calculated value obtained for the freely pseudorotating transition-state model, ca. 3–4 eu.[27]. Previous liquid-phase activation parameters report smaller activation entropies. As discussed above, the pressure dependence of the rate constants can be correctly predicted with this model although the quality of this agreement is not unique. Replacing the pseudorotation vibration with a harmonic vibration having a 3×10^{-4} cm^{-1} energy level spacing will also yield our experimental entropy difference.[41] Also, we obtain a unimolecular–bimolecular activation-energy difference of roughly 4 kT, which is also consistent with a transition state with a much larger partition function than the equlibrium chair conformation. All these features of our experimental results are consistent with a transition state with a large state density relative to the equilbrium configuration.

Another interesting experimental result is the observed phase dependence of the kinetic parameters. Gas-phase unimolecular ring-inversion rates for cyclohexane are ca. 2–3 times slower and the activation parameters are slightly higher than those obtained in liquid-phase studies. $\Delta G^{\ddagger}$ for conversion of the chair conformation of cyclohexane to the transition state is 10.4 (2) kcal/mol in the gas phase and 10.1 kcal/mol in CS_2 solutions (see Table II). The observed phase dependence is compatible with a negative activation volume. The partial derivative of $\Delta G^{\ddagger}$, the free energy of activation, with respect to pressure, equals the activation volume, $\Delta V^{\ddagger}$ for the process.[45] The internal pressure of an ideal gas is zero and that of liquid CS_2 at 298 K, is 3714 atm.[46] With use of these values and a $\Delta G^{\ddagger}$ of 370 cal, a $\Delta V^{\ddagger}$ value of ca. −4 cm^3/mol is obtained. Recently, variable-pressure and -temperature NMR studies of cyclohexane in several solvents have revealed that interconversion rates increase with increasing applied external pressure. The pressure dependence observed over a pressure range of 1–5000 bars yields activation volumes, $\Delta V^{\ddagger}$s, ranging from −5.0 cm^3/mol for an acetone solution to −1.5 cm^3/mol for a $C_6D_{11}Cd_3$ solution.[47] These results are consistent with earlier limited-pressure liquid studies.[48] These results are also qualitatively consistent with the slower gas-phase inversion rates reported in the present study and demonstrate that even in the absence of strong electrostatic interactions, kinetic parameters of molecules undergoing conformational exchange can be strongly phase dependent.

Acknowledgment. We are glad to acknowledge support from the National Science Foundation (Grant CHE82-10844), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Committee on Research, University of California, Davis. We thank Dr. Gerald B. Matson for his technical help and valuable suggestions, Miss Debra L. Decker for assistance with the data reduction and analysis associated with this study, and Professor Herbert L. Strauss of the University of California, Berkeley, for valuable information and comments.

Registry No. Cyclohexane, 110-82-7.

---

(45) R. J. Ouellette and S. H. Williams, *J. Am. Chem. Soc.*, **93**, 466–471 (1971).

(46) M. R. T. Dack, *Chem. Soc. Rev.*, **4**, 211–229 (1975).

(47) D. L. Hasha, T. Eguchi, and J. Jonas, *J. Am. Chem. Soc.*, **104**, 2290–2296 (1982).

(48) H. D. Ludeman, R. Rauchschwalbe, and E. Lang, *Angew. Chem., Int. Ed. Engl.*, **16**, 331–332 (1977).

(49) L. R. Pratt, C. S. Hue, and D. Chandler, *J. Chem. Phys.*, **68**, 4202–4212 (1978).

Na^+ and Li^+ Effects on the Photoreduction of Benzophenone: A Picosecond Absorption Study

John D. Simon and Kevin S. Peters*[‡]

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. *Received December 20, 1982*

Abstract: Picosecond absorption spectroscopy has been used to examine solvent effects on the ion-pair exchange reaction between alkali perchlorates and the ion-pair intermediate formed in the photoreduction of benzophenone by aromatic amines. In acetonitrile, the dynamics of exchange with $NaClO_4$ and $LiClO_4$ are similar. In DME the rate of exchange is found to be independent of $NaClO_4$ concentration but dependent on $LiClO_4$ concentration. No exchange is observed in Me_2SO; only solvent-separated ion pairs are observed. For an acetonitrile solution of equimolar 15-crown-5 and $NaClO_4$, exchange between the salt and the benzophenone radical anion/amine radical ion pair is prevented. The picosecond absorption spectrometer used in these studies is described in detail. Raman spectroscopy is used to probe the interactions between the solvent and the salts. In addition ground-state interactions between the alkali cation and the ketone are examined by using IR absorption spectroscopy.

The influence of the alkali cations Li^+ and Na^+ on the reduction of carbonyl compounds has been the subject of extensive investigation.[1] The rates of reaction as well as the overall chemistry have been shown to be highly sensitive to the particular cation present. Generally, the effects of added salts are discussed in terms of their complexation with the carbonyl moiety. The actual participation of the cation in the dynamic details of the reaction has never been fully addressed. The basis for an understanding of the role of the cation in the overall reaction must reside, in part, in the further elucidation of ion-pair dynamics.[2] By applying picosecond transient laser spectroscopy to the study of the photoreduction of benzophenone by *N,N*-diethylaniline in the presence of Na^+ and Li^+, we have developed a new probe into ion-pair chemistry; one which we believe can lead to a greater understanding of the effects of alkali cations on carbonyl chemistry.

The existence of ion pairs was postulated by Bjerrum[3] in an attempt to explain the behavior of ionophores in solvents of low dielectric. Since then, several advances have been made in our understanding of ion-pair structure, the most notable being those by Winstein,[4] Fuoss,[5] Grunwald,[6] and Hogen-Esch and Smid.[7]

[‡] Camille and Henry Dreyfus Teacher–Scholar.

(1) (a) Lefour, J. M.; Loupy, A. *Tetrahedron* **1978**, *34*, 2597. (b) Brown, H. C.; Ichikawa, K. *J. Am. Chem. Soc.* **1961**, *83*, 4372. (c) Ashby, E. C.; Boone, J. R. *Ibid.* **1976**, *98*, 5524.

(2) Szwarc, M. "Carbanions, Living Polymers and Electron Transfer Processes"; Wiley-Interscience: New York, 1968.

(3) Bjerrum, N. K. Dan. Vidensk. Selsk. **1926**, *7*, No. 9, 3.

0002-7863/83/1505-4875$01.50/0

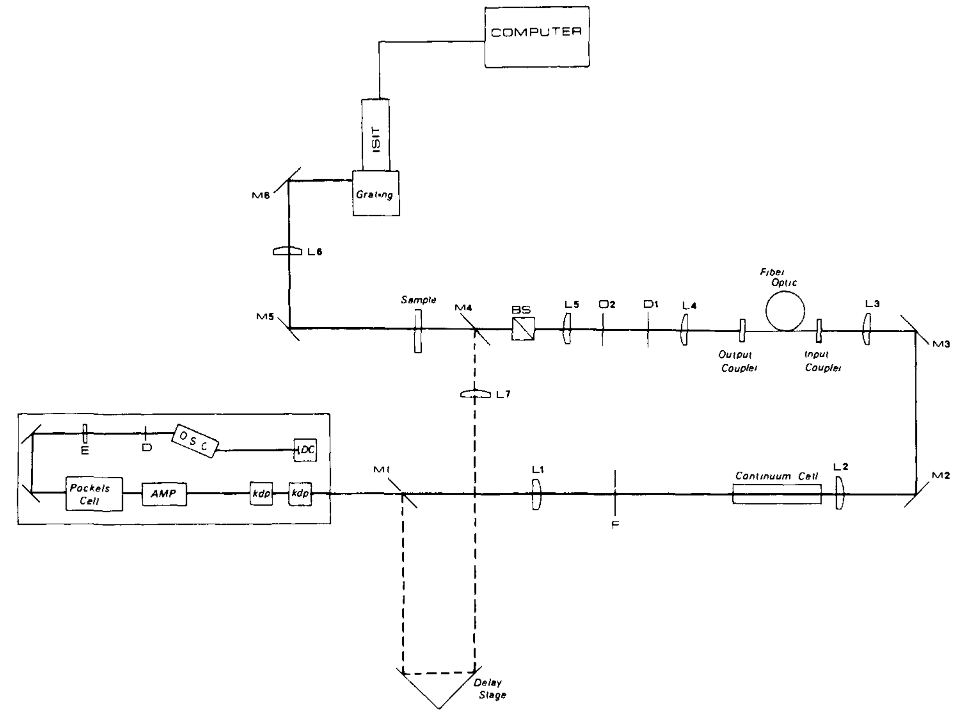
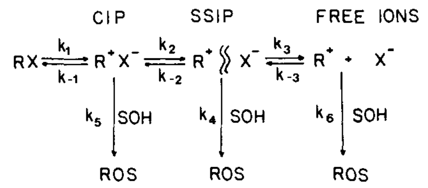


Figure 1. Schematic of the picosecond absorption spectrometer. Laser: Quantel YG-400 Nd^{+3}-YAG; DC, mode-locking dye cell; OCS, oscillator laser rod; E, etalon; AMP, amplifier laser rod; KDP, harmonic crystal. Optics: M1, 355 nm high reflector; L1, 50 cm focal length quartz lens; F, IR pass filter; L2, 15 cm focal length lens; M2, M3, silvered mirrors; L3, 5 cm focal length lens; L4, 10 cm focal length lens; D1, pinhole; D2, adjustable diaphram; L5; 20 cm focal length lens; BS, beam splitter; M4, 355 nm high reflector; sample cell, 1 cm path length quartz supersil cell; M5, M6, silvered mirrors; L6, 25 cm focal length lens; L7, 15 cm focal length lens.

Several excellent reviews are currently available.[8] Though a continuum of ion-pair forms are conceivable, their structures are usually categorized in terms of the contact and solvent-separated ion pair. The variety of spectroscopic techniques used in the study of ion pairs have mainly been limited to the examination of equilibrium distributions between these two ion-pair forms.[7] Thus, despite an active and growing interest in the role of ion pairs in chemical problems, little dynamical information has been obtained.[9] Until recently, no data were available on the effect of solvent interaction or solvent motion on the dynamics of interconversion between different ion-pair forms.[10]

Based on an observed increase in the rate for solvolysis reactions carried out in the presence of added lithium perchlorate, Winstein proposed the existence of an ion-pair exchange process between the salt and the organic ion pairs.[4b] The following mechanism was proposed:



The special salt effect was postulated to result from the prevention of return of the solvent separated ion pair to the contact ion pair due to an ion-pair exchange reaction between the organic and salt ion pairs. This mechanism has received much support,[4] although alternative mechanisms have been proposed.[6b–d] From picosecond flash photolysis studies, we have shown that the rate of ion-pair exchange in acetonitrile is at a maximum when the two ion-pair structures are of the same form, *either* solvent separated or contact.[10]

One would expect that the mechanism, as well as the rate of exchange, would depend not only on the types of ion pairs involved but also on the specific interactions which exist between the ions and the solvent. In the present paper we examine the dynamics of the ion-pair exchange between the alkali perchlorates, $NaClO_4$ and $LiClO_4$, and the ion-pair intermediate formed in the photoreduction of benzophenone by aromatic amines.[11] Ideally one would like to examine this process in solvents of both high and low dielectric, possessing both weak and strong affinities for cation solvation. In an attempt to elucidate the role of solvent interactions in the exchange mechanism, we have used picosecond absorption spectroscopy to study the dynamics of ion-pair exchange in acetonitrile, Me_2SO, and 1,2-dimethoxyethane. Despite the large change in dielectric constant between Me_2SO and 1,2-dimethoxyethane (Me_2SO, $\epsilon = 54$; 1,2-dimethoxyethane, $\epsilon = 7.2$) there is a variety of spectroscopic and conductivity[12] data which dem-

---

[4] (a) Winstein, S.; Robinson, G. C. *J. Am. Chem. Soc.* **1958**, *80*, 169. (b) Winstein, S.; Clippenger, E.; Fainberg, A.; Robinson, G. C. *Ibid.* **1954**, *76*, 2597. (c) Fainberg, A.; Winstein, S. *Ibid.* **1956**, *78*, 2767. (d) Fainberg, A.; Robinson, G.; Winstein, S. *Ibid.* **1956**, *78*, 2777. (e) Winstein, S.; Clippenger, E. *Ibid.* **1956**, *78*, 2784. (f) Jenny, E.; Winstein, S. *Helv. Chim. Acta* **1958**, *41*, 807.

[5] (a) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059. (b) Fuoss, R. M.; Kraus, C. A. *Ibid.* **1933**, *55*, 476. (c) Sadek, H.; Fuoss, R. M. *Ibid.* **1954**, *76*, 5897. (d) Sadek, H.; Fuoss, R. M. *Ibid.* **1954**, *76*, 5905. (e) Miller, R. C.; Fuoss, R. M. *Ibid.* **1953**, *75*, 3076. (f) Sadek, H.; Fuoss, R. M. *Ibid.* **1950**, *72*, 301. (g) Sacks, R. M.; Fuoss, R. M. *Ibid.* **1953**, *75*, 5172.

[6] (a) Grunwald, E.; Price, E. *J. Am. Chem. Soc.* **1964**, 45, 17. (b) Grunwald, E.; Puar, M. *Ibid.* **1967**, *89*, 6842. (c) Crampton, M.; Grunwald, E. *Ibid.* **1971**, *93*, 2987. (d) Crampton, M.; Grunwald, E. *Ibid.* **1971**, *93*, 2990. (e) Grunwald, E. *Anal. Chem.* **1954**, *26*, 1696.

[7] (a) Smid, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 2. (b) Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1966**, *88*, 307. (c) Smid, J. *Intersci. Chem. Rept.* **1973**, *7*, 75. (d) Hogen-Esch, T. E. *Adv. Phys. Org. Chem.* **1977**, *15*, 153. For studies in glyme solvents see: (e) Chan, L. L.; Smid, J. *J. Am. Chem. Soc.* **1967**, *89*, 4547. (f) Chan, L. L.; Wong, K. H.; Smid, J. *Ibid.* **1970**, *92*, 1955. (g) Smid, J., ref 8a, Vol. 1, p 86.

[8] (a) Szwarc, M., Ed. "Ions and Ion Pairs in Organic Reactions"; Wiley-Interscience: New York, 1972; Vol. 1 and 2. (b) Meyer, U. *Pure Appl. Chem.* **1975**, *41*, 291. (c) Schneider, H. *Top. Curr. Chem.* **1976**, *68*, 105. (d) Szwarc, M. *Acc. Chem. Res.* **1969**, *2*, 87.

[9] (a) Kessler, H.; Feigel, M. *Acc. Chem. Res.* **1982**, *15*, 2. (b) Hirota, N.; Carraway, R.; Schook, W. *J. Am. Chem. Soc.* **1968**, *90*, 3612. (c) Crowley, A.; Hirota, N.; Kreilich, R. *J. Chem. Phys.* **1967**, *46*, 4815. (d) Hirota, N. *Ibid.* **1967**, *71*, 127.

[10] Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1982**, *104*, 6142.

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

onstrate that both solvents strongly solvate alkali cations. This should result in an increase in the thermodynamic barrier for the exchange process; a strong cation–solvent interaction could result in prevention of ion-pair exchange. In addition the difference between the radii of the Li^+ and Na^+ cations[13] could significantly alter both the equilibrium ion-pair distributions and the solvent–cation interactions.

Experimental Section

The Picosecond Absorption Spectrometer. A schematic of the picosecond absorption spectrometer used in this study is shown in Figure 1. A passively mode-locked Nd^{+3}-YAG laser (Quantel International YG-400) is used to generate a train of 25-ps pulses; the time between pulses is approximately 7 ns. For our experiment, the average pulse train contains 9–11-ps pulses. A single pulse is extracted by using a Pockels cell. The rejected pulse train is monitored by a Tektronix oscilloscope, Model 7834. Periodically, the output pulse of the Pockels cell is examined to ensure that only a single pulse is being extracted. The extracted picosecond pulse is amplified—frequency doubled (KDP λ 530 nm) and tripled (KDP λ 355 nm). In previous studies[14] we have also used the fourth harmonic (KDP λ 266 nm) for photolysis. For a typical laser pulse, the energies at 1.06 μ, 530 nm, and 355 nm are 5.0 mJ, 2.0 mJ, and 0.5 mJ, respectively.

The general design of the experiment is similar to that of previous flash photolysis apparatuses.[15] Time resolution is obtained by varying the path length traversed by the excitation wavelength (in our case 355 nm) and the probe beam. A change in path length of 0.2 in. results in a temporal change of 17.2 ps. Given the constraints of various optical tables and the problem of beam divergence, the actual changing of the optical path with use of conventional optics would result in the ability to examine time delays on the order of 10 ns. Since flash lamps and mechanical shutters do not operate on the picosecond time scale, it is not possible to use conventional broad-band light sources for interrogation. Our interrogation beam is a picosecond continuum generated by focusing the fundamental laser line into a liquid solution. The composition of the continuum cell depends on the spectral region of interest. For the region between 500 and 800 nm, a 1:1 mixture of carbon tetrachloride and chloroform is used. For the region between 400 and 600 nm D_2O is used. This picosecond continuum is then passed through a short optical fiber which is permanently built into the beam path. Passing the beam through the fiber results in the depolarization of the continuum light. The output of the fiber is then passed through a beam splitter, resulting in a double-beam spectrometer. One of the continuum beams is made colinear with the excitation beam, and the other beam is passed through the sample cell at a different point. Both continuum and excitation beams are focused onto the sample. The sample is placed at the focal point of the probe beam. The focus of the excitation beam is then determined so that the entire probe beam is spatially inside the region excited by the UV radiation. Both continuum beams are then focused onto the slits of a monochrometer (JY-200, 50 μm slits, holographic grating 200–800 nm) and dispersed onto the face of an ISIT Vidicon detection system (PAR Model 1216, 1215, 1205I).

For time delays up to 2 ns, the optical path of the photolysis beam is shortened while the continuum path remains constant. Recently we have used fiber optics to obtain temporal delays between 2 and 250 ns. The desired length fiber (Math Associates) is inserted in place of the permanently mounted fiber located on the path traversed by the continuum light. The advantage of using fiber optics is that they can be changed without moving the input and output couplers, ensuring that the optical axis remains constant as the two beams (excitation and probe) are delayed with respect to one another. This results in a *constant* overlap of the excitation and probe beams at the sample, allowing for an accurate determination of changes in absorption intensity as a function of time. In this way, we are able to circumvent the constraints conventional optics places on the time domains accessible to our experiment. The light loss in a fiber optic is extremely small and in practice it is quite simple to change the delay between the excitation and interrogation beams from 25 ps to hundreds of ns. In principle, transient absorption spectra microseconds after photolysis can be probed with suitable length fibers. To establish zero time, an acetonitrile solution of benzophenone is used to determine the location of the delay stage which ensures that the beam paths for the excitation and probe pulses are equal. We are able to use this compound as the intersystem crossing rate of benzophenone occurs on a much faster time scale than can be resolved with use of pulses of 25-ps duration.[15] Thus the appearance of the triplet-state absorption spectrum of benzophenone to 50% of its maximum absorbance is used to define $t = 0$.

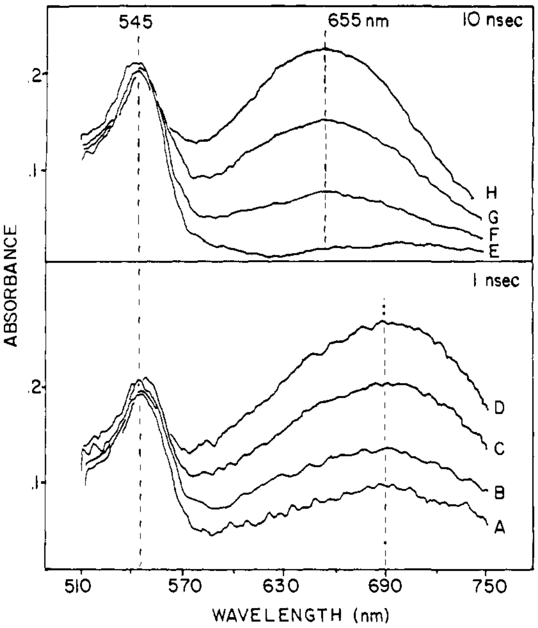


Figure 2. Transient absorption spectra for the photoreduction of 0.2 M benzophenone by 1.0 M DEA in 1,2-dimethoxyethane. Effect of added $NaClO_4$: 1 ns after photolysis, (A) no salt, (B) 0.1 M $NaClO_4$, (C) 0.5 M $NaClO_4$, (D) 1.0 M $NaClO_4$; 10 ns after photolysis, (E) no salt, (F) 0.1 M $NaClO_4$, (G) 0.5 M $NaClO_4$, (H) 1.0 M $NaClO_4$.

The actual procedure for obtaining a transient absorption spectrum involves the recording of the I and I_0 beams with and without excitation. The absorption spectrum is then calculated by:

$$A = \log\left[\frac{I_0}{I}\right]_{\text{with excitation}} - \log\left[\frac{I_0}{I}\right]_{\text{without excitation}}$$

For each transient absorption spectrum, over 500 laser shots are averaged. The noise level for an absorbance of 0.1 OD is generally less than 0.001 OD. In order to prevent the photolysis of photoproducts, a 1.0-cm cell equipped with magnetic stirring is used. Under certain conditions, a flow cell is also used. The transient absorption spectra are calibrated by using a low-pressure Hg-arc lamp (Spectroline Model SCT-1).

Vibrational Spectra. Infrared absorption spectra were obtained by using a Nicolet Model 7199 FT-IR. A solution cell (1.0-mm path length) with CaF_2 windows was used. The number of transform and data points accumulated resulted in an uncertainty of 0.5 cm^{-1} in band position.

Raman spectra were obtained by using a Spectra Physics Model 164 Argon Ion Laser (1.0 W at 514.5 nm). The scattered light was collected by using a back-scattering arrangement and focused onto the slits of a monochrometer (JY-HRS 2, equipped with a grating blazed at 500 nm, 1800 groves/mm). The slits were usually set at 100 μm; no narrowing in bandwidths was observed at smaller slit settings. The monochrometer was interfaced to a cooled SIT vidicon tube (PAR Model 1212 Vidicon Cooled Housing, 1205 Vidicon Tube, 1215-1216 controller-computer). The Raman apparatus was calibrated by using a low-pressure Hg-arc lamp. Using the Hg doublet centered at 579 nm, we find that the grating results in dispersing approximately 350 cm^{-1} across the face of the vidicon tube. This results in an accuracy of 2 cm^{-1} in our determination of band positions.

Chemicals. Spectrograde acetonitrile (Aldrich) was used. 1,2-Dimethoxyethane (DME, Aldrich) was dried by standard techniques and stored under argon and over molecular sieves. $NaClO_4$ (Aldrich) and $LiClO_4$ (Aldrich) were dried by heating under reduced pressure. 15-Crown-5 (Aldrich) and Me_2SO (Aldrich) were used without further purification. Benzophenone (MCB) was recrystallized from ethanol.

---

(12) (a) Detellier, C.; Laszlo, P. *Helv. Chim. Acta* **1976**, *59*, 1346. (b) Detellier, C.; Laszlo, P. *Bull. Chim. Belg.* **1975**, *84*, 1081. (c) Detellier, C.; Laszlo, P. *Helv. Chim. Acta* **1976**, *59*, 1333. (d) O'Brien, D. H.; Russell, C. R.; Hart, A. *J. Am. Chem. Soc.* **1979**, 101, 633. (e) Grutzner, J. B.; Lawlor, J. M.; Jackman, L. M. *Ibid.* **1972**, *94*, 2306. (f) Greenberg, M. S.; Bodner, R. L.; Popov, A. *J. Phys. Chem.* **1973**, *77*, 2449 and references within.

(13) Pauling crystal radii are 0.6 Å for Li^+ and 0.95 Å for Na^+. Pauling, L. "Nature of the Chemical Bond and the Structure of Molecules and Crystals"; 3rd ed.; Cornell University Press: New York, 1960.

(14) Freilich, S. C.; Peters, K. S. *J. Am. Chem. Soc.*, submitted for publication.

(15) Greene, B. I.; Hochstrasser, R. M.; Weisman, R. B. *J. Chem. Phys.* **1979**, *70*, 1247.

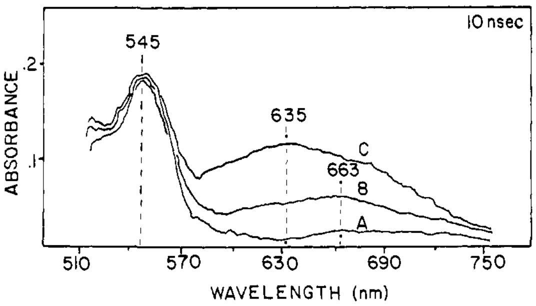


Figure 3. Transient absorption spectra for the photoreduction of 0.2 M benzophenone by 1.0 M DEA in 1,2-dimethoxyethane. Effect of added $LiClO_4$: 10 nsec after photolysis, (A) no salt, (B) 0.1 M $LiClO_4$, (C) 0.5 M $LiClO_4$.

N,N-Diethylaniline (Aldrich), and *N,N*-dimethylaniline (Aldrich) were refluxed over KOH, distilled under reduced pressure, and stored under argon.

Results

Transient absorption spectra for the photoreduction of benzophenone by 1.0 M DEA in 1,2-dimethoxyethane in the presence of added $NaClO_4$ are shown in Figure 2. We have previously reported[11] that the photolysis of an acetonitrile solution of 0.2 M benzophenone and 1.0 M DEA results in a rapid electron transfer generating a solvent-separated ion pair comprised of the amine radical cation and the benzophenone radical anion λ_{max} 720 nm. These species then diffuse together to form a contact ion pair, λ_{max} 690 nm, with a half-life of 200 ps. No proton transfer is observed on the nanosecond time scale ($t < 50$ ns). For the photolysis of 0.2 M benzophenone and 1.0 M DEA in 1,2-dimethoxyethane, we also observe rapid electron transfer generating a solvent-separated ion pair, λ_{max} 720 nm. The resulting solvent-separated ion pair collapses to form a contact ion pair, $\tau \approx 200$ ps. However, unlike in acetonitrile, once the contact ion pair is formed in DME, proton transfer to form the benzhydrol radical, λ_{max} 545 nm, is observed on the nanosecond time scale. By 50 ns following photolysis, proton transfer has gone to completion. The overall generation of the benzhydrol radical is dramatically decreased in the presence of either $LiClO_4$ or $NaClO_4$. At 1.0 ns following photolysis in the presence of $NaClO_4$ we observe a shift in the distribution between the ion pair and the ketyl radical, Figure 2, A–D. We note that for 0.1 M $NaClO_4$ [B] and 1.0 M $NaClO_4$ [D], no shift in the absorption maximum is observed. This indicates that the change in the ion pair/radical pair distribution results from an ionic strength effect, not the formation of the more stable sodium contact ion pair. At 10 ns following photolysis, we observe a shift in the absorption maximum to λ_{max} 655 nm. The rate of the shift is independent of the $NaClO_4$ concentration for the salt concentrations examined, 0.1 M $\leq$ $NaClO_4$ $\leq$ 1.0 M. No shift in the absorption maximum is observed between 10 and 250 ns following photolysis. On the basis of previous observation,[10,16] this band is assigned to the sodium contact ion pair. Once the sodium contact ion pair is formed, no further proton transfer is observed.

Different behavior is observed in the presence of $LiClO_4$ ([$LiClO_4$] = 0.1–0.5 M). In Figure 3, we present transient absorption spectra recorded 10 ns after photolysis for the photoreduction of benzophenone by 1.0 M DEA in DME in the presence of added $LiClO_4$. Unlike the results with $NaClO_4$, the rate of shift of the radical anion absorption is dependent on the concentration of $LiClO_4$. The effect of added salt on the radical anion absorption is shown graphically in Figure 4. It is evidant that the rate of exchange is dependent upon the concentration of $LiClO_4$. In addition at 1.0 ns following photolysis, we observe indications of exchange occurring with 0.5 M $LiClO_4$, $\lambda_{max} < 690$ nm, but no sign of exchange is detected with 0.5 M $NaClO_4$ or 0.1 M $LiClO_4$. However, in Figure 4 for $NaClO_4$ there is no change in the anion absorption maximum between 10 and 50 ns while the absorption spectra continue to blue-shift on this time scale in the presence of $LiClO_4$. Thus, the overall exchange occurs faster with 0.5 M $NaClO_4$ than with 0.5 M $LiClO_4$. A larger blue-shift is observed with $LiClO_4$ than with $NaClO_4$; at 50 ns following photolysis in the presence of 0.5 M $LiClO_4$, the absorption spectrum of the radical anion of benzophenone has shifted to 608 nm. No change is observed between 50 and 250 ns following photolysis. This spectrum is assigned to the lithium contact ion pair.[8] As observed with $NaClO_4$, once the lithium contact ion pair is formed, no further evidence of proton transfer is observed.

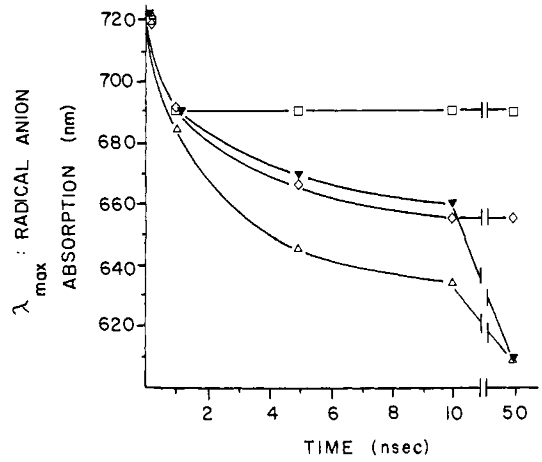


Figure 4. Absorption maximum of the radical anion of benzophenone as a function of time in 1,2-dimethoxyethane/salt solutions. All solutions contain 0.2 M benzophenone and 1.0 M DEA. No salt (□); 0.1 M $LiClO_4$ (▼); 0.1 M $NaClO_4$ (◇); 0.5 M $LiClO_4$ (△).

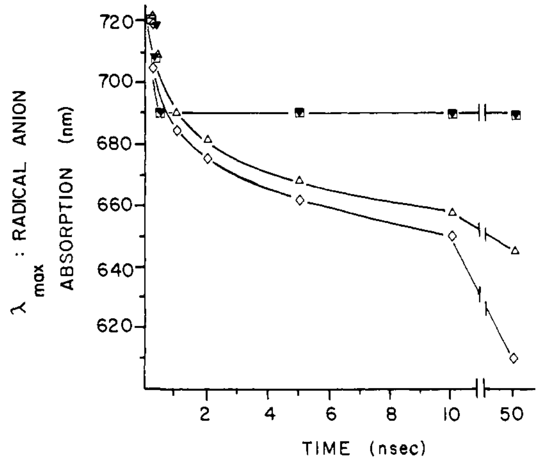


Figure 5. Absorption maximum of the radical anion of benzophenone as a function of time in acetonitrile/salt solutions. All solutions contain 0.2 M benzophenone and 1.0 M DEA. No salt (□); 0.5 M $NaClO_4$, 0.5 M 15-C-5 (▼); 0.1 M $NaClO_4$ (△); 0.1 M $LiClO_4$ (◇).

In Figure 5 we present a similar plot for the effect of added salt on the time-dependent absorption maximum of the radical anion absorption in acetonitrile solutions. At 1.0 ns following photolysis, we observe that the maximum of the radical anion absorption is dependent on the added salt. In addition, unlike DME, we observe a larger blue-shift upon increasing $NaClO_4$ concentration. At 1 ns following photolysis, we observe an absorption maximum of the radical anion for benzophenone of 690, 680, and 660 nm for 0.1, 0.5, and 1.0 M $NaClO_4$, respectively.[10] Between 1 and 10 ns following photolysis we observe an increase in the blue-shift to 660, 645, and 645 nm for 0.1, 0.5, and 1.0 M salt, respectively. We have previously reported[10] a bimolecular rate constant for the rate of ion pair exchange between $NaClO_4$ and the benzophenone radical anion/DEA radical cation ion pair in acetonitrile of $k = 7.4 \times 10^8$ mol^{-1} s^{-1}. The formation of the sodium contact ion pair involved initial exchange between two

---

(16) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.*, submitted for publication.

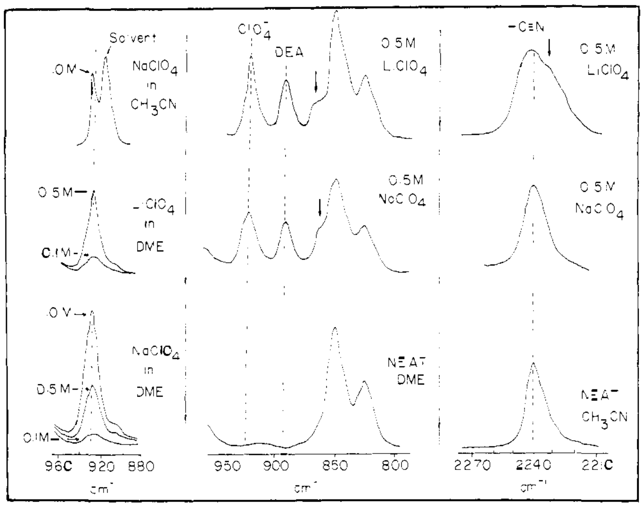


Figure 6. Raman spectra. All DME solutions contain 1.0 M DEA (concentration used in picosecond absorption studies). Left: Examination of the perchlorate stretch as a function of salt concentration in 1,2-dimethoxyethane and acetonitrile. Middle: The effect of salt concentration on Raman active bands of 1,2-dimethoxyethane. Right: The effect of salt concentration on the -C≡N Raman active band of acetonitrile.

solvent-separated ion pairs. As depicted in Figure 5, we observe initially a faster rate of blue-shifting in the absorption maximum of the radical anion in the presence of 0.1 M $LiClO_4$ than with 0.1 M $NaClO_4$. However, in comparison to $NaClO_4$, the overall rate of exchange with $LiClO_4$ is slower by at least a factor of 5, $k \leq 1.5 \times 10^8$ mol^{-1} s^{-1}. This is similar to the behavior observed at high $LiClO_4$ concentrations in DME.

For the photoreduction of benzophenone by 1.0 M DEA in Me_2SO, we observe the formation of the solvent-separated ion pair λ_{max} 720 nm. This band is not observed to shift within the first 250 ns following photolysis. In light of the results in acetonitrile, one would expect this ion pair to undergo exchange with the solvent-separated $NaClO_4$ ion pair. However, in the presence of 0.5 M $NaClO_4$, the absorption maximum of the radical anion undergoes only a slight blue-shift to λ_{max} 705 nm. This could be indicative of a slight interaction between the sodium cation and the benzophenone radical anion, but not the formation of a sodium contact ion pair.[17]

This observation indicates that the addition of a strong cation complexing agent could result in the prevention of ion-pair exchange. In order to obtain a better understanding of this phenomenon, we examined the effect of crown ethers on the rate of ion-pair exchange between $NaClO_4$ and the benzophenone radical anion/DEA radical cation ion pair in acetonitrile. The macrocyclic polyether, 15-crown-5, has a high affinity for complexing sodium[18] and addition of an equimolar amount of crown should result in efficient if not quantitative complex formation. Examining the photoreduction in the presence of 0.5 M $NaClO_4$/0.5 M 15-crown-5, we do not observe exchange between the crown complexed salt and the amine/ketone ion pair. The radical anion absorption observed at all times examined after photolysis is identical with that found in the absence of salt, Figure 5. This result indicates that the crown complex is substantially more stable than the sodium contact ion pair. Furthermore, these results clearly demonstrate that the association between a solvent molecule, or in this case a complexing agent, and the Na^+ cation could either result in a decrease in the rate of ion-pair exchange or prevent ion-pair exchange entirely.

Table I. Raman Stretching Frequencies for $NaClO_4$ and $LiClO_4$ Salt Solutions in DME and Acetonitrile (All Solutions Unless Otherwise Stated Contain 1.0 M *N*,*N*-Diethylaniline)

Perchlorate Stretching Frequencies

salt	ν_{max}, cm^{-1}	width, cm^{-1}	solvent	comment
0.1 M $NaClO_4$	928	15	DME	no amine
0.1-1.0 M $NaClO_4$	928	15	DME	
0.1 M $LiClO_4$	928	15	DME	no amine
0.1-0.5 M $LiClO_4$	928	15	DME	
0.1 M $NaClO_4$	935	6^a	CH_3CN	no amine
0.1-1.0 M $NaClO_4$	935	6^a	CH_3CN	
0.1 M $LiClO_4$	935	6^a	CH_3CN	

Solvent Bands

solvent	ν_{max}, cm^{-1}	added salt	comments
DME	847		*c*
		$NaClO_4$	shoulder 856 cm^{-1} *b*
		$LiClO_4$	shoulder 865 cm^{-1} *b*
CH_3CN	2241		
		$NaClO_4$	slight red broadening
		$LiClO_4$	substantial line broadening, shoulder 2233 cm^{-1}

[a] Based on deconvolution of acetonitrile band. [b] Band intensity is linear with added salt concentration. [c] Band observed is the overlapping of two Raman active bands which cannot be resolved by the apparatus.

Table II. Carbonyl Stretching Frequencies

solvent	amine	salt	$\nu_{C=O}$, cm^{-1}
CH_3CN			1660.7
	1.0 M DEA		1660.7
	1.0 M DEA	1.0 M $NaClO_4$	1660.4
	1.0 M DEA	0.1 M $LiClO_4$	1660.5
DME			1662.5
	1.0 M DEA		1662.4
	1.0 M DEA	0.5 M $NaClO_4$	1661.5
	1.0 M DEA	0.5 M $LiClO_4$	1661.3

In order to elucidate the mechanism of ion-pair exchange on a molecular level, it is important to know the various species of ion pairs present in solution. We have obtained Raman spectra for several of the salt solutions discussed above (under experimental conditions—with 1.0 M amine) which demonstrate that both alkali salts, $LiClO_4$ and $NaClO_4$, are predominantly solvent separated under experimental conditions. The data are given in Figure 6 and Table I. Raman spectra for the perchlorate stretch as a function of salt concentration are shown in the left portion of Figure 6. For $NaClO_4$ in DME, we observe a stretching frequency of 928 cm^{-1}. A slight shift and line narrowing is observed in acetonitrile, λ_{max} 935 cm^{-1}; these changes could be a result of a change in solvent structure, not necessarily a measure of ion pairing. The observed stretching frequencies are similar to previous observations.[19] In both DME and acetonitrile, no change in band shape or position is observed for $NaClO_4$ concentrations between 0.1 and 1.0 M. This indicates similar ion pairing in all solutions.[20] In addition, upon comparison to $NaClO_4$, identical band shapes are observed for $LiClO_4$ (0.1–0.5 M) in DME. Examination of

---

(17) The absorption spectra of contact ion pairs are found to be sensitive to solvent, ref 7. In Me_2SO one could have the formation of solvated contact ion pairs. However, usually the result of a solvated contact ion pair is manifested by a shift on the order of only a few nanometers in the absorption spectrum. In addition,[7] the addition of a small amount of Me_2SO to a dioxane solution of fluorenyl–sodium ion pairs results in complete formation of the solvent-separated form.

(18) (a) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017. (b) Izatt, R. M.; Eatough, D. J.; Christensen, J. J. *Struct. Bonding (Berlin)* **1973**, *16*, 161. (c) Izatt, R. M.; Nelson, D. P.; Rytting, J. H.; Haymore, B. L.; Christensen, J. J. *J. Am. Chem. Soc.* **1971**, *93*, 1619. (d) Ting-Po, I.; Grunwald, E. *Ibid.* **1974**, *96*, 2879. The diameter of the cavity in 15-crown-5 is 1.7–2.2 Å depending on the various possible configurations. From ref 11, the ionic diameter of Na^+ is 1.90 Å.

(19) Wong, M. K.; McKinney, W. J.; Popov, A. J. *J. Phys. Chem.* **1971**, *75*, 56.

(20) In ref 19, Popov et al. have demonstrated that the perchlorate stretch is a sensitive probe to ion pairing. In addition to observing changes in this band, they simultaneously observed changes in the solvent Raman bands. In our study, solvent bands are affected but the line shape and position of the perchlorate band is uneffected by increasing salt concentration.

the perchlorate stretch in acetonitrile reveals identical band shapes for 0.1 M $NaClO_4$ and 0.1 M $LiClO_4$. In the center portion of Figure 6, we present several DME Raman active bands which demonstrated the effect of the cation on solvent structure. The distortion of the DME Raman bands[21] is greater with $LiClO_4$ than with $NaClO_4$. No significant change in relative intensities is observed. Also, no change is observed in the amine Raman bands upon addition of salt. The nature of the vibrational modes associated with these bands and the resulting implications with respect to cation solvation will be discussed later. In Figure 6 we have also shown the effect of added salt on the $-C{\equiv}N$ stretch in acetonitrile. Addition of 0.5 M $NaClO_4$ results in a slight broadening on the Raman band (width of band increases from 12 cm^{-1} to 15 cm^{-1}). However, upon addition of 0.5 M $LiClO_4$, the band is observed to broaden significantly and develop a shoulder to higher energy. These results indicate a stronger solvent–cation interaction with Li^+ than with Na^+.

In order to investigate the possibility of ground-state interactions between the alkali cations and the carbonyl moiety of benzophenone, we have examined the effect of added salt on the $C{=}O$ stretching frequency with use of IR absorption spectroscopy.[22] The results are given in Table II. For benzophenone in acetonitrile, the carbonyl stretching frequency is found at 1660.7 ± 0.5 cm^{-1}. This band is found to be insensitive to added salt (0.1–1.0 M $NaClO_4$; 0.1 M $LiClO_4$). In addition no change in line width is observed. For benzophenone in DME, the carbonyl stretching frequency is found at 1662.5 cm^{-1}. Addition of 0.5 M salt (either $NaClO_4$ or $LiClO_4$) results in a slight red shift in the stretching frequency to 1661.3 cm^{-1}. This could result from either a change in the dielectric properties of the solvent at such high salt concentration[23] or an interaction between the cation and the ground-state carbonyl. No significant change in line width is observed.

Discussion

The factors which determine the equilibrium structure of an ion pair in solution are not solely limited to electrostatic interactions. The ability of the solvent to stabilize a specific ion pair form can determine the overall reactivity of the ion-pair intermediate; solvent basicity, steric hindrance near the coordination site, as well as the presence of multiple coordination sites must all be considered. Single parameters like macroscopic dielectric, ϵ, dipole moment, μ, Kosower's Z,[24] and Gutman's donor numbers[25] have limited value in predicting tendencies of various solvents to preferentially solvate a particular ion-pair form. In this paper we examine the ion-pair exchange in DME, Me_2SO, and acetonitrile. Before a detailed understanding of this process can be achieved, the equilibrium structures of the ion pairs undergoing exchange must be determined.

Ion-Pair Structure of $LiClO_4$ and $NaClO_4$ in DME, Me_2SO, and Acetonitrile. It is commonly accepted that $NaClO_4$ exclusively forms solvent-separated ion pairs in nonaqueous solvents. In acetonitrile, $^{23}Na^+$ NMR has demonstrated[26] that the chemical shift is independent of concentration (0.1–1.0 M, [$NaClO_4$]). These results have been interpreted by postulating that $NaClO_4$ forms only solvent-separated ion pairs in acetonitrile. Meanwhile, salts such as NaI do show a concentration-dependent chemical shift, indicating ion pairing.[26] Similar studies support the predominance of solvent-separated ion pairs for $NaClO_4$ in Me_2SO.[27] For acetonitrile solutions of $LiClO_4$ ($[LiClO_4] \leq 0.2$ M) no change in the $^7Li^+$ chemical shift is observed, once again supporting the conclusion that the equilibrium structure is a solvent-separated ion pair.[28] This result has also been confirmed by examining the ^{35}Cl chemical shift as a function of salt concentration.[28a] In addition to NMR, ion pairing of alkali perchlorates in nonaqueous solvents has been examined by using Raman spectroscopy. From the examination of the dependence of the perchlorate stretch (ν_1, A_1, 935 cm^{-1}) on salt concentration in nitromethane–THF mixtures, it was concluded that a change in line shape is associated with ion pairing.[19]

Our results, Table I and Figure 6, confirm the ion-pair structures deduced from NMR spectroscopy. No change in line shape or position is observed for the perchlorate stretch of $LiClO_4$ (0.1 M) or $NaClO_4$ (0.1–1.0 M) in acetonitrile. However, the two salts have dramatically different effects on the solvent $-C{\equiv}N$ Raman band. Addition of 0.5 M $NaClO_4$ results in only a slight broadening of the band while 0.5 M $LiClO_4$ significantly changes the band shape. It is reasonable to assume that the solvation of the cation involves interaction with the $-C{\equiv}N$ terminal group of the nitrile. In addition, on the basis of the smaller size of the lithium cation (Li^+, $r = 0.6$ Å; Na^+, $r = 0.95$ Å[13]), one predicts a stronger electrostatic interaction between Li^+ and the dipolar solvent molecules.[29] This would be manifested in a decrease in the electron density in the $-C{\equiv}N$ bond resulting in a decrease in both bond order and the energy associated with the vibration; this is experimentally observed.

Unfortunately, no alkali metal NMR studies aimed at elucidating ion pairing for $NaClO_4$ and $LiClO_4$ in DME have been carried out. However, there are several investigations which present chemical evidence for a strong Li^+–DME interaction.[30] Information concerning $NaClO_4$ and $LiClO_4$ ion-pair structure in DME can be gleaned from various dielectric relaxation and conductivity studies.[31] The characteristic rotation time of DME ($t_p \approx 30$ ps) was found to decrease by approximately an order of magnitude in the presence of either salt, $t_p = 350$ ps for $LiClO_4$ and 300 ps for $NaClO_4$. On the basis of these results it was postulated that the solvation of the cation most likely involved more than a single solvent molecule. The Stokes radius for Na^+ in DME has been determined to be 3.3 Å,[2] indicating that the cation is probably solvated by two DME molecules. In addition, conductivity studies show identical behavior for the two salts, indicating similar ion-pair structures. Although DME has a low dielectric constant, the coordinating ability of ethers is well known. In addition the interaction of the Na^+ cation with ethereal oxygens is generally weaker than with Li^+.[7g] Solvation by greater than one solvent molecule significantly lowers the entropy of the solvent. At high salt concentrations, it is conceivable that an equilibrium exists between cations which are solvated by single DME molecules and cations solvated by several solvent molecules.

In order for a more complete understanding of the interaction of DME with $LiClO_4$ and $NaClO_4$ to be obtained, Raman spectroscopy was used to examine both the perchlorate stretch and the solvent vibrations. The band shape and position of the perchlorate stretch were found to be concentration independent for both $LiClO_4$ and $NaClO_4$. The identical Raman bands observed along with the results from conductivity and dielectric relaxation studies support the conclusion that both salts exist as solvent-separated ion pairs. The coordination of an alkali cation by DME is predicted to significantly perturb the vibrational

---

[21] For a complete vibrational assignment of 1,2-dimethoxyethane, see: Synder, R. G.; Zerbi, G. *Spectrochim. Acta, Part A* **1967**, *23A*, 391. For conformational studies see: (a) Podo, F.; Nemethy, G.; Indovina, P. L.; Radics, L.; Viti, V. *Mol. Phys.* **1974**, *27*, 521. (b) Viti, V.; Indovina, P. L.; Podo, F.; Radics, L.; Nemethy, G. *Ibid.* **1974**, *27*, 541.

[22] IR absorption spectroscopy provides a sensitive probe in determining changes in solvation and the presence of ground-state complexes. For examples see: (a) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1982**, *104*, 6542. (b) Bellamy, L. J.; Williams, R. L. *Trans. Faraday Soc.* **1959**, *55*, 14.

[23] Reichardt, C. "Solvent Effects in Organic Chemistry"; Verlag Chemie: Germany 1978, Chapter 6.

[24] (a) Kosower, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 3253. (b) Kosower, E. M.; Mohammad, M. *Ibid.* **1968**, *90*, 3271.

[25] Gutman, V. "The Donor-Acceptor Approach to Molecular Interactions"; Plenum Publishing Corp.: New York, 1978. Donor numbers for Me_2SO and DME are 27.8 and 24.0 kcal/mol, respectively.

[26] (a) Erlich, R. H.; Roach, E.; Popov, A. I. *J. Am. Chem. Soc.* **1970**, *92*, 4989. (b) Greenberg, M. S.; Bodner, R. L.; Popov, A. I. *J. Phys. Chem.* **1973**, *77*, 2449.

[27] Green, R. D.; Martin, J. S. *Can. J. Chem.* **1972**, *50*, 3935.

[28] (a) Cohen, Y. M.; Hardy, P. R.; Roach, E. T.; Popov, A. I. *J. Phys. Chem.* **1975**, *79*, 80. (b) Maciel, G. E.; Hancock, J. K.; Lafferty, L. F.; Mueller, P. A.; Musker, W. K. *Inorg. Chem.* **1966**, *5*, 554.

[29] Borisova, V. B.; Akopyan, S. K.; Shevyakov, A. M.; Bakhshiev, N. G. *Dokl. Acad. Nauk SSSR* **1978**, *240* (*3*), 598.

[30] (a) Wittig, G.; Polster, R. *Ann.* **1956**, *1*, 599 (b) Wittig, G. *Naturwissenshaften* **1942**, *30*, 696.

[31] Cachet, H.; Fekir, M.; Lestrade, J. C. *Can. J. Chem.* **1981**, *59*, 1051.

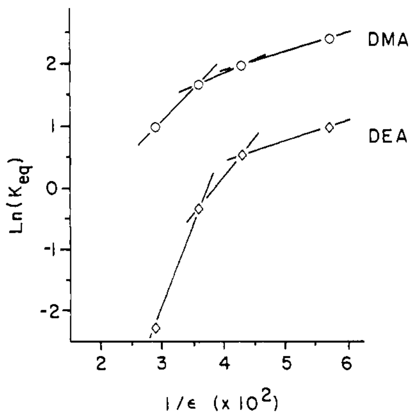


Figure 7. Plot of log (K_{eq}) vs. $1/\epsilon$ for the ketyl radical/radical anion equilibrium observed in the photoreduction of benzophenone by 1.0 M DEA and 1.0 M DMA. Solvents used are a series of nitriles. In order of decreasing dielectric constant they are as follows: acetonitrile, propionitrile, butyronitrile, and hexanenitrile. Data are from ref 11. K_{eq} = [ketyl radical]/[radical anion].

frequencies characteristic of the solvent molecule. Examination of the DME Raman lines centered at 847 cm^{-1} indicates a broadening in the presence of salt. These overlapping bands have been assigned to the following skeletal modes: C–O stretch, C–C stretch, and C–O–C bend.[21] These observations support previous suggestions[20] that increasing the salt concentration does not result in contact ion pair formation but merely increases the concentration of the solvent–salt complexes.

Structure of the Amine/Ketone Ion Pair. We have previously reported[11] that in acetonitrile the initial electron transfer from DEA to benzophenone results in the formation of a solvent-separated ion pair. These species diffuse together to form a contact ion pair, τ = 200 ps. These observations are based on absorption spectra associated with the radical anion in the different ion-pair forms. In the present study, identical spectral behavior is observed for the photolysis of benzophenone/DEA in DME, supporting the existence of the same types of ion-pair intermediates. On the basis of our previous study on ion-pair exchange phenomena,[10] the absorption of the radical anion at 690 nm was shown to arise from an equilibrium distribution of solvent-separated ion pair and contact ion pair (CIP:SSIP ≥ 5:1).

A better understanding of the equilibrium ion-pair distribution can be obtained by examining the relative effect of dielectric on the ion pair/radical pair equilibrium formed in the photoreduction of benzophenone by DEA and *N,N*-dimethylaniline (DMA). We have chosen to examine this equilibrium as a function of dielectric in a series of alkyl nitriles. In this way, the specific solvation of the nitrile group is preserved as the dielectric is changed. From previous work, it has been shown that proton transfer to form the benzhydrol radical occurs only from the contact ion pair.[11] When it is assumed that the energy of the ketyl radical is insensitive to changes in dielectric, the change in equilibrium constant, K_{eq}, with dielectric can be expressed as:[32]

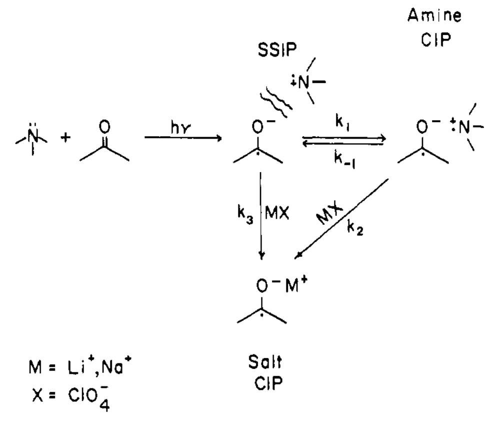
$$\frac{d(\ln K_{eq})}{d(1/\epsilon)} = \frac{N_0 e^2}{RT}\left(\frac{1}{2a_+} + \frac{1}{2a_-} - \frac{1}{D}\right)$$

where

$$K_{eq} = \frac{[\text{ketyl radical}]}{[\text{radical anion}]}$$

and a_+, a_-, and D are the radii of the cation and anion and the interionic distance, respectively. A plot of ln (K_{eq}) vs. $1/\epsilon$ for the photoreduction of benzophenone by DEA and DMA is shown in Figure 7. Since, for a given amine, the radii of the cation and anion are constant in the series of nitriles, the difference in response to dielectric must be the result of changes in the interionic distance.

Scheme I



Thus, the nonlinearity of the plots indicates a change in ion pairing. For the region between butyronitrile, ϵ = 23.2, and hexanenitrile, ϵ = 17.3, the same response is observed for photoreduction by both amines. However, between acetonitrile, ϵ = 34.5, and butyronitrile, the ion pair/radical pair equilibrium is more sensitive to a change in dielectric in the case of photoreduction by DEA than in the case of DMA. In the low dielectric limit, the similarity of the responses for the two amines indicates similar ion-pair structures are involved. Most probably, the equilibrium in these solvents lies exclusively in favor of the contact ion pair. The overall greater response observed in the case of DEA at high dielectric supports the conclusion that a greater percentage of solvent-separated ion pair exists in these system than in the corresponding DMA solutions. This conclusion is consistent with the relative stabilities of the two amine radical cations.

Due to the low dielectric of DME, one would predict that the contact ion pair would be more stable than the solvent-separated ion pair. However, the coordinative abilities of the ethereal oxygens could stabilize the amine radical cation resulting in the formation of some solvent-separated ion pairs. The exact equilibrium distribution in this solvent has not been determined.

Ion-Pair Exchange. Before we examine the effect of salt and solvent on the exchange process, it is important to clarify how the exchange process is being monitored. The time evolution of the transient absorption spectra of the radical anion of benzophenone shows a continuous change in the absorption maximum. The absorption bands corresponding to the salt and amine contact ion pairs are too broad to produce distinct peaks; thus only a gradual change in absorption maximum is expected. However, the existence of two distinct bands can be revealed by a study of bandwidth.[7,33] If two distict species are present in solution, one expects to observe a band broadening as one species converts into the other, followed by a band narrowing when only one species is present; the systems studied in this paper conform to this behavior. In addition, the transient absorption spectra observed have been shown to correlate with those predicted by coinvolving the absorption spectra of the two distinct ion-pair species.[11] Thus, although we have reported a time-dependent change in absorption maximum, this reveals information concerning the dynamics of the exchange process.

The possible mechanisms for ion-pair exchange between alkali perchlorates and the radical anion of benzophenone/radical cation of DEA ion pair are shown in Scheme I. In principle, exchange can occur from either of the possible amine/ketone ion-pair structures: the solvent-separated ion pair or the contact ion pair. For $NaClO_4$ in acetonitrile, several of these rates have previously been reported: $k_1 = 5 \times 10^9$ s^{-1},[10] $k_{-1} = 1 \times 10^9$ s^{-1} [estimated, see ref 11], $k_3 = 7.4 \times 10^8$ mol^{-1} s^{-1},[10] and $k_2 \ll k_3$.[10] For $NaClO_4$, exchange was only observed with the organic solvent-separated ion pair. However, in the presence of NaI (>97% contact ion pair in acetonitrile[34]), $k_2 \gg k_3$, and exchange was only observed with

---

[32] Denison, J. J.; Ramsey, J. B. *J. Am. Chem. Soc.* **1955**, *77*, 2615.

[33] Waack, R.; Doran, M. A.; Stevenson, P. E. *J. Am. Chem. Soc.* **1966**, *88*, 2109.

the organic contact ion pair. On the basis of the examination of several other exchange reactions, we found that the maximum rate of exchange was observed when the two ion pairs were of the same form.[10]

Since we have shown that the equilibrium structure of both $NaClO_4$ and $LiClO_4$ in DME and acetonitrile is predominantly the solvent-separated ion pair, the exchange reaction will preferentially occur with the organic solvent-separated ion pair, k_3. Thus for all reactions examined in this study, we will assume on the basis of our previous work[10] that $k_3[MX] \gg k_2[MX]$. The change in dynamics observed for the two salts in DME and acetonitrile must then be due to changes in the rates k_1, k_{-1}, and $k_3[MX]$.

For acetonitrile, the observed bimolecular rate of exchange with $NaClO_4$ indicates that $k_3[NaClO_4] < k_{-1}$ as the observed rate of exchange was dependent on salt concentration. Furthermore, the rate of exchange with $LiClO_4$ is slower by a factor of 5, and thus $k_3[LiClO_4] < k_3[NaClO_4]$. The difference in the overall rates of ion-pair exchange observed for equimolar $NaClO_4$ and $LiClO_4$ can be explained in terms of solvation energies. The larger shift to lower energy observed in the Raman analysis of acetonitrile salt solutions confirmed that lithium formed a tighter association with the solvent molecules than sodium. As a result, there will be a higher barrier associated with the desolvation of Li^+ than Na^+. For ion-pair exchange to occur, these ion–dipole forces must be overcome. Therefore, in acetonitrile, the rate-limiting step for ion-pair exchange is not the separation of the amine/ketone ion pair but the formation of the alkali contact ion pair, $k_3[LiClO_4] < k_3[NaClO_4] < k_{-1}$.

In the case of exchange with $LiClO_4$ in DME, the rate is found to be dependent on salt concentration. In addition, the overall exchange rate with $LiClO_4$ is observed to be slower than that with $NaClO_4$. This situation is analogous to that observed in acetonitrile and can be explained in terms of an increased activation energy for the desolvation of Li^+ compared to Na^+. The observed concentration dependence on the exchange rate with $LiClO_4$ indicates that the greater solvation of this cation has resulted in the rate of formation of the lithium contact ion pair being rate limiting in the exchange process, $k_{-1} > k_3[LiClO_4]$. However, in DME, the rate of exchange is observed to be independent of the concentration of $NaClO_4$ indicating that the rate-determining step is not the rate $k_3[NaClO_4]$. In terms of Scheme I, this would be manifested by the rate of formation of the sodium contact ion pair being faster than the rate of separation of the amine/ketone ion pair, $k_3[NaClO_4] > k_{-1}$ ($[NaClO_4] = 0.1–1.0$ M). The change in the relative ordering of the rates for the exchange process in DME and acetonitrile is due to one or both of the following: k_{-1}(DME) $<$ k_{-1}(acetonitrile) or the rate of desolvation of sodium in DME is faster than the rate of desolvation in acetonitrile, $k_3[NaClO_4]$(DME) $>$ $k_3[NaClO_4]$(acetonitrile).

These conclusions are confirmed by examining the rate of exchange in the presence of crown ether. The solvation of cations by DME is similar to that of the crown ethers. However, the complexation of alkali cations by linear polyethers is accompanied by a much more unfavorable entropy change than with the crowns.[7g] Thus the addition of crown should result in increased cation solvation and a higher activation barrier for the ion-pair exchange. In the presence of equimolar salt:crown concentration in acetonitrile, no ion-pair exchange is observed. Thus the addition of the crown ethers has slowed down the rate of exchange ($\tau >$ 1 μs), or prevented it entirely. In addition, the effect of cation solvation by a high dielectric solvent is exemplified by studying the ion-pair exchange in Me_2SO. Although Me_2SO is similar to DME in its donor ability,[25] no indications of exchange are observed in the first 250 ns following photolysis.

Summary. In conclusion we have examined solvent effects on the ion-pair exchange reactions between $NaClO_4$, $LiClO_4$, and the radical anion of benzophenone/radical cation of the DEA ion pair. Although exchange occurs from the solvent-separated ion pair for all systems examined, the rate of exchange is found to be very sensitive to the cation and solvent. In reference to Scheme I, the following conclusion were reached. (1) For exchange in acetonitrile, $k_3[LiClO_4] < k_3[NaClO_4] < k_{-1}$. (2) For exchange in DME, $k_3[NaClO_4] > k_{-1} > k_3[LiClO_4]$. In addition, we have shown that in order to fully understand the dynamics of ion-pair exchange reactions, one must understand the nature of the ion pairs involved as well as their interaction with the solvent.

Acknowledgment. This work is supported by a grant from the National Science Foundation, CHE-8117519, and the Henry and Camille Dreyfus Foundation.

Registry No. Benzophenone, 119-61-9; acetonitrile, 75-05-8; $PhNEt_2$, 91-66-7; $PhNEt_2$, 91-66-7; $NaClO_4$, 7601-89-0; $LiClO_4$, 7791-03-9; DME, 110-71-4; Na^+, 17341-25-2; Li^+, 17341-24-1; ClO_4^-, 14797-73-0.

---

(34) Richard Minasz, *Diss. Abstr., B* **1975**, *35* (*9*), 4393.

(35) Carvajal, C.; Tolle, K.; Smid, J.; Szwarc, M. *J. Am. Chem. Soc.* **1965**, *87*, 5548.