Transient Species in Electron Transfer: Reactions of Chloranil with Donor Aromatic Compounds

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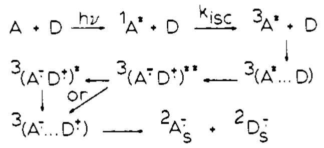
Abstract: Light-induced intermolecular electron-transfer reactions, particularly the dynamics of the early stages, were studied by means of picosecond absorption spectroscopy. The donor (D)/acceptor (A) systems studied in acetonitrile were naphthalene (NAP)/chloranil (CHL), 9,10-dihydrophenanthrene (DHP)/CHL, and indene (IN)/CHL. Difference absorption spectra taken at selected delay times after excitation of the sample by a 355-nm, 25-ps fwhm laser pulse revealed the sequence of events and the identities of the species involved in the electron-transfer reaction. With this spectroscopic information, we were able to elucidate events which occur in the early stages of the electron-transfer reaction. From the data, we infer that the initially formed ion pair relaxes to an equilibrated cation-anion-solvent complex.

Electron-transfer reactions are important steps in many chemical and biological processes. Light-induced electron transfer can result, in general, from three distinct types of excitation, absorption of a photon by either (1) a donor molecular (D), (2) an acceptor molecule (A), or (3) an electron-donor-acceptor (EDA) complex formed between D and A in their ground states. Past studies on the mechanism of electron transfer were performed by means of conventional flash photolysis,[1] nanosecond spectroscopy,[2] and, lately, picosecond spectroscopy.[3] One of the species suitable for accepting electrons in studies of electron-transfer processes is chloranil (CHL) which when excited in the presence of donor molecules generates radical ions.[2a,b,4]

Experimental data obtained, by means of nanosecond absorption spectroscopy, in the study of the chloranil/naphthalene system by Gschwind and Haselbach[2a] suggested that a Weller-type[1] quenching mechanism for electron transfer was operative. According to the results obtained by Weller and co-workers,[1,5] formation yields and therefore lifetimes of the exciplex composed of D and A are reduced in polar solvents as a result of ionic dissociation between the D-A pairs. In a more detailed mechanism (Scheme I) than considered by Gshwind and Haselbach,[2a] Weller and co-workers[1,5] proposed that a non-relaxed exciplex $^{1,3}(D^{+}\cdot A^{-}\cdot)^{**}$ is formed from the initial encounter complex $^{1,3}(D\cdots A)^{*}$ which results when a photoexcited molecule (D^{*} or A^{*}) approaches a complementary ground-state molecule. The non-relaxed exciplex $^{1,3}(D^{+}\cdot A^{-}\cdot)^{**}$ may relax to the fluorescent exciplex $^{1,3}(D^{+}\cdot A^{-}\cdot)^{*}$ state or, in polar solvents, ionize directly to a "solvent-shared" ion pair $^{1,3}(^{2}D\cdot^{+}\cdots{}^{2}A^{-}\cdot)$. The ground-state pair $(^{2}D\cdot^{+}\cdots{}^{2}A^{-}\cdot)$ may subsequently diffuse apart into the separated, solvated ions $^{2}D_{s}{}^{+}\cdot$ and $^{2}A_{s}{}^{-}\cdot$. The nanosecond spectroscopic experiment by Gshwind and Haselbach[2a] had sufficient time resolution to detect only $^{3}CHL^{*}$ and the solvent-separated ions, $CHL^{-}\cdot$ and $NAP^{+}\cdot$.

We have extended the investigation of the mechanism of photoinduced electron transfer between chloranil (CHL) and the arenes, naphthalene (NAP), 9,10-dihydrophenanthrene (DHP), and indene (IN), in an effort to gain a clearer understanding of the events which occur in the early stages of electron transfer. With use of picosecond absorption spectroscopy, we obtained direct information on the transient species involved in the electron-transfer process which was not possible to obtain by the previous studies with nanosecond time resolution.

Scheme I



Experimental Section

The experimental apparatus used to obtain the transient absorption spectra of the species involved in the electron-transfer reactions studied here has been described in previous publications.[6-8] Briefly, it consists of a passively mode-locked Nd^{3+}:YAG oscillator which produces a train of 25-ps fwhm 1064-nm pulses. A single pulse is selected by means of a Pockels cell and crossed polarizers. This single pulse is amplified by two Nd^{3+}:YAG amplifiers and passed through a KDP crystal to generate 532-nm light. The 355-nm excitation pulse (~1.5 mJ per pulse) is generated by passing the 532-nm light and residual 1064-nm light through a third harmonic generating crystal and is directed appropriately to the sample. The probe continuum is produced by passing the 1064-nm pulse, which exists after third harmonic generation, through a cell containing D_2O/H_2O. The continuum pulse is split into probe and reference pulses before reaching the sample. Both continuum pulses are focused through a 0.25-m spectrometer to a PAR ISIT vidicon interfaced with a PAR 1215 OMA2 and a Data General Eclipse S/130 minicomputer. The system was operated in gated-free-run mode at ~1.5 Hz. Each difference spectrum is the result of at least 120 no-excitation/excitation pairs of laser shots.

Chloranil (Aldrich) was purified by recrystallization from acetonitrile. Naphthalene (Prinz grade, Princeton Organics) and 9,10-dihydrophenanthrene (Aldrich) were purified by sublimation before use. Indene (Aldrich, 99+%) and acetonitrile (MCB, OMNISOLV) were used without further purification.

The sample cell for these studies was a 2-mm quartz optical cell which did not show any absorption either alone or with the solvent over the spectral region of interest. Absorption spectra of samples of CHL/NAP, CHL/DHP, and CHL/IN in acetonitrile were recorded with a Cary 15 spectrophotometer. The absorption spectra of CHL/NAP and CHL/DHP systems taken before and after the picosecond spectroscopic measurements revealed that no sample degradation resulted from laser photolysis. However, in the case of CHL/IN in acetonitrile, we found that photochemical degradation of the sample occurred when the sample was subjected to the amount of 355-nm picosecond-pulsed excitation required to obtain transient difference absorption spectra at only three delay times after excitation. Therefore, in the work reported here, a fresh CHL/IN sample taken from a volume of stock solution was used to obtain the difference absorption spectrum taken at each selected delay time after excitation. With the amount of irradiation required to obtain the dif-

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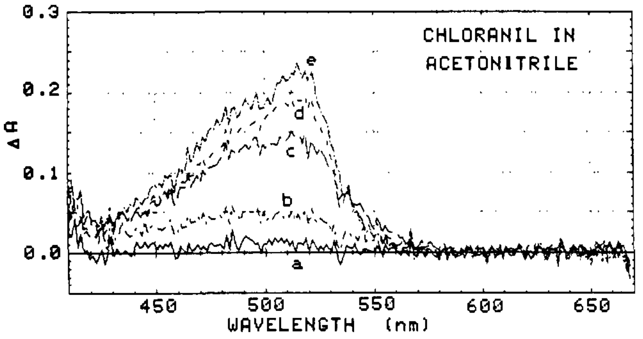

Figure 1. Difference absorption spectra obtained with 355-nm excitation for a 0.035 M solution of CHL in acetonitrile. (a) 0 ps, (b) 15 ps, (c) 40 ps, (d) 65 ps, and (e) 290 ps after excitation.

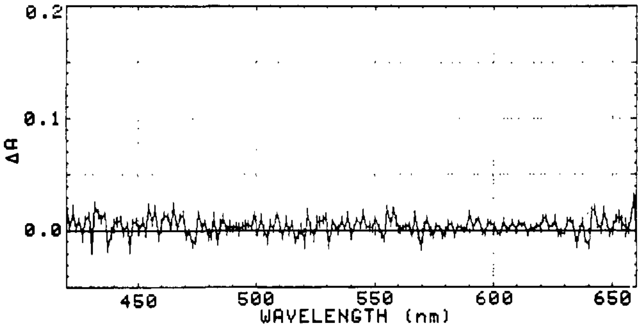

Figure 2. Difference absorption spectra obtained with 355-nm excitation for a 0.078 M solution of NAP in acetonitrile at 600 ps after excitation.

ference spectrum at one delay time, no significant sample degradation occurred, as was revealed by its absorption spectrum.

Results and Discussion

The main goal of this study was to elucidate the detailed mechanism of electron transfer between CHL and the arenes, NAP, DHP, and IN in acetonitrile by means of identifying the absorbing intermediate species generated after 355-nm excitation. When a solution of CHL in acetonitrile is irradiated with a 355-nm pulse, a new broad absorption band is observed between 420 nm and 540 nm which evolves in time into a spectrum possessing maxima at 490 and 515 nm (Figure 1). On the basis of previous published research,[9] the latter absorption spectrum which develops within 300 ps and remains unchanged for a time longer than 8 ns after excitation is assigned to the $T_n \leftarrow T_1$ transition of CHL. We assign the broad initially observed absorption band to the $S_n \leftarrow S_1$ transition of CHL. The decay rate of the $S_n \leftarrow S_1$ band at 420–520 nm and the growth of the $T_n \leftarrow T_1$ band permit us to obtain an intersystem crossing rate constant of $\sim 3 \times 10^{10}\ \mathrm{s}^{-1}$ for $^1\mathrm{CHL}^* \rightarrow {}^3\mathrm{CHL}^*$. Although the rate of intersystem crossing was not known prior to our measurement, the near unit quantum efficiency of the singelt–triplet intersystem crossing process had been determined previously.[9]

CHL possesses a $\pi^* \leftarrow n$ transition ($\lambda_{\max}$ 367 nm, $\epsilon_{367} = 180$ $\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$). However, neither NAP, DHP, nor IN appreciably absorb 355-nm light ($A_{355} < 0.03$) at the concentrations of solutions used in this work. Figure 2 shows the difference absorption spectrum obtained at 600 ps after excitation of a sample of NAP in acetonitrile by 355-nm laser pulses. No transient absorption was detected at this delay time or at 0, 25, or 300 ps after excitation, under our experimental conditions of 1.5-mJ pulse energy and 0.078 M concentration of NAP in acetonitrile, as was quite apparent by the flat ΔA vs. λ lines centered at $\Delta A = 0$ for the several delay times. Similarly, no transient absorption was detected for samples of DHP in acetonitrile and IN in acetonitrile when excited by 355-nm laser pulses.

The formation of strong transient absorptions, however, was observed when the sample solution which contained both CHL and NAP in acetonitrile was irradiated with the same type of laser pulse as used for samples of each compound individually. The changes in ΔA vs. λ were monitored by means of picosecond continuum pulse. In order to measure the growth of the population of transient species as a function of time, the probing continuum was delayed and arrived at the sample several tens to hundreds of picoseconds after the excitation pulse. The growth of the transient species population is revealed by the spectra illustrated in Figures 3 and 4. Observation of the difference absorption spectra was accomplished with two spectrometer settings which provided windows of ~400–670 nm and 555–770 nm. The transient absorption spectra within the two spectral windows were obtained under the following slightly different conditions: (a) 420–670 nm, 0.027M CHL, 0.078 M NAP, 1.5-mJ 355-nm pulses; (b) 555–770 nm, 0.029 M CHL, 0.070 M NAP, 1.9-mJ 355-nm pulses. The reasons for these different conditions will be explained below.

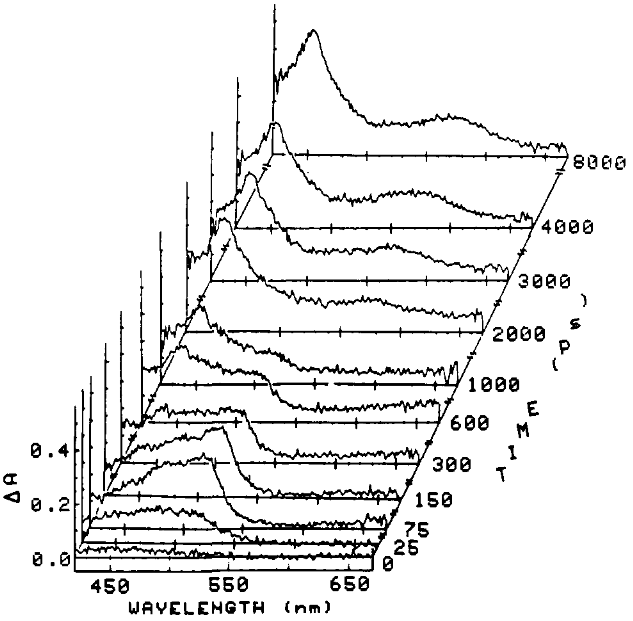

Figure 3. Difference absorption spectra obtained with 355-nm excitation for 0.027 M CHL/0.078 M NAP in acetonitrile in the 420–670-nm spectral range at selected times after excitation.

Previous investigations[9] have assigned the absorption bands to the following species and transitions:

$\lambda_{\max}$	species	transition
510 nm	CHL*	$T_n \leftarrow T_1$
450 nm	$\mathrm{CHL}^{-}\cdot$	$D_n \leftarrow D_0$
690 nm	$\mathrm{NAP}^{+}\cdot$	$D_n \leftarrow D_0$
570 nm	$(\mathrm{NAP})_2{}^{+}\cdot$	$D_n \leftarrow D_0$

The rate of this electron-transfer reaction has been measured and found to be diffusion limited.[2a]

Irradiation of a solution of CHL and DHP in acetonitrile with 355-nm laser pulses gave rise to analogous transient absorptions with the exception of $(\mathrm{DHP})_2{}^{+}\cdot$ (Figure 5). The absence of this species has been observed by Delcourt and Rossi[2b] who performed a similar experiment with use of nanosecond absorption spectroscopy.

Irradiation of a sample of CHL and IN in acetonitrile also gave rise to transient absorption bands of previously observed $^3\mathrm{CHL}^*$, $^2\mathrm{CHL}^{-}\cdot$, and, for the first time, to our knowledge, $^2\mathrm{IN}^{+}\cdot$ ($\lambda_{\max} \simeq$ 560 nm). We base the assignment of the 560-nm band to a $^2D_n \leftarrow D_0$ transition of $\mathrm{IN}^{+}\cdot$ upon the generation of other radical cations in the presence of $^3\mathrm{CHL}^*$ and upon the similarity between the position of the 560-nm absorption band and the absorption spectrum of styrene radical cation[10] generated by γ-irradiation of styrene in *sec*-butyl chloride at 77 K. The similarity between the π-electronic systems of In and styrene has been utilized previously[11] in a comparison of the photoelectron spectrum of IN, the optical spectrum of the styrene cation radical, and the results

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[9] References 2a and references cited therein.

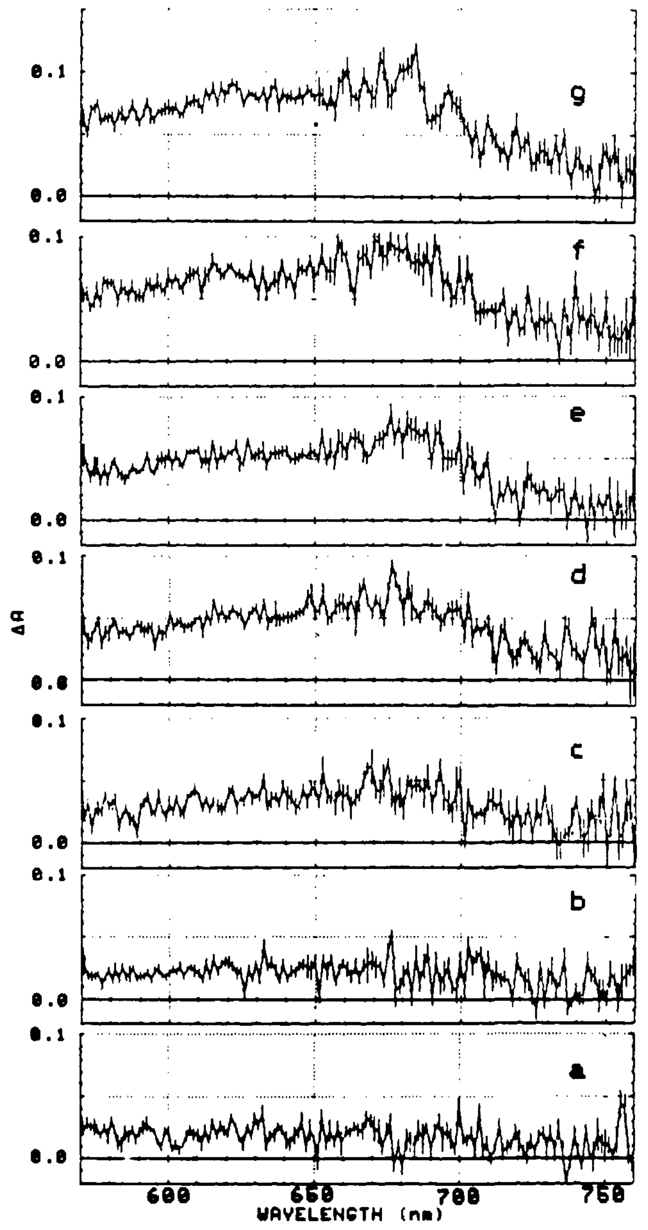

Figure 4. Difference absorption spectra obtained with 355-nm excitation for 0.029 M CHL/0.070 M NAP in acetonitrile in the 555–770-nm spectral range at (a) 75 ps, (b) 100 ps, (c) 200 ps, (d) 300 ps, (e) 400 ps, (f) 500 ps, and (g) 600 ps after excitation.

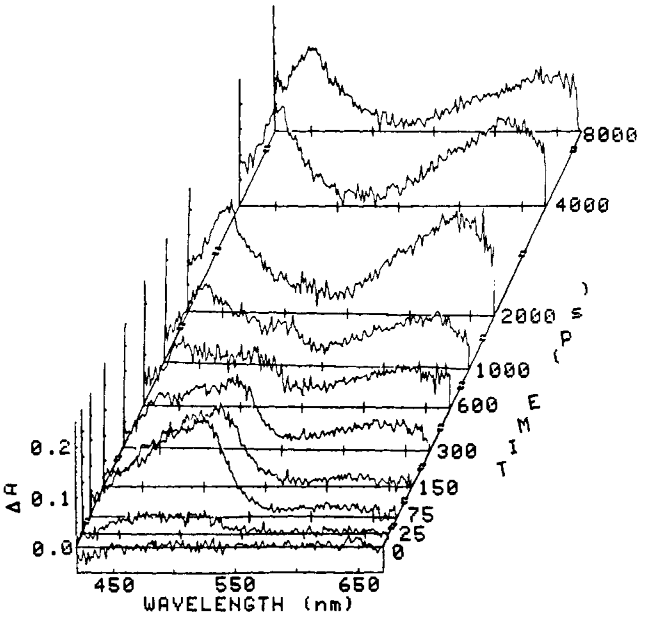

Figure 5. Difference absorption spectra obtained with 355-nm excitation for 0.027 M CHL/0.080 M DHP in acetonitrile.

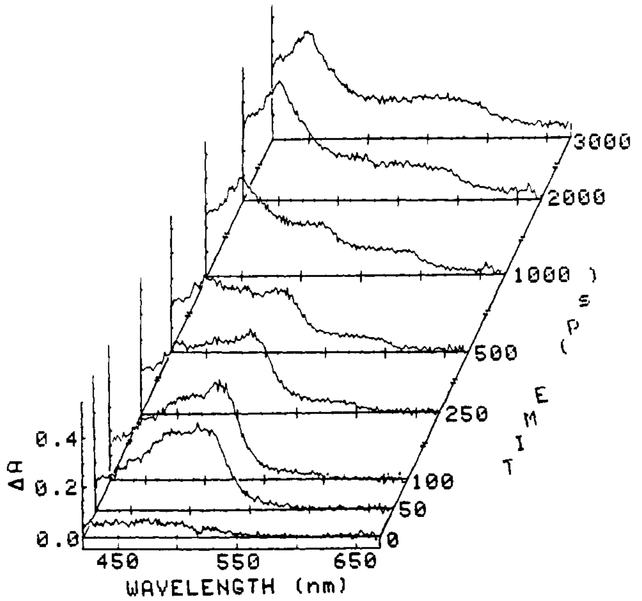

Figure 6. Difference absorption spectra obtained with 355-nm excitation for 0.029 M CHL/0.086 M IN in acetonitrile.

of theoretical calculations. As in the case of the CHL/DHP system, we do not observe the formation of a dimer, $(IN)_2{}^{+}\cdot$.

In previous studies it was proposed that the process of exciplex formation with subsequent electron transfer was the operative mechanism of the reaction. In the present study of CHL and the arenes, NAP, DHP, and IN, it is accepted that an excited-state molecule, either D* or A* depending upon wavelength of excitation, approaches a ground-state molecule of the remaining type by diffusion to form an encounter complex which collapses to an intermediate unrelaxed electron-transfer state.[5] In the case of CHL and the arenes, the acceptor, CHL, is excited to ^{1}CHL* which intersystem crosses faster than diffusion, a process which proceeds with a bimolecular rate constant of $\sim 10^{10}$ M^{-1} s^{-1}, to ^{3}CHL*. The intermediate non-relaxed state, $^{3}(D^{+}\cdot A^{-}\cdot)^{**}$, may be produced by interaction between the molecular components of the encounter complex, $^{3}(D\cdots A)^{*}$. This unrelaxed complex then may minimize its total energy by changing the relative possitions of D and A and also by solvent reorientation. Depending upon such factors as solvent polarity and relative oxidation and reduction potentials of D and A, this nonrelaxed intermediate may either form an exciplex $^{3}(D^{+}\cdot A^{-}\cdot)^{*}$ or the radical anion and cation. With acetonitrile, the solvent used in this study, ion formation is the preferred path. Previous nanosecond studies of the CHL/NAP system measured the kinetics of formation of the radical ions and found the process to proceed with a diffusion-controlled rate constant.[2a] Our study indicates that, as expected, the electron-transfer reactions between CHL and DHP and between CHL and IN proceed at rates comparable to those of the CHL/NAP system, and therefore they also proceed with diffusion-controlled rate constants.

In this picosecond spectroscopic study, we are interested in observing the events which occur prior to and in the early stages of ion formation. Over the range of wavelengths and times after excitation monitored for the CHL/IN system, the absorption bands which correspond to CHL$^{-}\cdot$ and IN$^{+}\cdot$ do not appear to have their absorption maxima shifting with respect to time as would be expected for dynamic effects upon vibrational levels or electronic states as a function of inter-ion distance or degree of solvent–ion interaction. However, the presence of the ^{3}CHL* absorption band may be obscuring these spectral shifts in the early stages of ion formation.

We became interested in the indene radical cation in connection with another study.[12] Since it was necessary to confirm the identity of $IN^{+}\cdot$ in other reaction systems, we utilized this straightforward method of cation radical generation to observe the absorption spectrum of $IN^{+}\cdot$ in solution for the first ime. The spectra of the styrene radical cation[10] generated via γ-irradiation of styrene in *sec*-butyl chloride and of the IN^{+} generated in this study in acetonitrile are quite similar. The transition which has an absorption maximum at 560 nm for IN^{+} in acetonitrile is red shifted to ~620 nm for styrene radical cation in *sec*-butyl chloride. Aside from a consideration of structural difference between the two cation radicals, this shift may be due partly to the difference in dielectric constants of the two media[13] and the different methods of radical cation generation which were used.

In the study of the CHL/NAP system, observation of transient species was performed with two spectral windows which covered the range of wavelengths from 420 to 770 nm. During the course of the electron-transfer reaction, absorption bands which correspond to $^{1}CHL^{*}$, $^{3}CHL^{*}$, $^{2}CHL^{-}\cdot$, $^{2}NAP^{+}\cdot$, and $^{2}(NAP)_2{}^{+}\cdot$ were observed (Figures 3 and 4).

As mentioned previously, the experimental conditions used for each spectral window were slightly different. In the shorter wavelength range (420–670 nm), we wished to observe the rate of formation of $^{2}(NAP)_2{}^{+}\cdot$ in addition to monitoring the transient states and species involved in the early stages of the electron-transfer process. In the previous nanosecond spectroscopic study,[2a] the following observations were made: at low NAP concentrations, $NAP^{+}\cdot$ and $CHL^{-}\cdot$ were detected before the ultimate back electron transfer to regenerate CHL and NAP occurred; at high NAP concentrations, $^{2}(NAP)_2{}^{+}\cdot$ and $CHL^{-}\cdot$ were detected prior to backward electron transfer, but the formation rate of $^{2}(NAP)_2{}^{+}\cdot$ could not be measured because of the time resolution of the experiment. It was assumed that the reaction was limited by diffusion. In our picosecond study, we see that $^{2}(NAP)_2{}^{+}\cdot$ reaches its maximum absorption intensity within ~4 ns after excitation, which is of the proper magnitude for a diffusion-limited rate at the concentration of NAP used.

To observe the absorption band of $^{2}NAP^{+}\cdot$ using the 555–770-nm window, we changed the starting concentrations of CHL and NAP to avoid perturbation of the $^{2}NAP^{+}\cdot$ absorption band by the absorption of $^{2}(NAP)_2{}^{+}\cdot$ in the early stages of the reaction. The appearance of the absorption band does change appearance over times ranging from 200 to 600 ps. At times after excitation which are longer than 600 ps, the shape of the absorption band of $^{2}NAP^{+}\cdot$ is affected by the presence of $^{2}(NAP)_2{}^{+}\cdot$. The spectral change, which appears to be a change in the vibrational intensities of the electronic absorption band, appears to reach its final equilibrium, appearance at ~600 ps. The half-life for the change is ~150 ps. This change of vibrational structure intensity in the $NAP^{+}\cdot$ absorption band occurs over too long a time period to be associated with vibrational relaxation of hot $NAP^{+}\cdot$ in a condensed medium or with solvent reorientation required for solvation of $NAP^{+}\cdot$. It does appear to be of the proper time period for a diffusional process associated with establishment of a cation–anion–solvent equilibrium geometry.[14] There is no apparent shift of the absorption maximum as was observed by Simons and Peters[14] for the photoreduction of benzophenone by organic amines such as diethylaniline, dimethylaniline, and 1,4-diazabicyclo[2.2.2]octane in acetonitrile.

For the reaction system CHL/DHP in acetonitrile, a red shift of ~10 nm of the absorption maximum of $DHP^{+}\cdot$ occurs from ~75 ps after excitation to ~600 ps after excitation. In their picosecond study of the photoreduction of benzophenone by amines, Simons and Peters[14] observed blue shifts of the absorption maximum of benzophenone radical anion of 25 to 55 nm with half-lives of 100 to 150 ps, depending upon the identities of the amine and solvent. They interpreted this blue shift in terms of previous work,[15] to indicate that electron transfer occurs when excited benzophenone and an amine molecule are ~7 Å apart. This initial ion pair, which is separated by solvent molecules, diffuses together to form a contact ion pair. This relative motion of the cation and anion gives rise to the blue shift of the absorption band of the initially formed benzophenone radical anion. In our case of CHL/DHP, the red shifting of the absorption maximum appears to indicate that the initial ion pair is in closer contact that the final equilibrium geometry which minimizes the energy for the $CHL^{-}\cdot$–$DHP^{+}\cdot$ pair in acetonitrile.

In none of the reaction systems studied did we observe any changes in the appearance of the absorption band of $CHL^{-}\cdot$. We believe that any shifts which might be occurring may be obscured by the broad $T_n \leftarrow T_1$ absorption of $^{3}CHL^{*}$.

Conclusions

In the systems of CHL/NAP, CHL/IN, and CHL/DHP in acetonitrile, dynamic processes which occur in electron-transfer reactions appear to manifest themselves in varying degrees, in terms of spectral changes. There are no apparent absorption shifts which occur in the CHL/IN system as a result of diffusive reorientation. Only slight vibrational structure intensity changes are apparent in the CHL/NAP system. While a more dramatic absorption maximum shift is observed for the CHL/DHP system, although this shift also may only be the result of vibrational structure intensity changes of the absorption band of $DHP^{+}\cdot$. In none of the systems which we studied, did we observe any absorption bands which could be attributed to an encounter complex of any sort formed prior to electron transfer. Our picosecond spectroscopic data did not reveal the existence of a discrete encounter complex, unrelaxed exciplex, or exciplex as proposed in the Weller mechanism. If present under these particular reaction conditions, their absorption bands possibly may be obscured by the $T_n \leftarrow T_1$ absorption of CHL. However, in acetonitrile solvent, electron transfer indeed occurs very rapidly and may therefore decrease the lifetimes of these intermediates below the limit of detection. Unfortunately, the low solubility of CHL in less polar solvents prohibited our testing of Weller's proposal that exciplex lifetimes would be increased with decreasing solvent polarity. Comparing our results of this study with those of Simons and Peters,[14] there appear to be subtle energetic criteria which alter the equilibrium geometry of an ion pair in solution. Further investigations of the effects of structures of ions which compose an ion pair and the effect of solvation on ion pairs will lead to a greater understanding of a complex species, an ion pair in solution, which is so important in chemical reactions.

We are currently investigating electron-transfer reactions between D and A molecules which form ground-state EDA complexes. Our preliminary findings[12] indicate that, unlike the CHL/arene systems described here in which the electron-transfer process evolves over a time period of hundreds of picoseconds, excitation of ground-state complexes leads to a much faster electron-transfer rate.

Acknowledgment. The authors thank M. J. Rossi for helpful discussions.

Registry No. $IN^{+}\cdot$, 42949-13-3; chloranil, 118-75-2; naphthalene, 91-20-3; 9,10-dihydrophenanthrene, 776-35-2; indene, 95-13-6.

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