested that, in the vapor-phase exciplex of TCNB–*p*-xylene, the rate constant of the exciplex formation (7×10^{12} dm^3 mol^{-1} s^{-1}) between the vibrationally hot electron acceptor, $A^*(\nu_h)$, *via* the S_2 excitation and the ground state of the electron donor is 10 times greater than that of the formation of $(DA)^*(\nu_l)$, measured for excitation into S_1. Further, the rate constant of the intramolecular exciplex formation from the $A^*(\nu_h)$ and D moieties in the collision-free vapor of DCAN was determined to be much greater than that from the $A^*(\nu_l)$ and D moieties.[9] Therefore, if the rate constant of the $(DA)^*(\nu_h)$ formation in the DCN–PMB vapor is assumed to be 5—10 times greater than the value of 1.2×10^{11} dm^3 mol^{-1} s^{-1} obtained in the $(DA)^*(\nu_l)$ formation, the rate constant of the $(DA)^*(\nu_h)$

formation is estimated to be approximately 10^{12} dm^3 mol^{-1} s^{-1}. On the other hand, the concentration of PMB (10^{-2}—10^{-3} mol dm^{-3}) corresponds to the gas pressure of 50 Torr and to the collisional relaxation rate of 5×10^8 s^{-1} obtained by the use of a hard-sphere collision model.[4,10] Therefore, the rate of the $(DA)^*(\nu_h)$ formation *via* S_2 excitation ($\approx10^{12}[D]$ s^{-1}) is greater than the decay of $A^*(\nu_h)$ and the vibrational relaxation by $\approx$50 Torr of PMB. However, since the decay-rate constant of $(DA)^*(\nu_h)$ is assumed to be approximately 3×10^7 s^{-1}, the vibrational relaxation of the upper vibrational state of $(DA)^*(\nu_h)$ by PMB vapor may proceed at the rate of 5×10^8 s^{-1}, followed by the fluorescent decay from $(DA)^*(\nu_l)$. These arguments are consistent with the absence of the excitation-wavelength dependence of the fluorescence lifetimes of the exciplex. The fluorescence-intensity ratio of the exciplex and DCN is not very much dependent on the absence or presence of the buffer gas, though the intensity ratio shows a slight increase in the latter, as shown in Fig. 1. This fact suggests that the exciplex formation and emission may take place according to the reaction scheme mentioned above. In the scheme, D and R are PMB as the electron donor and also as the vibrational relaxer.

The rate constants of the exciplex formation and decay kinetics were obtained in the DCN-d_6 and PMB system, as summarized in Table 1. Figure 3 compares the fluorescence spectrum of DCN-d_6 and PMB vapor with that of DCN–PMB vapor determined under identical conditions. The fluorescence-intensity ratio of the exciplex and DCN in DCN-d_6–PMB slightly increases in comparison with that of DCN–PMB. However, the rate constant of the exciplex formation (k_3) and the quenching constant (k_q) obtained from the plots shown in Figs. 2, show no significant difference between DCN-d_6 and DCN, as summarized in Table 1.[11] Okajima and Lim[4] reported that the Stern-Volmer quenching constant in the TCNB-*p*-xylene-d_{10} vapor is smaller by a factor of 1.4 than that for TCNB-*p*-xylene, and they suggested the occurence of important vibrational effects in the photoassociation. However, the lack of any significant effects of the deuterium substitution in DCN reported here suggests a slight contribution of C–D stretching to the high-frequency vibrational mode of a large molecule such as DCN in the exciplex formation and the radiationless deactivation.

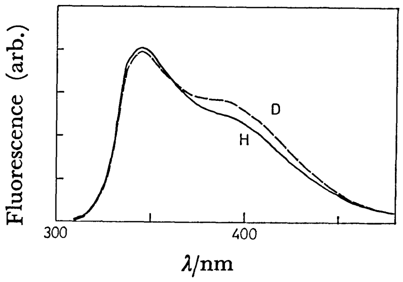

Fig. 3. (H) Fluorescence spectrum of 1,4-dicyanonaphthalene (6.7×10^{-6} mol dm^{-3}) and pentamethylbenzene (3.8×10^{-3} mol dm^{-3}) in the vapor phase at $\approx$503 K. (D) Fluorescence spectrum of 1,4-dicyanonaphthalene-d_6 (6.7×10^{-6} mol dm^{-3}) and pentamethylbenzene (3.8×10^{-3} mol dm^{-3}) determined in the identical condition with (H).

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11) During the spectral determination in the vapor phase at a high temperature, it was confirmed that no H-D exchange reaction between DCN-d_6 and PMB occured, as mentioned in the Experimental section.