Picosecond Dynamics of Proton Transfers

Lewis E. Manring[†] and Kevin S. Peters*[‡]

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. *Received January 21, 1985*

Abstract: The dynamics of proton transfer within an acid-base pair, which is created by a photoinduced electron transfer from an amine to a ketone, is investigated through picosecond absorption spectroscopy. Questions relating to molecular motion within the encounter complex and the distance dependence of proton transfer are addressed. Specifically, for substituted benzophenones and diphenylmethylamine, isotope and solvent dependence studies reveal that, although an acid-base pair is formed as an encounter complex, prior reorientation within the complex must take place before proton transfer. Other systems investigated include the transfer of a proton from the radical cation of *N*-methylacridan to the radical anions of benzophenone and anthraquinone as well as an intramolecular proton transfer for a molecule containing dimethylaniline linked to benzophenone by a methylene bridge.

Proton transfer reactions are of interest in many areas of chemistry. The effect of molecular motion immediately preceding and following a proton transfer in solution on the observed rates for proton transfer has recently been discussed by Murdoch.[1] A simple mechanism for proton transfer is Eigen's three-step proposal:[2]

$$AH^+ + B^- \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} [AH\cdots B] \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} [A\cdots HB] \overset{k_c}{\underset{k_{-c}}{\rightleftharpoons}} A + HB \quad (1)$$

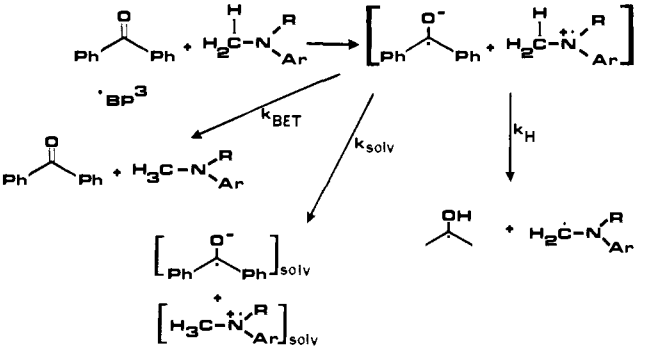
encounter proton transfer separation

Of special interest in this scheme is k_b, the rate of proton transfer. It is now apparent that direct measurement of k_b independent of the other five contributing steps (with rates k_a, k_{-a}, k_{-b}, k_c, and k_{-c}) is exceedingly difficult.[1] The coupling of the various steps is especially troublesome when $\Delta G^{\mp}$ for step b is $\simeq 0$; i.e., k_b is very fast. In this case k_b can be faster than k_a and the rate-determining step is diffusion to form the encounter complex. The observed rate is no longer dependent on the proton transfer step. Further complications arise when $\Delta G°$ is also small. In this case k_{-b} can be faster than k_c, causing back reactions to occur faster than product separation.

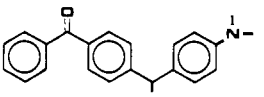
In this paper we report results obtained by picosecond absorption spectroscopy of a system which photochemically generates the acid-base pair in an encounter complex. In principle, formation of the acid-base pair in an encounter complex removes the complication of the diffusional process on the rate of observable proton transfer. Furthermore, for the systems studied herein, proton transfer is exothermic ($\Delta G° << 0$) which removes the complications of back proton transfer, k_{-b}, on the time scale of the experiment. In these studies the bases are various benzophenone radical anions while the acids are aromatic *N*-methylamine radical cations. The acid-base pair is generated as a contact pair by photochemically induced electron transfer from the amine to triplet excited-state benzophenone (^{3}BP*) in a nonpolar solvent. A general mechanism for the photoreduction of benzophenone by aromatic amines is shown in Scheme I. Photoexcitation of benzophenone (BP) creates ^{3}BP* within 10 ps.[5] Upon the encounter of ^{3}BP* with a tertiary aromatic amine, electron transfer occurs to form the benzophenone radical anion and the amine radical cation as a triplet pair. Determination of the rate of disappearance of the radical ion pair is a direct measure of the proton transfer rate as long as k_{solv} and k_{BET} are much slower than k_H.

The results from three benzophenone-amine systems are reported herein. The first involves proton transfer from di-

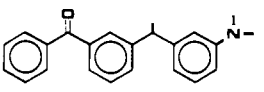
Scheme I



phenylmethylamine radical cation ($DPMA^{+}\cdot$) to various substituted benzophenone radical anions ($BP^{-}\cdot$). Both isotope and solvent effects are studied in this system. The results indicate that although the acid-base pair is formed in an encounter complex, prior reorientation within the complex must still take place before proton transfer occurs. The second system is *N*-methylacridan radical cation ($NMA^{+}\cdot$) proton transfer to $BP^{-}\cdot$ and anthraquinone radical anions ($AQ^{-}\cdot$).[6] In this system, proton transfer can occur from either the *N*-methyl group or the 9-methylene position. The position from which proton transfer occurs is dictated by the relative position of the proton to the basic site in the encounter complex. The third system involves dimethylaniline linked to benzophenone by a methylene bridge. The compounds investigated are designated PPDMAB and MMDMAB to indicate the para-



PPDMAB



MMDMAB

para and meta-meta isomers, respectively.

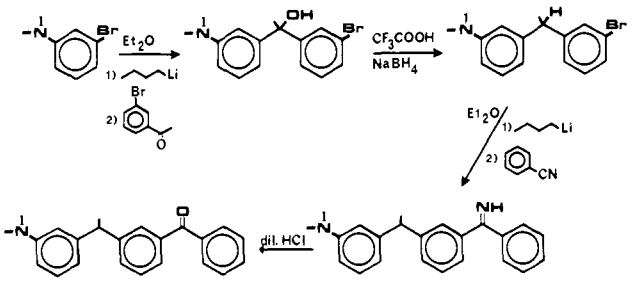
Previously reported nanosecond flash studies on a system very similar to PPDMAB suggests that hydrogen atom transfer proceeds by an intramolecular process in benzene;[7] however, our results are more consistent with an intermolecular interaction leading to proton transfer.

[†]Current address: Central Research and Development Department, E. I. du Pont de Nemours and Co., Experimental Station, Wilmington, DE 19898.
[‡]Current address: Department of Chemistry, University of Colorado, Boulder, CO 80309.

(1) Murdoch, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 71.
(2) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.
(3) Cohen, S. G.; Parola, A. H.; Parsons, G. H., Jr. *Chem. Rev.* **1973**, *73*, 141.
(4) Schaefer, C. G.; Peters, K. S. *J. Am. Chem. Soc.* **1980**, *102*, 7566.
(5) Anderson, R. W., Jr.; Hochstrasser, R. M.; Lutz, H.; Scott, G. W. *Chem. Phys. Lett.* **1974**, *28*, 153.
(6) Part of these results has been reported previously in a communication: Manring, L. E.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 5708.
(7) Masuhara, H.; Maeda, Y.; Mataga, N. *Chem. Phys. Lett.* **1980**, *69*, 182.

0002-7863/85/1507-6452$01.50/0

Scheme II



Experimental Section

Materials. Benzene, *o*-xylene, diethyl ether, chlorobenzene, dimethoxyethane, pyridine, methylene chloride, and ethyl acetate are all commercially available and were used without further purification.

All chemicals were from Aldrich unless otherwise noted. Benzophenone (MCB) and anthraquinone (MCB) were recrystallized from ethanol before use. 4-Chlorobenzophenone (Pfaltz and Bauer) and 4,4′-dichlorobenzophenone were used without further purification. Leucomalachite green was recrystallized twice from ethanol, and 4,4′-methylenebis(*N,N*-dimethylaniline) was sublimed. Diphenylmethylamine and *N,N*-dimethyl-4-toluidine were distilled from acetic anhydride (to remove non- and monoalkylated amine as the amide) at reduced pressure.

Diphenylmethyl-d_3-amine was prepared by condensation of diphenylamine and CD_3OD with P_2O_5. In a 250-mL flask were placed 10 g of P_2O_5 (0.06 mol), 6 mL of CD_3OD (0.15 mol), and a magnetic stir bar. The mixture was heated until it became fluid (~100 °C); then 10 g of diphenylamine (0.06 mol) was added and the mixture left stirring at 150 °C overnight. After cooling, the remaining phosphoric acid glass was dissolved with $NaHCO_3$ solution and the organic extracted into diethyl ether to yield 9 g of diphenylmethyl-d_3-amine. This product was distilled from acetic anhydride to remove nonreacted diphenylamine. The NMR spectrum indicated >99% CD_3.

The *N*-methylacridan and *N*-methyl-d_3-acridan were prepared by $NaBH_4$ reduction of the corresponding *N*-methylacridinium iodide or *N*-methyl-d_3-acridinium iodide by literature procedures.[8] The *N*-methyl-d_3-acridinium iodide was prepared by reaction of CD_3I and acridine in acetonitrile. NMR and mass spectral analysis indicated the *N*-methyl-d_3-acridan was >99% methyl-d_3. The *N*-methylacridan-9,9-d_2 was prepared by $NaBD_4$ reduction of *N*-methylacridone. In a 500-mL flask were placed 1.6 g of *N*-methylacridone (7.7 mmol), 0.8 g of $NaBD_4$ (21 mmol), 200 mL of 2-propanol, and a magnetic stir bar. The solution was heated to 80 °C until the acridone fluorescence had disappeared (~14 h). The 2-propanol was removed and the residue taken up in diethyl ether. The residue was washed and dried; the ether was removed yielding 1.2 g of crude yellow product. The crude product was recrystallized from methanol yielding white crystals, mp 93.1–93.8 °C. NMR and mass spectral analysis indicated >93% d_2, ~6% d_1, and <1% d_0.

Since the two linked benzophenone–dimethylaniline compounds PPDMAB and MMDMAB were prepared by similar procedures, only the preparation of MMDMAB is described. The general synthesis is shown in Scheme II.

2-Bromodimethylaniline was prepared by condensation of methanol and 2-bromoaniline with P_2O_5 as described above. 2-Dimethylamino-2′-bromomethylcarbinol was prepared by the reaction of 2-dimethylaminophenyllithium with 2-bromoacetophenone. To a dry 250-mL round-bottom flask fitted with a rubber septum and stir bar were added 19 g of 3-bromo-*N,N*-dimethylaniline (0.09 mol) and 150 mL of dry diethyl ether. The solution was cooled to 0 °C and 1 equiv of butyllithium in hexane was added via syringe. This solution was transferred to a second flask precooled to 0 °C containing 20.0 g of 3-bromoacetophenone (0.1 mol). The solution was allowed to stir for 1 h at 0 °C. The mixture was then quenched with 50 mL of H_2O and washed three more times with 50-mL portions of H_2O. Removal of the solvent yielded ~30 g of material which was ~50% the desired product. The crude material was purified by column chromatography (eluted on silica with a $CCl_4 \rightarrow CH_2Cl_2$ gradient) yielding ~15 g of the carbinol. The carbinol was reduced by the action of $NaBH_4$ in trifluoroacetic acid.[9] To 50 mL of CF_3COOH in a 250-mL three-neck flask under N_2 was added 10 8-mm $NaBH_4$ pellets (Ventron). To this mixture was added 15 g of the carbinol in 10 mL of CH_2Cl_2 over a 15-min period. The solution was allowed to stir an additional 2 h, after which time the solution was neutralized by aqueous NaOH and extracted into diethyl ether. Removal of the solvent and chromatography of the crude mixture yielded 3.8 g of 2-bromophenyl-2′-dimethylaminophenylethane. A major side product was the olefin formed by dehydration of the carbinol.

The final product was prepared by lithiation of the 2-bromophenyl-2′-dimethylaminophenylethane, reaction with benzonitrile, and subsequent hydrolysis of the resulting imine. To a dry 250-mL round-bottom flask fitted with a rubber septum and a stir bar were added 3.8 g of the 2-bromophenyl-2′-dimethylaminophenylethane and 100 mL of dry diethyl ether. The solution was cooled to 0 °C and 1 equiv of butyllithium in hexane was added via syringe. After ~30 min of stirring, 2 mL of C_6H_5CN in 50 mL of dry diethyl ether was transferred to the flask. The solution was allowed to stir for 1 h and then quenched with dilute HCl. After washing, the ether was removed and chromatography of the crude mixture (eluted on silica with a $CCl_4 \rightarrow CH_2Cl_2$ gradient) yielded ~1 g of pure MMDMAB as a yellow oil: NMR ($CDCl_3$) δ 1.66 [d, 3 H, CCH_3, J_{CH-CH_3} = 7.2 Hz], 2.91 [s, 6 H, $N(CH_3)_2$], 4.17 [q, 1 H, Ar–CHR–Ar, J_{CH-CH_3} = 7.2 Hz], 6.57–6.60 [mult, 2 H, ortho to $N(CH_3)_2$], 7.14–7.79 [mult, 11 H, aromatic protons]; IR (CH_2Cl_2) 1659 cm^{-1}.

The other coupled system PPDMAB was a yellow solid, mp 63.5–65.0 °C: NMR ($CDCl_3$) δ 1.63 [d, 3 H, CCH_3, J_{CH-CH_3} = 7.2 Hz], 2.93 [s, 6 H, $N(CH_3)_2$], 4.13 [q, 1 H, Ar–CHR–Ar, $J_CH_{-CH_3}$ = 7.2 Hz], 6.68 [d, 2 H, ortho to $N(CH_3)_2$, $J_{-HC=CH-}$ = 8.7 Hz], 7.09 [d, 2 H, meta to $N(CH_3)_2$, $J_{-HC=CH-}$ = 8.7 Hz], 7.31 [d, 2 H, ortho to bridging ethyl group, $J_{-HC=CH-}$ = 8.2 Hz], 7.71 [d, 2 H, meta to bridging ethyl group, $J_{-H,C=CH-}$ = 8.3 Hz], 7.4–7.8 [mult, 3 H, remaining aromatic protons]; IR (CH_2Cl_2) 1657 cm^{-1}.

NMR spectra were recorded on a Bruker 300-MHz instrument. UV–visible absorption spectra were recorded on a Perkin-Elmer Lambda-3 spectrophotometer.

Picosecond Laser Experiments. The laser apparatus has been described in detail.[10] Briefly, the picosecond absorption spectrometer consists of a 10-Hz Nd^{3+}–YAG laser (Quantel International, YG-400) with a pulse width of 25 ps. The detector is an OMAII Vidicon (PAR-1215-1216-1217) interfaced to a 200-mm spectrograph (JY-UFS-200). The 355-nm pulse used to excite benzophenone was ~0.2 mJ focused to an area of ~5 mm^2. Each spectrum is from the accumulation of at least 200 laser pulses. Solutions were deaerated by sealing the sample cuvette with a septum and bubbling N_2 through the solution for at least 4 min.

Results

Diphenylmethylamine-CH_3 and -CD_3. Laser irradiation (355 nm) of a 0.05 M solution of benzophenone (BP) in any of the solvents studied creates the benzophenone triplet ($^3BP^*$) within 25 ps with λ_{max} at 525 nm. In the presence of 1.0 M diphenylmethylamine (DPMA), the triplet state is quenched within 50 ps by an electron transfer process yielding the benzophenone radical anion ($BP^{-}\cdot$, λ_{max} ~690 nm) and the diphenylmethylamine radical cation ($DPMA^{+}\cdot$, λ_{max} 635 nm) as an ion pair in solution. The observed absorption spectrum from the ion pair is a superposition of those obtained from the individual ions.

Figure 1a shows the spectrum observed in chlorobenzene ~40 ps after excitation. Subsequent to ion pair formation, proton transfer occurs from $DPMA^{+}\cdot$ to $BP^{-}\cdot$ yielding benzophenone ketyl radical (BPH·, λ_{max} 545 nm) and diphenylmethylamine radical (DPMA·, no visible absorption). A spectrum of BPH· observed 10 ns after excitation of BP and DPMA in benzene is shown in Figure 1b. It is apparent that BPH· does not absorb light at 635 nm where the ion pair has its λ_{max} (Figure 1a). If the only path leading to loss of the ion pair is proton transfer with rate k_H, Scheme I, then monitoring the rate of loss of absorbance at 635 nm is a direct measure of the rate of proton transfer. Scheme I indicates two paths that will compete with proton transfer within the ion pair. The first is solvation of the ions (k_{solv}) which depends on the association constant for the ion pair which is solvent dependent.

$$K_{assoc} = \frac{[A^-D^+]}{[A^-][D^+]} = \frac{k_{-solv}}{k_{solv}} \qquad (2)$$

In the experiments reported, the solvent dielectric constants are kept below ϵ ~12. Typical association constants for ion pairs in solvents with ϵ ~12 are >5000 M^{-1}.[11] If it assumed that the fastest possible rate for k_{-solv} is diffusion controlled (~1×10^{10}

(8) Colter, A. K.; Saito, G.; Sharom, F. J. *Can. J. Chem.* **1977**, *55*, 2741.
(9) Gribble, G. W.; Leese, R. M.; Evans, B. E. *Synthesis* **1977**, 172.
(10) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 4875.
(11) Gordon, J. E. "The Organic Chemistry of Electrolyte Solutions"; Olah, G. A., Ed.; Wiley-Interscience: New York; p 373.

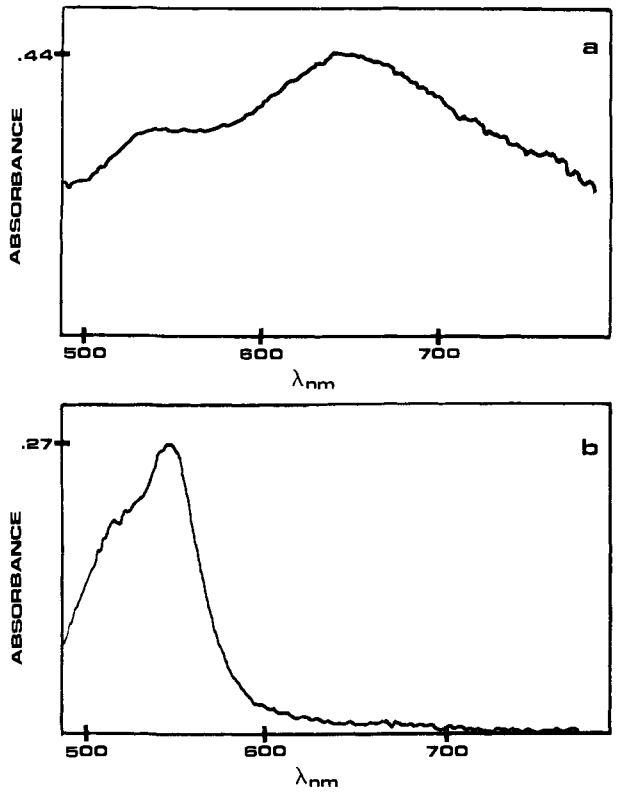


Figure 1. Absorption spectrum at (a) 40 ps and (b) 10 ns following 355-nm excitation of 0.05 M benzophenone–1.0 M diphenylmethylamine in benzene.

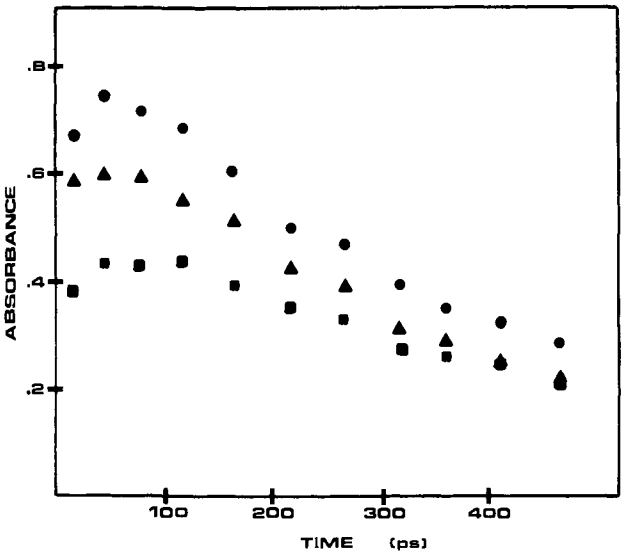


Figure 2. Time evolution of the absorbance at 635 nm following 355-nm excitation of 0.05 M benzophenone in dimethoxyethane in the presence of 1 M (●), 0.5 M (▲), and 0.25 M (■) diphenylmethylamine.

s^{-1} M^{-1} for most organic solvents),[12] then an estimate for an upper limit for k_{solv} is $\sim 2 \times 10^6$ s^{-1}. The proton transfers reported herein all occur faster than 5×10^8 s^{-1}; therefore, ion solvation will not compete with proton transfer. The second path that may compete with proton transfer is back electron transfer to give ground-state BP and DPMA. The contribution of back electron transfer, k_{BET}, to the decay of the triplet ion pair cannot be easily dismissed. However, the deuterium isotope experiments to be discussed indicate that k_{BET} can only be a minor pathway. It is also important to consider that the high concentration of amine required to trap the ^{3}BP* within 50 ps (1 M) might trap some ^{1}BP* before it

(12) Calvert, J. G.; Pitts, J. N., Jr. "Photochemistry"; Wiley: New York; p 627.

Table I. Solvent Effects on Proton Transfer Rates[a]

solvent	τ(DPMA), ps	τ(DPMA-CD_3), ps	k_H/k_D
o-xylene	200		
benzene	180	340	1.9
diethyl ether	230		
chlorobenzene	420	1100	2.6
dimethoxyethane	410		
pyridine	670	1660	2.5
methylene chloride	660	1590	2.4

[a] Error is ±10%.

Table II. Effect of Benzophenone Chlorination on Proton Transfer Rates in Benzene[a]

ketone	τ(DPMA), ps	τ(DPMA-CD_3), ps	k_H/k_D
benzophenone	180	340	1.9
4-chlorobenzophenone	270	750	2.8
4,4'-dichlorobenzophenone	400	1200	3.0

[a] Error is ±10%.

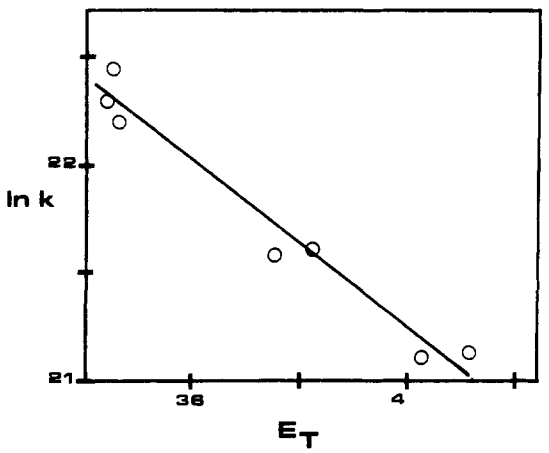


Figure 3. Correlation of ln k for proton transfer from $DPMA^{+\cdot}$ to $BP^{-\cdot}$ with E_T for the solvents listed in Table I.

intersystem crosses.[10] The singlet ion pair could undergo more facile back electron transfer, and the observed disappearance of the absorption at 635 nm would not be entirely due to proton transfer. That electron transfer to ^{1}BP* is not a major contributor to ion-pair formation is illustrated in Figure 2 which shows the appearance and disappearance of absorbance at 635 nm after BP excitation in dimethoxyethane at various DPMA concentrations. With 1 M DPMA present, the ion pair appears within 50 ps, and then decays with a lifetime of 410 ± 30 ps. When the DPMA concentration is reduced to ~0.5 M, the ion pair takes somewhat longer to appear but then decays with the same lifetime as seen at 1 M DPMA, 410 ps. If a large percentage of ^{1}BP* is being trapped at the higher DPMA concentration (leading to increased back electron transfer as a source of ion-pair loss), the rate of ion-pair decay would be dependent upon DPMA concentrations. When the DPMA concentration is reduced to 0.25 M, the disappearance of the ion pair occurs with a lifetime of ~500 ps. This apparent decrease in proton transfer rate is actually due to the much slower rate of ^{3}BP* quenching at the lower DPMA concentration. The above observations indicate that the major path for ion-pair loss in these systems is proton transfer.

The rate of proton transfer from $DPMA^{+\cdot}$ to $BP^{-\cdot}$ was determined in a number of solvents of varying polarities (Table I). It is apparent that as the solvent polarity increases, the rate of proton transfer decreases, going from a lifetime of ~200 ps in benzene and *o*-xylene to ~650 ps in pyridine and methylene chloride. Figure 3 is a plot of the natural logarithm of the observed rates vs. Dimroth's E_T values for the various solvents.[13] The plot is

(13) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Justus Liebigs Ann. Chem.* **1963**, *661*, 1.

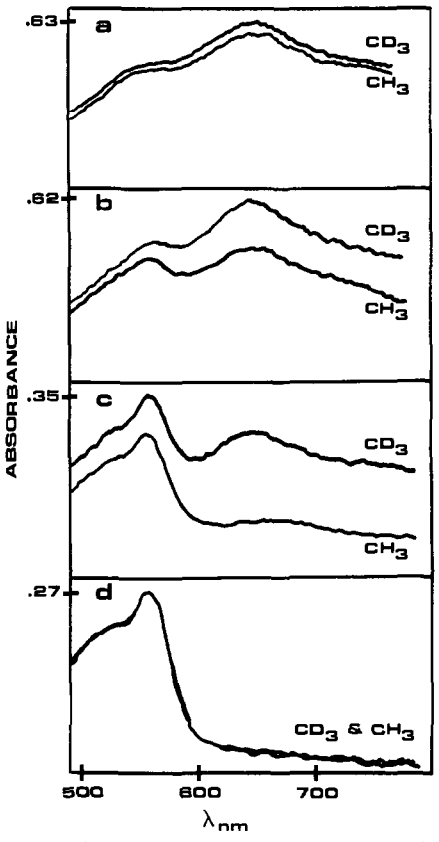


Figure 4. Absorption spectrum following 355-nm excitation of 4-chlorobenzophenone in the presence of 1 M DPMA-d_3 and 1 M DPMA at (a) 40 ps, (b) 130 ps, (c) 600 ps, (d) 50 ns.

fairly linear with a negative slope indicating the ion pair is stabilized more by polar solvents than is the transition state leading to proton transfer.

The basic oxide center in $BP^{-}\cdot$ can be stabilized by placing electron-withdrawing groups on the benzophenone. Table II lists the lifetimes for proton transfer from DPMA· to $BP^{-}\cdot$, 4-Cl-$BP^{-}\cdot$ and 4,4′-Cl_2-$BP^{-}\cdot$. The rate of proton transfer slows considerably as the benzophenone radical anion is stabilized by the electron-withdrawing groups.

Deuterium isotope effects on the observed rates were determined by replacing the DPMA with DPMA-d_3. Table I shows the lifetimes for deuterium transfer in a few of the solvents and Table II lists the lifetimes for deuterium transfer to chlorinated benzophenones. Figure 4 compares the spectra from DPMA and DPMA-d_3 with 4-Cl-BP in benzene. At 40 ps (Figure 4a) the two spectra are very similar as the predominant reaction at this time is electron transfer (the rate of electron transfer from DPMA and DPMA-d_3 should be almost identical). By 130 ps (Figure 4b) it is apparent that the proton from DPMA is being transferred faster than the deuterium from DPMA-d_3. Furthermore, the DPMA system has formed more 4-Cl-BPH· (λ_{max} 560 nm) than the DPMA-d_3 system. The same trend is seen at 600 ps (Figure 4c); however, by 50 ns (Figure 4d) the same amount of 4-Cl-BPH· has formed from DPMA and DPMA-d_3. Based on this latter observation, we conclude that k_{BET} is at least an order of magnitude less than k_H. If k_{BET} had been of the same magnitude as k_H the amounts of ketyl radical formed at 50 ns would have been different from DPMA and DPMA-d_3.

This observation supports the conclusions drawn by Linschitz and Cohen[14] in their investigation of quantum yields for ketyl radical formation in the photoreduction of benzophenone by amines. They proposed that the rate of back electron transfer for the triplet ion pair is not competitive with the rate of proton transfer within the ion pair. In order to rationalize the low overall

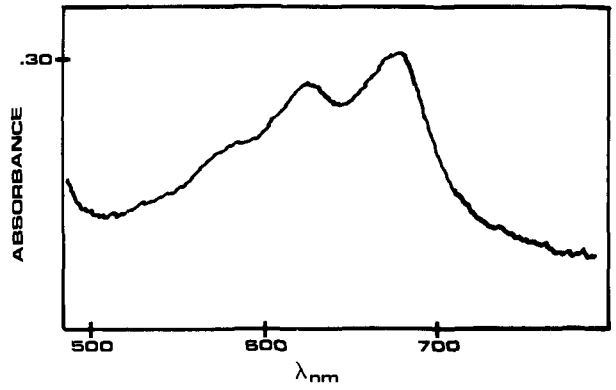
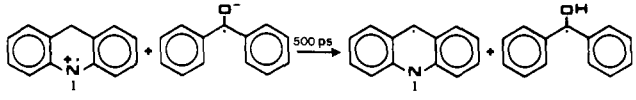


Figure 5. Absorption spectrum at 25 ps following 355-nm excitation of 0.01 M anthraquinone in benzene.

quantum yield of product formation, subsequent back reactions, such as diproportionation of the radical pair, must regenerate starting material.

***N*-Methylacridan-CH_3, -CD_3, and -CO_2^{-}·.** Laser excitation (355 nm) of a 0.05 M solution of BP with 1.0 M *N*-methylacridan (NMA) in benzene produced the radical ion pair composed of $BP^{-}\cdot$ and $NMA^{+}\cdot$ (λ_{max} 640 nm) within 50 ps. Subsequent to electron transfer, proton transfer occurs from $NMA^{+}\cdot$ to $BP^{-}\cdot$ with τ = 500 ± 50 ps to yield BPH· (λ_{max} 545 nm) and the *N*-methylacridanyl radical (NMA·; λ_{max} 520 nm).



640 nm 690 nm 520 nm 545 nm

Excitation of a 1.0 M 9,9-dideuterio-*N*-methlacridan (NMA-9,9-d_2) solution with 0.05 M BP under identical conditions yields k_H/k_D = 1.00 ± 0.03 as determined by the rate of ion-pair disappearance. However, when 1.0 M *N*-methylacridan-*methyl*-d_3 (NMA-CD_3) is present, k_H/k_D is 1.4 ± 0.05. These results indicate that proton transfer actually occurs from the *N*-methyl position rather than the 9-methylene position. The ratios of BPH· to NMA· (determined by the ratio of the 545- and 520-nm peaks) are the same for all three systems studied at all times after the laser flash indicating that although initial proton transfer occurs from the *N*-methyl position forming an NMA ylide, NMA· (which has lost a proton from the 9-methylene position) appears at a rate similar to that for BPH·.

Further evidence that initial proton transfer occurs from the *N*-methyl position was obtained by NMR analysis. A solution of 1.0 M BP with 0.015 M NMA-CD_3 in C_6D_6 was irradiated to ~50% conversion of the acridan. NMR analysis of the mixture before irradiation showed a peak at 3.66 ppm due to the methylene bridge protons and a very small peak at 2.80 ppm due to the <0.2% NMA-CHD_2 in the starting material. After irradiation, NMA-CHD_2 (2.80 ppm, pentet) accounts for >20% of the remaining starting material and pentets appear at 2.69 and 2.60 ppm. We assign the pentet at 2.60 ppm to the 9,9′-(NMA-CHD_2) dimer because a sample of 9,9′-NMA dimer shows a singlet at 2.63 ppm. The pentet at 2.69 is possibly due to the mixed dimer from the acridanyl and BPH· radicals. The position of the NMA-CHD_2 peak in the starting material (2.80 ppm) and in the 9,9′-(NMA-CHD_2) dimer (2.60 ppm) are shifted upfield from NMA-CH_3 groups in the corresponding compounds, 2.83 and 2.63 ppm, respectively.[15]

The proton transer from $NMA^{+}\cdot$ to anthraquinone radical anion $AQ^{-}\cdot$ was also studied. Laser excitation (355 nm) of 0.01 M AQ in benzene creates the anthraquinone triplet ($^3AQ^*$) within 25 ps with λ_{max} at 677 nm and shoulders at 582 and 623 nm (Figure 5).[16] In the presence of 1.0 M NMA a ground-state charge-

(14) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1980**, *102*, 1419.

(15) For isotope effects on chemical shifts see: Gutowsky, H. S. *J. Chem. Phys.* **1959**, *31*, 1683.

(16) Astier, R.; Meyer, Y. *J. Chim. Phys.* **1967**, *64*, 919.

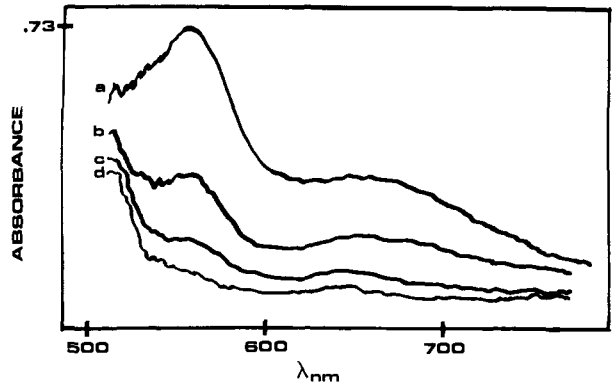


Figure 6. Absorption spectrum following 355-nm excitation of 0.01 M anthraquinone–1.0 M *N*-methylacridan in benzene at (a) 25 ps, (b) 100 ps, (c) 190 ps, (d) 280 ps.

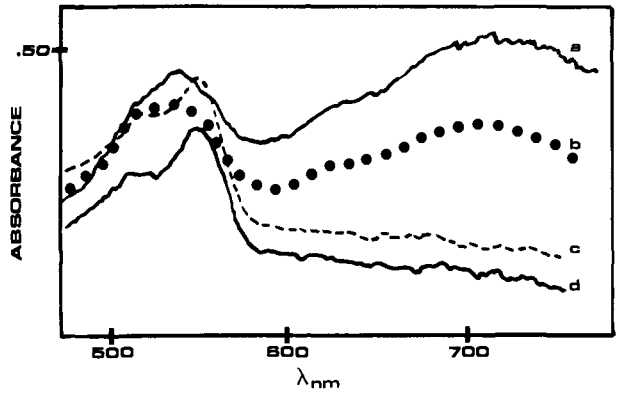


Figure 7. Absorption spectrum following 355-nm excitation of 0.06 M PPDMAB in benzene at (a) 50 ps, (b) 350 ps, (c) 4.3 ns, (d) 18.8 ns.

transfer complex forms between AQ and NMA which has a broad visible absorbance (λ_{max} 450 nm, A_{450} = 1.2) extending beyond 600 nm (A_{600} = 0.07). A Benesi–Hildebrand study on the ground-state charge-transfer complex indicates the association constant is 0.6 ± 0.1 M^{-1}. With 1.0 M NMA and 0.01 M AQ, the AQ–NMA charge-transfer complex absorbs ~80% and the AQ absorbs ~20% of the 355-nm light. Laser excitation (355 nm) of a 0.01 M solution of AQ with 1.0 M NMA in benzene creates an ion pair, $AQ^{-}\cdot$ (λ_{max} 550 nm)[17] and $NMA^{+}\cdot$ (λ_{max} 640 nm) (Figure 6). Subsequent to its formation, the ion pair disappears with τ = 140 ± 30 ps forming a new transient with an absorption at ~520 nm. Unfortunately the loss of probe light due to absorption by the ground-state complex makes data acquisition below 520 nm impossible. However, the increase in absorbance at 520 nm is consistent with NMA· formation. When the 1.0 M NMA is replaced by NMA-*9,9*-d_2 or NMA-CD_3, the lifetimes of ion-pair disappearance are 210 ± 30 and 190 ± 30 ps, respectively. This observation indicates that in the $AQ^{-}\cdot NMA^{+}\cdot$ radical ion pair, proton transer occurs from both the *N*-methyl position and the 9-methylene position of $NMA^{+}\cdot$.

Dimethylaniline Linked to Benzophenone. Laser excitation of 0.06 M PPDMAB in benzene produces the transient spectra shown in Figure 7a–d. At 50 ps after laser excitation there is a mixture of benzophenone radical anion λ_{max} 720 nm, and a peak at 540 nm, probably due to a mixture of $^3BP^*$ and BPH·. By 4.3 ns the $BP^{-}\cdot$ has almost completely decayed and BPH· accounts for most of the remaining absorbance. Excitation of PPDMAB at various concentrations (Figure 8a–c) indicates that bimolecular reactions are a major contributor to the dynamics of proton transfer. With 0.002 M PPDMAB, $BP^{-}\cdot$ is still present at 4.2 ns whereas for 0.06 M PPDMAB only ketyl radical is observed. Similar results are obtained with MMDMAB after 355-nm excitation in benzene.

Excitation of 3.6 × 10^{-3} M PPDMAB in ethyl acetate produces the $BP^{-}\cdot$ spectrum within the time of the laser pulse. The im-

(17) Fujihira, M.; Hayano, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 644.

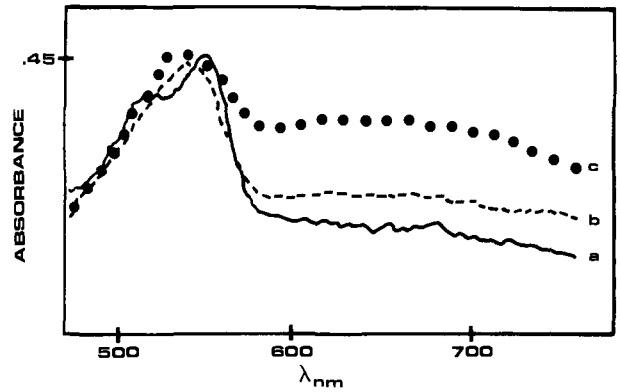


Figure 8. Absorption spectrum 4.2 ns after 355-nm excitation of (a) 0.06 M, (b) 0.012 M, and (c) 0.002 M PPDMAB in benzene.

mediate appearance of $BP^{-}\cdot$ at this PPDMAB concentration indicates it is formed by an intramolecular electron transfer. The anion decays with a lifetime of 10 ± 2 ns producing the ketyl radical. Excitation of a solution containing 3.6 × 10^{-3} M PPDMAB and 0.05 M *N,N*-dimethyl-4-toluidine (DMT) in ethyl acetate also produces $BP^{-}\cdot$ within the laser pulse; however, in this case the anion decays with τ = 3.8 ± 1.0 ns. At 50 ns the solution without DMT contains both $BP^{-}\cdot$ and BPH· while the solution with DMT contains only BP· at a concentration three times greater than the solution without DMT.

Discussion

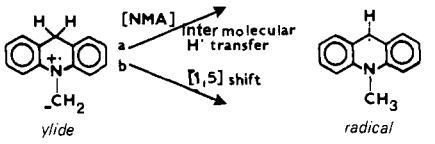
The driving force for proton transfer in the systems described is the increased stability of the radical pair relative to the ion pair. The observed solvent effects (Table I) are consistent with the anticipated loss of charge separation in the transition state leading to proton transfer. The correlation with Dimroth's E_T values (Figure 3) is not surprising since the E_T values are based on the loss of charge separation in an electronic transition.[13] The data in Table I indicate that the isotope effects increase with increasing solvent polarity (going from k_H/k_D ~ 1.9 in benzene to k_H/k_D ~ 2.5 in chlorobenzene, pyridine, and methylene chloride). However, it does not approach the expected value of ~7. It has been observed[18] previously that k_H/k_D varies with $\Delta G°$ for the overall reaction with a maximum at $\Delta G°$ = 0, consistent with Westheimer's original proposal that k_H/k_D will have a maximum value for a symmetrical transition state.[19] The proton transfer from $DPMA^{+}\cdot$ to $BP^{-}\cdot$ is certainly exothermic in all of the solvents studied but should be less exothermic in the more polar solvents. However, the isotope effect does not change significantly in going from chlorobenzene (E_T = 37.5) to methylene chloride (E_T = 41.1) even though $\Delta G°$ is certainly less negative in the latter solvent. A possible explanation for this observation is that the proton transfer is coupled to molecular reorientation within the radical ion pair ($DPMA^{+}\cdot BP^{-}\cdot$). This would indicate that although the ion pair is formed as an encounter complex, thereby avoiding diffusion of the acid–base pair, the equilibrium geometry is not optimum for proton transfer to occur. In this case proton transfer requires two steps with rates k_1 and k_2.

$$A \xrightarrow[\Delta G^{\mp}_{reo}]{k_1} B \xrightarrow[\Delta G^{\mp}_{pro}]{k_2} C \qquad (3)$$

In eq 3, B is the ion pair from which proton transfer occurs yet is spectroscopically indistinguishable from A by our technique. The actual isotope effect for proton transfer will not be observed even when ΔG = 0 unless $\Delta G^{\mp}_{reo} << \Delta G^{\mp}_{pro}$. It is likely that stabilization of the ion pair by adjusting the solvent polarity will effect both $\Delta G^{\mp}_{reo}$ and $\Delta G^{\mp}_{pro}$. When $\delta\Delta G^{\mp}_{reo}/\delta\Delta G^{\mp}_{pro} < 1$, the observed isotope effect will increase as the ion pair is stabilized. When $\delta\Delta G^{\mp}_{reo}/\delta\Delta G^{\mp}_{pro} \sim 1$, the observed isotope effect will remain constant, and when $\delta\Delta G^{\mp}_{reo}/\delta\Delta G^{\mp}_{pro} > 1$, the observed

(18) Bell, R. P. *Faraday Symp. Chem. Soc.* **1975**, *10*, 1.
(19) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265.

Scheme III

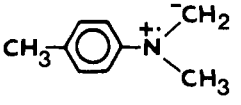


isotope effect will decrease as the ion pair is stabilized. Substitution of electron-withdrawing groups on $BP^{-}\cdot$ will stabilize the anion (reducing its basicity) which should have a greater effect on $\Delta G^{\mp}_{pro}$ than on $\Delta G^{\mp}_{reo}$. Indeed the observed rates are consistent with this expectation, as k_H/k_D increases from 1.9 to 2.8 and 3.0 in benzene when $BP^{-}\cdot$ is chlorinated and dichlorinated. A Hammett plot for the chlorinated benzophenone data in benzene[20] (with our limited number of data points) indicates that DPMA-d_3 has a more negative ρ value than DPMA; i.e., deuterium transfer is more sensitive to benzophenone substitution than proton transfer. This observation can be explained by considering the coupling of molecular reorientation to proton transfer: $\Delta G^{\mp}_{reo}$ will not be affected by deuterium substitution, whereas $\Delta G^{\mp}_{pro}$ will increase upon deuterium substitution. The results suggest that the faster proton transfer is slowed more by the reorientation step than the slower deuterium transfer.

These same general conclusions, regarding specific orientation for proton transfer, had been reached by Wagner[21] in his investigation of type II photoreactions of α-, γ-, and δ-dialkylamine ketones. The low efficiency of γ-proton transfer to the oxygen anion was attributed to geometrical constraints of the charge-transfer complex limiting the rate of proton transfer.

Proton transfer from $NMA^{+}\cdot$ can occur, in principle, from either the *N*-methyl position or the 9-methylene position of $NMA^{+}\cdot$ to $BP^{-}\cdot$. The observation of NMA· (λ_{max} 520 nm) formation suggests that proton transfer is occurring from the 9-methylene position. This is consistent with mass spectral results which indicate that hydrogen atom loss occurs predominately from the 9-methylene position in the gas phase.[22] Our mass spectral analyses of NMA, NMA-*9,9*-d_2, and NMA-CD_3 confirm this previous conclusion indicating that <1% of the hdyrogen loss occurs from the *N*-methyl position in the gas phase. However, the observation of no isotope effect upon deuteration of the methylene position (k_H/k_D = 1.00 ± 0.03) coupled with the isotope effect seen when the methyl group is deuterated (k_H/k_D = 1.40 ± 0.05) indicates that proton transfer is occurring from the methyl position. This possibility is confirmed by the NMR analysis which shows the appearance of -CHD_2 products upon excitation of NMA-CD_3 in benzene-d_6 with BP present.

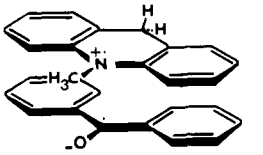
Initial proton transfer from the *N*-methyl position will create an ylide. Since NMA· appears as fast as BPH·, the ylide must be converted to NMA· within 500 ps. Two mechanisms can account for the conversion of the ylide to NMA·: paths a and b in Scheme III. Path a is an *inter*molecular hydrogen atom transfer from the 9-position of acridan to the ylide yielding NMA· and acridan. If path a is occurring, we anticipate that other ylides similar to the NMA ylide would also abstract a hydrogen atom from NMA. *N,N*-Dimethyl-4-toluidine (DMT) undergoes electron-proton transfer to ^3BP in benzene at rates similar to those for NMA. Proton transfer from $DMT^{+}\cdot$ to $BP^{-}\cdot$ will create a DMT ylide similar to the NMA ylide.



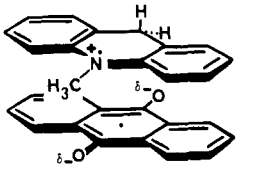
DMT–*ylide*

Laser excitation of 0.05 M BP with 1.0 M NMA and 1.0 M DMT in benzene shows the same amount of BPH· (5 ns after excitation) as a solution with only 1.0 M NMA but shows only half as much NMA·. This result indicates that the DMT ylide does not abstract a hydrogen atom from NMA and rules out path a as the mechanism for NMA· formation. By exclusion pathway b, an *intra*molecular [1,5] shift, is occurring.

The reason for kinetically favored proton abstraction from the *N*-methyl group rather than the thermodynamically favored 9-position is due to the geometry of the ion pair. The results from $DPMA^{+}\cdot$ proton transfer to $BP^{-}\cdot$ suggest that reorientation occurs prior to proton transfer. This reorientation is due to movement away from the initially formed ion-pair geometry. It is anticipated that the favored geometry in either the $DPMA^{+}\cdot BP^{-}\cdot$ or the $NMA^{+}\cdot BP^{-}\cdot$ ion pair will allow maximum π-system overlap between the two aromatic systems with strong association of the negative charge on $BP^{-}\cdot$ (located predominantly on the oxygen) with the positive charge on the radical cation (located on the nitrogen). A structure that satisfies this requirement is shown below.

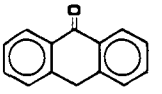


Interaction between the oxide center and the methylene protons of $NMA^{+}\cdot$ requires major restructuring of the complex, whereas interaction with the *N*-methyl protons (to give the observed proton transfer) can readily occur. It is likely that movement toward the methyl group to form a hydrogen-bonded species is the reorientation required prior to proton transfer. If BP is replaced by anthraquinone (AQ), an ion pair would be formed similar to that shown below.

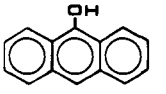


In this ion pair two resonance structures are available, one with the basic site near the methyl position and a second with the basic site near the methylene position. No major restructuring is required for the methylene proton to be removed. Our results indicate that in $NMA^{+}\cdot AQ^{-}\cdot$ the proton transfer can occur from either position with k_H/k_D of ~1.5 and ~1.4 for NMA-*9,9*-d_2 and NMA-CD_3, respectively.

Another system similar to NMA where intramolecular hydrogen transfer will be exothermic is anthrone. Excitation of



triplet ~72 kcal

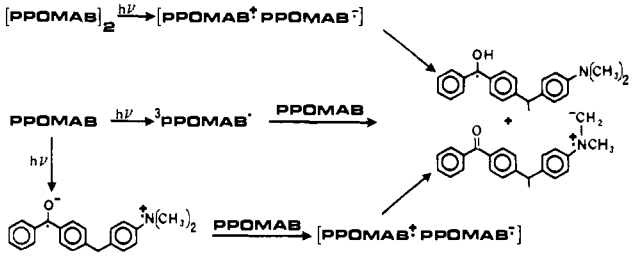


triplet ~43 kcal

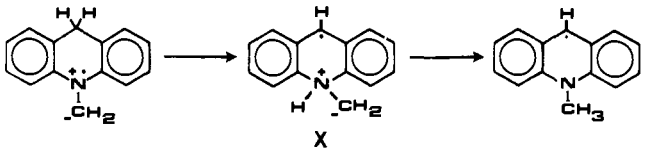
anthrone creates the triplet state within 50 ps[23] which is 71.5 kcal above the ground state.[24] A [1,5] shift of a hydrogen from the methylene position to the oxygen would create triplet 9-hydroxyanthracene. The triplet state of anthracene is ~43 kcal above the ground state.[25] Therefore, this [1,5] shift will be exothermic by ~26 kcal[26] and yet it does not occur.[23] This contrast with the fast [1,5] shift that occurs with the NMA ylide to form NMA·. The difference in the observed rates for these

(20) Brockman, R. W.; Pearson, D. E. *J. Am. Chem. Soc.* **1952**, *74*, 4128.
(21) Wagner, P. J.; Kemppainen, A. E.; Jellinek, T., *J. Am. Chem. Soc.* **1972**, *94*, 7512.
(22) Clark, J.; Bakavoli, M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1966.
(23) Damschen, D. E.; Merritt, C. D.; Perry, D. L.; Scott, G. W.; Talley, L. D. *J. Phys. Chem.* **1978**, *82*, 2268.
(24) Kobayashi, T.; Nagakura, S. *Chem. Phys. Lett.* **1976**, *43*, 429.
(25) Herkstroeter, W. G.; Lamola, A. A.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 4537.
(26) The enthalpy change for conversion of anthrone to 9-hydroxyanthracene in benzene is −2.6 kcal/mol. See: Baba, H.; Takemura, T. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1241.

Scheme IV



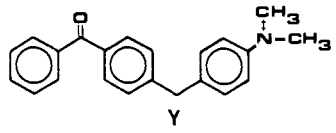
[1,5] shifts may be accounted for by the presence, in NMA, of the nitrogen ortho to the methylene position. Hydrogen transfer from the 9-methylene position to nitrogen would create the intermediate X. Intermediate X contains an ammonium center



X

stabilized by an α-carbanion and a diphenylmethyl radical. Direct contact between the methylene and the ortho nitrogen is possible, whereas contact between the carbanion and methylene is unlikely.

The observed inability of hydrogens to transfer over large distances raised our interest in a literature report that a methylene-linked dimethylaniline–benzophenone system (Y) underwent

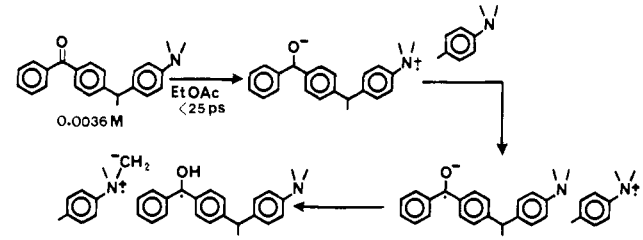


Y

intramolecular hydrogen atom transfer in benzene.[5] Analysis of molecular models of Y indicate that the closest approach of a methyl proton to the carbonyl oxygen is ~7 Å. Transfer over such a large distance is somewhat surprising in light of the above discussion. Wagner[27] recently proposed that the observed ketyl radical formation in Y in fact may be the result of a bimolecular reaction. The experiments with PPDMAB (which is identical with Y except for the methyl group on the methylene bridge) indeed are more consistent with proton transfer occurring by an intermolecular process. Three mechanisms which lead to facile intermolecular proton transfer are shown in Scheme IV. The first mechanism involves the photoexcitation of PPDMAB charge-transfer dimer. The extent to which ground-state complexation occurs is not known but certainly should be present at higher PPDMAB concentrations and probably accounts for PPDMAB being yellow rather than white. The second mechanism involves quenching of the triplet state of one PPDMAB molecule by diffusion encounter of a second PPDMAB molecule. This mechanism is certainly not occurring in ethyl acetate where only $BP^{-}\cdot$ and dimethylamine radical cation are observed immediately after the laser flash but could be occurring in benzene where some $^3BP^*$ at 4.2 ns is observed when lower concentrations of PPDMAB are used. The third mechanism accounts for most of the BPH· observed in ethyl acetate. In this case, photoexcitation of PPDMAB creates the intramolecular zwitterion within the time resolution of our experiment. Subsequent to its formation the zwitterion encounters a ground-state PPDMAB molecule. Electron transfer from the neutral aniline moiety (or to the neutral BP moiety) will be approximately isoenergetic and will occur at a diffusion-controlled rate. After formation of the $PPDMAB^{+}\cdot PPDMAB^{-}\cdot$ ion pair and reorientation, proton transfer occurs which is detected as BPH· formation. That the latter mechanism is viable is illustrated by adding DMT to act as an intermolecular aid to proton transfer.

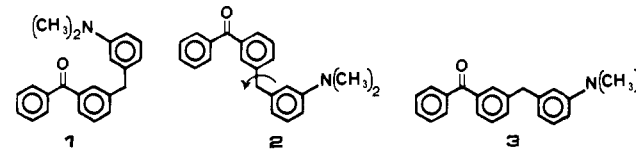
(27) Wagner, P. J. *Acc. Chem. Res.* **1983**, *16*, 461.

Scheme V



Photoexcitation of a 0.0036 M solution of PPDMAB (Scheme V) created the zwitterion within 25 ps. Comparison of a solution containing 0.05 M DMT (which cannot compete with the intramolecular process for electron transfer to $^3BP^*$) to one without DMT indicates that the absorption due to $BP^{-}\cdot$ decays ~2.6 times faster when the DMT is present. At 50 ns no $BP^{-}\cdot$ is observed in the solution with DMT while $BP^{-}\cdot$ is present without DMT. Furthermore, the sample with DMT showed ca. three time as much absorbance due to the BPH· moiety as the sample without DMT.

The synthesis of MMDMAB was undertaken because molecular models revealed that the closest approach of a methyl proton to the carbonyl oxygen is <3 Å. The results obtained with MMDMAB are similar to those from PPDMAB; proton transfer occurs from bimolecular interaction. MMDMAB may exist in one of three conformations (**1**, **2**, or **3**). Of these conformations,



only **1** has the methyl protons close to the oxide center. We do not know if the similarity of the results from PPDMAB and MMDMAB is due to a lack of conformer **1** being present or that proton transfer does not occur over a 3-Å distance.

Conclusions

The details of proton transfer processes within an encounter complex have been of great interest to chemists. Through picosecond absorption spectroscopy, we have shown that geometrical restructuring within the encounter complex can make a significant contribution to the overall rate of proton transfer as revealed by the energetic and isotope studies of the benzophenone–diphenylmethylamine system. On the other hand, large amplitude rearrangement within the complex can be slow relative to the actual transfer of the proton. This is illustrated by the transfer of a proton from the radical cation of *N*-methylacridan to the radical anion of benzophenone, where the thermodynamically most stable product is not formed. Finally, contrary to previous reports, long-range proton transfer (3 to 7 Å) from the radical cation of dimethylaniline to the radical anion of benzophenone, linked by a methylene bridge, is not observed on the 1 to 10 ns time scale.

Acknowledgment. This work is supported by a grant from the National Science Foundation, No. CHE-8418611. K.S.P. acknowledges support from the Henry and Camille Dreyfus Foundation for a teacher–scholar grant and the Alfred P. Sloan Foundation.

Registry No. MMDMAB, 98509-09-2; PPDMAB, 98509-10-5; CH_3OD, 811-98-3; CH_3OH, 67-56-1; C_6H_5CN, 100-47-0; diphenylmethylamine, 552-82-9; *N*-methylacridan, 4217-54-3; benzophenone anion radical, 16592-08-8; anthraquinone anion radical, 3426-73-1; benzophenone, 119-61-9; 4-chlorobenzophenone, 134-85-0; 4,4′-dichlorobenzophenone, 90-98-2; methyl-d_3-diphenylamine, 95469-17-3; diphenylamine, 122-39-4; *N*-methyl-d_3-acridan, 98482-15-6; *N*-methylacridone, 719-54-0; *N*-methylacridan-9,9-d_2, 66228-30-6; 3-bromodimethylaniline, 16518-62-0; 3-bromoaniline, 591-19-5; 3-bromoacetophenone, 2142-63-4; 2-dimethylamino-2′-bromoethylcarbinol, 98482-16-7; 2-bromophenyl-2′-dimethylaminophenylethane, 98482-17-8; deuterium, 7782-39-0.