reactants, etc. The core, however, is distinctly rigid and inhibits diffusion so that selection and energy transfer over distances of 10 Å are readily observed, as diffusion processes are inhibited. This behavior is useful in promoting long-range chemical processes of interest, and may also be used to enmesh or capture one of the reactants, on a long-term basis. The permanent nature of the polymerized particles enables the construction of a system containing two simple but distinct colloidal species, namely, the particle and a micelle. This provides the opportunity for promoting different photochemical reactions each with particle, followed by a pooling of the products in the aqueous bulk. Further studies to this end are now in progress.

Registry No. CTAB, 57-09-0; CPC, 123-03-5; PBA, 25338-56-1; PDA, 73451-05-5; I^-, 20461-54-5; styrene–divinylbenzene, 9003-70-7; pyrene, 129-00-0; oxygen, 7782-44-7.

Picosecond Laser Studies of Intramolecular Excited-State Charge-Transfer Dynamics and Small-Chain Relaxation

Y. Wang, M. C. Crawford,† and K. B. Eisenthal*

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. *Received January 12, 1982*

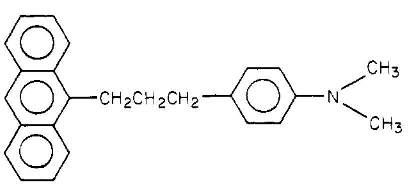
Abstract: Intramolecular charge transfer has been observed for the molecule anthracene-$(CH_2)_3$-*N*,*N*-dimethylaniline [9-[3-[4-(dimethylamino)phenyl]propyl]anthracene] in nonpolar solvents of varying viscosities. The technique employed was picosecond time-resolved fluorescence utilizing a Nd^{3+}:phosphate glass laser and streak camera. Measurements of the fluorescence decay of the excited-state acceptor (anthracene moiety) and the fluorescence rise of the exciplex demonstrate that there is no intermediate nonfluorescent state existing prior to exciplex formation and that the end-to-end cyclization of the four-bond methylene chain is exponential in time. This exponentiality has not been previously demonstrated. 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. Each conformer has a different viscosity dependence for the formation of an exciplex. General conclusions concerning charge-transfer dynamics in solution are presented on the basis of these and related studies.

Charge-transfer (CT) interactions of excited molecules with neighboring molecules play a vital role in electronic energy relaxation. The quenching of excited-state fluorescence and either the appearance of a new, red-shifted exciplex emission or the formation of ion radicals are manifestations of charge-transfer phenomena. The widespread interest and importance of these light-driven charge generation processes is reflected by the numerous studies[1] on this subject since the discovery of the perylene–dimethylaniline exciplex by Leonhardt and Weller.[2] Two questions concerning the nature of the excited CT interaction are particularly interesting, namely the dependence of reaction on distance and geometry. From studies of *intermolecular* exciplex formation between anthracene and diethylaniline molecules using picosecond transient absorption,[3] it has been concluded that when the two molecules are separated by $\simeq 8$ Å, rapid exciplex formation (10^{11} M^{-1} s^{-1}) occurs. For study of the geometric requirements for exciplex formation, one approach is to restrict the relative orientation of the electron donor and acceptor molecules by connecting them with a number of methylene groups.[4-11] The effect of this restriction on the formation of the *intramolecular* exciplex is then studied.

Table I. Time Constants for Intramolecular Exciplex Formation in Various Solvents; Uncertainty in Lifetimes Is ±10%

solvent	iso-pentane	hexane	decane	tetra-decane
viscosity, cp	0.22	0.33	0.92	2.18
dielectric constant	1.84	1.89	1.99	
anthracene moiety decay at 410 nm, ns	1.4	1.9	2.8	3.8
CT formation at 480 and 520 nm, ns	1.4	1.9	2.9	4.1
CT formation at 570 and 600 nm, ns	2.0	2.6	3.8	5.5

In an earlier communication,[11] we reported preliminary results on the study of the intramolecular exciplex 9-anthracene-$(CH_2)_3$-*p*-*N*,*N*-dimethylaniline in isopentane solution. On the basis of the dynamics we concluded that internal rotational motions are required to achieve a favorable geometry for the formation of the intramolecular exciplex in the nonpolar solvent. The observation of a dependence of exciplex rise time upon the fluorescence wavelength monitored was interpreted as evidence for two groups of distinct ground-state conformers. We have now extended this study to solvents of widely



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† IBM predoctoral fellow.

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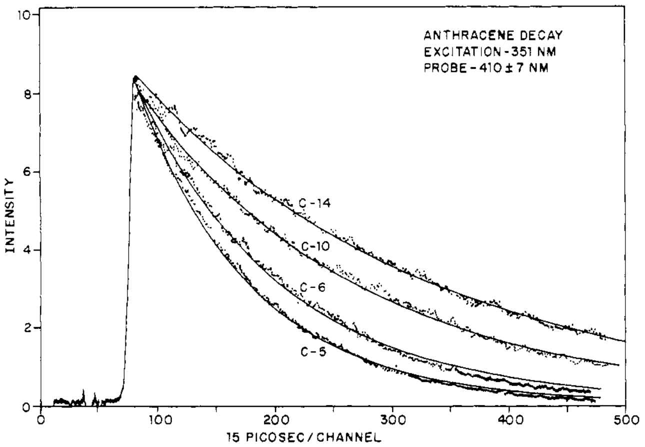

Figure 1. Decay of the excited anthracene moiety in isopentane (C-5), hexane (C-6), decane (C-10), and tetradecane (C-14). The points are experimental; the solid curves are theoretical.

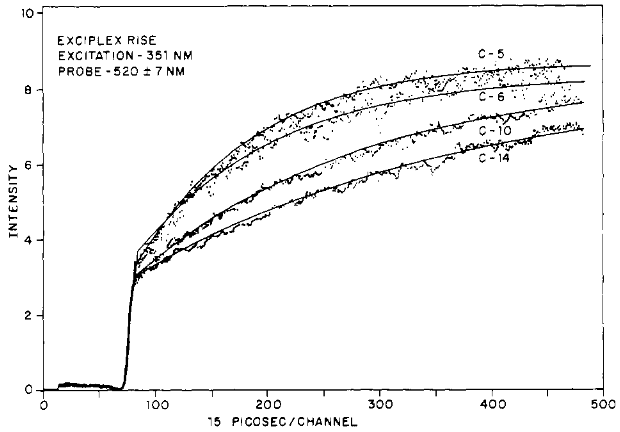

Figure 2. Rise of the intramolecular exciplex of anthracene-$(CH_2)_3$-DMA in isopentane (C-5), hexane (C-6), decane (C-10), and tetradecane (C-14). The initial fast rise is due to residual excited anthracene moiety emission at 520 nm. The points are experimental; the solid curves are theoretical.

varying viscosities. The role of the starting ground-state conformation on the dynamics of exciplex formation and the dependence of the intramolecular motion on viscosity are discussed.

Experimental Section

A TEM_{00}, 4–8 ps, third-harmonic pulse (351 nm) 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 the streak camera–OMA response function is corrected in each shot.

The synthesis of 9-anthracene-$(CH_2)_3$-*N*,*N*-dimethylaniline has been described before.[5] 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 HPLC 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 performed with the recrystallized compound and the compound further purified by chromatography yielded identical results. Solvents were obtained from Aldrich (isopentane 99+%, decane, and tetradecane 99%) and Fisher Scientific (hexane, spectral grade). All solvents were purified by passage through a neutral alumina column before use, and the sample solutions were deoxygenated by repetitive freeze–pump–thaw cycles. All experiments were done at 20 °C at a solute concentration of 2.5×10^{-3} M.

Results and Discussion

Geometric Effects. A 351-nm picosecond laser pulse was used to excite the anthracene moiety in the model compound. The decay of anthracene fluorescence in four nonpolar solvents (isopentane, hexane, decane, and tetradecane) was monitored at 410 nm, and the results are shown in Figure 1. The decay curves are exponential in form with time constants ranging from 1.4 ns in isopentane to 3.8 ns in tetradecane (Table I). These rather slow rates indicate that intramolecular rotational motions are required to bring the two moieties to a geometry favorable for charge transfer.[11] This conclusion is based on previous studies of intermolecular exciplex[5] formation between free anthracene and dimethylaniline molecules where there is no restraint on their rotational motions. For this latter case of the unattached donor and acceptor molecules, a very rapid formation of the exciplex absorption ($\leq$10 ps) is observed.[5] These results show that in nonpolar solvents the formation of an intramolecular exciplex in the molecule A-$(CH_2)_3$-D can only be achieved in certain geometrical positions. This is consistent with the observation[7] that no exciplex is formed when either one or two methylene groups (CH_2) separate the anthracene and dimethylaniline chromophores.

Different behavior, however, is exhibited by other exciplex systems. Chandross and Thomas,[4] in their studies of the naphthalene-$(CH_2)_{3n}$-$N(CH_3)_2$ system in methylcyclohexane and isopentane solutions, found no strong geometrical preference for exciplex formation. This conclusion was based on the observation that exciplexes were formed when *n* = 2, 3, or 4. Davidson and Trethewey[6] reached the same conclusion for this series of molecules. In the study of intramolecular exciplex formation for the molecule *N*-carbazolyl-$(CH_2)_n$-tetrachlorophthalimide in cyclohexane solution, Borkent et al.[9] concluded that there are *no* geometric requirements for exciplex formation. This was based on the following: (1) the exciplex can be formed for chains in which *n* = 2, 3, 4, and 7, and (2) the formation rates are extremely fast (shorter than 200 ps) and virtually independent of solvent viscosity. These different observations can be rationalized by assuming that the degree of geometric constraint imposed on exciplex formation becomes less important as the driving force of the reaction increases. A measure of the driving force is the free energy change of the reaction which can be expressed in terms of the experimentally measured energy separation between the locally excited singlet and exciplex states.[1b] These energy differences are about 1.0, 0.5, and 0.13 eV for *N*-carbazolyl-$(CH_2)_n$-tetrachlorophthalimide, naphthalene-$(CH_2)_n$-$N(CH_3)_2$, and anthracene-$(CH_2)_n$-dimethylaniline, respectively, which is consistent with the observed trend of geometric constraint on exciplex formation. This view is further supported by the observation[7] than an exciplex A-$(CH_2)_n$-D will form in polar solvents but not in nonpolar solvents when *n* = 1 or 2. This result can be understood by considering the decrease in the free energy change (i.e., ΔG becomes more negative) as the solvent polarity increases. The resulting increased driving force reduces the importance of the geometric constraint on exciplex formation. As the solvent dielectric constant increases further, there will be progressively less geometric constraint on charge transfer. Eventually solvent stabilization will make an ion-pair state accessible from the exciplex state as well as from the locally excited state. This latter pathway opens up a direct electron-transfer channel for energy relaxation and has indeed been observed to occur in acetonitrile where the electron-transfer rate[12] was found to be 7 ps for the anthracene-$(CH_2)_3$-*N*,*N*-dimethylaniline molecule.

The Role of Starting Ground-State Conformations

By probing the exciplex emission band at several different wavelengths in isopentane solutions, we have found that there are two distinct spectral regions, each having a characteristic rise time.[11] This was interpreted as evidence for two ground-state conformations, each leading to the formation of a different exciplex. The same phenomenon has now been observed in the nonpolar solvents hexane, decane, and tetradecane. In Figure 2 we show the rise of exciplex fluorescence in these solvents monitored at 520 ± 7 nm, and in Figure 3 the rises monitored at 570

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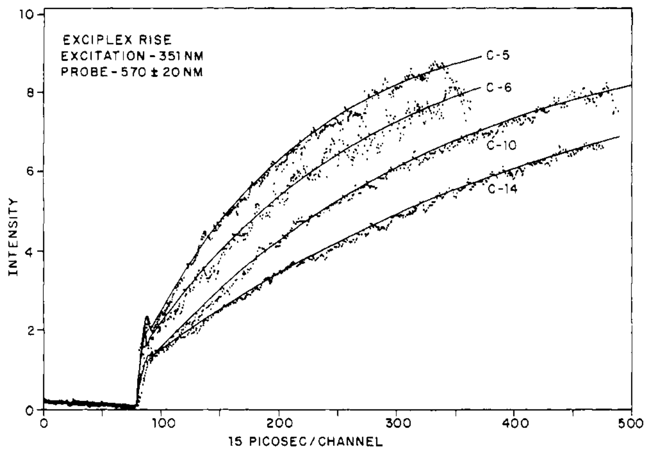
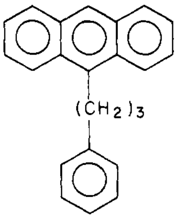


Figure 3. Rise of the intramolecular exciplex of anthracene-$(CH_2)_3$-DMA in isopentane (C-5), hexane (C-6), decane (C-10), and tetradecane (C-14). The initial fast rise is due to residual excited anthracene moiety emission at 570 nm. The points are experimental; the solid curves are theoretical.

± 20 nm are shown. The very rapid initial rise (within the laser pulse width) is due to the tail of the overlapping anthracene emission (not observed at 600 ± 10 nm). This overlapping emission was subtracted from the total emission yielding exponential formation curves (Table I). In all cases the dominant shorter wavelength exciplex emission has a rise time equal to the decay time of the anthracene emission while the long wavelength emission rises more slowly. The anthracene decay corresponding to this slow rise is masked by the much more intense emission from the dominant conformer.



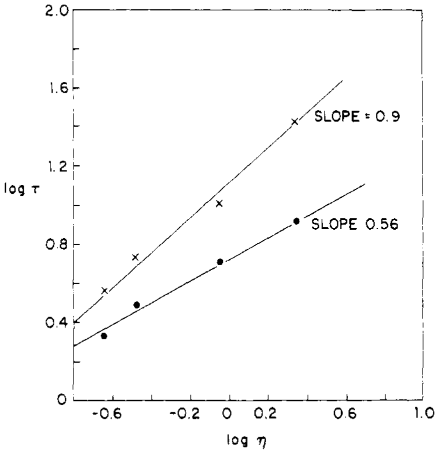


Figure 4. Plot of log of rotational relaxation time vs. log of solvent viscosity for two conformers of anthracene-$(CH_2)_3$-DMA in isopentane, hexane, decane, and tetradecane.

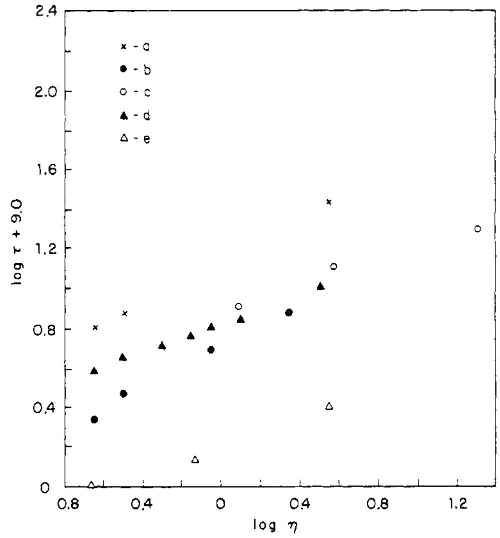


Figure 5. Plot of log of literature values of chain relaxation time vs. log of solvent viscosity. The points lie on a line of slope 0.5 ± 0.1, implying that $\tau \sim \eta^{0.5\pm0.1}$. (a) Reference 36; (b) this work; (c) ref 35; (d) ref 33; (e) ref 34.

By using 9-(3-phenylpropyl)anthracene[37,38] as a reference molecule, we correct for the decay of the anthracene moiety in the model compound that results from relaxation by processes other than exciplex formation. The observed exciplex formation time τ_{CT}, given in Table I, is related to the internal rotational time τ_{rot}, and the time τ_0, due to processes other than exciplex formation by

$$1/\tau_{CT} = 1/\tau_{rot} + 1/\tau_0$$

The values of τ_0 for the different solvent viscosities[37,38] are combined with the values of τ_{CT} measured in this work to yield the chain relaxation time, τ_{rot}. The log of these rotational lifetimes are plotted against the log of the solvent viscosities as shown in

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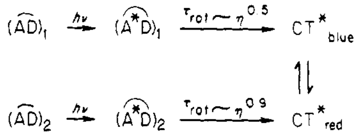
(38) The lifetimes of 9-(3-phenylpropyl)anthracene in various solvents either interpolated or obtained directly from ref 37.

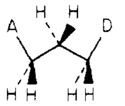
Figure 5. It is seen that the viscosity dependence is different for the formation of the two different exciplexes, yielding $\tau_{rot} \sim \eta^{0.5\pm0.1}$ for the short-wavelength exciplex and $\tau_{rot} \sim \eta^{0.9\pm0.1}$ for the long-wavelength one. This result provides additional support of our conclusion that two distinct groups of ground-state conformers go through different internal rotations and form exciplexes having different emission energies. It should also be noted that although the formation rates of the blue and red exciplexes differ, their lifetimes are equal in both hexane and tetradecane solutions. This implies that the blue and red exciplexes equilibrate on a time scale fast compared to their lifetimes ($\simeq$100 ns). The equality of the lifetimes of the two exciplexes in both hexane and tetradecane further supports the idea that we are indeed observing distinct conformers of our model compound rather than the compound and an impurity. If the red conformer was an impurity, the probability that it would have the same lifetime as our model compound in hexane (120 ns) as well as in tetradecane (140 ns) would be very small. We can summarize the above results as follows:



where $(\widehat{AD})_1$ and $(\widehat{AD})_2$ represent different ground-state conformations, $(\widehat{AD})_1$ being the dominant one, and CT^*_{blue} and CT^*_{red} represent the short-wavelength and long-wavelength exciplexes, respectively.

Recent studies by De Schryver and co-workers[13,14] on the different intramolecular exciplexes phenyl-$(CH_2)_3$-$N(CH_3)_2$ and 2-naphthalene-$(CH_2)_2$-pyridine reached similar conclusions. In the former case they found there were two ground-state conformations leading to the formation of the same exciplex at different rates, while in the latter case they concluded that of the two ground-state conformations only one was able to reach the geometry necessary for exciplex formation. These results suggest it may be a general phenomenon that the dynamics of exciplex formation in nonpolar solvents can be controlled by the starting ground-state conformation.

From previous studies on several analogous compounds,[40,41] i.e., 2,4-disubstituted pentanes, three possible ground-state conformations for our model compound can be suggested, as well as a likely conformation for the exciplex. For minimization of the repulsive interactions between the donor and acceptor groups conformers, **1**, **2** and **3** are reasonable ground-state conformations.[40,41] Conformer **4**, although unstable (repulsive) in the ground state, is expected to be the most stable exciplex conformation due to the maximal orbital overlap of A and D.[40,41] The exciplex formation rates we measured would then be the transition rates from conformers **1**, **2**, or **3** to conformer **4**. This conformational transition is achieved by rotations about the C–C bonds of the methylene chain. Support for this conclusion is gained from the following considerations.



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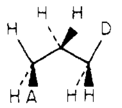

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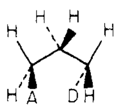

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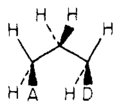

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Inspection of a molecular model shows that rotation around the anthracene–C bond, the aniline–C bond, or the N–benzene bond in the extended conformations **1**, **2**, and **3** cannot bring the anthracene and aniline groups to the overlapping position for exciplex formation. Furthermore, estimates of these rates based on bond rotations in related molecules indicate they are too rapid to account for our data; i.e., rotation about the N–benzene bond occurs in 20 ps for the molecule *p*-cyanodimethylaniline,[29] and the C–benzene bond rotation in crystal violet[30] occurs in 50–100 ps.

The remaining bond to consider in our model compound is the C–C bond, of which there are two in the methylene chain. Although theoretical studies predict that C–C bond rotations hindered by the trans–gauche energy barrier occur on the picosecond time scale for a simple alkane chains such as butane,[25,31,32] computer simulations have demonstrated a marked decrease in these rates if there is a large group appended to the rotating bond.[25] Bond rotations that must drag large moieties through the solvent may require nanoseconds, a prediction consistent with our observations.

To further illustrate the effects of end groups on chain motions, we have collected scattered experimental data from the literature concerning intramolecular excimer and exciplex formation[33-36] for compounds in which there is a chain of three methylene groups. The logs of their intramolecular rotational lifetimes are plotted against the log of solvent viscosities, along with our own data, in Figure 5. As expected, there is a wide variation in rates among different excimers and exciplexes, reflecting the differences in size and geometry of the individual systems, in qualitative accord with computer simulation studies.[25] Despite the range of different systems, it turns out that the viscosity dependences of the rates are similar, the average dependence of τ_{rot} on η being $\tau_{rot} \sim \eta^{0.5\pm0.1}$. This supports the idea that it is the methylene chain relaxation, and indeed similar chain motions for all of these diverse systems, that determines the viscosity dependence. The different groups attached to the methylene chain appear to alter the relaxation rates but not the viscosity dependences for the cases considered here. This is analogous to Debye rotations for which the rates of orientational relaxation decrease with molecular size but scale linearly with viscosity.[39]

One final point to be made concerns the exponential time dependence of the observed exciplex formation. This exponential behavior extends from short times (few picoseconds) to long times (nanoseconds). To the best of our knowledge exponential (time) behavior for cyclization dynamics of a four-bond chain has not been demonstrated either experimentally or theoretically before the present work. Szabo, Schulten, and Schulten[22] have studied the end-to-end relaxation of a polymer chain possessing a harmonic spring interaction potential. The relaxation was assumed to be described by a Smoluchowski-type diffusion equation. They found that the probability that the two ends remain unreacted at time *t*, though not rigorously exponential, can be approximately represented by an exponential function. We also note the results of several computer simulation studies[17] that show that the autocorrelation function of the end-to-end distance decays exponentially in time. However, no explicit time dependences for the collision of the end groups, which would correspond to the cyclization dynamics that we measure, are reported in these studies. Perhaps the exponential time dependence we observe indicates that for rigid short-chain molecules the high-frequency chain modes are greatly restricted and the chain relaxation is dominated by slower global motions,[18] at least in the time domain we have investigated.

On the basis of the above discussion, two ideas emerge which bear directly on the general concept of using intramolecular excimer or exciplex formation as probes of chain relaxation. First, the observed rate of chain motion is considerably affected by the probe molecule used, its physical size, and its relative orientation to the main chain. In order to study chain dynamics, it is important to first understand the perturbation caused by attaching the probes to the chain molecule. Second, since different relaxation rates are often observed with different fluorescent or absorption probes (Figure 5), sometimes even with the same probe, as in the present study, additional information, e.g., viscosity or temperature dependence, other than the rate measurement itself may be needed to identify the relaxation mode.

Summary

(1) In nonpolar solvents, there is a fairly strong geometric requirement for intramolecular exciplex formation in the model

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compound 9-anthracene-$(CH_2)_3$-*p*-*N*,*N*-dimethylaniline. For exciplexes in general, the geometric effects on formation rates are greatly affected by the energy separation between the locally excited singlet state and the exciplex state. The geometric constraints become less stringent as the energy difference increases.

(2) We have established that the dynamics of exciplex formation are influenced by the starting ground-state conformations. For the model compound studied, it was found that exciplexes with different emission energies were formed independently from two distinct groups of ground-state conformers at different rates. The structures of these conformers are not known but possibly differ in the relative orientation of the anthracene and the dimethylaniline chromophores.

(3) The observed viscosity dependence we find, combined with literature values for other three-chain systems, points to the methylene chain motions as the key factor in determining the viscosity dependence of the rates. The attached end groups alter the formation rates but not the viscosity dependence of the rates for most of the cases considered.

(4) The experimentally observed exponential rise for intramolecular exciplex formation suggests that a single chain relaxation mode, perhaps the large-scale end-to-end relaxation mode, is dominant, at least in the picosecond to nanosecond time regime we have examined.

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Magnetic Field Dependence of ^{19}F Nuclear Spin Polarization. The System Tetrafluorobenzoquinone–Tetrafluorohydroquinone

Richard S. Hutton,[†] Heinz D. Roth,*[†] Marcia L. Manion Schilling,[†] Anthony M. Trozzolo,[‡] and Thomas M. Leslie[‡,§]

Contribution from Bell Laboratories, Murray Hill, New Jersey 07974, and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. *Received December 4, 1981*

Abstract: The magnetic field dependence of the ^{19}F polarization observed in the reaction of tetrafluorobenzoquinone with tetrafluorohydroquinone in benzene has been studied. The results can be interpreted in terms of three different polarization mechanisms. The effects observed at fields below 100 G can be ascribed to a radical-pair mechanism involving $S-T_\pm$ mixing. At fields of 1–20 kG two different contributions have been identified which can be observed separately under appropriate experimental conditions. One contribution showing a maximum near 4 kG is assigned to a biradical adduct between the triplet quinone and the solvent, benzene. The other contribution shows a monotonical increase with magnetic field strength. This effect is assigned to the triplet-Overhauser mechanism in the reaction of the triplet quinone with the hydroquinone.

Introduction

Recently, we reported the magnetic field dependence of the ^{19}F polarization generated in the photoreaction of trifluoroacetophenone with dimethoxybenzene.[1] We concluded that these effects, when evaluated in the light of supplementary experimental results, provided strong evidence for the triplet-Overhauser mechanism, a relatively rare spin polarization mechanism with electron-nuclear cross relaxation as a key step.[2] In the paper presented here, we report the magnetic field dependence of ^{19}F polarization effects observed during the irradiation of tetrafluorobenzoquinone (**1**) in the presence of tetrafluorohydroquinone (**2**) in benzene solution. This reaction was first studied by Vyas and Wan[3] who suggested tetrafluorosemiquinone (**3**) as an intermediate and ascribed the strong ^{19}F emission observed for the quinone to the triplet-Overhauser mechanism. Several experimental results were adduced in support of this assignment including the magnetic field dependence of this enhancement between 1 and 7 and at 14 kG. This dependence was compared with a theoretical prediction and appeared to match it reasonably well.[2a]

The theory underlying the triplet-Overhauser mechanism has been discussed in detail elsewhere[1,2] and only a brief recapitulation of its principal features will be given here. The intensity of the nuclear spin polarization (P_n) induced via this mechanism can be expressed as a function of two magnetic field dependent factors, the initial electron polarization (P_e) of a radical and the efficiency (ξ) of electron nuclear cross relaxation,

$$P_n \propto P_e \xi \qquad (1)$$

The initial electron polarization is determined by

$$P_e \propto \frac{\omega_z \tau_t}{\omega_{zfs}} {}^3T_{1e}^{-1} T^{\ddagger} \qquad (2)$$

Of these factors, ω_{zfs}, the zero-field splitting of the triplet species, and τ_t, the "rotational" correlation time, are independent of the magnetic field, whereas ω_z, the Zeeman splitting, ${}^3T_{1e}$, the electron relaxation time of the triplet, and $T^{\ddagger}$, the probability that the triplet is quenched, are magnetic field dependent.[1,2]

The efficiency of cross relaxation is a complex function of various relaxation rates. It can be evaluated by solving the different rate equations governing the populations of the spin levels of the substrates and the intermediate radicals. Adrian has solved these equations for the case of a radical whose unpaired electron

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[†] Bell Laboratories.

[‡] University of Notre Dame.

[§] Present address: Bell Laboratories.

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