Although part of the reason for examining pyramidal methylenes was to look for lower-energy S–T intersections, most of the intersections are actually higher than the intersection in Figure 10. In fact, many segments of the S–T intersection lie above the 1.5 kcal contour on the triplet surface (Figure 12) and have unfavorable Boltzmann factors. Other than this, the qualitative features of these surfaces are identical with those of Figures 8 and 9. Figure 11 shows that after isc occurs cyclopropane can be formed without activation, starting from any point on the S–T intersection. Figure 11 also shows that the intersection is 1 kcal below (0′,270′), a good approximation to the calculated[2a] geometry of the transition state for geometrical isomerization of cyclopropane. Since the transition state for propylene formation is known to be higher still, we presume that H transfer requires activation after the isc step. The basic conclusions of the previous section are therefore unchanged by pyramidalizing the terminal methylenes.

Summary and Conclusion

In this paper we have explored the relation between the S–T splitting and the geometry of trimethylene. In particular, we have identified some of the interactions responsible for S–T intersections. In many cases the S–T splitting can be understood as a competition between the orbital energy difference, favoring a singlet ground state, and the exchange integral between the terminal AOs, favoring a triplet ground state.

Examination of the singlet and triplet surfaces generated by twisting the terminal methylenes, both with and without pyramidalization, yielded several interesting conclusions. On the triplet surface single methylene rotation is faster than synchronous double rotation. The opposite is true on the singlet surface. Of the two possible double rotation pathways, singlet trimethylene prefers conrotation. Finally, the lack of propylene in the products from triplet-derived trimethylenes is ascribed to two features of the potential surfaces: (1) the S–T intersections accessible to the triplet are below the transition state for propylene formation on the singlet surface, and (2) the formation of propylene on the singlet surface is entropically unfavorable. Decay of triplet trimethylene thus appears to be an example of a photochemical reaction whose product distribution can be understood substantially on the basis of the potential surfaces alone. Explicit consideration of the dynamics or even of the S–T crossing probabilities does not seem to be needed.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE 7901138) for partial support of this research, and David Mullally for stimulating conversations.

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Picosecond Dynamics of Ion Pairs: The Effect of Hydrogen Bonding on Ion-Pair Intermediates

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Abstract: The dynamics of the interconversion between the solvent-separated ion pair and the contact ion-pair intermediates in the photoreduction of benzophenone by *N,N*-diethylaniline and diazabicyclo[2.2.2]octane have been elucidated by use of picosecond absorption spectroscopy. The dynamics were studied in ethanol/acetonitrile mixtures to ascertain the role of the solvent in the interconversion process.

The concept of the ion pair was introduced by Bjerrum[1] to account for the behavior of ionophores in solvents of low dielectric. Since then, intermediates in organic reactions have been frequently described as ion pairs.[2] Though a continuum in distribution of ion pairs may exist, their structures are usually formulated in terms of the solvent-separated ion pair and the contact ion pair.[3,4] Spectral changes resulting from the interconversion between the solvent-separated ion pair and the contact ion pair have been extensively studied.[5] However, our present understanding of ion pairs is restricted to equilibrium distributions among the various ion-pair forms; there have been no experimental or theoretical treatments of the dynamics of interconversion between ion-pair structures in solution. In this paper, we employ picosecond absorption spectroscopy to elucidate the effect of the solvent on ion-pair dynamics.

Ion-pair intermediates have been invoked for the photoreduction of aromatic ketones by amines.[6,7] We have recently reported that the photoreduction of benzophenone by *N,N*-dimethylaniline, *N,N*-diethylaniline, and diazabicyclo[2.2.2]octane[8] proceeds by electron transfer, resulting in the formation of the solvent-separated ion pair comprised of the radical cation of the amine and the radical anion of benzophenone. Subsequent to solvent-separated ion-pair formation, a contact ion pair is formed betwen these species. The half-lives of contact ion-pair formation from the solvent-separated ion pair for the photoreduction by *N,N*-diethylaniline and diazabicyclo[2.2.2]octane are 200 ± 50 ps and 100 ± 25 ps, respectively. Our studies in the photoreduction process were performed in acetonitrile, a solvent that is both a weak electron-pair donor and a weak electron-pair acceptor.[9] In acetonitrile, the equilibrium distribution between the ion-pair forms lies in favor of the contact ion pair. In this paper, we will dem-

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[1] Bjerrum, N. *K. Dan. Vidensk. Selsk.* **1926**, *7*, No. 9.

[2] Szwarc, M. "Carbanions, Living Polymers and Electron Transfer Processes"; Interscience: New York, 1968.

[3] Winstein, S.; Robinson, G. C. *J. Am. Chem. Soc.* **1958**, *80*, 169.

[4] Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.

[5] (a) Szwarc, M. *Acc. Chem. Res.* **1969**, *2*, 87. (b) Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1966**, *88*, 307.

[6] (a) Wagner, P. J. *Top. Ann. Chem.* **1976**, *66*, 1. (b) Wagner, P. J.; Leavitt, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 3669. (c) Wagner, P. J.; Lam, H. M. H. *Ibid.* **1980**, *102*, 4167.

[7] (a) Cohen, S. G.; Parola, A. H.; Parsons, G. H. *Chem. Rev.* **1973**, *73*, 141. (b) Parola, A. H.; Rosa, A. W.; Cohen, S. G. *J. Am. Chems. Soc.* **1975**, *97*, 6202. (c) Inbar, S.; Linschilz, H.; Cohen, S. G. *Ibid.* **1980**, *102*, 1419.

[8] Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1981**, *103*, 6403.

[9] Gutman, V. "The Donor-Acceptor Approach to Molecular Interactions"; Plenum Press: New York, 1978. For acetonitrile the donor and acceptor numbers are 14.1 kcal/mol and 18.9, respectively.

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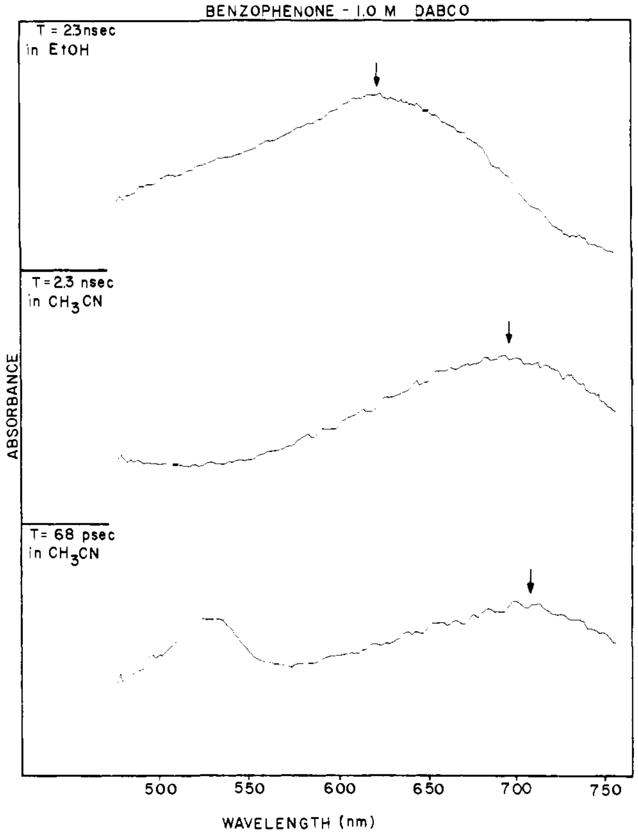

Figure 1. Transient absorption spectra for the photoreduction of 0.25 M benzophenone by 1.0 M Dabco. Bottom: solvent = acetonitrile, 68 ps following photolysis. Middle: solvent = acetonitrile, 2.3 ns following photolysis. Top: solvent = ethanol, 2.3 ns following photolysis.

onstrate that with the appropriate choice of solvent or solvent mixtures, the equilibrium distribution of the ion-pair intermediates can be shifted by stabilzing the solvent-separated ion pair relative to the contact ion pair. The dynamic role of the solvent in the interconversion of ion-pair forms can be elucidated by using solvent mixtures. In this paper, we will examine the role of the hydrogen bond in the dynamics of the interconversion of the ion-pair intermediates in the photoreduction of benzophenone by *N*,*N*-diethylaniline and diazabicyclo[2.2.2]octane in ethanol[10] and ethanol/acetonitrile mixtures.

Experimental Section

The picosecond absorption spectrometer consists of a 10-Hz Nd^{3+}–YAG laser (Quantel International, YG-400) with 25-ps time resolution. The detector is an OMA II Vidicon (PAR-1215-1216-1205I) interfaced to a 200-mm spectrograph (JY-UFS-200). The experiment utilizes a 1-mJ light pulse at 355 nm for photolysis. The transient absorption spectra are monitored by a picosecond continuum extending from 450 to 800 nm which can be delayed up to 10 ns following photolysis.

The picosecond absorption spectra were deconvoluted with a Commodore Pet Computer, Series 2000. The deconvolution routine is designed to minimize the variance between the calculated and observed spectrum.[8]

Fourier transform infrared spectra were recorded with a Nicolet Model 7199 FT-IR spectrometer. NaCl solution cells with a 0.1-cm path length were used. The benzophenone and amine concentrations used were identical with those employed in the time-resolved studies. The number of data points accumulated resulted in a resolution of ±0.5 cm^{-1} in band position.

Freshly distilled *N*,*N*-diethylaniline (Aldrich) and *N*,*N*-dimethylaniline (Aldrich) were used. Benzophenone (MCB) was recrystallized from ethanol. Diazabicyclo[2.2.2]octane (Aldrich) was purified by sublimation. Absolute ethanol (U.S. Industrial Chem. Co.), acetonitrile (Mallinckrodt), and trifluoroethanol (Tridom-Fluka) were used without further purification.

Table I. Rate of Electron Transfer for Dabco in Ethanol/Acetonitrile Mixtures

[EtOH]	rate, 10^{10} mol^{-1} s^{-1}
1.0 M	1.24 ± 0.12
5.0 M	0.63 ± 0.06
neat	0.23 ± 0.02

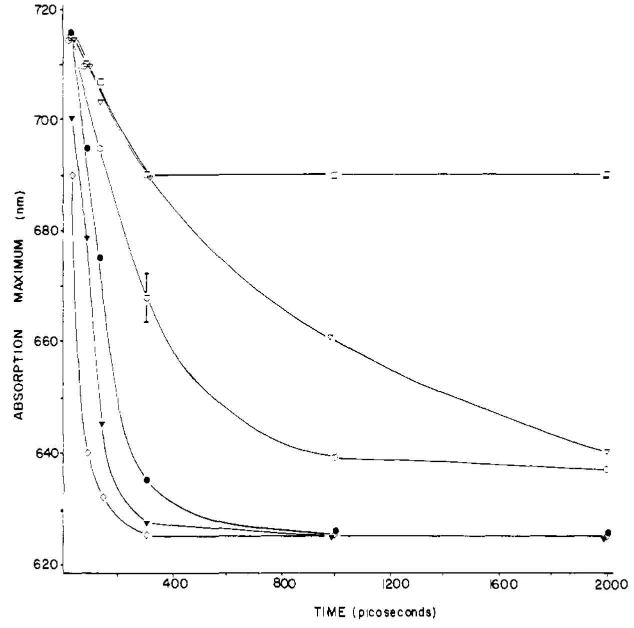

Figure 2. Absorption maximum of the radical anion absorption as a function of time for the photoreduction of 0.25 M benzophenone by 1.0 M DEA in ethanol/acetonitrile mixtures. (□) Neat acetonitrile; (▽) 1.0 M ethanol in acetonitrile; (○) 2.0 M ethanol in acetonitrile; (●) 5.0 M ethanol in acetonitrile;[a] (▼) 10.0 M ethanol in acetonitrile;[a] (◇) neat ethanol. [a] *For* $t > 800$ ps, absorption bands are broader to the red relative to neat ethanol.

Results

Transient absorption spectra for the photoreduction of benzophenone by 1.0 M diazabicyclo[2.2.2]octane (Dabco) are shown in Figure 1. Photolysis of 0.25 M benzophenone and 1.0 M Dabco in acetonitrile results in the decay of triplet benzophenone (λ_{max} = 525 nm) concomitant with the transfer of an electron to form the radical anion of benzophenone (λ_{max} = 715 nm). The absorption maximum of the radical anion subsequently shifts from 715 to 690 nm with a half-life of 100 ± 25 ps. We have previously assigned this shift to contact ion-pair formation.[8] In neat ethanol, the absorption maximum at 2 ns after photolysis for the radical anion (λ_{max} = 625 nm) is blue shifted from that observed for the contact ion pair. This band does not shift between 300 ps and 2 ns. This band is assigned to the hydrogen-bonded species on the basis of previous studies by Porter and Wilkinson.[11] The rates of electron transfer for the photoreduction of benzophenone by 1.0 M Dabco in ethanol/acetonitrile mixtures are give in Table I. We find that the rate of electron transfer decreases with increasing ethanol concentration.

We have also examined the dynamics of the ionic intermediates in the photoreduction of benzophenone by 1.0 M diethylaniline (DEA). In acetonitrile, the electron transfer has a rate constant of $k_{et} = 4.2 \times 10^{10}$ mol^{-1} s^{-1}.[8] No change in rate is observed either in neat ethanol or in ethanol/acetonitrile mixtures. In neat ethanol, the absorption maximum blue shifts from 690 to 625 nm with a half-life of 150 ± 50 ps. As we will discuss, this shift represents the formation of a solvent-separated ion pair from an initially formed contact ion pair. However, this explanation requires that the contact ion pair be formed immediately following the rapid

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[10] Donor and acceptor numbers for ethanol are 41.5 kcal/mol and 37.1, respectively.

[11] Porter, G.; Wilkinson, F. *Trans. Faraday Soc.* **1961**, *57*, 1686. For solvation in 1-propanol: Marignier, J.; Hickel, B. *Chem. Phys. Lett.* **1982**, *86*, 95.

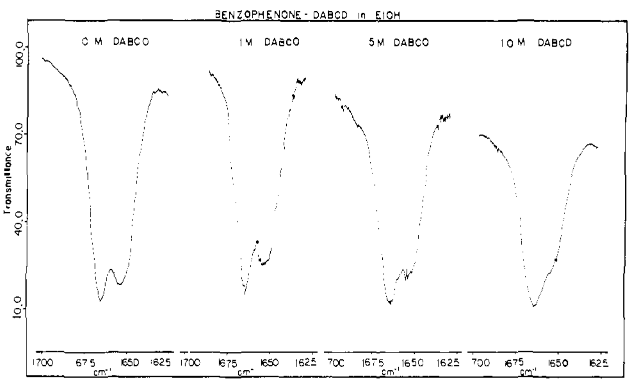

Figure 3. Fourier transfer infrared spectra of the carbonyl stretch of benzophenone in ethanol with varying Dabco concentration.

electron transfer. To understand these observations, we examined the dynamics of the ionic intermediates in ethanol/acetonitrile mixtures. In mixed solvents, the dynamics of the blue shift of the radical anion absorption is found to vary with changes in ethanol concentration. The absorption maximum of the radical anion is plotted as a function of time in Figure 2. Similar behavior is observed for the photoreduction by 1.0 M Dabco in solvent mixtures containing up to 5.0 M ethanol. At higher alcohol concentrations, the rate of electron transfer from Dabco is too slow to allow us to study the shifting of the radical anion absorption.

We have investigated the temperature dependence of the rate of shift of the radical anion absorption for the photoreduction of benzophenone by 1.0 M DEA in a solvent of 5.0 M ethanol in acetonitrile. The transient absorption spectra of the radical anion at 2 and 53 °C are identical up to 2 ns following photolysis, at which time the location of this band has reached a stationary value (Figure 2). The dynamics of the ionic intermediates in the above reaction were also examined in a solvent of 5.0 M trifluoroethanol in acetonitrile. Again, no change in the rate of shift for the absorption maximum of the radical anion was observed. At 2 ns following photolysis, the absorption maximum for the radical anion in the trifluoroethanol solvent mixture is found at 585 nm, a shift of 40 nm from that observed in the 5.0 M ethanol/acetonitrile mixture.

To investigate the possibility of ground-state interactions between the ketone and the amine, we have examined the effect of amine and solvent on the carbonyl stretching frequency of benzophenone. The data are presented in Table II and Figure 3. For benzophenone in acetonitrile, the carbonyl stretching frequency is found at 1660.7 ± 0.5 cm^{-1}. The stretching frequency is found to be insensitive to the presence of either 1.0 M DEA or 1.0 M DMA. Two carbonyl populations for benzophenone in neat ethanol are observed.[12] The stretching frequencies of these populations are 1664.3 ± 0.5 cm^{-1} and 1653.7 ± 0.5 cm^{-1}. Addition of Dabco is found to deplete the population at lower frequency (Figure 3). The stretching frequencies of both populations decrease in the presence of either 1.0 M DEA or 1.0 M DMA. These red shifts suggest the formation of a ground-state complex between benzophenone and DMA or DEA in neat ethanol. Two distinct carbonyl populations for benzophenone in ethanol/acetonitrile mixtures are not observed in mixtures of ethanol concentrations less than 10.0 M.

Discussion

The structure of the ion-pair intermediate initially formed in the photoreduction of benzophenone by amines is dependent on the spatial orientation of the ketone and the amine at the time of the electron transfer. For the photoreduction of benzophenone by 1.0 M amine (amine = DEA, DMA, Dabco) in acetonitrile, we have recently reported[8] that the electron transfer results in the formation of the solvent-separated ion pair. This structure rapidly collapses to form the contact ion pair. In the present study, we focus on the dynamics of the interconversion between these ion-pair forms in ethanol and ethanol/acetonitrile mixtures.

Table II. Stretching Frequencies of the Benzophenone Carbonyl

amine	solvent	C=O stretch, ±0.5 cm^{-1}
	acetonitrile	1660.7
	1.0 M EtOH/acetonitrile	1660.7
	2.0 M EtOH/acetonitrile	1660.7
	10.0 M EtOH/acetonitrile	1661.1, shoulder to lower energy
	EtOH	1664.3
		1653.7
0.1 M Dabco	EtOH	1664.2
		1653.5, same intensities as no amine
0.5 M Dabco	EtOH	1663.9
		1654.4, loss in intensity
1.0 M Dabco	EtOH	1663.5, shoulder to lower energy
1.0 M DMA	acetonitrile	1660.5
1.0 M DMA	EtOH	1663.2
		1651.8
1.0 M DEA	acetonitrile	1660.7
1.0 M DEA	1.0 M EtOH/acetonitrile	1660.7
1.0 M DEA	EtOH	1663.9
		1652.7

A. Electron Transfer: The Effect of Hydrogen Bonding. For the photoreduction of benzophenone by 1.0 M Dabco in ethanol/acetonitrile mixtures, we observe a decrease in the rate of electron transfer with increasing ethanol concentration. This cannot be explained in terms of a decrease in dielectric as we have previously found[8] that the rate of electron transfer in this system is only weakly dependent on medium dielectric. In addition, for the photoreduction of benzophenone by 1.0 M DEA in ethanol/acetonitrile mixtures, we do not observe a change in the electron-transfer rate with an increase in ethanol concentration.

We propose that the decrease in the electron-transfer rate for photoreduction of benzophenone by Dabco in ethanol/acetonitrile mixtures results from the formation of a hydrogen bond to the ground-state amine. This would increase the activation energy for the electron-transfer process, as the hydrogen bond must be broken prior to transfer. DEA is a much weaker base than Dabco and would not be expected to form as strong a hydrogen bond with the solvent. The insensitivity of the rate of electron transfer to changes in medium dielectric for the photoreduction of benzophenone by 1.0 M DEA in ethanol/acetonitrile mixtures can be explained in terms of the Marcus theory for electron transfer.[13] Marcus theory predicts that the rate of transfer will be sensitive to changes in medium dielectric only when the overall free energy change of the transfer process is less than 10 kcal/mol. For the photoreduction by 1.0 M DEA we calculate the electron-transfer process to be exothermic by at least 20 kcal/mol.

The conclusion that Dabco is hydrogen bonded in ethanol/acetonitrile mixtures is consistent with infrared studies of the effect of Dabco concentration on the carbonyl stretching frequency. In neat ethanol, two carbonyl populations are observed. Addition of Dabco results in the depletion of the low-frequency population. No such depletion is observed upon addition of either DEA or DMA. The depleted population is assigned to the hydrogen-bonded ketone. The addition of amine results in structural reorientation in solution resulting in hydrogen bonds to the amine, depleting the population of hydrogen-bonded ketone. Since no population depletion is observed upon addition of DEA or DMA, we conclude that the equilibrium between the hydrogen-bonded amine and the non-hydrogen-bonded amine lies strongly in favor of the non-hydrogen-bonded species in these systems.

From the observed electron-transfer rates for the photoreduction of benzophenone by 1.0 M Dabco in ethanol/acetonitrile mixtures, the equilibrium constant for the hydrogen-bonded amine/non-hydrogen-bonded amine equilibrium can be obtained. The

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[12] Bellamy, L. J.; Williams, R. L. *Trans. Faraday Soc.* **1959**, *55*, 14.

[13] Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 748.

equilibrium constant is expressed as

$$K_1 = \frac{[\text{Dabco}][\text{EtOH}]}{[\text{Dabco}\cdot\text{EtOH}]} \qquad (1)$$

The total concentration of Dabco in solution is 1.0 M so we can rewrite the above expression as

$$[\text{Dabco}] = \frac{K_1}{K_1 + [\text{EtOH}]} \qquad (2)$$

The rate of electron transfer is dependent on the concentration of free Dabco in solution. Thus the observed rate constant is expressed as

$$k_{\text{obsd}} = k_{\text{et}}[\text{Dabco}] \qquad (3)$$

where k_{et} is the rate constant in neat acetonitrile ($k_{\text{et}} = 1.7 \times 10^{10}$ mol^{-1} s^{-1}). From the above equations, the following expression for the hydrogen-bonded equilibrium constant is derived:

$$K_1 = \frac{k_{\text{obsd}}[\text{EtOH}]}{k_{\text{et}} - k_{\text{obsd}}} \qquad (4)$$

With the rate constants presented in Table I, the calculated equilibrium constant is $K_1 = 2.67 \pm 0.15$. This value indicates that a significant percentage of the amine molecules are hydrogen bonded, supporting the conclusion that hydrogen bonding to the amine is responsible for the decrease in the observed rate of electron transfer in ethanol/acetonitrile mixtures.

B. Ground-State Complexes between the Ketone and the Amine. For the photoreduction of benzophenone by 1.0 M DEA in neat ethanol, the absorption maximum of the radical anion of benzophenone first appears at 690 nm. In acetonitrile, the radical anion absorbance at 690 nm has been previously assigned to the contact ion pair comprised of the radical cation of the amine and the radical anion of the ketone.[8] Apparently, in ethanol the contact ion pair is formed immediately after the electron-transfer process. For this to occur, the amine and the ketone must be cosolvated in the ground state. Since amines are strong electron-pair donors and ketones are good electron-pair acceptors, we expect that cosolvation would result in the formation of an electron-pair donor/electron-pair acceptor (EPD/EPA) complex. The formation of a complex of this type would result in the transfer of electron density into the antibonding orbital of the carbonyl moiety of the ketone. The reduction in bonding would be manifested by a decrease in the carbonyl stretching frequency. In order to study the presence of ground-state complexes of this type, we have examined the carbonyl stretching frequency of benzophenone as a function of solvent and amine.

Upon examination of Table II, the location of the carbonyl stretching frequency of benzophenone in acetonitrile is found to be independent of the presence of amine, indicating that a ground-state complex is not formed in this solvent. This conclusion is supported by the observation that the solvent-separated ion pair is the initially formed ion-pair intermediate subsequent to the electron transfer. However, the two carbonyl populations observed for benzophenone in ethanol were found to undergo a red shift in the presence of either 1.0 M DEA or 1.0 M DMA. Consequently a ground-state complex between benzophenone and DMA (DEA) exists in ethanol solution. Subsequent to electron transfer, therefore, the two charged species exist as a contact ion pair. This contact ion pair corresponds to the radical anion absorption at 690 nm initially observed for the photoreduction of benzophenone by 1.0 M DEA in neat ethanol.

There is no evidence for ground-state complex formation between Dabco and benzophenone in acetonitrile, ethanol, or ethanol/acetonitrile mixtures. The degree of ground-state charge transfer will depend on the oxidation potential of the amine. Dabco has a higher ionization potential than DEA (0.89 eV for Dabco, 0.70 eV for DEA) and thus is less likely to form a ground-state complex.

C. Ion-Pair Dynamics. For the photoreduction of benzophenone by 1.0 M DEA in neat ethanol, the absorption maximum of the radical anion shifts from 690 to 625 nm with a half-life of 150 ± 50 ps. We have shown that the absorption at 690 nm corresponds to the contact ion pair while the absorption at 625 nm corresponds to the hydrogen-bonded anion.[11] This assignment is supported by the observation that more pronounced blue shifting (from 690 to 585 nm) occurs when the photoreduction of benzophenone by DEA is performed in trifluoroethanol. The larger blue shift in trifluoroethanol results from the stronger hydrogen bond relative to that formed between the radical anion and ethanol. A time-dependent blue shift in the absorption maximum of the radical anion was also observed when the photoreduction was studied in ethanol/acetonitrile mixtures. This blue shift represents the formation of the hydrogen-bonded anion from the contact ion pair formed in the photoreduction process. Upon solvent-separated ion-pair formation, the solvent must reorient to solvate both ionic species. On the basis of the relative donor and acceptor numbers, one would conclude that ethanol would be superior to acetonitrile at solvating both the benzophenone radical anion and the amine cation.

In order to obtain a rate constant for the formation of hydrogen-bonded anion from the contact ion pair, we assumed that the absorption at 625 nm corresponded to an entirely hydrogen-bonded population. By use of the spectrum of the 625-nm absorption and an absorption spectrum of the contact ion-pair radical anion ($\lambda_{\text{max}} = 690$ nm), the transient absorption spectra were deconvoluted to give the relative concentration of non-hydrogen-bonded anion as a function of time following photolysis.

The kinetics for the conversion of the contact ion pair into the solvent-separated ion pair can be represented by the general kinetic scheme $n\text{EtOH} + \text{CIP} \rightarrow \text{SSIP}$. The order of the reaction in ethanol concentration, n, can be determined from the analysis of the dependence of the kinetics of SSIP formation on the ethanol concentration. The integral equation expressing the contact ion pair concentration as a function of time can be written as

$$kt = \int \frac{1}{([\text{EtOH})_0 - nx)^n([\text{CIP}]_0 - x)} \mathrm{d}x \qquad (5)$$

where $[\text{EtOH}]_0$ and $[\text{CIP}]_0$ are the initial concentrations of ethanol and contact ion pair and x is the concentration of solvent-separated ion pair at time t. This integral can be simplified by noting that in our experiments $[\text{CIP}]_0 \approx 10^{-3}$ M. Since the concentration of solvent-separated ion pair is also of this order of magnitude, $[\text{EtOH}]_0 - nx \approx [\text{EtOH}]_0$ for all reasonable values of n. The integral is then easily solved, and applying the boundary condition that there is no solvent-separated ion pair at $t = 0$ ($t = 0$, $x = 0$), we arrive at the expression:

$$kt = \frac{1}{[\text{EtOH}]_0{}^n} \ln \frac{[\text{CIP}]_0}{[\text{CIP}]_0 - x} \qquad (6)$$

Thus for 1.0 M ethanol, the rate constant, k, is independent of the order of ethanol and represents the rate constant for the dynamics of ion-pair separation.

In the ensuing kinetic analysis, we have assumed that only monomer ethanol is involved in the formation of the solvent-separated ion pair. For a mixture of 1.0 M ethanol in acetonitrile, this assumption is valid, for greater than 90% of the ethanol molecules exist in the monomer form.[14] However, in neat ethanol, higher aggregates of ethanol as well as monomer ethanol are found. The concentration of monomer ethanol in neat ethanol has been determined by NMR spectroscopy to be 3.8 M.[15] Consequently, if we are to assume that only monomer ethanol is important in the dynamics of the separation of the contact ion pair, the concentration of ethanol used in our kinetic analysis of solvent-separated ion-pair formation in neat ethanol must be 3.8 M. If there is no change in the order of the reaction on going from 1.0 M ethanol to neat ethanol, then the order in ethanol, n, can be determined within the above approximation. From eq 6, the rate

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[14] The amount of monomer ethanol was determined by FT IR spectroscopy.

[15] Sakai, Y.; Sadaoka, Y.; Yamamoto, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3575.

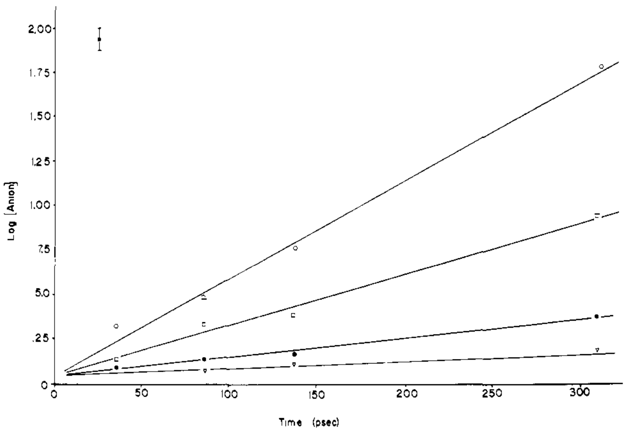


Figure 4. Rate plot for the formation of the solvent-separated ion pair from the contact ion pair for the photoreduction of 0.25 M benzophenone by 1.0 M DEA. (▽) 1.0 M Ethanol in acetonitrile; (●) 2.0 M ethanol in acetonitrile; (□) 5.0 M ethanol in acetonitrile; (○) 10.0 M ethanol in acetonitrile.

Table III. Observed Rates for the Formation of the Solvent-Separated Ion Pair

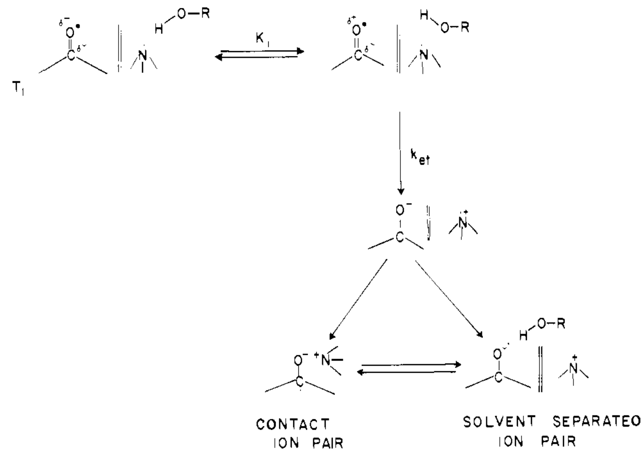
[EtOH]	$k_{\mathrm{obsd}}{}^{a}$
1.0 M	4.9×10^8
2.0 M	1.1×10^9
5.0 M	2.8×10^9
10.0 M	5.5×10^9
neat	6.7×10^9

[a] Rates ±10% accuracy.

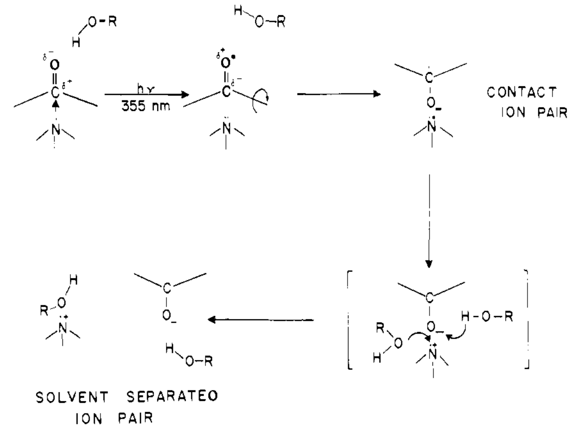
of solvent-separated ion-pair formation can be found by plotting ln [CIP] vs. time. Such a plot is presented in Figure 4, with the calculated rates given in Table III. The rate constant, k, for the ion-pair separation must be the same for both 1.0 M ethanol/acetonitrile and neat ethanol. The only integer value that fulfills this condition is $n = 2$, where the calculated rate constants for the ion-pair separation in 1.0 M ethanol/acetonitrile and neat ethanol are $k = 4.8 \times 10^8$ mol^{-2} s^{-1} and $k = 4.6 \times 10^8$ mol^{-2} s^{-1}, respectively. A second-order process in ethanol is not unexpected, as both the anion and the cation must be solvated in the transition state.[16]

Further insight into the mechanism of contact ion-pair separation can be obtained from the temperature dependence studies. Examining the ion-pair dynamics in 5.0 M ethanol/acetonitrile solution, the rate of solvent-separated ion-pair formation at 2 and 53 °C is the same. The insensitivity of the rate to the change in temperature indicates that the separation process has no enthalpy of activation barrier ($\Delta H = 0 \pm 0.1$ kcal/mol). This observation is further supported by the study of the ion-pair dynamics in trifluoroethanol/acetonitrile mixtures. The rates of solvent-separated ion-pair formation in 5.0 M ethanol/acetonitrile and 5.0 M trifluoroethanol/acetonitrile are identical. Since the enthalpy for hydrogen-bond formation by trifluoroethanol is greater than that of ethanol,[17] the dynamics of the rate-limiting step do not involve the breaking of a hydrogen bond. From the temperature dependence studies, we conclude that the formation of the solvent-separated ion pair from the contact ion pair is controlled by the entropy of activation. With the rate constant $k = 4.8 \times 10^8$ mol^{-2} s^{-1}, the entropy of activation from activated complex theory is −20.4 eu.[18]

Scheme I



Scheme II



Since the absorption spectra are constant from 2 to 10 ns after photolysis, the equilibrium constants for the contact ion-pair and the solvent-separated ion-pair equilibrium in 1.0 M ethanol/acetonitrile mixtures can be obtained. The equilibrium constants (K_{eq} = [SSIP]/[CIP][EtOH]^n) for these ion-pair intermediates formed in the photoreduction of benzophenone by 1.0 M Dabco and 1.0 M DEA in 1.0 M ethanol/acetonitrile are 0.49 ± 0.1 and 0.82 ± 0.1, respectively. Thus, the equilibrium between the ion-pair forms differs for the two amines studied. The decrease in solvent-separated ion-pair formation observed for the photoreduction of benzophenone by Dabco can be attributed to the increased charge localization in the Dabco radical cation relative to the DEA radical cation. This increased charge localization will result in a stronger Coulombic attraction and, hence, a stronger contact ion pair.

Conclusion

In summary, we have studied the dynamics of the ion-pair intermediates in the photoreduction of benzophenone by 1.0 M Dabco and 1.0 M DEA in neat ethanol and ethanol/acetonitrile mixtures. For the photoreduction of benzophenone by Dabco (Scheme I), the rate of electron transfer decreases with increasing alcohol concentration. This results from the formation of hydrogen-bonded amine ($K_1 = 2.7$). Electron transfer, k_{et}, results in solvent-separated ion-pair formation. The constituents of the solvent-separated ion pair either diffuse together to form a contact ion pair or become resolvated and remain in the solvent-separated form. For solvent mixtures containing up to 5.0 M ethanol, the contact ion pair is formed prior to hydrogen bonding. For mixtures containing greater than 5.0 M ethanol, the rate of electron transfer is too slow to allow us to elucidate the ion-pair dynamics.

For photoreduction of benzophenone by 1.0 M DEA in neat ethanol (Scheme II), the electron transfer results in contact ion-pair formation. This is supported by infrared data indicating a ground-state complex between the ketone and the amine.

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(16) On the basis of the relative donor and acceptor numbers,[9,10] ethanol would be superior to acetonitrile at solvating both the amine radical cation and the benzophenone radical anion.

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Subsequent to contact ion pair formation, the solvent-separated ion pair is formed. For ethanol/acetonitrile mixtures ([EtOH] < 10 M), the electron transfer results in the formation of the solvent-separated ion pair. We observe contact ion-pair formation prior to hydrogen bonding in these systems. The formation of the solvent-separated ion pair from the contact ion pair is found to be controlled by an entropy of activation. Furthermore, the kinetics are found to be termolecular, second order in ethanol monomer concentration.

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Registry No. Ph_2CO, 119-61-9; $PhNEt_2$, 91-66-7; Dabco, 280-57-9; Ph_2Co radical anion, 16592-08-8; Dabco radical cation, 54159-20-5; $PhNEt_2$ radical cation, 63224-14-6.

Anion-Exchange Properties of Ammonium Salts Immobilized on Silica Gel

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Abstract: The synthesis and aqueous anion-exchange properties are reported for ammonium salts immobilized on silica gel by alkyl chains of various lengths. Since the exchange properties of these systems are strongly affected by the polar inorganic matrix and its hydrophobic covering, these new anion-exchange supports have properties that are quite different from those of known polystyrene resins.

Benzyltrimethylammonium salts immobilized on insoluble polystyrene-type matrices are widely used as ion-exchange resins,[1] chromatographic supports,[2] and insoluble solid reagents.[3] When the methyl groups bound to the positive heteroatom are replaced with bulkier, lipophilic *n*-butyl groups, these systems can act as phase-transfer catalysts and activate the reagent anion in the organic phase, although they remain insoluble.[4] Tri-*n*-butyl onium salts have also been anchored to silica gel[5,6] and alumina[6] through alkyl chains, which on the one hand make the support more lipophilic, and on the other, when used as phase-transfer catalysts, facilitate anion exchange between the immiscible organic and aqueous phases. Silica gels with hydrophobic covering have been known for some time, and their application in the areas of chromatography and HPLC has been developed.[7] Lately, silica matrices supporting unspecified ammonium salts (presumably alkyltrimethyl) have become commercially available and their use is recommended in anion exchange, nucleotides, and enzyme chromatography.[8]

We report here the synthesis and anion-exchange properties of four new systems in which ammonium salts of different lipophilicities are anchored to silica gel via alkyl spacer chains of various lengths. These new systems have exchange, regeneration, and adsorption properties quite different from those of known polystyrene anion-exchange resins.

Table I. Regeneration and Anions Exchange on 4(Br^-) via Aqueous $NaHCO_3$[a]

$$\underset{(0.16)}{4(\mathrm{Br}^-)} \xrightarrow{\mathrm{NaHCO_3}\ 5\%} \underset{(<1 \times 10^{-3})}{4(\mathrm{HCO_3}^-)} \xrightarrow{\mathrm{HCl\ 0\ 2\ N}} \underset{(0.17)}{4(\mathrm{Cl}^-)} \xrightarrow{\mathrm{NaHCO_3}\ 5\%}$$

$$\underset{(<1 \times 10^{-3})}{4(\mathrm{HCO_3})} \xrightarrow{\mathrm{TsOH}^{b}\ 0.2\ \mathrm{N}} 4(\mathrm{TsO}^-) \xrightarrow{\mathrm{NaHCO_3}\ 5\%} \underset{(<1 \times 10^{-3})}{4(\mathrm{HCO_3}^-)}$$

$$\xrightarrow{\mathrm{HBr\ 0.2\ N}} \underset{(0.16)}{4(\mathrm{Br}^-)}$$

[a] These consecutive exchanges were carried out successively treating 6.0 g of 4(Br^-) with 50.0 mL of the reported aqueous solutions, slowly stirring for 5 min with $NaHCO_3$ 5% by weight and 2 min with acid solutions, at room temperature. In parentheses are the titers (Cl^- and Br^-) as mequiv of X^-/g. [b] *p*-Toluensulfonic acid.

Table II. Ammonium Chloride Functionalized Silica Gels Starting from the Corresponding Ammonium Bromide[a]

starting ammonium bromide (titer)	outcoming ammonium chloride (titer)
4(Br^-) (0.16)	4(Cl^-) (0.17)
6(Br^-) (0.23)	6(Cl^-) (0.24)
7(Br^-) (0.43)	7(Cl^-) (0.43)
8(Br^-) (0.79)	8(Cl^-) (0.79)

[a] The exchanges were carried out successively treating ammonium bromide functionalized silica gels (6.0 g) with $NaHCO_3$ 5% by weight (50.0 mL) and HCl 0.2 N (50.0 mL) according to eq 1. The number in parentheses are the titers as mequiv of X^-/g.

Results

All systems were prepared from nonfunctionalized silica gel (Merck No. 7734, pore diameter 60 Å, specific surface area 500 m^2/g) sieved to a 212–106 μm particle size (70–130 mesh).

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