EFFECTS OF CONFORMATION AND SOLVENT POLARITY ON INTRAMOLECULAR CHARGE TRANSFER: A PICOSECOND LASER STUDY

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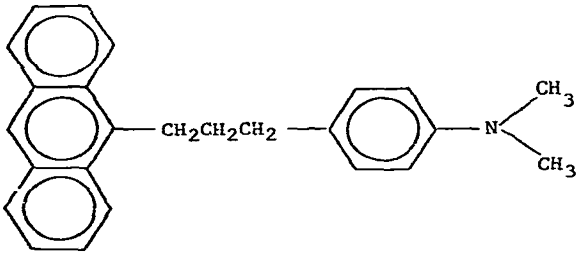
Picosecond dynamics of the intramolecular exciplex anthracene–$(CH_2)_3$–N,N-dimethylaniline have been measured in acetonitrile. The results indicate two processes. First, very rapid (7 ± 1 ps) electron transfer for molecules in extended conformations, producing solvated ion pairs without passing through the exciplex state. Second, folded conformers yield exciplexes within 2 ps, having a lifetime of 580 ± 30 ps.

1. Introduction

Charge-transfer (CT) interactions provide an important and common pathway for energy relaxation in excited-state molecules [1–8]. These interactions, though determined by the intrinsic properties of the donor and acceptor pair, are importantly modified by environmental effects [9–13]. In non-polar solvents the exciplex dynamics are greatly altered by geometric restrictions [10, 14–21]. An example of this is the relatively slow rate for intramolecular exciplex formation (ns) in A–$(CH_2)_3$–D



compared with the intermolecular exciplex formation (ps) of free A and D at comparable separations. It is to be noted that due to the charge separation associated with the CT interaction the solvent polarity can also play an important role [7,10,11]. To examine the interplay between geometric and solvent dielectric effects, we have studied A–$(CH_2)_3$–D in the strongly polar ($\epsilon = 37$) solvent acetonitrile using picosecond fluorescence as a probe method. This approach is complementary to transient absorption measurements and avoids complications due to overlapping absorptions.

2. Experimental

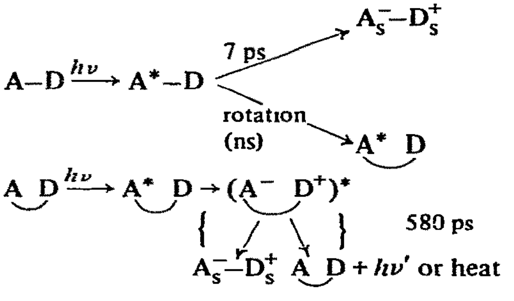
A TEM_{00}, 4–8 ps, third harmonic (351 nm) pulse from a passively mode-locked Nd^{3+} phosphate glass laser was used to excite the anthracene moiety. The fluorescence and the excitation pulse width were monitored with an Imacon streak camera coupled to a PAR optical multichannel analyzer. Streak speed is calibrated with an etalon. Linearity of the intensity response is checked in every experiment and each shot is corrected for the streak camera–OMA response function. All data are deconvoluted using both the measured response time of the detecting system and the laser pulse width. The synthesis of 9-anthracene–$(CH_2)_3$–N,N-dimethylaniline has been described before [17]. The purification procedure has been published elsewhere [22]. Acetonitrile was obtained from Eastman and purified by passing through a neutral alumina column before use. The sample solution was deoxygenated by repetitive freeze–pump–thaw cycles. In all experiments the sample concentration was 2.5×10^{-3} M and the temperature was 20°C.

3. Results and discussion

In marked contrast to the results in non-polar solvents [22], where the excited CT complex is formed in a few nanoseconds and lives for more than 100 ns, we have found in acetonitrile that it is formed in a time shorter than we can resolve (2 ps) and decays in 580 ± 30 ps, fig. 1 This is the first direct observation of the formation of the exciplex in acetonitrile. These results were obtained, following excitation of the anthracene moiety at 351 nm, by monitoring the weak CT complex emission in the 500–600 nm region.

Although the CT complex is formed "instantaneously", we find that the excited anthracene moiety, which is monitored at 411 nm, has a lifetime of 7 ± 1 ps, fig. 2. Since the CT rise is faster than the anthracene decay we conclude that these observed emissions correspond to independent processes.

The very fast CT rise suggests that only those molecules in a favorable ground-state conformation at the time of excitation lead to the excited CT complexes. For those molecules in unfavorable extended conformations a new non-radiative decay channel is responsible for the observed 7 ps lifetime of the excited anthracene moieties. This channel, which becomes accessible in highly polar acetonitrile, is direct formation of ion pairs For extended molecules, the excited anthracene decays directly to the ion pair since the internal rotational motions necessary for the formation of excited CT complexes are too slow to compete. The appearance of this new channel for energy dissipation in polar solvents is a result of solvent stabilization of the ion pair. On the other hand, in the non-polar solvents, e.g. 2-methylbutane, it is probable that the energy of $A^-{-}(CH_2)_3{-}D^+$ is higher than that of $A^*{-}(CH_2)_3{-}D$ in extended conformations The following scheme summarizes the results in very polar media·



(1)

(2)

where A D represents the sandwich conformation, A–D. an extended conformation, $A_s^-{-}D_s^+$ the solvent stabilized extended ion pair, and $(A^-\ D^+)^*$ the excited CT complex

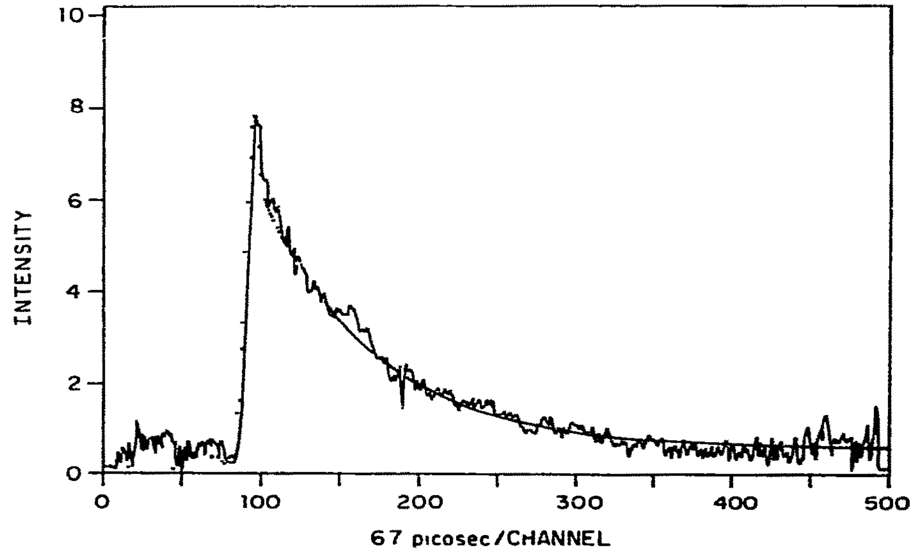


Fig. 1. Fluorescence of the excited CT complex in acetonitrile (2.5×10^{-3} M). The smooth curve is a theoretical fit to the experimental decay.

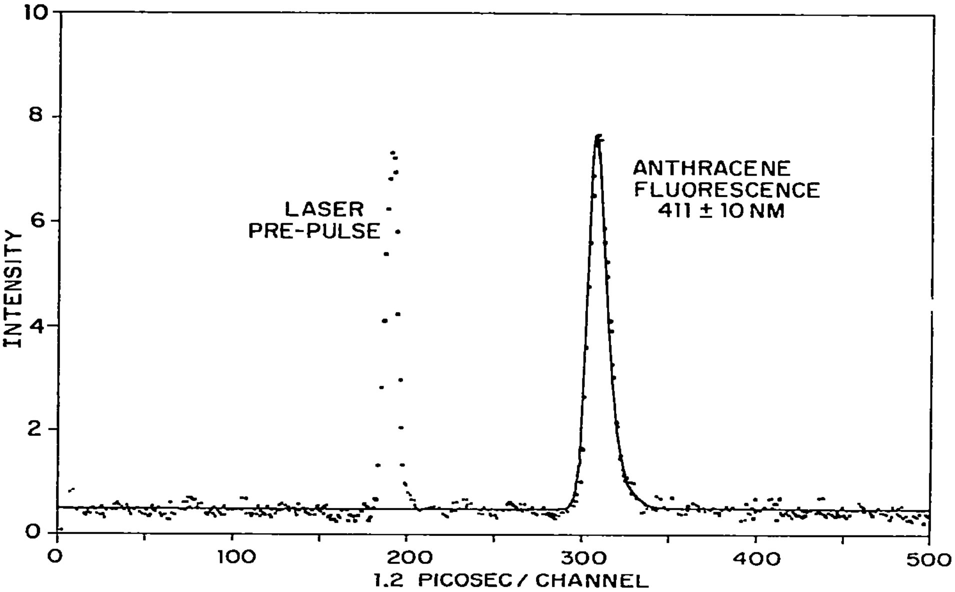


Fig. 2 Anthracene moiety fluorescence in acetonitrile. The laser pre-pulse is both a pulse width display and a time marker for signal averaging Solid curve is a theoretical fit to the experimental points

The lifetime of the excited CT complex in acetonitrile is more than two orders of magnitude shorter than in 2-methylbutane, i.e. 580 ps versus 126 ns [22]. There are several factors which can contribute to the marked decrease in lifetime. In the polar solvent the stabilization of the solvated ion pair state to an energy below that of the excited CT state opens a new pathway for decay of the excited CT complex. This energy relaxation channel is not available in non-polar solvents. Another decay route which can be solvent dependent is intersystem crossing in the excited CT complex. Shifts in energy levels and changes in Franck–Condon factors can alter the singlet to triplet rate constant. However it should be noted that in the intermolecular case there is no evidence for triplet formation on this short time scale [8]. Since the CT lifetime decreases as the solvent polarity increases in both intermolecular [12,23] and intramolecular systems it seems reasonable to attribute this trend to a common source, namely solvent stabilization of the ion pair.

In addition to the solvent-dependent non-radiative rate constant discussed above, a decrease in the radiative rate constant of the excited CT complex can occur as the solvent becomes more polar [23]. This latter possibility was first proposed for an intermolecular CT system to explain the observation that the CT fluorescence quantum yield decreased more rapidly than the CT lifetime as the solvent polarity increased [23]. It is to be noted that an alternative explanation for this disparity in the lifetimes and quantum yields has been offered for the intermolecular case [12]. This entails the direct formation of ion pairs from A^*D without passing through the excited CT complex Our results provide the first direct support for this mechanism, eq. (1), at least for the intramolecular system reported here However this does not eliminate the possibility of the CT radiative rate constant, eq. (2), varying with solvent polarity and thereby altering the quantum yield of CT fluorescence.

Combining the present findings in acetonitrile with our results in non-polar solvents [22] we can make some general remarks on the charge-transfer dynamics of $A-(CH_2)_3-D$ in liquids. The key to understanding the behavior of these intramolecular charge-transfer systems is the strong dependence of the energies of the excited charge-transfer complex and ion-pair states on both conformation and solvent polarity. The shifts in the energies of these states relative to each

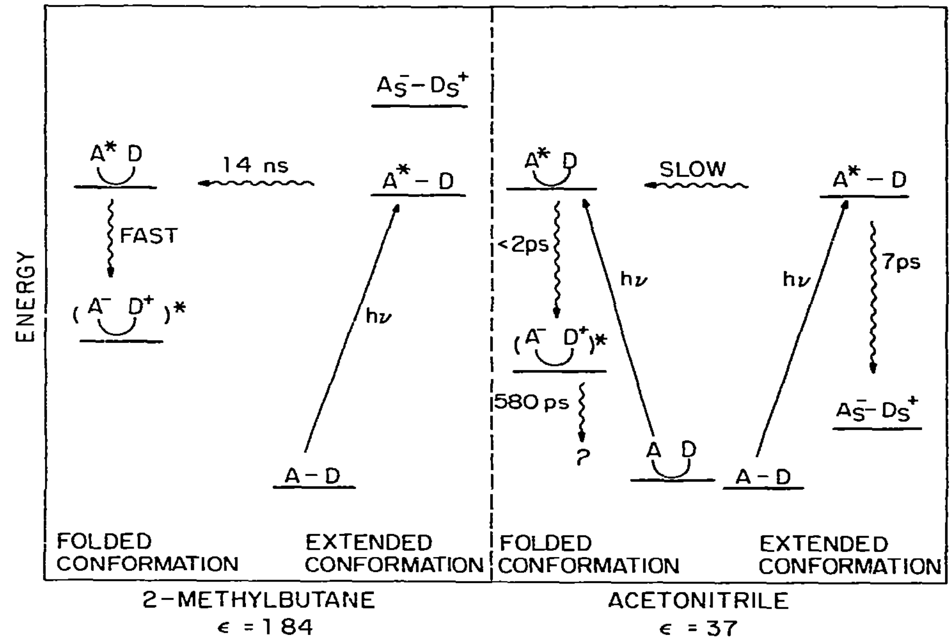


Fig. 3. Energy levels and dynamics of anthracene–$(CH_2)_3$–N,N-dimethylaniline in both a low- and high-polarity solvent. Relative energies are qualitative.

other and to the energy of the locally excited state (which is not very solvent or conformation sensitive) determine the decay channels. Our experimental results in acetonitrile and 3-methylbutane [22], presented in fig. 3, represent the extreme cases. In the non-polar solvent the lowest-energy state for the extended conformation is the locally excited one, A*–D. In the folded conformation the excited CT state $(A^- D^+)^*$ becomes more stable than A* D. Thus to effect charge transfer the extended molecules must assume the folded conformation. In acetonitrile, on the other hand, the lowest-energy state is the solvated extended ion-pair conformation, $A_s^- - D_s^+$. A direct electron transfer to go from A*–D to this state is therefore energetically feasible and extremely fast (7 ps). For the folded conformation, $(A^- D^+)^*$ is at a lower energy than A* D and thus exciplex formation becomes the most rapid energy decay route. We find this process to be faster than we can resolve (<2 ps). Since the solvated extended ion pair, $A_s^- - D_s^+$, is lower in energy than the folded excited CT complex, $(A^- D^+)^*$, one channel through which this latter species can relax is by unfolding and undergoing solvent stabilization. If we now consider liquids of intermediate polarity, the formation rate of the ion pair should slow down sufficiently (compared with the very rapid rate in acetonitrile) to permit the chain motions necessary for development of the folded excited CT complex from the extended form. Therefore both exciplex and direct ion-pair formation should be observed.

4. Conclusions

Photoexcitation of extended conformers of A–$(CH_2)_3$–D in acetonitrile is followed by vary rapid electron transfer yielding the solvated ion pair (7 ps). This occurs directly, i.e. without passing through an exciplex state. Since the extended conformers yield ion pairs, we conclude that there are no severe geometry requirements for formation of the ion pair. Using a sensitive streak camera–OMA system, the exciplex formation in acetonitrile has been observed for the first time, and is attributed to the excitation of folded ground-state conformers. The lifetime of the exciplex is found to be greatly reduced in acetonitrile (580 ps) compared with its value in non-polar solvents, e.g. 126 ns in 2-methylbutane. A likely possibility to account for this difference is the availability of exciplex decay to the ion pair in acetonitrile but not in 2-methylbutane.

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