but differ in electronic energies; in the Jahn–Teller literature this last difference is usually called a strain term. A molecular realization might involve dimers like **3** in a matrix which slightly shifts the diagonal energies or a species like **1** with a methyl group on one of the benzene rings.

The present theoretical treatment is based on some severe modeling assumptions. First is the neglect of electronic repulsions; these can be included, but we expect, and indeed the work of Cederbaum and co-workers[39] on vibronic problems has demonstrated, that the electron repulsion and the vibronic coupling problems can to a fair degree be separated. The second approximation is the neglect of frequency changes in the elastic energy (eq 4). Much of the study of mixed valence species is in fact based upon[4-6] frequency changes attendant upon electron localization. Inclusion of frequency changes is not a serious complication, and we hope to deal with it in future work. The present four-site model, though expected to be more adequate than

the two-site[35,40] or three-site[32] assumptions employed previously, is nevertheless insufficient if the excess electron orbital (HOMO) contains a nonnegligible contribution from atomic orbitals on bridge atoms (as has in fact been calculated[41] for Creutz–Taube ion). Under these conditions a five-site model, with the additional site representing the bridge, seems appropriate. Finally, as has been noted above, we have neglected any role of the solvent in promoting transfer or dissipating energy; work on this problem is also continuing.

(39) For example, H. Köppel, W. Domcke, L. S. Cederbaum, and W. von Niessen, *J. Chem. Phys.*, **69**, 4252 (1978).

(40) M. J. Ondrechen and M. A. Ratner, *J. Chem. Phys.*, **66**, 938 (1977); *Chem. Phys. Lett.*, **51**, 573 (1977).

(41) M. J. Ondrechen, D. E. Ellis, and M. A. Ratner, to be published.

Electronic Relaxation of Intra- and Intermolecular Exciplexes in the Vapor Phase

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Abstract: Intramolecular exciplex formations in the vapor phase of 1-(9,10-dicyano-2-anthryl)-3-(1- and 2-naphthyl)propanes ($\beta\alpha$- and $\beta\beta$-DCAN) have been studied in the presence and absence of a vibrational relaxer. In the collision-free vapor of DCAN (vapor pressure, approximately 10^{-2}–10^{-3} torr), excitation wavelength dependences in the spectral region of $S_1 \leftarrow S_0$ on the relative fluorescence quantum yield and lifetimes of the exciplex were observed. A considerable blue shift of the exciplex fluorescence (time-resolved spectra) of the collision-free vapor upon excitation of the upper vibrational states was observed in comparison with excitation of the lower vibrational state. The facts suggest fluorescent relaxation from the upper vibrational state of the exciplex. In the intermolecular system of 9,10-dicyanoanthracene (DCA) and 1,5-dimethylnaphthalene (1,5-DMN), exciplex fluorescence was observed in the vapor phase. However, no significant wavelength dependence of the exciplex fluorescence or the lifetime was observed even in the absence of the buffer gas. The formation and dissociation rate constants of the DCA–1,5-DMN exciplex were determined in the vapor phase. The obtained rates of exciplex formation and of vibrational relaxation suggest that 1,5-DMN seems to behave not only as an electron donor but also as a vibrational relaxer. The electronic relaxation process of the exciplex could be investigated only in the vapor phase of the collision-free condition of the intramolecular electron donor–acceptor system.

In the course of numerous investigations on the exciplex in solution, solvent participation in the formation and stabilization of the exciplex and in the inter- and intramolecular vibrational deactivation of the exciplex has been pointed out.[1,2] Therefore, the observation of exciplex formation in the vapor phase provides us 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. Previously, exciplex formation in the vapor phase was reported only in 9-cyanoanthracene or substituted 9-cyanoanthracene and alkylamine system.[3,4] Recently, Prochorow et al.[5] and Okajima and Lim[6]

reported the exciplex formation in the 1,2,4,5-tetracyanobenzene (TCNB) and *p*-xylene system in the vapor phase. They reported vibrational energy dependence and temperature dependence of the exciplex in the vapor phase, which suggest the importance of intermolecular vibrations in the formation and the radiationless deactivation of the exciplex.

Numerous investigations have been made on the intermolecular exciplex formation in solution of the electron donor–acceptor systems connected by trimethylene chains such as 1-(*N*,*N*-dimethylanilino)-3-(anthryl)propane[7] and 1-(9,10-dicyano-2-anthryl)-3-(1- or 2-naphthyl)propane ($\beta\alpha$- or $\beta\beta$-DCAN).[8] The association and dissociation processes in these intramolecular

(1) S. Nagakura in "Excited State", Vol. 2, E. C. Lim, Ed., Academic Press, New York, 1975, p 321.

(2) N. Mataga and M. Ottolenghi in "Molecular Association", Vol. 2, R. Foster, Ed., Academic Press, New York, 1979, p 1.

(3) S. Hirayama, G. D. Abbott, and D. Phillips, *Chem. Phys. Lett.*, **56**, 497 (1978).

(4) S. Hirayama, *Chem. Phys. Lett.*, **63**, 596 (1979).

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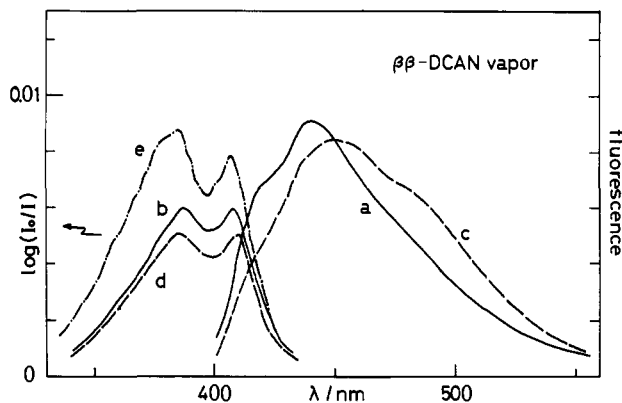
Figure 1. (a) Fluorescence (excited at 380 nm) and (b) excitation (monitored at 480 nm) spectra of $\beta\beta$-DCAN vapor. (c) Fluorescence (excited at 380 nm) and (d) excitation (monitored at 500 nm) spectra at 544 K of $\beta\beta$-DCAN vapor in the presence of $\sim$500 torr of hexane. (e) Absorption spectrum of $\beta\alpha$-DCAN in the vapor phase at 545 K. Fluorescence intensities are uncorrected.

systems were compared with those in the intermolecular exciplexes of the corresponding electron donor–acceptor systems. This paper describes the intramolecular exciplex formation and dissociation of DCAN in the vapor phase in comparison with the intermolecular system of 9,10-dicyanoanthracene (DCA) and 1,5-dimethylnaphthalene (1,5-DMN) or 2-methylnaphthalene.[9] In the intramolecular system of DCAN vapor, the electronic relaxation process of the exciplex can be investigated in the vapor phase of the collision-free condition, while a large amount of the fluorescence quencher needed for the study of the intermolecular electron donor–acceptor vapor prevents a similar investigation for the intermolecular system. It is because high pressures of the quencher may play the important role of the vibrational relaxer. The argument was confirmed by the determinations of the rate constants of the exciplex formation and the vibrational relaxation, which are comparable in magnitude.

The fluorescence lifetimes and relative quantum yield of the intramolecular exciplex in the collision-free vapor of DCAN exhibit a striking difference from those of the intermolecular exciplex of the vapor phase of DCA–1,5-DMN. The excitation wavelength dependences in the spectral region of $S_1 \leftarrow S_0$ on the exciplex formation and fluorescence lifetimes were determined in the vapor phase. A significant difference of the exciplex fluorescence (time-resolved spectra) was observed in the absence and presence of a vibrational relaxer. Further, the fluorescence spectra of the collision-free exciplex shift to the shorter wavelength region with increasing excitation energy. The facts suggest the fluorescent relaxation from the upper vibrational state of the exciplex.

Experimental Section

Materials were purified by the methods described in the previous papers.[8,10] The samples for measurements were prepared as follows. The rectangular quartz cell (10 mm) with graded seals containing solid DCAN (or DCA and alkylnaphthalene) was degassed by a high-vacuum line and sealed off from the vacuum line. In using hexane as a buffer gas, the cell containing samples and a trace of hexane corresponding to $\sim$500 torr at 510–560 K was degassed by freeze–pump–thaw cycles. The absorption and fluorescence spectra and the lifetimes were measured in a quartz dewar with the temperature controlled by heated air flow. The fluorescence and absorption spectra were measured by Hitachi MPF-4 and 220 spectrophotometers, respectively. The fluorescence lifetimes were determined in the excitations by a nitrogen gas laser (Molectron UV 12) and by a N₂ laser pumped dye laser (Molectron DL 14). Laser dyes are PBD, BBQ, DPS, Bis-MSB, and Coumarin 440 obtained from Molectron Corp. or Exciton Chem. Co. The fluorescence decays were detected by an HTV R666 photomultiplier and determined by a Tektronix oscilloscope 7904 and 7A19 and 7B85 plug-in units. Observed decay curves were analyzed by a computer-simulated deconvolution.[11]
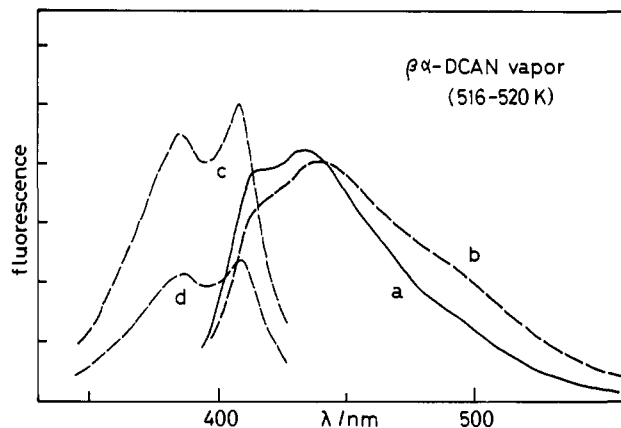
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Figure 2. (a) Fluorescence (excited at 380 nm) spectrum of $\beta\alpha$-DCAN. (b) Fluorescence (excited at 380 nm) and excitation spectra (c) monitored at 430 nm and (d) at 500 nm of $\beta\alpha$-DCAN in the presence of $\sim$500 torr of hexane.

Results and Discussion

Intramolecular Exciplex in the Vapor Phase. The fluorescence spectra of $\beta\beta$-DCAN in the vapor phase were measured in the absence and presence of the buffer gas ($\sim$500 torr of hexane) as a vibrational relaxer, as shown in Figure 1. Their fluorescence excitation spectra monitored at several wavelengths in the spectral region of 410–550 nm are in good consistency with the absorption spectrum of the 9,10-dicyanoanthryl moiety (DCA moiety) in $\beta\beta$-DCAN, though there is some difference in the spectral intensity distribution between the excitation and absorption spectra, as will be mentioned later. The fluorescence decay curve monitored at 550 nm of the DCAN vapor in the presence of the buffer gas exhibits a typical rise and decay of the fluorescence, while that monitored at the shorter wavelength region (410–450 nm) exhibits double exponential decay. The well known photochemical reaction scheme and decay kinetics are as follows:[12] where A and D
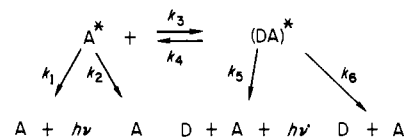
$$[A^*] = c_1 \exp(-\lambda_1 t) + c_2 \exp(-\lambda_2 t) \qquad (1)$$

$$[(DA)^*] = c_3 \exp(-\lambda_1 t) - c_3 \exp(-\lambda_2 t) \qquad (2)$$

$$\lambda_{1,2} = \tfrac{1}{2}[k_1 + k_2 + k_3 + k_4 + k_5 + k_6 \mp (\{k_1 + k_2 + k_3 - (k_4 + k_5 + k_6)\}^2 + 4k_3k_4)^{1/2}] \qquad (3)$$

are DCA and naphthyl moieties in DCAN, respectively. The time constants of the rise and decay in the excitation at 337 nm are in good consistency with those of the double exponential decay. Therefore, the fluorescence spectra at 450–500 nm are ascribed to an intramolecular exciplex in the vapor phase, though a considerable DCA moiety fluorescence is contained in the shorter wavelength region. Figure 2 shows the fluorescence and excitation spectra of vapor-phase $\beta\alpha$-DCAN in the absence and presence of the buffer gas, which are also ascribed to the intramolecular exciplex in the vapor phase. It should be noted that the exciplex fluorescence has a peak at $\sim$430 nm. On the other hand, the fluorescence spectra of $\beta\beta$- and $\beta\alpha$-DCAN in cyclohexyl at 490–520 K show the intramolecular exciplex fluorescence at $\sim$500 nm, which is almost identical with that in the usual liquid solution at room temperature.[10] In the presence of the buffer gas, the fluorescence maxima of the vapor-phase exciplex both in $\beta\beta$- and $\beta\alpha$-DCAN show a considerable blue shift from those in cyclohexyl at similar temperature. The shift of the vapor-phase exciplex seems to be attributable to the exciplex stabilization in solution.

Assuming an identical absorption intensity in the vapor phase to that in hexane, the concentration of DCAN in the vapor phase

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Intra- and Intermolecular Exciplexes in the Vapor Phase

J. Am. Chem. Soc., Vol. 103, No. 12, 1981 3273

Table I. Fluorescence Lifetimes[a] of DCAN Exciplexes in the Vapor Phase

	excitation wavelength, nm					
	337		385		430	
	T, K	τ, ns	T, K	τ, ns	T, K	τ, ns
$\beta\beta$-DCAN	527	18.4	525	25.0	525	27.5
$\beta\beta$-DCAN + hexane[b]	527	29.0	527	28.0	527	29.0
$\beta\alpha$-DCAN	524	24.5	526	30.5	525	35.0
$\beta\alpha$-DCAN + hexane[b]	526	36.0	523	35.5	529	35.6

[a] $\lambda_1^{-1} \simeq k_4 + k_5 + k_6$ $(=\tau)$. Errors of temperature and lifetimes are approximately ± 2 K and ± 1.5 ns, respectively. [b] ~500 torr.
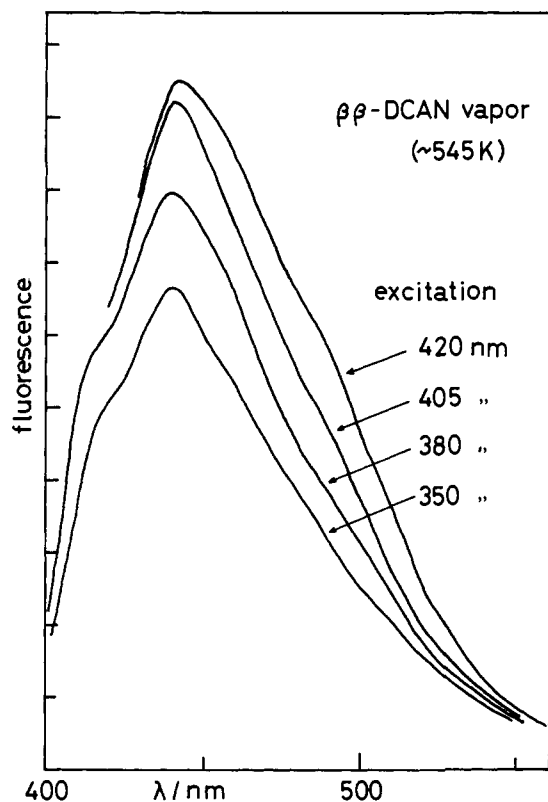

Figure 3. Relative fluorescence quantum spectra excited at several wavelengths of $\beta\beta$-DCAN vapor.

Figure 4. Plots of log $(k_4 + k_5 + k_6)$ vs. excitation energy in $\beta\beta$- and $\beta\alpha$-DCAN collision-free vapor at 525 K. $\lambda_1 \simeq k_4 + k_5 + k_6$.

at 520–560 K was estimated to be 10^{-7} M from the absorption spectrum shown in Figure 1, which corresponds to the gas pressure of 10^{-2}–10^{-3} torr. The intermolecular collisional rate constant (k_c) is expressed by $k_c = \sim 10^7$ torr^{-1} s^{-1} from a hard-sphere collision model and average collision time (τ_c) is also expressed by $\tau_c = 1/(k_c p)$, where p is a gas pressure. Since the decay rate constants of the intermolecular exciplex (λ_1) and the DCA moiety (λ_2) are at least $>3 \times 10^7$ s^{-1}, as will be mentioned later, the vapor-phase DCAN in the absence of the buffer gas can be considered to be in the collision-free condition or in an isolated molecular system. The intramolecular association and dissociation of the exciplex in DCAN occur in this collision-free condition. The fluorescence of the collision-free vapor of DCAN indicates that the fluorescence intensity ratio of the exciplex and DCA moiety decreases in comparison with that of the collisionally relaxed system by the buffer gas. The fluorescence lifetimes $(\lambda_1^{-1}$ in eq 2) of the vapor-phase exciplex in the presence of the buffer gas were determined in the excitations at several wavelengths, as summarized in Table I. The fluorescence lifetimes (λ_1^{-1}) and spectra of the exciplex in the collisionally relaxed condition of DCAN are independent of the excitation wavelength. The collision-free vapors of $\beta\beta$- and $\beta\alpha$-DCAN excited in the longest wavelength band (420–430 nm) of the vibrational structure of the S_1 state in the DCA moiety show the same fluorescence lifetimes as those in the collisionally relaxed system of the corresponding compounds, as summarized in Table I. In the excitation of the shorter wavelength
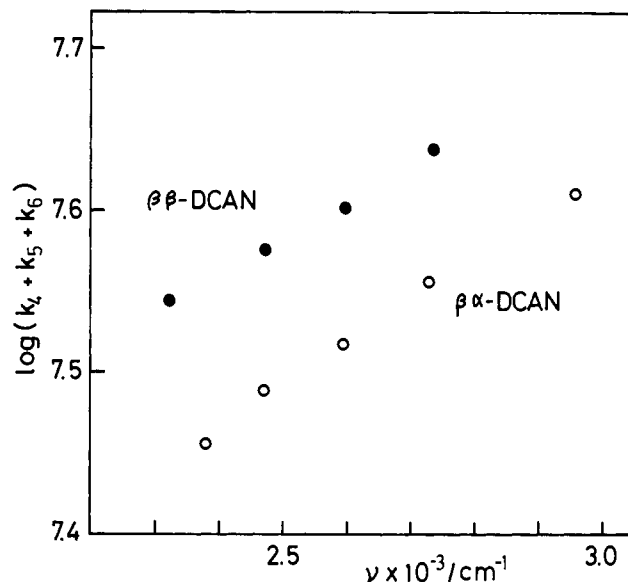
region (337–405 nm) of the S_1 state, however, the fluorescence lifetimes of the exciplex in the collision-free system demonstrate a considerable dependence on the excitation wavelength: 18–28 ns in $\beta\beta$-DCAN and 25–36 ns in $\beta\alpha$-DCAN at ~525 K. Further, Figure 3 shows the excitation dependence of the relative fluorescence quantum spectra of the exciplex in the collision-free vapor of $\beta\beta$-DCAN. The relative fluorescence quantum yields of the exciplex both in $\beta\beta$- and $\beta\alpha$-DCAN decrease when the excitation wavelength shifts to the shorter wavelength.

Okajima and Lim[6] reported that the fluorescence yield of the exciplex in the TCNB and p-xylene system in the absence of the buffer gas was independent of the excitation wavelength in the spectral region of $S_1 \leftarrow S_0$ absorption. The formation of the exciplex can be expressed by the following scheme

$$A^*(\nu_h) + D \rightarrow (DA)^*(\nu_h)$$

$$A^*(\nu_h) + R \rightarrow A^*(\nu_l)$$

$$A^*(\nu_l) + D \rightarrow (DA)^*(\nu_l)$$
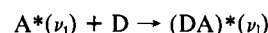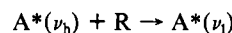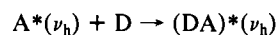
where ν_h and ν_l denote upper and low levels of the vibrational excitation, respectively, and R is a vibrational relaxer. Okajima and Lim suggested that the exciplex $(DA)^*(\nu_h)$ formed between the vibrationally hot acceptor and the ground state donor is nonfluorescent or very weakly fluorescent and decays rapidly via a nonradiative process. This explains the weakness of the exciplex fluorescence in the absence of the buffer gas, as mentioned above.

In the intramolecular collision-free system reported here, the fluorescence yield and the lifetimes (λ_1^{-1}) of the exciplex remarkably depend on the excitation wavelength in the spectral region of $S_1 \leftarrow S_0$, as shown in Figure 3 and Table I. The fluorescence quantum yields and lifetimes (λ_1^{-1}) decrease in parallel with each other with increasing excitation energy. These excitation wavelength dependences suggest that the upper vibrational level of the exciplex is also fluorescent. On the other hand, the dissociation rate constant of the excimer of 1,3-di(biphenyl)propane was reported to be much smaller than the association rate constant.[13] The association and dissociation behavior in the intramolecular exciplex may be similar to that in the excimer. Therefore, if the dissociation rate constant, k_4, is assumed to be much smaller than the association rate constant, k_3, in the reaction scheme mentioned above, the decay rate constant λ_1 of the exciplex is reduced approximately to $k_4 + k_5 + k_6$.[12] Figure 4 shows plots of the decay rate constant of the collision free

(12) W. R. Ware, D. Watt, and D. Holmes, *J. Am. Chem. Soc.*, **96**, 7853 (1974).

(13) K. A. Zachariasse, W. Kuhnle, and A. Weller, *Chem. Phys. Lett.*, **59**, 375 (1978).
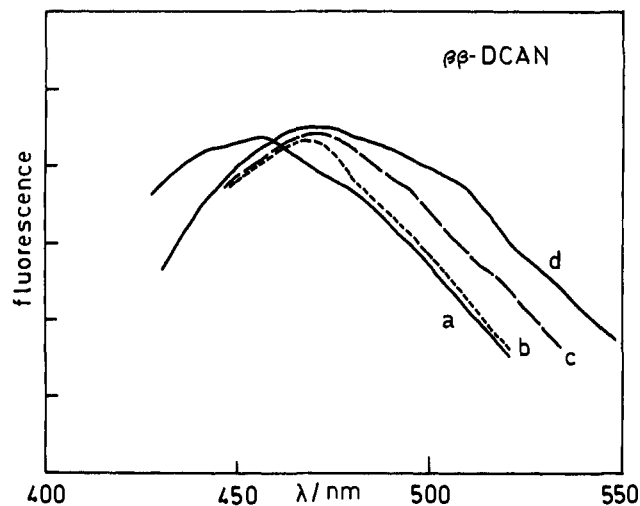
Figure 5. Time-resolved fluorescence spectra of $\beta\beta$-DCAN vapor in the excitations at several wavelengths. The spectra were depicted at ~50 ns: (a) 337 nm, (b) 385 nm, and (c) 430 nm. (d) Time-resolved fluorescence spectrum of $\beta\beta$-DCAN vapor in the presence of ~500 torr of hexane excited at 337 nm. The spectra were determined at 535–540 K.

exciplex, $\lambda_1 \simeq (k_4 + k_5 + k_6)$, against the excitation energy. Since the dissociation rate constant, k_4, does not seem to depend very much on the excitation energy, the excitation wavelength dependence of the decay rate constants shown in Figure 4 suggests that the radiative and nonradiative rate constants of the exciplex depend on the energy level of the vibrational state of the exciplex. Spears and Rice[14] and Ware et al.[15] reported in the single vibronic level (SVL) fluorescence of benzene that nonradiative rate constant remarkably increases with increasing vibrational energy level while radiative rate constant slightly decreases. Therefore, the excitation energy dependence of the exciplex fluorescence lifetimes (λ_1^{-1}) seems to suggest that nonradiative and radiative rate constants increase and decrease with increasing vibrational energy of the exciplex, respectively. Further, Figure 5 shows the time-resolved fluorescence spectra of the collision-free $\beta\beta$-DCAN vapor in the excitations at several wavelengths. The spectra exhibit a significant blue shift from that of the vibrationally relaxed system. These time-resolved fluorescence spectra shown in Figure 5 demonstrate that the exciplex $(DA)^*(\nu_h)$ formed from the vibrationally hot DCA moiety and the ground state naphthyl moiety exhibits fluorescence with a considerablly blue-shifted spectral distribution in comparison with that of the vibrationally relaxed exciplex.

Halpern and Gartman[16] reported that the fluorescence spectrum of N,N'-dimethylpiperazine (NNDMP) vapor exhibits blue shift with increasing excitation energy and remarkable red shift in the addition of ~50 torr of hexane gas. Further, they reported nonexponential fluorescence decay of NNDMP vapor consisting of fluorescences from the Franck-Condon state and from the conformationally and electronically relaxed state. Fluorescence decays of the collision-free exciplex of DCAN reported here exhibit approximately a single exponential decay, as mentioned above. The arguments on the fluorescence from the upper vibrational state of the exciplex, $(DA)^*(\nu_h)$, suggest that the fluorescence decay of $(DA)^*(\nu_h)$ might be multiexponential. In the molecular complex (exciplex) of the complex molecules, however, it is likely that the multiexponential decay may be averaged and show approximately a single exponential decay. Since the rate constant of the exciplex formation in the presence of the buffer gas is much smaller than the collisional relaxation rate of the upper vibrational S_1 state of the DCA moiety (~500 torr of the buffer gas corresponds to the rate constant of 5×10^9 s^{-1}), the exciplex formation of $(DA)^*(\nu_h)$ from the vibrationally excited DCA moiety is ne-

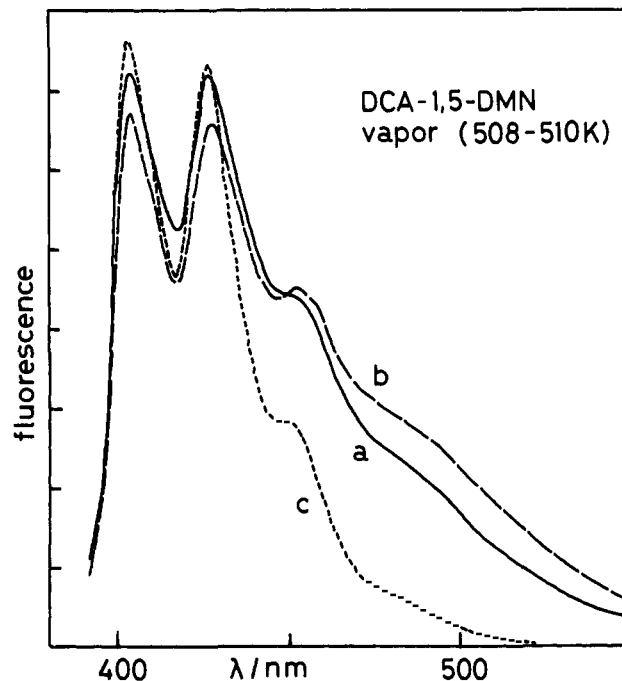(14) K. G. Spears and S. A. Rice, *J. Chem. Phys.*, **55**, 5561 (1971).
(15) W. R. Ware, A. M. Garcia, C. S. Paramenter, M. D. Schuh, and K. Y. Tang, *Chem. Phys.*, **17**, 377 (1976).
(16) A. M. Halpern and T. Gartman, *J. Am. Chem. Soc.*, **96**, 1393 (1974).

Figure 6. Fluorescence spectra of (a) DCA-1,5-DMN (DCA, 10^{-6}M; 1,5-DMN, 2.5×10^{-2}M), (b) that in the presence of ~500 torr of hexane, and (c) that in DCA vapor. The spectra are uncorrected.
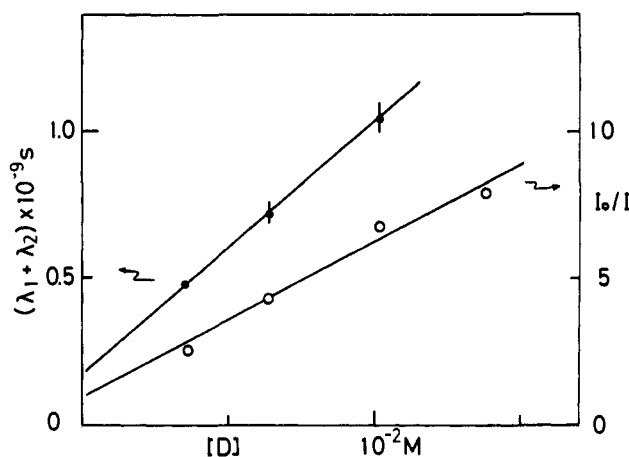

Figure 7. Plots of $\lambda_1 + \lambda_2$ vs. [D] and I_0/I vs. [D] in DCA-1,5-DMN at 513 K.

glected in the presence of the buffer gas. Therefore, it is reasonable that the fluorescence decay of the exciplex in the collisionally relaxed system excited at the upper vibrational states is the same within experimental error as that of the collision-free exciplex from the DCA moiety $A^*(\nu_l)$ excited at the longest absorption edge (430 nm), as mentioned above.

Intermolecular Exciplex Formation in the Vapor Phase. Figure 6 shows the fluorescence and excitation spectra of 9,10-dicyanoanthracene (DCA) and 1,5-dimethylnaphthalene (1,5-DMN) vapor in the absence and presence of the buffer gas (~500 torr of hexane). The longer wavelength fluorescence may be ascribed to the exciplex, though the fluorescence shows no significant fluorescence maximum even in the presence of the buffer gas. The exciplex fluorescence exhibits a typical rise and decay, of which time constants in eq 2 are in good consistency with those of the double exponential decay of DCA fluorescence (eq 1). In the intermolecular exciplex formation, the rate constant k_3 in the reaction scheme and kinetics is replaced by k_3'[D], where k_3' and [D] are the rate constant of the exciplex formation and the concentration of 1,5-DMN, respectively. The time constants λ_1 and λ_2 were determined in several concentrations of 1,5-DMN. Figure 7 shows plots 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'

Table II. Fluorescence Lifetimes and Rate Constants of DCA-1,5-DMN Exciplex in the Vapor Phase $(\tau = \lambda_1^{-1})^a$

excitation wavelength, nm			
385		420	
T, K	τ, ns	T, K	τ, ns
DCA (1×10^{-6} M) + 1,5-DMN (2×10^{-2} M)			
496	40.8	505	40.0
516	37.0	514	37.4
527	34.5	529	34.4
541	33.6	544	31.7

	rate constant		
	k_3', M^{-1} s^{-1}	k_4, s^{-1}	$(k_5 + k_6)$, s^{-1}
DCA + 1,5-DMN	9.1×10^{10}	1.2×10^7	1.5×10^7

^{a} Errors of fluorescence lifetimes are approximately ±1. Rate constants were determined at 513 K.

$= 9.1 \times 10^{10}$ M^{-1} s^{-1}. The fluorescence intensity ratio of DCA in the absence (I_0) and presence (I) of the electron donor is expressed by the following equation:[12]

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

Plots of I_0/I vs. [D] are shown in Figure 7. Combining the slope of these plots with k_3' and the lifetimes of the exciplex and the DCA fluorescence, the dissociation rate constant of the exciplex (k_4) was obtained to be 1.2×10^7 s^{-1} as summarized in Table II. It is noteworthy that the dissociation rate constant of the exciplex is significantly large in comparison with $k_5 + k_6$ as summarized in Table II, which implies that the dissociation process to DCA and 1,5-DMN is unusually important in the deactivation of the exciplex.

The fluorescence lifetimes of the exciplex of DCA-1,5-DMN vapor in the absence of the buffer gas are independent of the excitation wavelength, while those of the collision-free exciplex in DCAN are remarkably dependent, as mentioned above. In the intermolecular exciplex formation in the vapor phase, the concentration of 1,5-DMN (10^{-2}–10^{-3} M) as the electron donor corresponds to the gas pressure of ~50 torr and the rate of the exciplex formation ($k_3'[D]$) is approximately 10^8–10^9 s^{-1}. The collisional relaxation rate by 1,5-DMN itself is estimated to be 5×10^8 s^{-1} from the hard-sphere collision model, which is comparable to the rate of the exciplex formation. These arguments of the reaction rates suggest that 1,5-DMN act not only as an electron donor but also as a relaxer of the upper vibrational state of the S$_1$ state of DCA. Therefore, the exciplex fluorescence lifetimes of DCA-1,5-DMN vapor even in the absence of the buffer gas cannot depend on the excitation wavelength.

Prochorow et al.[5] suggested that the radiationless decay of the gas-phase TCNB–*p*-xylene exciplex was very sensitive to temperature variation and that the low-frequency intermolecular deactivation played an important role in the radiationless deactivation of the exciplex. The exciplex fluorescence in the DCA–1,5-DMN vapor decreases in intensity in comparison with that of DCA fluorescence with increasing temperature, while the intramolecular exciplex in DCAN vapor shows less significant temperature dependence. The dissociation process of the intermolecular exciplex in the DCA–1,5-DMN vapor is important in the deactivation of the exciplex, as mentioned above. In the intramolecular exciplex, however, the dissociation rate constant is known to be much lower than the association rate constant, and also much lower than the dissociation rate constant in the corresponding intermolecular system. Therefore, the facts in the DCAN vapor suggest that the dissociation of the DCAN exciplex to DCA and naphthyl moieties does not seem to be the most important decay channel of the radiationless deactivation of the exciplex.

A Theoretical Investigation of the Structure and Rotational Barriers of Peroxyformimidic Acid. The Mechanism of Stereomutation at the Carbon–Nitrogen Double Bond

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Abstract: The relative energies of the eight planar structures of peroxyformimidic acid have been studied employing ab initio MO calculations. The minimum energy conformer has the *Z* configuration about the C=N bond and an anti configuration about the O–O bond. The C–O and O–O rotational barriers were calculated to be 6.61 and 3.75 kcal/mol, respectively, employing a 6-31G basis set. The inversion barrier at nitrogen was calculated to be 15.9 kcal/mol (6-31G) and compared to a calculated topomerization barrier in methylenimine of 25.2 kcal/mol. The relevance of these calculations to the epoxidation of alkenes with peroxyformimidic acid is discussed.

Introduction

A significant role is played by 1,2-epoxides (oxiranes) in both biological and industrial chemical processes. Synthetic intermediates containing this highly reactive[1] functional group are typically prepared from alkenes on an industrial scale by the use of organic peroxides and metal catalysts,[2] whereas in the laboratory use is made of a variety of peroxy acids.[3] The latter method appears to require the intermediacy of a weakly basic heteroatom that is intramolecularly hydrogen bonded to a hydroperoxide.

Despite the extensive use of such reagents, the ground-state structures of this important class of organic peroxides have not

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