acid groups[2,3] with the carbonyl oxygen during enolization reactions contrasts sharply with the results of a number of studies of intramolecular general base catalyzed enolization reactions.[20-23] The observed rates for these reactions were found to be similar to those that could be achieved by the use of only modest concentration of base in the corresponding intermolecular reaction. These results would suggest that to achieve large increases in the rates of enolization or

ionization of simple ketones, it is necessary to stabilize the developing negative charge on the carbonyl oxygen.

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Picosecond Studies of the Excited Charge-Transfer Interactions in Anthracene-$(CH_2)_3$-N,N-Dimethylaniline Systems

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Abstract: The excited inter- and intramolecular charge-transfer interactions in N,N-dimethyl-4-[3-(9-anthryl)-propyl]aniline systems have been studied using methods of picosecond laser photolysis. The rates of intramolecular rotation about the methylene bonds of the model compound, the rates of orientational relaxation of the excited charge-transfer complex, and the kinetics of electron transfer are determined and discussed.

It has been established for some time that the kinetics of charge-transfer (CT) interaction between an electron donor (D) and an acceptor (A) are determined by the transitional motion of the particles and the inherent characters of the interacting species. These properties may include the ionization potential of the donor, the electron affinity of the acceptor, and the solvation and Columbic interactions.[1] Little is known, however, regarding the molecular geometric requirements for electron-transfer reactions. Recently, Chandross,[2,3] Okada,[4] and their coworkers made a series of studies on the intramolecular exciplex formation to elucidate this problem. Chandross,[2] *et al.*, showed that in the naphthalene-$(CH_2)_n$-$N(CH_3)_2$ system naphthalene and alkylamine readily form an exciplex when electronically excited. The exciplex did not seem to have strong geometrical preferences. In the anthracene-$(CH_2)_n$-dimethylaniline systems, Okada, *et al.*,[4] found that while for $n = 3$ charge-transfer complex formed easily in all solvents, the excited complex could not form for $n = 1$ or 2 in solvents of low polarity, *e.g.*, n-hexane and cyclohexane. They, nevertheless, concluded that a parallel

sandwich geometrical structure might be favorable but not necessary for the exciplex formation.

We approach the problem from the molecular dynamic point of view. We choose N,N-dimethyl-4-[3-(9-anthryl)propyl]aniline as a model molecule (A-$(CH_2)_3$-DMA). In the previous report,[5] we established that upon excitation anthracene would accept an electron from N,N-diethylaniline (DEA) with the intermolecular reaction distance of 8 Å. Since dimethylaniline has the same electron donating properties as diethylaniline and the three-methylene bond distance is much less than 8 Å, this model molecule should form an exciplex as rapidly as the free anthracene and dimethylaniline system, if there is no orientational requirement for interaction. On the other hand, if the time courses for exciplex formations are different, then we know molecular motions other than translational modes must be involved. Theoretically, absolute fluorescence quantum yield and radiative lifetime measurements may provide similar information about these systems. Yet, as Okada, *et al.*, have shown, the lifetime and quantum yield varies from system to system and quantitative measurements and interpretation are difficult. Furthermore, time-dependent measurement can reveal the dynamic feature of the molecular process and the measurement is possible for nonfluorescent

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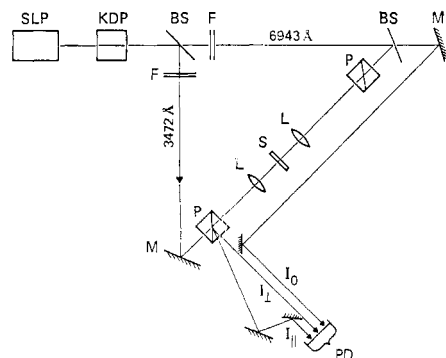(5) T. J. Chuang and K. B. Eisenthal, *J. Chem. Phys.*, 59, 2140 (1973).

Figure 1. Experimental arrangement for monitoring $I_{||}$ and $I_{\perp}$ transmissions at 6943 Å following photoexcitation of anthracene by a 3472-Å light pulse: (SLP) single laser pulse at 6943 Å from the laser oscillator, single pulse selector and laser amplifier systems; (KDP) second harmonic crystal; (BS) beam splitter; (F) filter; (M) mirror; (P) polarizer; (L) lens; (S) sample; (PD) photodiode.

Figure 2. Absorption and fluorescence spectra of A–(CH₂)₃–DMA in n-hexane.

systems. Neither of these can be achieved by the steady state methods. We also report in this paper the rotational relaxation process of this model molecule. This is a part of the program we set up to study the kinetics of the electron transfer reactions using picosecond laser pulses.[5,6]

Experimental Section

The experimental arrangement is shown in Figure 1. The details of this setup have been published elsewhere.[5] Here, it suffices to mention that the picosecond pulse at 3472 Å from a mode-locked ruby laser system is used to excite anthrane into its first excited singlet state. The fundamental pulse at 6943 Å then probes the formation of the charge-transfer complex which absorbs this wavelength corresponding to $(A^-D^+) \rightarrow (A^{-*}D^+)$ transition. The pulse width of the laser is about seven picoseconds and approximately Gaussian in shape. The probe pulse is optically delayed with respect to the exciting pulse and the delay time which has a picosecond in resolution is varied from zero to a time region longer than a nanosecond.[5] We use polarizers to measure the parallel and perpendicular components of the transmitted intensities, from which the dynamics of orientational relaxation and charge-transfer complex formation are deduced. For the fluorescence lifetime measurement, the same 3472-Å pulse is used as the excitation source. An ITT photodiode and Tektronix 519 Oscilloscope (~0.5-nsec resolution) are used to monitor the fluorescence decay curve.

The preparation of the model compound N,N-dimethyl-4-[3-(9-anthryl)propyl]aniline is as follows.

N,N-Dimethyl-4-[3-(9-anthryl)-1-oxo-2-propyl]aniline. A solution of 4-dimethylaminoacetophenone[7] in dimethyl sulfoxide was treated with a small amount of base. This solution was added to a solution of 9-anthraldehyde in dimethyl sulfoxide. The precipitate which formed after 1.5 hr stirring was filtered and recrystallized from ethanol. It melted at 157–158° and was formed in 50% yield: nmr (CDCl₃) δ 2.96 (s, 6), 6.58 (d, 2), 7.40 (m, 5), 7.90 (m, 4), 8.30 (m, 4), 8.62 (d, 1).

N,N-Dimethyl-4-[3-(9-anthryl)-1-oxopropyl]aniline. A solution of N,N-dimethyl-4-[3-(9-anthryl)-1-oxo-2-propyl]aniline was reduced in a Parr hydrogenation apparatus using a 10% palladium on carbon catalyst and acetone solvent. A crude product melting at 145° after recrystallization from ethanol–water and from hexane was obtained. This was used directly in the next reaction. A sample which was purified by column chromatography melted at 159–160°: nmr (CDCl₃) δ 2.85 (s, 6), 3.20 (t, 2), 3.90 (t, 2), 6.43 (d, 2), 7.30 (m, 4), 7.80 (m, 6), 8.18 (s, 1).

N,N-Dimethyl-4-[3-(9-anthryl)propyl]aniline. The crude ketone was reduced in diethylene glycol with hydrazine hydrate and potassium hydroxide. The oily solids obtained after pouring into aqueous ethanol were recrystallized first from ethanol–water and
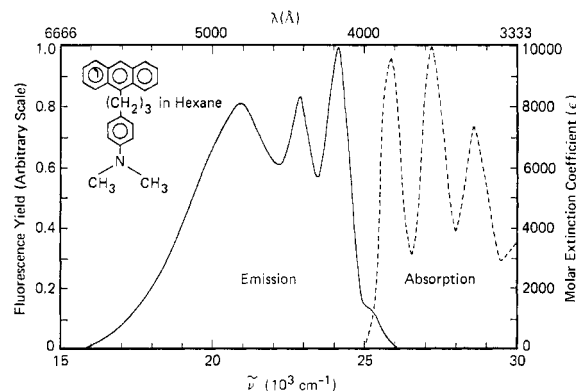
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then from petroleum ether. The product melted at 98.5–100°: nmr (CDCl₃) δ 2.10 (m, 2), 2.80 (t, 2), 2.90 (s, 6), 3.58 (t, 2), 6.67 (d, 2), 7.10 (d, 2), 7.30–8.20 (m, 8), 8.26 (s, 1). Anal. Calcd for C₂₅H₂₅N: C, 88.45; H, 7.42; N, 4.12. Found: C, 87.99; H, 7.46; N, 4.32.

The concentration of the sample is fixed at 2.5×10^{-3} M. The solution is saturated with nitrogen to avoid oxygen quenching processes. Unless indicated, all experiments are carried out at room temperature.

Results and Discussion

The absorption and fluorescence spectra of the model molecule in n-hexane is shown in Figure 2. The absorption spectrum from 3300 to 4000 Å is identical with that of 9-methylanthracene alone in hexane indicating that there is no significant ground state interaction between the anthracene and dimethylaniline groups. This is consistent with the results of Chandross and Okada, et al. The fluorescence of the charge-transfer complex peaks at 4800 Å, very similar to that of the dilute hexane solution of anthracene and diethylaniline. It has a lifetime of 50 nsec which is very long in comparison with the lifetime of anthracene (5 nsec) but much shorter than that reported by Okada, et al. The discrepancy is primarily due to the fact that we simply saturated our solutions with nitrogen while Okada, et al., deaerated their solutions entirely. In any event, this lifetime does not affect the dynamic processes we are going to analyze and discuss below.

We first realize that linearly polarized light is used to excite one of the three sample axes; therefore, an anisotropic distribution in the orientation of the excited molecules is created. Consequently, the observed probe transmissions, $I_{||}(t)/I_0$ and $I_{\perp}(t)/I_0$, will be functions of not just the kinetics of the electron-transfer reactions but also the dynamics of the rotational motion of the molecules. That is

$$I_{||}(t)/I_0 = \exp\left\{-\epsilon_{CT}l\int_\Omega n_{CT}(\Omega,t)\alpha_{||}d\Omega\right\} \quad (1a)$$

and

$$I_{\perp}(t)/I_0 = \exp\left\{-\epsilon_{CT}l\int_\Omega n_{CT}(\Omega,t)\alpha_{\perp}d\Omega\right\} \quad (1b)$$

where ϵ_{CT} is the absorption coefficient of the CT complex at 6943 Å, l is the length of optical path, $n_{CT}(\Omega,t)$ is the concentration of the CT complex with its transition vector oriented at an angle Ω at time t, and α's are the projections of the transition vector along the parallel and perpendicular axes. Since the details of the de-
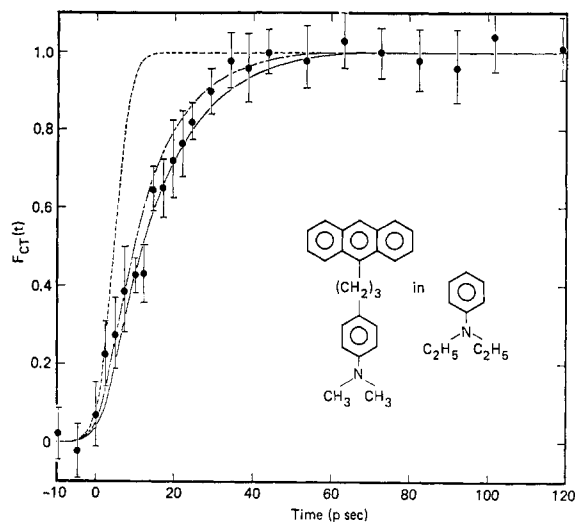
Figure 3. Charge-transfer complex formation F_{CT} vs. time for A-(CH$_2$)$_3$-DMA in DEA. The curves are calculated formation function convoluted with the pulse widths of the excitation and probe light pulses. The rate constant is 7×10^{10} sec^{-1} for (——); 9×10^{10} sec^{-1} for (———); $\gtrsim 66 \times 10^{10}$ sec^{-1} for (---).
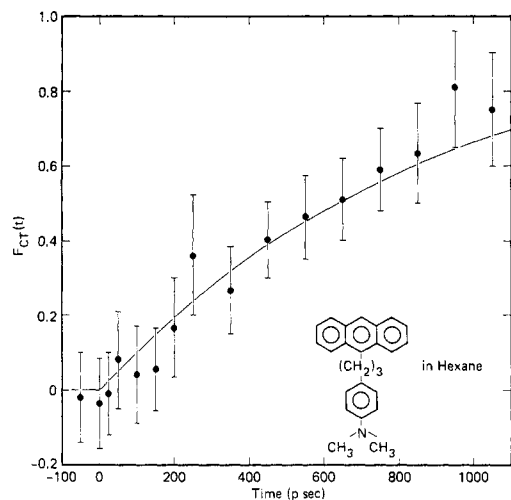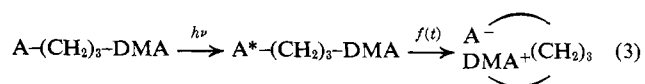

Figure 4. Charge-transfer complex formation F_{CT} vs. time for A-(CH$_2$)$_3$-DMA in n-hexane. The curve is a calculated exponential formation function.

rivation are given in the subsequent paper,[6] we present only the formula we need for the data analysis

$$F_{CT}(t) \equiv [-\ln (I_{||}/I_0)^*(I_\perp/I_0)^2]/\epsilon_{CT}lC_A(0) =$$

$$1 - \exp\left(-\int_0^t f(t')\mathrm{d}t'\right) \quad (2)$$

where $C_A(0)$ is the initial concentration of excited anthracene molecules created by the excitation pulse and $f(t)$ is the rate function of the electron transfer reaction

$$\text{A-(CH}_2)_3\text{-DMA} \xrightarrow{h\nu} \text{A*-(CH}_2)_3\text{-DMA} \xrightarrow{f(t)} \overbrace{\text{DMA}^+\text{(CH}_2)_3}^{\text{A}^-} \quad (3)$$

We recognize that $F_{CT}(t)$ is a function of the rate of formation of the CT complex and is independent of the orientational motion of the particle. This is because we have taken the sum of the absorbances for the probe light polarized parallel and polarized in the two orthogonal directions which is in dependent of orientation.
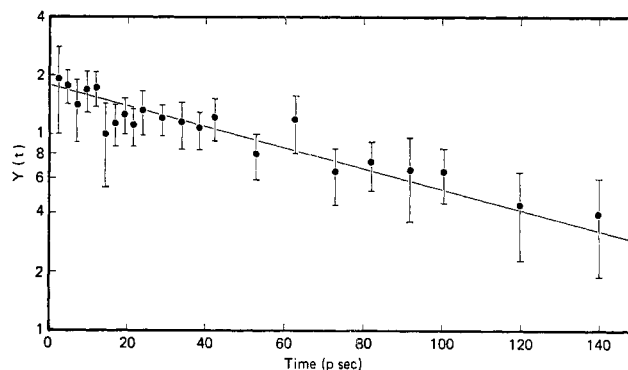
Figure 5. Plot of log $Y(t)$ vs. time for A-(CH$_2$)$_3$-DMA in DEA.

By so doing, we monitor the concentration of the complex oriented in all directions and therefore the rotational motion of the molecule has no effect. To obtain the rate of orientational relaxation, we take the ratio $I_{||}/I_\perp$. The expression for this ratio is much more complicated. If we assume, however, that the rate function is a constant and the rotational motion of the molecule is isotropic, the expression can be reduced to

$$R \equiv I_{||}/I_\perp = \exp\left\{\frac{-\epsilon_{CT}lC_A(0)C_S f}{f + 6(D_A - D_{CT})} \times \right.$$

$$\left. [\exp(-6D_{CT}t) - \exp(-ft - 6D_At)]\right\} \quad (4)$$

where D_A and D_{CT} are the rotational diffusion constants of the excited anthracene and the CT complex, respectively, and C_S is just a constant. Since the rate function f can be obtained independently from eq 2, the values of D_A and D_{CT} can be obtained from eq 4.

The experimental results for A-(CH$_2$)$_3$-DMA in DEA and hexane are shown in Figures 3 and 4, respectively. The experimentally obtained formation curves are convoluted with the excitation and probe pulses because of their finite width. However, this is not crucial since our data are not pulse width limited as is clearly shown in Figure 3. The growth curves for the formation of the charge-transfer complex are found to be exponential in both the DEA and hexane solvents and yield rate constants of 7.5×10^{10} and 1.1×10^9 sec^{-1}, respectively. Since the electron-transfer process in hexane is relatively slow, we have taken the lifetime of the excited anthracene into account to obtain the charge transfer rate constant in hexane.

The rotational diffusion constants are obtained by combining the experimentally determined rate of electron transfer with the measured values of $I_{||}/I_\perp$. In practice, we find that the ln $(I_{||}/I_\perp)$ values divided by the relative concentration of the CT complex, i.e., $[1 - \exp(-ft)]$, follow an exponential time dependence indicating that the orientational relaxation times of the excited model compound and the charge-transfer complex are equal within the accuracy of our measurements. Thus combining $D_A \approx D_{CT} = D$ with eq 4, we obtain

$$Y(t) \equiv (\ln R)/[1 - \exp(-ft)]$$

$$= -\epsilon_{CT}lC_A(0)C_S \exp(-6Dt) \quad (5)$$

The result of this analysis for the model molecule in DEA is shown in Figure 5. The orientational relaxa-

tion time, i.e., $^1/_6 D$, is about 80 psec. Unlike our measurements in the DEA solvent, we did not observe significant anisotropy, i.e., ln $R \approx 0$ for all time, for the complex in hexane solution. This is readily understandable since the rate of CT formation is slow and the rate of rotation of the molecule is much faster in in hexane than in DEA. DEA is about seven times as viscous as hexane.

In hexane solutions, we have determined earlier[5] that electron transfer can occur very rapidly ($\sim$10 psec) when the free donor and acceptor molecules are separated by 8 Å or less. Here, in the model molecule, A and DMA are separated by only three methylene groups ($\sim$4 Å), yet it takes 900 psec to form the CT complex. We conclude that this is due to the effect of the methylene bonds on the rotational motion of the donor and the acceptor groups. Therefore the observed kinetics shown in Figure 4 is due to the internal orientational motion of the model molecule. Considering that the potential barrier of internal rotation of simple alkanes is about 3–4 kcal/mol,[8] it is not surprising that the two end groups would orient so slowly into the favorable geometry for interaction.

In this discussion, we have ruled out the possibility that the observed slow rate of CT interaction in the hexane system is due to the intermolecular rather than intramolecular interaction. Intermolecular charge transfer, i.e., A–$(CH_2)_3$–DMA$^+$–A$^-$–$(CH_2)_3$–DMA, is a diffusion-controlled process under these conditions. The translational diffusion rate constant for anthracene and diethylaniline in hexane is 1.65×10^{10} M^{-1} sec^{-1}.[9] For the model molecule, this rate constant must be even smaller. Therefore, the time constant for intermolecular reaction in our solutions would be 24 nsec or longer.

Our observation of a single exponential function for the charge-transfer complex formation and the relatively long time constant for formation (900 psec) also strongly indicates that at thermal equilibrium the fraction of ground state molecules in the configuration necessary for electron transfer is negligible. If there was a significant population in the configuration favorable for electron transfer, we would expect to observe a faster rate with two or more distinct rates of formation. The fact that we do not see this is furthermore consistent with the spectral data indicating that there is no appreciable interaction between the ground states of A and DMA groups.

The rate of CT complex formation of the model molecule in DEA is very rapid (Figure 3). Apparently, the excited anthracene portion of the molecule interacts directly with the solvent DEA molecules to form the intermolecular charge-transfer complex, i.e.

$$\text{DEA} + \text{A*–}(CH_2)_3\text{–DMA} \longrightarrow (\text{DEA}^+\text{–A}^-)\text{–}(CH_2)_3\text{–DMA} \quad (6)$$
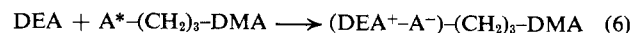
There is a very interesting dynamic feature in this reaction. The reaction rate between DEA and A–$(CH_2)_3$–DMA seems a little bit (about 35%) slower than that of DEA and free anthracene.[5,6] We also recognize that the rotational diffusion rate of A–$(CH_2)_3$–DMA system is slower than that of the free anthracene system by about 30%. The former has a rotational relaxation time of 80 psec while the latter is about 60 psec.[6] This indicates that in pure DEA solutions both excited A and A–$(CH_2)_3$–DMA molecules as well as DEA have to undergo some reorientation in order to react. Yet extensive reorientational readjustment is not necessary, otherwise the process would be much slower. The very fast rates of CT formation in DEA are not surprising in either the free molecule or the model compound since they are surrounded by many DEA molecules and a significant fraction of donor–acceptor pairs are in a fairly favorable orientation before reaction.

In conclusion, we infer from picosecond time-dependent studies that relative molecular reorientation is an important and necessary process for excited charge-transfer complex formation. We have determined the rates of intramolecular rotation about the methylene bonds of the model compound, the rates of electron transfer, and the orientational relaxation of the excited charge-transfer complex.

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