Intramolecular Excited-State Charge-Transfer Interactions and the Role of Ground-State Conformations

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The dynamics of formation of the intramolecular exciplex, anthracene- $(CH_2)_3$ -N,N-dimethylaniline, has been investigated by using a picosecond laser-streak camera system. Measurement of the fluorescences of both the excited-state acceptor decay and exciplex rise demonstrate that there is no intermediate nonfluorescent state prior to exciplex formation and that the end-to-end relaxation is exponential. Furthermore, a dependence of exciplex rise time upon the fluorescence wavelength is found and interpreted as evidence for two distinct ground-state conformers, one being dominant.

Introduction

An electronically excited molecule can relax its energy through charge-transfer (CT) interactions with surrounding ground-state molecules, leading to exciplex formation in nonpolar solvents and the formation of ions in polar solvents. The diverse physical and chemical nature of these processes have been extensively studied since the pioneering work of Leonhardt and Weller.¹ Of particular interest is the role of geometric effects, i.e., the relative orientations of the donor and acceptor molecules on the dynamics of exciplex formation. From our previous studies² on the intermolecular exciplex formation between anthracene and N,N-diethylaniline (DEA) molecules it was established that upon excitation of anthracene an electron can jump from DEA to the excited anthracene over a reaction distance of 8 Å within 10 ps. By connecting the anthracene and DEA molecules with three methylene groups (I), the relative orientations of the molecules are



restricted while still maintaining their close proximity, maximum separation between them being less than 4 Å.

Upon excitation, this model molecule should form an intramolecular exciplex as rapidly as the free anthracene and DEA system, if there are no significant orientational requirements for CT interaction. On the other hand, if the time course for exciplex formation is different for the two cases, then molecular motions to achieve a favorable geometry must be involved and can be directly followed in the formation of the intramolecular exciplex. This principle has been applied in previous studies^{3,4} by monitoring the exciplex adsorption at 694 nm. However, the results obtained in these studies were in conflict possibly due to nonlinear intensity-dependent absorption which would produce species absorbing in the exciplex region. This could be responsible for the rapid rise time observed in one of the studies.⁴

To avoid these complications lower laser intensities were used in the present study. Furthermore, a complementary technique, namely picosecond time-resolved fluorescence

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of both the excited anthracene decay and exciplex formation at several different wavelengths, is employed to obtain the dynamics of the charge-transfer process. The results confirm the finding of one of the previous studies.³ In addition, we have observed an unexpected dependence of the rate of exciplex formation on the fluorescence wavelength monitored. This observation is interpreted in terms of the effect of different ground-state conformations upon the rate of intramolecular exciplex formation.

Experimental Section

A TEM₀₀, 4–8 ps, third-harmonic pulse (351 nm) from a passively mode-locked Nd³⁺-phosphate glass laser was used to excite the anthracene moiety. The fluorescence and the excitation pulse width were monitored with an Imacon streak camera coupled to a PAR optical multichannel analyzer. Streak speed is calibrated with an etalon. Linearity of the intensity response is checked in every experiment and the streak camera–OMA response function is corrected in each shot.

The synthesis of 9-anthracene- $(CH_2)_3$ -N,N-dimethyl-aniline has been described before.³ The crude compound was first purified by recrystallization from ethanol-water and petroleum ether. A portion was then further purified by thin-layer and spinning-band chromatography and checked by high-performance LC and NMR. Fluorescence spectra show no difference between the compound purified by chromatography and that purified by recrystallization only. Excitation spectra taken at several different wavelengths (410, 480, 560 nm) are in excellent agreement. Experiments were performed with the recrystallized compound and the chromatographically purified compound and yielded identical results. Isopentane was obtained from Aldrich (99+%). It was purified by passing through a neutral alumina column before use. The sample solution was deoxygenated by repetitive freeze-pump-thaw cycles. All experiments were done at 20 °C.

Results and Discussion

A 351-nm picosecond laser pulse was used to excite the anthracene moiety in the model compound. The decay of anthracene fluorescence in isopentane was monitored at 410 nm and the result is shown in Figure 1. It can be fitted with an exponential curve with decay constant of 1.4 ± 0.1 ns. The observed single exponential decay is quite different from the two exponential decay behavior which is characteristic of the reverse dissociation generally observed in other exciplex and excimer systems. This reflects the unusual stability of the anthracene-(CH₂)₃-

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Figure 1. Decay of the anthracene molety and the formation of the exciplex at several different wavelengths. The dots are experimental points and the curves are theoretical calculations.

N,N-dimethylaniline exciplex. The fluorescence rise of exciplex was monitored at 520 nm. At this wavelength the fluorescence curve consists of a very rapid initial rise (within the laser pulse width) which is due to the tail of the overlapping anthracene emission, followed by a much slower rise. By subtracting the contribution of the anthracene emission, obtained in the same experiment, an exponential exciplex formation curve with rise time of 1.4 \pm 0.1 ns was obtained as shown in Figure 1. The fluorescence rise time of the exciplex was thus found to be the same as the anthracene decay time. If there were no geometric requirements for exciplex formation, then we know from our earlier work² on intermolecular exciplex kinetics that a rise time of less than 10 ps should be observed. The much slower formation time we find in the intramolecular case confirms our earlier work which indicated that rotational motions are required to bring the two moieties into a favorable conformation to form the exciplex. The time dependence of this motion thus provides direct information about the end-to-end relaxation dynamics of this short-chain molecule. The exponential behavior observed and possible models of it will be discussed in detail in a forthcoming paper. The observation that the rate of anthracene decay and exciplex rise are equal indicates that there is no intermediate nonfluorescent state present before the formation of the fluorescent exciplex. However, the presence of such nonfluorescent intermediates has been suggested by many workers based on studies of related systems.⁵⁻⁸ We therefore emphasize that these intermediates are not necessarily a general phenomenon in exciplex formation.

An interesting and unexpected result was observed when we probed the low-energy side of the exciplex emission spectrum. The rise time of exciplex fluorescence at 600 nm, 2.1 ± 0.2 ns, was found to be slower than both the rise time of exciplex monitored at 520 nm, 1.4 ± 0.1 ns, and the decay of anthracene monitored at 410 nm, 1.4 ± 0.1 ns. By probing at four different wavelengths in the exciplex emission band, we have shown that there are two distinct regions each having a characteristic rise time. The formation rates at longer wavelengths (570 and 600 nm) are found to be the same but slower than those at shorter wavelengths (480 and 520 nm). These results are summarized in Figure 1. The extensive purification and checking procedures employed, which included excitation spectra, fluorescence, NMR and high-performance LC (details presented in the Experimental Section), argue strongly against the possibility that the long wavelength emission is due to an impurity. The fact that there are

two kinetically distinguishable regions in the emission spectrum indicates the exciplex has two different conformations with different emission energies. This is consistent with studies, using X-ray and fluorescent methods,⁹⁻¹³ of intramolecular excimers in which more than one excimer conformation was found. However, this is indeed the first time, to the best of our knowledge, that it is observed among exciplexes. The lifetimes of the two complexes, measured by the photon-counting technique, were found to be the same, being 126 ± 3 ns in isopentane. This observation not only provides further strong evidence that the long wavelength complex is not due to an impurity, it also implies that either the two exciplexes have the same radiative and nonradiative rate constants or they reach equilibrium on a time scale which is short relative to their decay times.

In order to explain the origin of different exciplexes formed with different rates, we have considered many possible mechanisms. Here we briefly mention two important possibilities. For the convenience of discussion we will refer to the short wavelength and the long wavelength exciplexes as the blue and the red exciplexes, respectively. One possibility is that the blue emission is due to an unrelaxed exciplex, which on solvent and/or structural changes evolves into the more stable red exciplex form. Since the decay of the blue exciplex would correlate with the appearance time of the red exciplex if this model was correct, which it does not, we can eliminate this scheme. A second possibility is that there is a small fraction of ground-state charge-transfer complexes present which on excitation yield the red emission. This indeed was suggested to be occurring in the compound 9,10-dicyanoanthracene- $(CH_2)_3$ -naphthalene. In our case this possibility can be ruled out on the basis of our time-resolved measurements which show that the red emission appears slowly (2.1 ns) rather than the instantaneous rise that would occur if the emission was due to the direct excitation of a ground-state charge-transfer complex.

A model consistent with all of our data is based upon two different ground state conformations, one being dominant. Each of these forms go through different rotational motions leading to the formation of different exciplexes. The blue complex is derived from the dominant groundstate conformation. The formation dynamics are shown in the following scheme:



where $(A D)_1$ and $(A D)_2$ represent different ground state conformations, $(A D)_1$ being the dominant one. The ratio of the relative populations of the two groundstate conformations is estimated to be larger than 10:1 on the basis of their relative fluorescence intensities and their formation rates. Because of the large difference in relative populations of the two ground-state conformations, the anthracene fluorescence decay reflects only the existence of the dominant one within our experimental limits. The interesting phenomenon that we have observed is, however, readily revealed by monitoring the exciplex fluorescences at the blue and red wavelengths since the two exciplex emissions do not significantly overlap in wavelength.

At present, it is not clear what structures actually correspond to the ground-state conformers in the model compound. Nor do we understand the exact nature of the two different rotational motions. We are currently investigating the viscosity and temperature dependence of these dynamic processes in order to gain a better understanding of these issues. Preliminary results show the same behavior in hexane solution, where the formation rate of exciplex at 570 nm is slower than at 520 nm, being 2.6 and 1.9 ns, respectively.

Note

During the course of writing this paper, two relevant articles appeared in the literature. Van der Auweraer et al.¹⁴ studied the intramolecular exciplex formation of 3phenyl-1-(dimethylamino)propane and reached the similar conclusion that there are two different ground-state conformers leading to the exciplex formation with different rates. However, only one exciplex emission was detected in their system. Another paper by Migita et al.¹⁵ reported a time-resolved fluorescence study on the same intramolecular exciplex system investigated here. They determined the exciplex formation time in hexane to be 2.6 ns in the wavelength region 540 nm and above, which is exactly what we find. However, they did not monitor the fluorescence rise at shorter wavelengths where we detected the faster exciplex formation.

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