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separated from it by a significant activation barrier.

The aluminocyclopentene forms two strong interactions and two weak interactions to butadiene and is characterized by substantial spin density on aluminum in an orbital 70% s. In contrast, the spin density in aluminomethylallyl is mostly on the allylic fragment.

Three structures were considered for the complex formed between aluminum and benzene. The lowest energy structure, the 1,4-addition complex, agrees with experiment and is bound by 7.4 kcal/mol at the highest level of theory. A natural population analysis (NPA) indicates that nearly a full negative charge is transferred from aluminum to benzene.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. Computer time for this study was made available by the Alabama Supercomputer Network and the NSF-supported Pittsburgh Supercomputer Center.

Picosecond and Nanosecond Studies of the Photoreduction of Benzophenone by *N*,*N*-Diethylaniline and Triethylamine

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The photoreduction of benzophenone by *N*,*N*-diethylaniline and triethylamine has been examined in a number of solvents by both nano- and picosecond laser photolysis. With diethylaniline, electron transfer is the primary step and the spectrum of the ion pair has been detected even in nonpolar solvents such as benzene and cyclohexane. Rapid proton transfer then takes place to form a high yield of the ketyl radical. The lifetime of the ion pair in benzene is about 900 ps. In acetonitrile, the ion pair dissociates into individual ions which then decay by back electron transfer and proton transfer. A spectral shift to the red occurs over 100 ps as the contact ion pair dissociates. In acidic alcohols such as methanol and trifluoroethanol, proton transfer from the alcohol occurs to produce the ketyl radical. In the case of triethylamine, no distinct absorption band for benzophenone anion was seen in picosecond experiments but difference spectra, which removed much of the spectrum of benzophenone triplet, clearly showed some contribution from the anion. For this compound, it is likely that electron transfer occurs first followed by very fast proton transfer.

Introduction

The photoreduction of benzophenone (BP) by amines has been studied for a long time. Some of the earlier work relevant to the present observations is in papers by Cohen and co-workers[1-3] and Wagner and Kemppainen.[4] Cohen et al.[5] and also Wagner[6] have covered photoreduction by amines in reviews. Cohen and Cohen[7] and also Davidson and Lambeth[8] proposed electron transfer from tertiary amines to triplet (substituted) BP followed by proton transfer and the possibility of an ion pair or charge-transfer intermediate was suggested by Cohen and Chao.[3] Cohen and Baumgarten[2] noted marked effects of composition in mixed solvents of 2-propanol and benzene or hydrocarbon. Wagner and Kemppainen[4] have reported observations in accord with an initial electron transfer but observe that the lack of an effect of solvent polarity on quenching rate constant does not agree with that idea. Wagner[6] has reviewed the arguments for and against electron transfer. These discussions mainly predated the use of laser flash photolysis which directly affirms that charge or electron transfer has occurred when an intermediate of character like the BP anion or amine cation can be seen in the spectrum. The question of partial or complete charge transfer and the designation of the intermediate as an exciplex or ion pair is a more difficult question. We shall use the term ion pair.

A previous paper[9] presented results of pico- and nanosecond laser photolysis experiments on the quenching of ^{3}BP by 1,4-diazabicyclo[2.2.2]octane (DABCO) in a wide variety of solvents. In all cases, it was concluded that the first step is electron transfer to form a contact ion pair (CIP) in the triplet state. The subsequent reactions of the ion pair, which involve solvation to form a solvent-separated ion pair (SSIP), proton transfer to form neutral radicals, and back electron transfer to re-form the starting materials, are controlled by a complex interplay between the rate of intersystem crossing, rate of proton transfer, and the rate of back electron transfer. The observed reactions generally follow the overall scheme proposed by Cohen and co-workers[10-12] and the picosecond observations agree with those reported by Peters and co-workers[13-15] except in the case of acetonitrile where evidence for a conversion of CIP to SSIP was found rather than the reverse. The present work represents an extension of similar studies to the amines *N*,*N*-diethylaniline (DEA) and triethylamine (TEA) for comparison with the results for DABCO. In the case of DEA, the cation is stabilized by conjugation with the aromatic ring while with TEA there is no stabilization of the cation and the molecule is not rigid like DABCO so proton transfer from the amine cation may be faster. The specific aim is to identify the nature of the transient intermediate in various solvents and to examine its mode of decay.

The photoreduction of BP by DEA has been studied extensively by nano- and picosecond laser photolysis and ESR methods. Arimitsu et al.[16] studied this photochemical reaction by nanosecond laser photolysis and proposed that, in ACN, electron transfer from DEA to ^{3}BP triplet takes place and then the ion pair dissociates

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into separate ions without forming ketyl radicals. Further, they reported that the absorption maximum of BP^- in ACN is 660 nm which is not in agreement with the value of 720 nm seen in the previous study.[9] Even though they were not able to observe BP^- in benzene and other nonpolar solvents, they suggested that the reaction proceeds by electron transfer followed by fast proton transfer thus leading to the formation of ketyl radicals. Hoshino and co-workers[17,18] studied the quenching of BP by DEA in 2-methyltetrahydrofuran and in neat DEA and observed the formation of ketyl radical alone at room temperature. However, at lower temperatures, below 165 K in 2-methyltetrahydrofuran and at 77 K in neat DEA, they were able to observe BP^- with an absorption peak at 740 nm in 2-methyltetrahydrofuran and at 780 nm in neat DEA. They were also able to identify DEA^+ in 2-methyltetrahydrofuran and in neat DEA at low temperatures with λ_{max} at 470 and 450 nm, respectively. Their study also did not report observation of BP^- in benzene or in nonpolar aliphatic hydrocarbon solvents at room temperature. Miyagawa et al.[19] studied the same photochemical reaction in ACN and cyclohexane by using ESR, which is useful for the unambiguous identification of radicals. Despite their failure to observe BP^- and DEA^+ in cyclohexane, they also concluded that the mechanism involves electron transfer followed by proton transfer. However, they differed from Arimitsu et al.[16] in proposing the formation of ketyl radicals in ACN.

Simon and Peters[14,15] studied the photoreduction of BP by DEA using picosecond laser spectroscopy. They reported observing a blue spectral shift from 715 to 690 nm in ACN and from 690 to 625 nm in ethanol much like their results for BP–DABCO. They added the additional step of equilibrium between BP^- and ketyl radical in ACN for the BP–DEA system. However, their study was limited to the highly polar solvents ACN and ethanol and was not extended to nonpolar solvents. Further, their study failed to characterize the absorption spectrum of DEA^+ even in ACN. Most recently, after the present work was largely completed, Borisevich et al.[20] reported observation of the (BP^-DEA^+) ion pair in hexane.

One important distinction between DABCO and DEA is that DEA forms a ground-state complex with BP in polar, nonpolar, and alcoholic solvents. Steady-state absorption and phosphorescence studies have proved the existence of the ground-state complex in these solvents. Hoshino et al.[17,18] reported the phosphorescence spectrum of the BP–DEA complex which was red-shifted from the phosphorescence of BP. In addition, spectral broadening of the $S_0 \rightarrow S_1$ absorption band of BP in the presence of DEA in polar and nonpolar solvents has been reported.[17,21]

Previous studies of the BP/TEA system with nano- and picosecond laser photolysis by a number of groups[11,16,20,22-24] did not demonstrate the presence of a polar transient in any solvent. Schaefer and Peters[13] did report observing a CT complex with an absorption band having λ_{max} at 610 nm in ACN. They used a laser system with 10-ps time resolution and 100 mM BP and 3 M TEA and monitored the formation of the complex which decayed with a half-life of 15 ps. Later, Ohtani et al.,[23] using 20-ps laser pulses, could not observe any evidence for a CT complex or an ion pair in the photoreduction of BP by TEA in ACN and in neat TEA. Further, Borisevich and co-workers[20,24] studied this photoreaction in diethyl ether using 6-ps pulses and came to the conclusion that the photoreduction of BP by TEA proceeds by direct hydrogen abstraction. Obviously, the nanosecond flash photolysis experiments at room temperature were unable to provide any evidence for the presence of an ion pair as a transient in the reaction. Ohtani et al.[23] examined the photoreduction of BP in neat TEA in the temperature range 300–77 K and could not detect any transient absorption ascribable to the CT complex. Hence, the identification of the transient and elucidation of the mechanism of the photoreduction of BP by TEA is a challenging task which requires a careful examination of the intermediates involved in this reaction. The present study provides some further insight into this mechanism by probing the reaction in polar, nonpolar, and alcoholic solvents with nano- and picosecond laser photolysis.

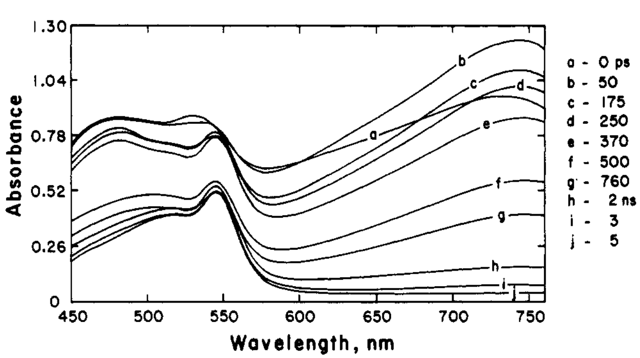

Figure 1. Transient absorption spectra for BP (10 nM) and DEA (0.75 M) in benzene at different time delays after the laser pulse.

Experimental Section

The laser photolysis experiments (both nano- and picosecond) were as described in the previous work.[9] The picosecond experiments had approximately 30 ps rise time. Most solvents were used as received. Benzene was dried by passage through alumina and was stored over molecular sieves. Previous experience[9] showed that fresh acetonitrile from Burdick and Jackson (99.995%) was dry enough that further drying did not change the results significantly. The *N,N*-diethylaniline (from Mallinckrodt) was distilled under vacuum and stored under argon. Triethylamine from Aldrich Chemical Co. was distilled. The various benzophenones were all from Aldrich and were recrystallized from aqueous ethanol. All experiments used 10 mM of benzophenone unless otherwise indicated. The temperature was 22 °C if not specified.

Results and Discussion

A. *N,N*-Diethylaniline. 1. Nonpolar Solvents. Most nanosecond experiments with DEA were carried out with 355-nm pulses from a Nd:YAG laser since DEA has a small absorption at 337.1 nm (N_2 laser) and it was desired to avoid complications from excited DEA which is known to photoionize on excitation. When a solution of BP and DEA (20 mM) in benzene was excited at 355 nm, ^3BP was formed and rapidly quenched by DEA forming neutral ketyl radicals. Spectra were taken at various times after the pulse but no evidence for the intermediacy of the (BP^-DEA^+) ion pair (particularly absorption by BP^- at longer wavelengths in the range 600–700 nm) could be observed in benzene. A similar result was obtained for cyclohexane solutions. Addition of small amounts of methanol (1%) to benzene solutions did not appear to have any effect on either the stability of the ion pair or the yield of ketyl radical. This behavior contrasts with that found with BP–DABCO[9] where the lifetime of the ion pair (BP^-DABCO^+) was doubled and the ketyl radical yield greatly reduced on addition of 1% methanol. The ion pair (if it is present) is not stabilized sufficiently by small amounts of alcohol to make it observable.

When the BP–DEA system was studied by picosecond laser photolysis using 0.75 M DEA in benzene, the characteristic absorption band for BP^- with a peak at 735 nm and another for DEA^+ with λ_{max} at 470 nm were observed as shown in Figure 1. (The absorption at 550 nm as in the spectra at 2 or 5 ns is from the neutral ketyl radical.) The absorption maximum for BP^- (735 nm) is slightly red-shifted from 725 nm as observed for BP–

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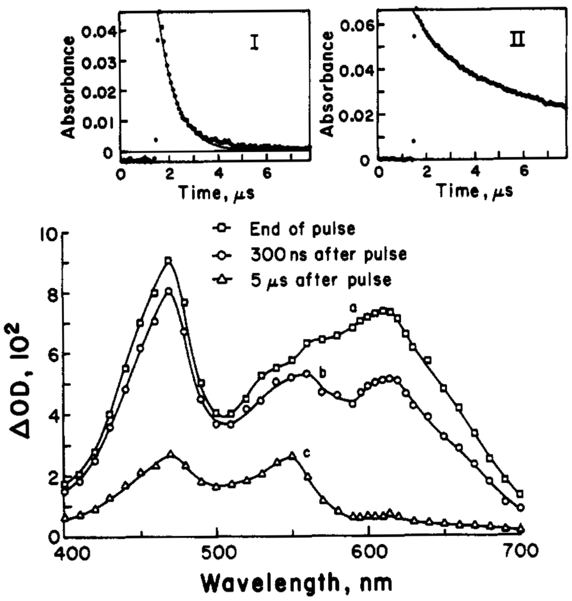

Figure 2. Transient absorption spectra of a methanol solution of BP (10 mM) and DEA (20 mM) at different time intervals after laser photolysis: (a) end of pulse, (b) 300 ns, (c) 5 μs. Inset I shows a kinetic trace taken at 615 nm and inset II shows the trace at 470 nm.

DABCO. This shift is not unexpected as the peak position can be affected by the size of the cation counter radical. As can be seen in the figure, the absorbance of BP^- is negligible after 5 ns as the ion has already decayed to ketyl radicals. The corresponding lifetime is 875 ps. This series of spectra clearly indicates that the (BP^-DEA^+) ion pair is an intermediate in the photoreduction of BP by DEA in benzene. When this experiment was repeated in cyclohexane (with 0.75 M DEA), a similar series of spectra indicating the presence of the ion pair was obtained. The lifetime was about 300 ps. Just as with benzene, the absorbance for BP^- at 5 ns after photolysis is negligible. This short lifetime of the ion pair, due to fast proton transfer in the ion pair to form ketyl radical, makes the observation of the ion pair in nonpolar solvents impossible in the nanosecond experiment. Unlike with DABCO, the absorption spectrum of the aromatic amine radical cation (DEA^+) was clearly evident (450–500 nm).

2. Methanol. The photoreduction of BP by DEA, when carried out in methanol, clearly indicates the presence of the (BP^-DEA^+) ion pair as the transient in the reaction. Figure 2 shows the transient absorption spectra in the nanosecond experiment at different time intervals. The two characteristic bands for BP^- and DEA^+ are clearly seen (Figure 2 a). The absorption maximum for BP^- is at 615 nm as a result of H bonding and that for DEA^+ is at 470 nm. The spectra at 300 ns and 5 μs after the photolysis (Figure 2, b and c) indicate that BP^- decays faster than DEA^+. The unequal decay rates suggest that BP^- decays by a channel other than the proton transfer from DEA^+. Insets I and II are kinetic traces for the decay of BP^- and DEA^+, respectively, monitored at 615 and 470 nm (their respective absorption maxima). BP^- decays with first-order kinetics with a lifetime of 775 ns, and a small residual absorbance at longer time implies that a small portion of the ion pairs separate into individual ions whereas the decay of DEA^+ follows clean second-order kinetics. Hence, BP^- must decay with the assistance of methanol, the only compound present other than DEA and DEA^+. The only possible mode of decay is the transfer of a proton from methanol to BP^- and this proton should come from the hydroxylic group. To test this assumption, the reaction was conducted in methanol and deuterated methanol (CH_3OD). Figure 3, a and b, shows the decay of BP^- and DEA^+, respectively, in methanol and Figure 3, c and d, shows results for deuterated methanol. On comparing the decay of BP^- in both solvents (Figure 3a,c), it is evident that the decay is slower in the deuterated solvent. The ratio of the two decay rate constants k_H/k_D is 1.84. This isotope effect definitely confirms that the proton transfer takes place from the solvent. The second-order rate constants for the decay of DEA^+ in the two solvents do not differ much (Figure 3b,d).

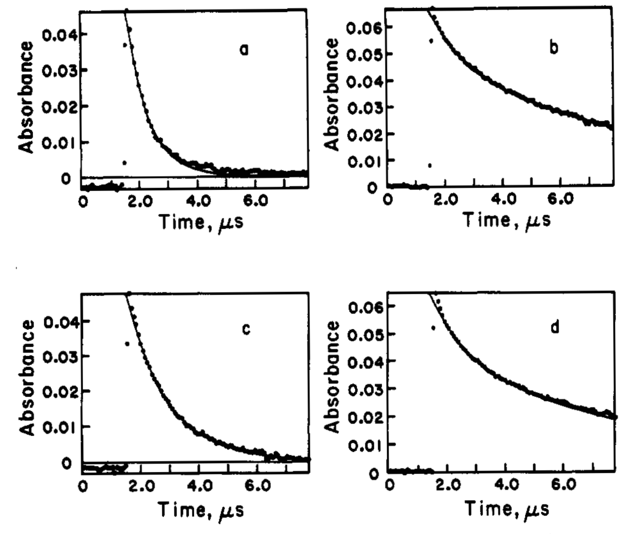

Figure 3. Top: Kinetic traces for the decay of the (BP^- DEA^+) ion pair in methanol monitored at (a) 615 nm and (b) 470 nm. Bottom: Kinetic traces for the decay of the ion pair in deuterated methanol monitored at (c) 615 nm and (d) 470 nm.

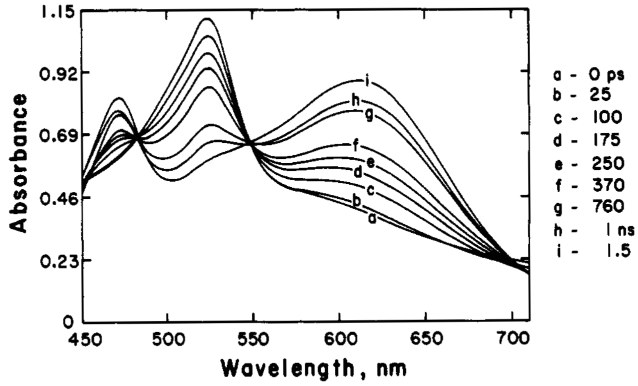

Figure 4. Transient absorption spectra for BP (10 mM) and DEA (0.1 M) in methanol at different time delays after the laser pulse.

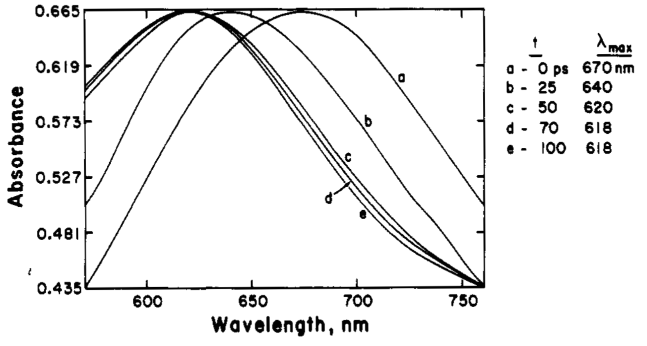

Figure 5. Time-dependent spectral shift for BP (10 mM) and DEA (1 M) in methanol over the initial 100 ps.

Figure 4 shows the transient absorption spectra obtained at different time delays in the picosecond experiment for methanol solution. As can be seen from the figure, the absorption bands with maxima at 470 nm (DEA^+) and at 618 nm (BP^-) grow as the peak at 525 nm corresponding to ^3BP decays. Two nice isosbestic points are evident in this system showing that no changes in the spectra occur as the BP triplet is replaced by the ion pair. Thus with this concentration of DEA (0.1 M), no shift with time in the peak position for BP^- was observed. However, when a higher concentration of DEA (1.0 M) was used, a blue shift from 670 to 618 nm was observed for 70 ps after photolysis. This shift is similar to that noticed in the BP–DABCO system. Figure 5 illustrates the time-dependent spectral shift observed in methanol.

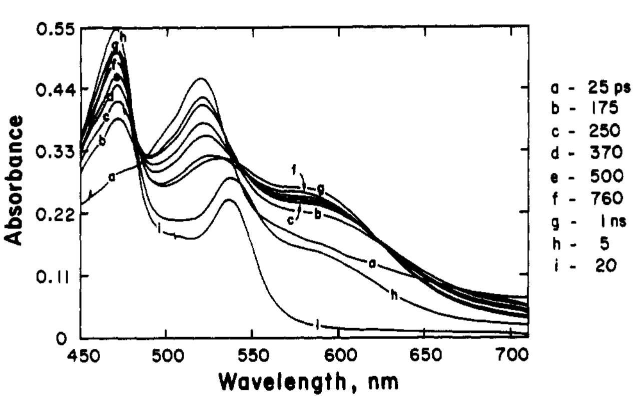

Figure 6. Transient absorption spectra for BP (10 mM) and DEA (0.2 M) in trifluoroethanol at different time delays after the laser pulse.

Because of fast electron transfer from DEA to BP triplet in methanol (compared to DABCO) the absorption bands are clear at early times and the peaks are distinct. This blue shift is ascribed to the formation of H bonds between BP$^-$ and methanol molecules as discussed for the BP–DABCO system.[9] This result agrees with the observations reported by Simon and Peters.[14,15]

To test the conclusions derived from the nanosecond results in methanol that proton transfer takes place from alcohol to BP$^-$, the photoreduction was studied in trifluoroethanol (TFE) with both nano- and picosecond laser photolysis. TFE is quite acidic and is a good proton donor so that, if a proton is transferred from the alcohol, a very fast decay of BP$^-$ is expected. In the nanosecond experiment, the presence of BP$^-$ was evident by the appearance of a small absorption band with a peak around 600 nm at the end of the pulse. However, the absorption band of DEA$^+$ was intense even after the complete decay of BP$^-$ and it decayed with second-order kinetics. A series of transient absorption spectra obtained at different time delays in the picosecond experiment is shown in Figure 6. As the band for BP triplet decays, that for DEA$^+$ is seen growing with peak at 470 nm. The absorption band for BP$^-$ appears as a shoulder with a peak around 590 nm but it decays quickly. As seen from Figure 6i, the decay of BP$^-$ is complete at 20 ns after photolysis and only the absorption bands for DEA$^+$ and ketyl radical remain. This fast decay of BP$^-$ without a corresponding decay of DEA$^+$ confirms the result obtained in methanol that a proton is transferred from the alcohol molecule. The behavior of BP–DEA in TFE is entirely different from that of BP–DABCO in TFE where the electron transfer from DABCO to BP triplet is so inhibited by H bonding to DABCO that the quenching rate constant is 3 orders of magnitude less than the expected value. In the present system the interaction between BP and DEA is so great that the electron transfer is very fast despite the strong H-bonding ability of TFE.

3. *tert*-Butyl Alcohol. The nature of the (BP$^-$DEA$^+$) ion pair in *tert*-butyl alcohol is strikingly different from that observed in methanol and TFE. As discussed earlier, BP$^-$ receives a proton from either methanol or TFE to form ketyl radical. This leaves DEA$^+$ to decay more slowly by bimolecular reaction. In the nanosecond experiment, the ion pair was not observed in *tert*-butyl alcohol and the only species noticed after the decay of BP triplet was ketyl radical. The absorption bands for both BP$^-$ and DEA$^+$ were absent. However, in the picosecond experiment, a weak band with λ_{max} around 470 nm and another band with a maximum around 660 nm were seen. Unlike the behavior in methanol and TFE, the bands of BP$^-$ and DEA$^+$ seem to decay simultaneously. The similar decay rates for BP$^-$ and DEA$^+$ reveal that proton transfer from alcohol to BP$^-$ does not occur in *tert*-butyl alcohol. Since this alcohol is not acidic in nature, donation of a proton to BP$^-$ is energetically not favorable. These results point to the fact that the nature of the ion pair in *tert*-butyl alcohol is different from that in methanol and TFE. Since a proton is transferred from DEA$^+$ to BP$^-$ the ion pair must be a contact ion pair (CIP). The weak H bonding between BP$^-$ and the alcohol does not prevent the proton transfer from DEA$^+$. Anomalous behavior in *tert*-butyl alcohol was also seen for BP–DABCO where the ion pair has a short lifetime and the ketyl radical yield was essentially zero. This solvent alone among those with $\epsilon > 10$, stabilized the CIP for BP–DABCO. In the BP–DEA system, the DEA$^+$ readily donates a proton to form the ketyl radical.

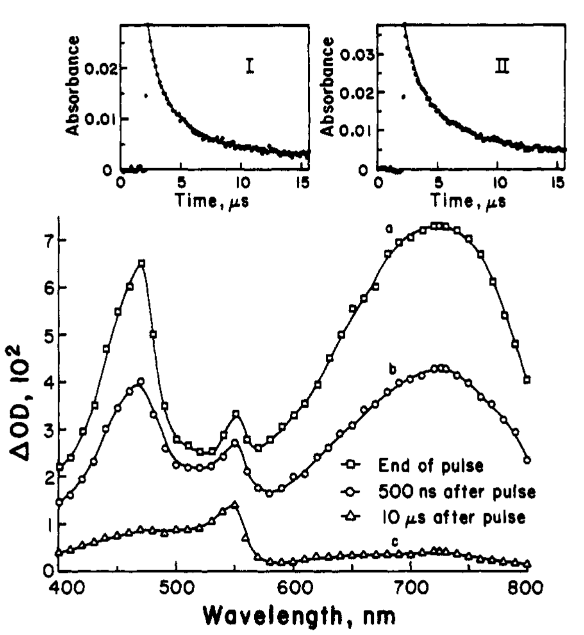

Figure 7. Transient absorption spectra of an acetonitrile solution of BP (10 mM) and DEA (20 mM) at different time intervals after laser photolysis: (a) end of pulse, (b) 500 ns, (c) 10 µs. Inset I shows a kinetic trace taken at 690 nm and inset II shows the trace at 470 nm.

4. 2-Propanol. In 2-propanol, the ion pair decays by two channels. The absorption at 620 nm decays with 110-ns lifetime to a plateau. This residual absorbance at longer time indicates that the ion pair dissociates into separate ions. Considerable absorption also remains at 550 nm so ketyl radical is also formed during the decay of the ion pair. Since 2-propanol is not very acidic, the proton added to BP$^-$ probably comes from DEA$^+$.

5. Acetonitrile. The photoreduction of BP by DEA was also carried out in acetonitrile (ACN), an aprotic polar solvent. Figure 7 shows the transient absorption spectra obtained at different (nanosecond) time intervals in ACN. Three distinct absorption bands from DEA$^+$ (λ_{max} at 470 nm), ketyl radical (λ_{max} at 550 nm), and BP$^-$ (725 nm) are seen. The latter absorption maximum differs from the value of 660 nm reported by Arimitsu et al.[16] With the decay of DEA$^+$ and BP$^-$ there is no corresponding proportionate growth in the absorbance of the ketyl radical. Inset I shows the decay of BP$^-$ monitored at 690 nm. The transient decays with clean second-order kinetics. Inset II describes the decay of DEA$^+$, monitored at 470 nm, which also follows second-order kinetics. The latter decay is slightly slower than the former because of some overlap with the spectrum of the ketyl radical. This second-order kinetics implies that the transient exists as separate radical ions in ACN. Dissociation of the ion pair into separated ions in ACN is energetically favorable. Formation of some ketyl radical is observed as the ions decay. (The central peak from ketyl radical in Figure 7 is larger at longer times.) The bimolecular reaction of the ions must, in part, lead to neutral radicals.

There are several striking differences between the nature of the transient in the BP–DABCO and BP–DEA systems in ACN. First and foremost is the dissociation of the ion pair into separate radical ions in the BP–DEA system as evidenced by the second-order decay of BP$^-$ and DEA$^+$. This behavior contrasts with the first-order decay observed in the BP–DABCO system. The rate of the decay of BP$^-$ and DEA$^+$ approaches the diffusion-controlled rate. The second difference is the formation of ketyl radical in the BP–DEA system. This observation also differs from the result of Arimitsu and co-workers[16] who mentioned the absence of ketyl radical in ACN in their nanosecond study and confirms the observation by Miyagawa et al.[19] of ketyl radical by ESR in the same system. However, in the BP–DABCO system the ion pair decayed

TABLE I: **Quenching Rate Constants for BP–DEA in Different Solvents**

solvent	dielectric const[a]	ΔG(CIP),[b] eV	ΔG(SSIP),[b] eV	k_q, M^{-1} s^{-1}	rel ketyl radical yield[c]
cyclohexane	2.02	−0.19	+0.60	3.3×10^9	0.87
benzene	2.28	−0.21	+0.45	6.3×10^9	0.85
o-dichlorobenzene	9.93	−0.36	−0.43	3.3×10^9	0.86
acetone	20.70	−0.39	−0.56	9.4×10^9	0.67
methanol	32.70	−0.40	−0.61	7.9×10^9	0.50
acetonitrile	37.50	−0.40	−0.62	11.3×10^9	0.20

[a] From: Marcus, Y. *Ion Solvation*; Wiley: Chichester, U.K., 1985. [b] Calculated from Weller's equation (Weller A. *Z. Phys. Chem.* **1982**, *133*, 93). The value 0.75 eV was used for μ^2/ρ^3. [c] Based on the ratio of the absorbance of the ketyl radical to the initial absorbance by ^{3}BP measured at 545 nm (uncorrected for differences in absorption coefficients).

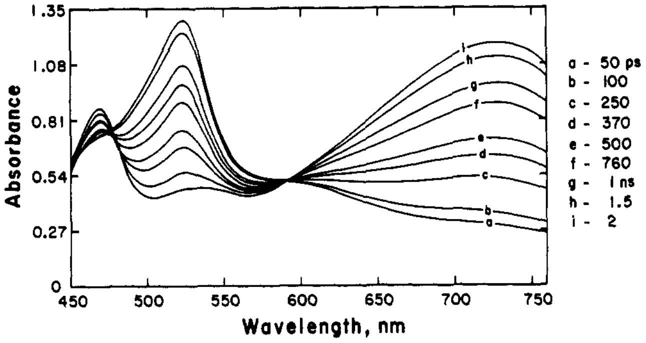

Figure 8. Transient absorption spectra for BP (10 mM) and DEA (50 mM) in acetonitrile at different time delays after the laser pulse.

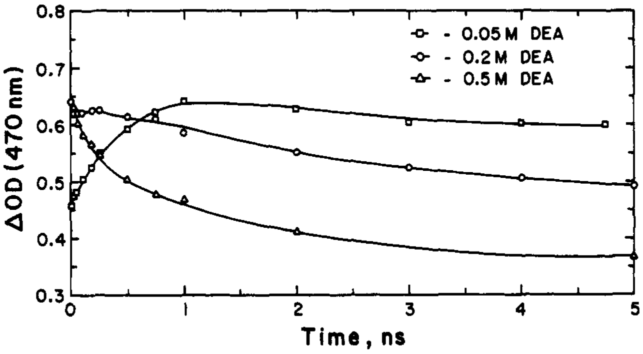

Figure 9. Decay traces at short times for DEA$^+$ at 470 nm for three different concentrations of DEA.

mostly by back-electron transfer without forming any ketyl radical. The low ketyl radical yield in polar solvents in the BP–DEA system when compared to nonpolar solvents indicates that the main mode of decay of the transient in polar solvents is back-electron transfer and only a small fraction decays by proton transfer. The absorption maximum of BP$^-$ is slightly red-shifted from 720 nm, the value observed with BP–DABCO, to 725 nm in the present system. Unlike the very long lifetime of the (BP$^-$DABCO$^+$) ion pair in moderately polar dichloromethane (ϵ = 8.93), the lifetime of the transient in the case of BP–DEA is very short as in other nonpolar solvents and the ketyl radical yield is also high. The ability of DEA$^+$ to transfer a proton readily reduces the lifetime of the ion pair in these solvents.

In the picosecond experiment, the decay of BP triplet and the formation of BP$^-$ and DEA$^+$ were directly observed in ACN as in methanol. Figure 8 shows the series of spectra obtained at different time delays in ACN. With this small concentration of DEA (50 mM), two isosbestic points are noticed and, correspondingly, no spectral shift is observed. The absorption maximum of BP$^-$ in ACN is 727 nm which coincides with the value observed in the nanosecond experiment. When the concentration of DEA was increased to 1.0 M, a red shift from 702 nm at 0 ps to 727 nm at 50 ps was observed for the spectral maximum of BP$^-$. This spectral shift is similar to that observed in the BP–DABCO system and denotes the transformation of CIP to solvent-separated ion pair (SSIP) or free ions. (No shift was seen in Figure 8 because the time scale for the shift is shorter than that for the bimolecular quenching of ^{3}BP.) This observation contradicts the report by Simon and Peters[14] who proposed a conversion of SSIP to CIP even at 5.0 M DEA. A simple calculation shows that with 5 M DEA in ACN (that means 80% DEA and 20% ACN by volume) the amount of solvent would be 3.8 M only. Since the quencher molecules outnumber solvent molecules, the suggestion that a SSIP is formed by long-range electron transfer is problematic. Again, the long ion lifetime and second-order decay kinetics rule out the existence of a CIP.

An interesting feature observed in ACN with higher amounts of DEA is the faster decay of DEA$^+$ than BP$^-$ over the first 3 ns. With 50 mM DEA, both DEA$^+$ and BP$^-$ grow for 2 ns as ^{3}BP decays as in Figure 8. When the concentration of DEA was increased to 0.2 M, BP$^-$ was seen to grow for 760 ps but DEA$^+$ was found to remain constant. This observation implies that the rates of formation and decay of DEA$^+$ are equal ($k = 4.5 \times 10^9$ s^{-1}). With 0.5 M DEA, BP$^-$ grew for 175 ps but DEA$^+$ actually decayed starting at 0 ps. This unusual behavior of DEA$^+$ is illustrated in Figure 9. It appears that higher concentrations of DEA can quench DEA$^+$. This quenching cannot be the result of electron transfer from DEA to DEA$^+$. Formation of an amide dimer cation radical (DEA DEA$^+$) is possible. Such a species has been observed in the quenching of *trans*-stilbene by amines.[25]

6. Quenching Rate Constants and Ketyl Radical Yield. The quenching rate constants were determined from plots of the pseudo-first-order rate constants for decay of ^{3}BP as a function of DEA concentration. These rate constants are listed in Table I for six solvents. As expected, the reactions are close to diffusion-controlled. Similar values were observed in the picosecond experiments. An important difference between the quenching behavior of DEA and DABCO[9] is the 6-fold increase in the k_q value in methanol. (The k_q value for the BP–DABCO system in methanol is 1.2×10^9 M^{-1} s^{-1} and that for BP–DEA system is 7.9×10^9 M^{-1} s^{-1}.) Since both DABCO and DEA have similar oxidation potentials (E_{ox} = 0.69 V), the quenching rate constants are expected to be similar. As discussed in the earlier paper,[9] H bonding between DABCO and methanol slows down the electron transfer from DABCO to BP triplet. In DEA, the electron transfer is fast since a ground-state complex is formed between BP and DEA. The ΔG values (shown in Table I) indicate that the formation of the CIP is energetically favorable in benzene and cyclohexane and this was confirmed in the picosecond study. The relative ketyl radical yields in different solvents are given in the last column of the table. The yield decreases with increasing polarity of the solvent. In less polar solvents, the transient is a CIP which favors the transfer of a proton from DEA$^+$ to BP$^-$, thus giving the higher ketyl radical yield. The ease of proton transfer from DEA$^+$ contrasts with the behavior of DABCO$^+$ where the proton transfer is believed to be hindered by stereoelectronic effects.[9,26] In methanol and TFE, the proton is transferred from the alcohols, thereby increasing the ketyl radical yield. In ACN and acetone, the ion pair separates into individual ions and the ketyl radical is formed by bimolecular combination. In benzene, the presence of small amounts of an alcohol has no

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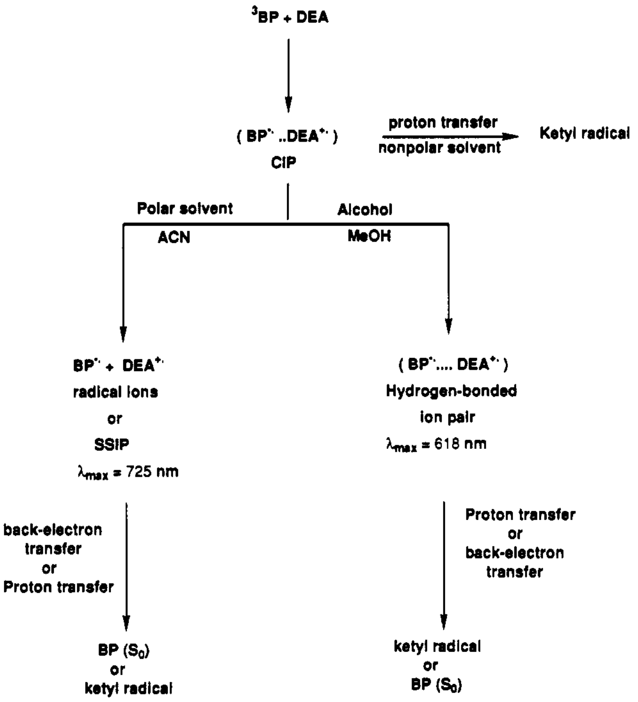
SCHEME I



effect on the ketyl radical yield.

7. **Mechanism for DEA.** The reaction mechanism proposed to account for the results obtained with BP/DEA is shown in Scheme I. The initial step in all solvents studied is an electron transfer from DEA to BP triplet to form a CIP (BP^-DEA^+). In highly polar solvents, the CIP dissociates into separate ions and in alcohols BP^- is H-bonded to the alcohol. In nonpolar solvents like benzene, proton transfer in the CIP from DEA^+ to BP^- takes place and the ketyl radical is formed within a few nanoseconds. In alcohols which are capable of donating a proton, this proton is transferred from the alcohol molecule to BP^- to yield the ketyl radical. In TFE, proton transfer from TFE to BP^- is so swift that BP^- could not be observed clearly in the nanosecond experiment. In *tert*-butyl alcohol, which is a weak H-bonding alcohol and poor proton donor, the transient remains as a CIP and proton transfer takes place from DEA^+ to BP^- to form the ketyl radical. In acetonitrile, the decay of the radical ion follows second-order kinetics and the main mode of decay is back electron transfer from BP^- to DEA^+. A small fraction in this case undergoes proton transfer from DEA^+ to BP^-. The ketyl radical yield depends on the polarity of the solvent and it decreases with increasing polarity. A small amount of alcohol in benzene does not affect either the nature of the transient or the yield of ketyl radical. The high value of k_q in methanol shows that interaction between BP and DEA is greater than the H bonding between DEA and methanol. With the decay of BP triplet, the growth of BP^- and the aromatic DEA^+ was clearly observed.

B. Triethylamine. 1. Spectra and Kinetics. When a solution of BP was photolyzed with nanosecond laser pulses in the presence of TEA (20 mM) in polar and nonpolar solvents, ^{3}BP was quenched to form ketyl radicals. The transient absorption spectra obtained in benzene, methanol, and ACN did not have any distinct band for the ion pair, which is the intermediate in the photoreduction of BP by DABCO and DEA. Therefore, the nanosecond experiments failed to provide any direct evidence for the presence of the ion pair in the photoreduction of BP by TEA. However, a few pieces of indirect evidence exist for the intermediacy of an ion pair. The high values of the quenching rate constants (k_q) for the BP–TEA system in different solvents indicate that direct hydrogen abstraction may not be the initial step in the photoreduction. The values found here are listed in Table II and are above 10^9 M^{-1} s^{-1} in all solvents studied except methanol. Similar values have been reported for some of the solvents[4,12] and the reduction in value from benzene to methanol has been noted.[4] The values are at least 2 orders of magnitude larger than the rate constants for hydrogen abstraction. For example, the reported rate constant for hydrogen abstraction by ^{3}BP is 9×10^6 M^{-1} s^{-1} in benzhydrol[4] and 1.8×10^6 M^{-1} s^{-1} in 2-propanol.[4] Both alcohols are excellent hydrogen donors. Arguments for electron rather than hydrogen transfer based on the high reactivity of amines have been made before.[2,3,7]

TABLE II: Quenching Rate Constants for BP–TEA in Different Solvents

solvent	dielectric const	ΔG(CIP),[a] eV	k_q, M^{-1} s^{-1}
cyclohexane	2.02	−0.09	2.8×10^9
benzene	2.28	−0.11	2.9×10^9
o-dichlorobenzene	9.93	−0.26	1.4×10^9
acetone	20.70	−0.29	3.8×10^9
methanol	32.70	−0.30	0.8×10^9
acetonitrile	37.50	−0.30	3.2×10^9

[a] Calculated as in Table I.

The dielectric constants of the solvents listed in Table II range widely from 2.02 to 37.50. These rate constants are somewhat lower than those determined for the BP–DABCO and BP–DEA systems. Lower values for TEA are expected because the ΔG values for electron transfer in these solvents are decreased by about 0.1 eV (E_{ox} = 0.79 V for TEA and 0.69 V for DABCO and DEA). However, electron transfer from TEA to BP triplet is expected to be exothermic in all the six solvents studied even with a reduced ΔG.

To determine the effect of changing the energetics, experiments were carried out with substituted benzophenones like 4,4′-difluoro-BP, 4-chloro-BP, and 4,4′-dichloro-BP for which the anion is stabilized by the presence of electron-withdrawing groups. None of these compounds gave a detectable absorption band for BP^- in ACN. Since the ΔG values for these substituted BP's are more exothermic, the k_q values are also higher than that for the unsubstituted BP. (Only approximate values from one concentration of amine were determined.) As direct hydrogen transfer involves bond breaking and bond making, it is expected to be slower in these cases whereas electron transfer followed by proton transfer can be faster. Therefore, quenching by TEA must involve a faster process than direct hydrogen abstraction.

The response of the quenching rate constant to changes in solvent is different for DEA and TEA (see Tables I and II). The rate constants for DEA increase with polarity, with that in acetonitrile twice that in benzene, while for TEA there is little variation from benzene to acetonitrile except for a sizable decrease for methanol. For DABCO, where electron transfer is clearly evident, there is an increase in rate from benzene to acetonitrile (as for DEA) but there is also a big decrease for methanol (as with TEA), implying that H bonding slows down the electron transfer. Thus the solvent effects do not seem to be a strong indicator of the nature of the reaction. The parallel with DABCO is strong enough that the intermediate in the reaction of ^{3}BP with TEA can be an ion pair.

The relative ketyl radical yield with DEA is high in all solvents studied. Small amounts of alcohol did not have any effect on the ketyl radical yield, although it slightly decreased the quenching rate. A flexible geometry and absence of conjugative stabilization in TEA^+ lead to fast proton transfer to form the ketyl radical. The photoreduction was also carried out at lower temperatures in the range 22 to −40 °C to see if the proton transfer could be delayed. However, no absorption spectrum for the ion pair was observed and this clearly shows that the proton transfer is ultrafast.

The slow rate of quenching in methanol suggested that the experiment also should be done in TFE, a more acidic alcohol. If the primary process is an electron transfer, then in TFE the rate would be drastically reduced due to a strong H-bonding interaction between TEA and TFE (as with DABCO). As expected, the quenching rate constant was reduced by about 2 orders of magnitude to 1.8×10^7 M^{-1} s^{-1}. The availability of an electron in the nonbonding orbital of nitrogen in TEA is reduced by the overlap of that orbital with the H atom of TFE. Because of

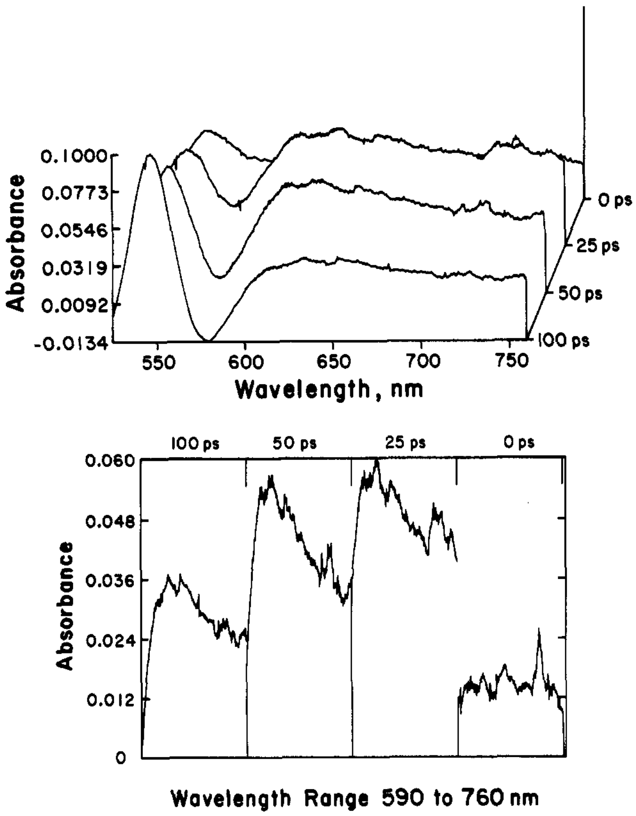


Figure 10. Top: Difference spectra obtained as discussed in the text for BP (10 mM) and TEA (1 M) in acetonitrile at different time delays. Bottom: Spectra which show the absorption band for BP$^-$ only.

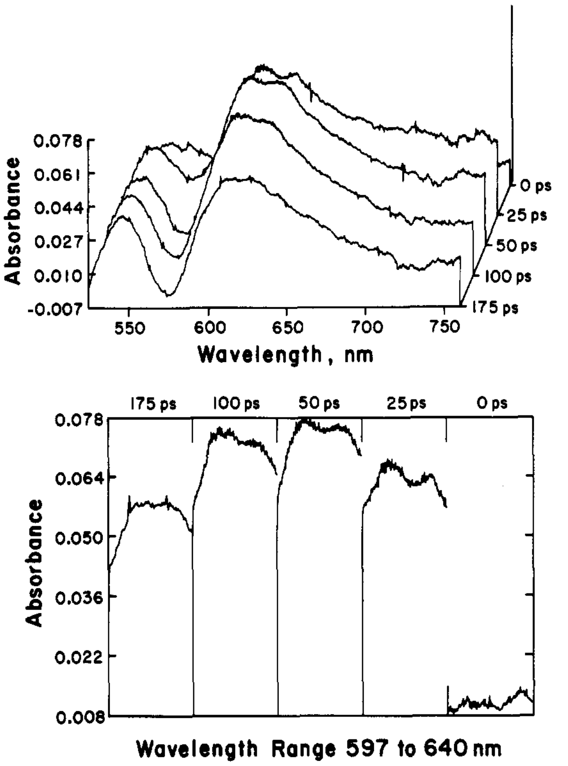
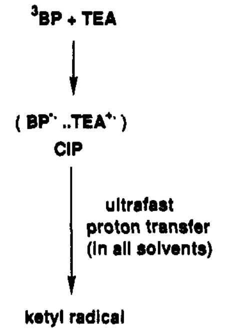


Figure 11. Top: Difference spectra obtained for BP (10 mM) and TEA (1 M) in methanol at different time delays. Bottom: Spectra of BP$^-$ only.

TABLE III: Rate Constants for the Decay of BP Triplet and the Growth of BP$^-$ in Acetonitrile with Three Amines

amine	rate const for BP triplet decay, s^{-1}	rate constant for BP$^-$ growth, s^{-1}
DABCO	1.0×10^9	1.0×10^9
DEA	1.2×10^9	1.2×10^9
TEA	4.0×10^8	

SCHEME II



inefficient electron transfer, the ketyl radical yield is also reduced substantially. This slowing of the primary process in TFE strongly proves that electron transfer is the initial step in the photoreduction.

Other indirect evidence for the electron transfer in the photoreduction comes from the study of the photoreduction of 4-phenyl-BP by TEA. This aromatic ketone is known to have a π–π^* T_1 electronic state. Therefore, unlike BP which has an n–π^* T_1 state, 4-PhBP does not abstract hydrogen from hydrogen-donating solvents like methanol, 2-propanol, and cyclohexane. This reaction is so sluggish with 4-PhBP that the triplet has a lifetime on the order of microseconds in these solvents and the ketyl radical yield is also negligible. However, in the presence of TEA, the triplet is readily quenched and a significant amount of ketyl radical is also formed. In methanol and ACN, small absorption bands from 4-PhBP$^-$ were observed at longer wavelengths. This observation clearly proves that an ion pair (4-PhBP$^-$TEA$^+$) is produced in the photoreduction of 4-PhBP by TEA. With DABCO and DEA, 4-PhBP behaves like BP but with longer lifetimes of the ion pairs. Thus it can be confidently said that (BP$^-$TEA$^+$) is the transient in the photoreduction of BP by TEA. It must be concluded that proton transfer in the ion pair is faster than can be resolved in this experiment.

When the photoreduction was studied in the picosecond experiment, no absorption band for BP$^-$ could directly be observed during the decay of BP triplet. Figures 10 and 11 show, at the bottom, spectra for ACN and methanol. Though this result was disappointing initially, an attempt was made to subtract the contribution of ^{3}BP to the spectrum. Difference spectra were obtained by subtracting the known spectrum of BP triplet which was normalized to the maximum absorbance at the peak of the short-time spectrum. Such spectra obtained with ACN and methanol are shown at the top in Figure 10 and 11, respectively. In ACN, the remaining absorption band has a maximum at 633 nm and the band grows for 25 ps and then decays rapidly. In methanol, as expected, the peak is blue-shifted to 612 nm and the band grows for 50 ps and then decays. Although these decompositions are not unique, there is clearly excess absorption above about 600 nm which is of the shape expected for the (BP$^-$TEA$^+$) ion pair. An ion pair thus seems to be an intermediate in the photoreduction of BP by TEA. Its lifetime is estimated to be <20 ps. The ion pair must be a CIP in both solvents since subsequent proton transfer takes place at an ultrafast rate. The rate constants for the decay of ^{3}BP in the presence of 50 mM of the three amines in ACN are given in Table III. The values for these rate constants are similar for the three amines and suggest that the primary process for the quenching must be similar. Since DABCO and DEA involve electron transfer as the initial step and an ion pair is formed, TEA most probably also reacts by electron transfer and an ion pair is formed. This situation is shown in Scheme II.

2. Deprotonation of Ketyl Radicals and Secondary Reduction. One important observation made during the study of the photoreduction of BP by TEA is the formation of BP$^-$ at longer times in methanol. The formation of BP$^-$ in this system may be from the deprotonation of the initially formed ketyl radicals or the secondary reduction of ground-state BP by the neutral α-aminoalkyl radical (methyl(diethylamino)methyl radical) formed from

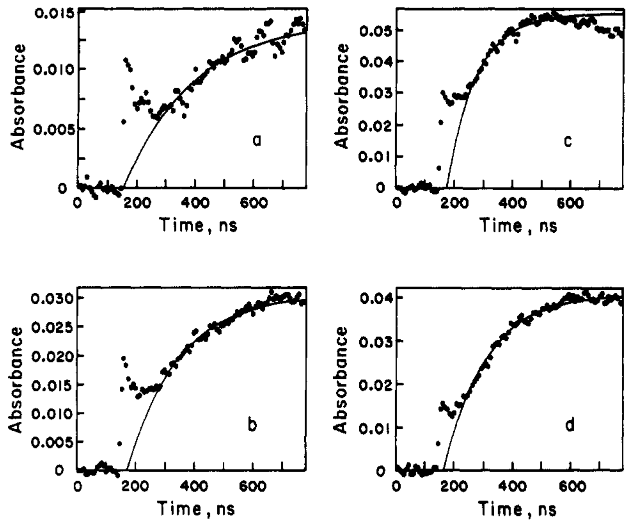


Figure 12. Kinetic traces at 620 nm for the growth of BP^- in methanol with (a) BP (5 mM) and TEA (20 mM), (b) BP (10 mM) and TEA (20 mM), (c) BP (25 mM) and TEA (20 mM), and (d) BP (10 mM) and TEA (50 mM).

TEA by the net transfer of an H atom to ^3BP. Since TEA itself is basic, deprotonation of the ketyl radical is expected. However, such a reaction occurs extensively in methanol alone. To see which mechanism operates in the generation of BP^-, the photoreduction was conducted with a fixed concentration of BP (10 mM) and varying amounts of TEA (5–50 mM) and also another series of experiments with a constant amount of TEA (20 mM) and different concentrations of BP (5–25 mM). Figure 12a–c shows the growth of BP^- monitored at 620 nm with 20 mM of TEA and 5, 10, and 25 mM concentration of BP in methanol. The first-order rate constants for the growth are 4.1×10^6, 5.6×10^6, and 9.7×10^6 s^{-1}, respectively. The increase of rate constant with increasing BP concentration indicates that secondary reduction of ground-state BP as suggested by Cohen and Baumgarten[1] occurs. This observation establishes the rate constant of reaction at about 3×10^8 M^{-1} s^{-1}.

$$(C_2H_5)_2N\text{–}\dot{C}H\text{–}CH_3 + (C_6H_5)_2C{=}O \rightarrow (C_2H_5)_2N\text{—}CH{=}CH_2 + (C_6H_5)_2\dot{C}\text{–}OH$$

Figure 12, b and d, shows the growth of BP^- with 10 mM BP and 20 and 50 mM, respectively, of TEA. The corresponding rate constants for the growth of BP^- are 5.6×10^6 and 7.0×10^6 s^{-1}. Although the increase is not proportional to the concentration of TEA, there is a definite increase in the rate constant with increasing TEA. This result implies that the deprotonation of ketyl radicals also occurs.

$$(C_6H_5)_2\dot{C}\text{–}OH + N(C_2H_5)_3 \rightarrow (C_6H_5)_2\dot{C}\text{–}O^- + HN^+(C_2H_5)_3$$

TEA differs from DABCO and DEA in the deprotonation process and the secondary reduction of ground-state BP. Similar reactions have been observed by Scaiano[27] in the quenching of benzil by TEA in wet ACN and of BP by TEA in alkaline water–ACN mixed solvent by Das and co-workers.[28] Hence, this process is unique to TEA.

Conclusion

The photoreduction of ^3BP by DEA is initiated by electron transfer to form an ion pair. Direct observation of the contact ion pair so formed has been possible in picosecond experiments in the nonpolar solvents benzene and cyclohexane. Rapid transfer of a proton within the ion pair leads to formation of neutral radicals. In polar solvents, the ion pair dissociates into free ions which decay by back electron transfer or proton transfer. A rapid spectral shift to the red is seen in ACN as the CIP dissociates. Proton transfer from the solvent to BP^- occurs in acidic alcohols such as methanol and trifluoroethanol. The photoreduction of ^3BP by TEA is accompanied by a very rapid formation of neutral radicals on the picosecond time scale. However, if difference spectra to remove the contribution from ^3BP are constructed, then it is possible to detect adsorption by BP^- in an ion pair. This reaction thus appears to proceed by electron transfer followed by a very rapid proton transfer.

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