

Figure 6. SERS excitation profile for dielectric coated silver sphere in water with radial ratios $q = 0.5$ and coating dielectric constant (1) 1.77 (water), (2) 1 (air), (3) 3.06, (4) 4.0, and (5) 11.6. Raman shift is 1010 cm^{-1} . Raman dipoles form a monolayer on the Ag surface.

Figure 6 depicts the SERS excitation profiles for such dielectric-coated Ag spheres in water with $q = 0.5$ and coating dielectric constants $m_2^2 = 1, 3.06, 4.0,$ and 11.6 .⁵¹ In this case the Raman dipoles have been located at the interface between the silver core and the dielectric coating. There is a fivefold increase in the peak enhancement and a shift of the peak to longer wavelengths as m_2^2 increases from 1.77 (pure silver in water) to 4.0.

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Further increases in m_2^2 result in continued wavelength shift of the peak enhancement but not its magnitude. The excitation profile also depends sensitively upon the thickness of the dielectric layer as well as the actual distribution of the dipoles within the layer.⁵¹

Concluding Remarks

The classical electromagnetic model of colloid optics which is extended here to encompass SERS is able to account for the major experimental features of that phenomena. The electromagnetic field near a small metal particle is strongly enhanced at frequencies for which the incident radiation excites resonant surface plasmons within the particle. SERS occurs because of the coupling of the excitation of a Raman active molecule by this incident field with a similar resonance which occurs upon reradiation at the Raman shifted frequency.

The perturbation of electromagnetic fields near the surfaces of small particles is a sufficiently general phenomenon to affect other optical processes. Indeed, the methods of this *Account* may be extended to include four-wave mixing,^{52,53} coherent anti-Stokes Raman scattering (CARS),⁵⁴ and double resonance at dielectric surfaces.⁵⁵

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Picosecond Studies of Organic Photoreactions

JOHN D. SIMON and KEVIN S. PETERS*†

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

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Interest in the molecular motions associated with reactions in solution has sparked a rapid growth in the application of picosecond laser technology to the study of organic photochemical systems. Frequently, fast photochemical dynamics are discussed in terms of a

Kevin Peters received his B.S. from the University of Oklahoma. After obtaining his Ph.D. from Yale University in 1975, studying with Professor Ken Wilberg, he continued for a year as a postdoctoral fellow for Professor Fred Richards. He then began his work in picosecond spectroscopy during a postdoctoral appointment with Professor M. Applebury and Dr. Peter Rentzepis. In 1978 he was appointed to the faculty at Harvard University. He is currently Associate Professor of Chemistry at the University of Colorado. He is an Alfred P. Sloan Fellow and a Henry and Camille Dreyfus Teacher-Scholar.

John Simon received his B. A. from Williams College. Studying with Kevin Peters, he received his Ph.D. from Harvard in 1983. He is currently a postdoctoral fellow in Professor M. A. El-Sayed's group at U.C.L.A. and in Jan 1985, will join the faculty of the Department of Chemistry, University of California at San Diego.

“diffusion-controlled” regime.¹ Resulting in part from the limitations of various experimental techniques, there has developed, unfortunately, a common tendency to describe reaction dynamics in terms of diffusional properties, completely ignoring the question of coupling of molecular motions between reacting and solvent molecules. Since nanosecond flash photolysis is unable to resolve photochemical events faster than the rates associated with the diffusion of reactants in solution, this technique cannot be used to elucidate the molecular dynamics that occur once the reactive species have formed an “encounter pair”. Picosecond techniques, however, offer the time resolution needed to study the

† Alfred P. Sloan Fellow and Camille and Henry Dreyfus Teacher-Scholar.

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"microdynamics"² of the reaction process.

Several important intermolecular reactions (electron,³ proton,⁴ and hydride⁵) and intramolecular reactions (isomerization⁶ and photodissociation⁷) have been the subject of numerous picosecond studies. With more organic processes being scrutinized on the picosecond time scale, increasing attention is being paid to the role of solvent motion and its influence on reactions. As a result, for a variety of organic photochemical reactions, the "diffusion-controlled" models are being replaced by new molecular pictures incorporating solvation dynamics. Although these models are simplistic in their scope, one must remember that they represent the beginning of our unravelling of the molecular aspects of chemical processes. Complimenting statistical mechanics and kinetic theory,⁸ which are developing new molecular models of rate processes, picosecond spectroscopy has the potential to play a major role in enhancing our understanding of reaction dynamics in solution.

In this Account, we will focus on several areas of organic molecular photochemistry. Our goal is to emphasize the unique contribution picosecond studies have made to our overall understanding of reaction dynamics on the molecular level. It is not within the scope of this treatment to address the technological aspects of the field. This has been done adequately by several researchers, and the reader is referred to the literature for a discussion of experimental details.⁹

Photoisomerization: What Comprises the Barrier to Rotation?

One of the most intensely studied photochemical reaction has been the cis-trans isomerization of *trans*-stilbene. Though many aspects of the isomeri-

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zation process were elucidated prior to picosecond laser studies,¹⁰ several important questions relating to the energy barrier to isomerization and the coupling of solvent motion to the reaction coordinate remained unanswered.

The picosecond laser studies of Hochstrasser and co-workers^{6a-c} have contributed much to our understanding of the excited-state dynamics of *trans*-stilbene in solution. Excitation of *trans*-stilbene dissolved in benzene by an 8-ps pulse at 265 nm produced a strong transient absorption with a maximum at 585 nm. Successive absorption spectra recorded at 12, 28, and 53 ps after photolysis revealed a narrowing in the absorption band profile with an exponential time constant of 25 ps. In addition, the intensity of the transient absorption decays with an exponential time constant of 90 ± 5 ps. The transient absorption band was assigned to an $^1S_n \leftarrow ^1B$ transition. The 90-ps decay was attributed to the formation of an intermediate twisted about the ethylenic double bond. In addition, the narrowing of the absorption band was proposed to result from vibrational relaxation within the first excited singlet state. It is reasonable to postulate that during the 25 ps in which *trans*-stilbene is vibrationally hot, an increased rate of isomerization could be observed. This would be manifested in a nonexponential decay of the transient absorption; however, the data presented are found to correspond to a single exponential time decay of 90 ps. Thus, it appears that the excess vibrational energy does not find its way into the active torsional mode responsible for isomerization.

The magnitude of the barrier to excited-state isomerization of *trans*-stilbene has been the subject of gas, solution, and molecular beam studies. The rate of isomerization is found to be independent of excitation wavelength in solution. However, in the gas-phase excitation at 262 nm (8000 cm^{-1} excess energy) and 287 nm (5200 cm^{-1}) results in an excited-state lifetime of 15 and 55 ps, respectively,^{6b} while excitation of the 0,0 band leads to a lifetime of 1.6 ns. From these data, the barrier to isomerization was placed between 1000 and 2000 cm^{-1} . More recently, Zewail and co-workers have measured an intrinsic barrier of 1200 cm^{-1} by using picosecond excitation of jet-cooled collision-free *trans*-stilbene.^{6e}

The Effect of Solvent on Isomerization Barriers

As a molecule undergoes isomerization in solution, it will experience forces that are absent in the gas phase. First, one must consider that the intrinsic intramolecular barrier will be modified by static interactions with solvent molecules.¹¹ However, even more important is the dynamic interaction between the isomerizing molecule and the surrounding solvent molecules. In order to analyze these reactions using transition-state theory, one assumes that each crossing of the barrier top leads to product formation.¹² However, "collisional buffeting"¹³ may effect repeated barrier crossings prior to the ultimate formation of product. Depending on the microdynamics of the isomerization process, the rate

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of product formation could be substantially less than that predicted by transition-state theory.

Currently, the standard theoretical framework used to interpret isomerization dynamics is based upon the work of Kramers.¹⁴ Using the steady-state Fokker-Planck equation to describe the motion of a particle across the barrier in the presence of friction, Kramers derived the following rate equation

$$k = \omega_r / \omega_B \tau_v \{ [1 + (2\omega_B \tau_v)^2]^{1/2} - 1 \} \exp(-E_0/RT)$$

where ω_r is the frequency of the reactant well, ω_B is the curvature at the barrier top, τ_v is the velocity relaxation time of the reaction coordinate, and E_0 is the activation energy. The friction experienced by the molecule as it passes through the region near the top of the barrier is assumed to be linearly related to the velocity relaxation time.^{6g} Furthermore, with use of hydrodynamics to model the friction, the reciprocal of the velocity relaxation time is set proportional to the bulk solvent viscosity.^{6g} A comparison of the rate derived from transition-state theory to that calculated by using Kramers' approach enables one to examine the dynamic interaction between the solvent and isomerizing molecule.

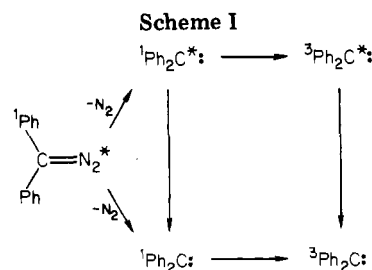
For calculation of the rate according to transition-state theory, the magnitude of the intrinsic barrier must be determined. An elegant experimental method by which one can determine the barrier height was developed by Fleming and co-workers.^{6f-h} The rate of isomerization was modeled according to the equation

$$k = F(\eta) \exp(-E_0/RT)$$

where E is the intrinsic barrier to isomerization and only $F(\eta)$, the preexponential factor, contains the viscosity dependence. The key to the analysis lies in the determination of E_0 . Fleming demonstrated^{6f-h} that one could determine the magnitude of the barrier by examining the temperature dependence of the isomerization rate at constant viscosity. For diphenylbutadiene, the "isoviscosity plots" yielded an activation energy of 4.7 ± 0.5 kcal/mol; this value is less than that measured by a normal Arrhenius approach, $E_a = 5.6$ kcal/mol in hexane. Using the determined intrinsic barrier, it was possible to correlate the preexponential factor, $F(\eta)$, as a function of viscosity and compare these results to those predicted by Kramers.

Many important conclusions were derived from these studies. Specifically, for both diphenylbutadiene and 3,3'-diethyloxadicarbocyanine iodide (DODCI), the Arrhenius activation energies derive a significant contribution from the solvent viscosity. For diphenylbutadiene in linear alkane solvents and DODCI in linear alcohol solvents, the preexponential factor is *not* well characterized by Kramers' theory using a hydrodynamic model for the friction. Similar results have recently been reported for stilbene.⁶ⁱ This perhaps surprising result supports the recent proposal that a frequency-dependent friction must be taken into account as the bulk viscosity (zero frequency component) may not adequately describe the friction felt by the isomerizing molecule.⁶ⁱ Consequently, further picosecond investigations as well as theoretical studies are needed before we can fully understand the molecular dynamics of isomerization in solution.

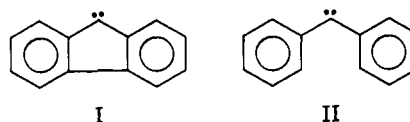
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Photochemistry of Diazo and Azo Compounds

Diazo and azo compounds provide convenient routes for the photogeneration of carbenes and diradicals. The dynamics and physical properties of these reactive intermediates have attracted both experimental and theoretical interest.¹⁵ Although significant advances have been made in the determination of ground-state spin configurations, our understanding of the dynamics of these molecules has been hampered by an inability to resolve the details of the photodissociation event. Using nanosecond flash photolysis, one finds that the photoelimination of nitrogen (as well as any intersystem crossing dynamics in the resulting diradical or carbene) occurs within the time resolution of the experiment. Through a combination of picosecond absorption and fluorescence, the spin dynamics and photodissociative pathways of a wide variety of diazo compounds have now been elucidated. These rate data have significantly enhanced our understanding of the differences in the reactivities of the singlet and triplet states of the resulting carbenes.

In the field of carbene chemistry the major research efforts have focussed on fluorenylidene (I)^{7h} and diphenylmethylene (II).^{7c-e} Picosecond studies have revealed that although these two carbenes are similar in structure, their reactivity and spin dynamics vary significantly.



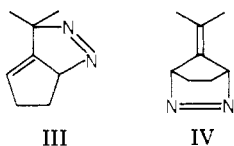
Photolysis of the diazo precursors to I and II results in efficient formation of carbenes and nitrogen. On the picosecond time scale, emission is observed when diphenyldiazomethane is photolyzed at 266 nm. From time-resolved fluorescence quenching experiments, Eisenthal and co-workers have demonstrated that the emission is derived from the excited triplet carbene.^{7c} This conclusion indicates that two competitive dissociative pathways are available to the excited diazo compound (Scheme I). Furthermore, the reactivity of the excited triplet carbene was found to be similar to that of singlet diphenylcarbene, preferentially attacking the O-H bond rather than the C-H bonds of alcohols.^{7e} Picosecond laser-induced fluorescence^{7d} was used to determine the rate of intersystem crossing from the initially formed singlet carbene to the ground-state

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triplet carbene, $k_{gt} = (9.1 \pm 1) \times 10^9 \text{ s}^{-1}$. This rate, combined with the rate of carbene quenching by methanol, enabled the determination of the singlet-triplet splitting. In acetonitrile, the energy gap between the singlet and triplet carbene is $5.1 \pm 1 \text{ kcal/mol}$. This value is sensitive to the solvent.^{7d}

Photolysis of 9-diazafluorene in acetonitrile results in the formation of triplet fluorenylidene with a first-order rise time of $280 \pm 90 \text{ ps}$.^{7h} Similar behavior is observed in other solvents, although slight variations in rise time are observed. As triplet fluorenylidene is not formed instantaneously subsequent to photolysis, two reasonable precursors can be proposed: singlet fluorenylidene and triplet 9-diazafluorene. Unlike diphenyldiazomethane, the precursor to triplet fluorenylidene has not unambiguously been determined. However, recent chemical and spectroscopic evidence presented by Schuster and co-workers supports the intermediacy of singlet fluorenylidene.^{7h} The observed rise time of triplet fluorenylidene would then correspond to the intersystem crossing rate from singlet to triplet fluorenylidene, $k_{gt} = 2.5 \times 10^9 \text{ s}^{-1}$, in acetonitrile. This rate is a factor of 4 slower than that observed for diphenylcarbene. In addition (through quenching studies) Schuster has determined that the singlet-triplet splitting in fluorenylidene is at most 1.1 kcal/mol .^{7h} In comparison to diphenylcarbene, this would result in a 150-fold difference in the equilibrium population of the respective singlet carbenes, explaining in part the observed enhanced reactivity of fluorenylidene with a variety of compounds.

Rentzepis and co-workers have examined the formation of substituted trimethylenemethanes (from III and IV).^{7a,b} These studies suggest that the photoelimination



of nitrogen from the excited azo molecule is a concerted process unlike the stepwise dissociation proposed for their thermal reactions. Intersystem crossing rates as well as reaction rates for various quenchers were examined.

Endoperoxides

Evidence supporting the adiabaticity of the photodissociation of oxygen from endoperoxides of anthracene has largely rested on the detection of chemiluminescence from singlet oxygen.¹⁶ Using picosecond spectroscopy to directly observe the primary photofragments following excitation of the endoperoxide of 1,4-dimethyl-9,10-diphenylanthracene, Eisenthal and co-workers observed efficient formation of excited 1,4-dimethyl-9,10-diphenylanthracene and singlet oxygen within 5 ps of excitation.^{7f,g} These results directly verified that the photoelimination is an adiabatic process. In addition, thermodynamic arguments conclusively showed that singlet oxygen could not be formed in the $^1\Sigma_g^+$ state and hence must be formed in the $^1\Delta_g^+$ state. Rise time data under varying conditions indicate that the photoelimination of oxygen might be a stepwise

process, although this question has not been definitely answered.^{7g}

Ion-Pair Dynamics

Ion pairs are frequently invoked as intermediates in organic reactions.¹⁷ Recent studies of the reactions of ketones have indicated that single electron transfer and hence ion-pair formation may play an important role in Wittig,¹⁸ Grignard,¹⁹ hydride,⁵ and condensation reaction.²⁰ However, due to the fast rate of electron-transfer processes, the microdynamics of the subsequent ion pairs are difficult to study. The remainder of this Account will focus on our studies in these and related areas.

Several types of ion pairs can exist in solution. The two most common ion pairs are the contact ion pair and solvent-separated ion pair. Ion-pair aggregation has also been observed, but this topic is beyond the scope of our discussion.¹⁷ There has been extensive spectroscopic work aimed at elucidating the thermodynamic properties of various ion-pair forms.²¹ Reaction rates, as well as overall product distributions, are sensitive to the particular ion-pair structures involved.²² However, despite the wealth of information that has been obtained on these intermediates, the dynamics and solvent effects upon the rates of interconversion between various ion-pair forms in solution have remained virtually unstudied. Picosecond technology can be used to examine these important processes.

Before we can adequately address the effect of solvent and counterions on ion-pair reactions, it is necessary to choose and characterize a given reaction that involves ion-pair intermediates. For this purpose we examined the photoreduction of benzophenone by aromatic amines. From nanosecond quenching studies, Cohen,²³ Davidson,²⁴ and Wagner²⁵ proposed that the reaction proceeds by rapid formation of a charge-transfer complex, followed by proton transfer to give the ketyl and amine radicals. Using *N,N*-diethylaniline as a quencher, Magata and co-workers²⁶ observed formation of the benzophenone radical anion on the picosecond time scale in acetonitrile. In benzene, ketyl radical formation was also observed, substantiating the proposed mechanism. Despite the depth of our understanding of this reaction, prior to our picosecond studies several significant questions remained unanswered. It was not known whether a specific spatial relationship between the ketone and amine is necessary for electron transfer to occur. The relative contributions of first or second solvent shell electron transfer had not been addressed. In addition, assuming electron transfer did occur from outside the first solvent sphere, the question of whether contact ion-pair formation is necessary prior to proton

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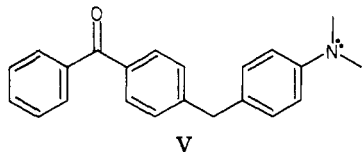
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transfer remained unanswered.

Photoreduction of benzophenone by 1.0 M diethylaniline in acetonitrile results in complete electron transfer within 25 ps to form the radical anion of benzophenone with an absorption maximum of 720 nm. From 25 to 400 ps following photolysis, we observed a shift in absorption maximum from 720 to 690 nm.²⁷ In order to ascertain the source of the time-dependent hypsochromic shift, we examined the corresponding intramolecular system 4-(*p*-(dimethylamino)benzyl)-benzophenone, V²⁷ (DMABB). For this molecule, the



photostimulated electron transfer results in the formation of a charge-transfer intermediate that is analogous to the intermolecular solvent-separated ion pair. The methylene bridge prevents collapse to the corresponding contact ion pair. Photolysis of DMABB in acetonitrile results in rapid electron transfer (<20 ps) to form the radical anion with an absorption maximum of 720 nm. Unlike the intermolecular system, no shift in absorption maximum is observed.²⁸ These studies suggest that the spectral shift observed for the intermolecular system must correspond to reorganization of the ion pair on the molecular level. Based on equilibrium studies of benzophenone-amine ion pairs, we concluded that the hypsochromic shift arises from the formation of a contact ion pair from the initially formed ion-pair structure. However, from our experiments, we cannot determine the geometry of the primary ion pair. It is possible that the 720-nm absorption band could arise from either a structure in which a solvent molecule separates the two ions (solvent-separated) or a non-contact structure in which the diethylaniline radical cation and benzophenone radical anion are cosolvated but must undergo rotational diffusion to attain the equilibrium contact ion-pair geometry.

Two important conclusions resulted from these studies. First, as the energetically more stable ion pair, the contact ion pair, is not initially formed in acetonitrile, the electron transfer must occur over distances larger than the van der Waals' contact distance. There have been several recent reports supporting electron-transfer distances up to 15 Å.^{29,30} Second, the proton transfer is observed to occur only after contact ion pair formation; thus, proton transfer occurs only over short distances in these systems.

Dynamics of Hydrogen Bond Formation

The distribution among ion-pair forms is sensitive to the donor and acceptor properties of the solvent. Alcohols are found to favor formation of solvent-separated ion pairs by virtue of their ability to both hydrogen bond to anions and donate electrons to cations.³¹ In

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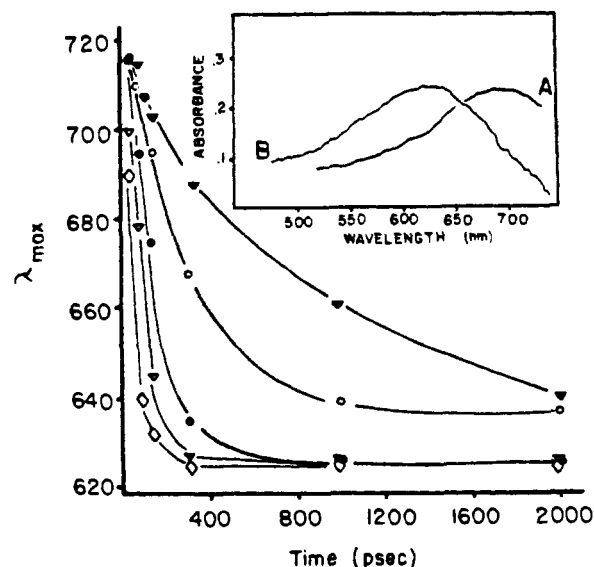
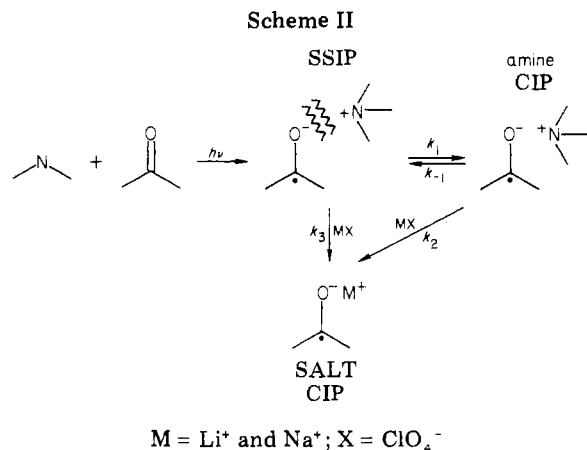


Figure 1. Time evolution of the absorption maximum of the radical anion of benzophenone in ethanol and ethanol-acetonitrile mixtures: \diamond , neat ethanol; ∇ , 10 M ethanol (for $t > 800$ ps, the absorption bands are broader to the red relative to neat ethanol); \bullet , 5 M ethanol; \circ , 2 M ethanol; ∇ , 1 M ethanol. Insert: transient absorption spectra of the radical anion of benzophenone: A, contact ion pair with the diethylaniline radical cation in acetonitrile; B, the hydrogen-bonded radical anion in neat ethanol.

order to probe the molecular dynamics of solvation in protic media, we studied the photolysis of benzophenone and diethylaniline in ethanol and ethanol-acetonitrile mixtures.³²

Photolysis of benzophenone-diethylaniline in neat ethanol resulted in immediate formation of a contact ion pair, $\lambda_{\max} = 690$ nm. The initial formation of a contact ion pair in ethanol, as opposed to the solvent-separated ion pair observed in acetonitrile, was attributed to photolysis of a ground-state complex between the amine and ketone in the alcoholic solvent.³² However, between 50 and 300 ps following photolysis, the radical anion absorption band shifts from 690 to 625 nm. No further shifting is observed from 300 ps to 50 ns following photolysis. The band at 625 nm has previously been assigned to the hydrogen-bonded benzophenone radical anion.³³ Thus, the dynamics entail the disruption of the contact ion pair by solvent molecules to form the thermodynamically more stable hydrogen-bonded ion. In order to elucidate a molecular picture for the solvation dynamics, we determined the rate of hydrogen bond formation in acetonitrile-ethanol mixture. The results are shown graphically in Figure 1. Deconvolution of the absorption data revealed that the process was second order in ethanol monomer concentration, with a termolecular rate constant of $(4.7 \pm 0.5) \times 10^8 \text{ mol}^{-2} \text{ s}^{-1}$.³² Studies with 2,2,2-trifluoroethanol also revealed the importance of monomer alcohol in the separation process. The intermolecular rate constant reveals that two molecules of ethanol are involved in the separation of the contact ion pair. Presumably one ethanol hydrogen bonds to the anion while the second ethanol stabilizes the cation. The thermodynamic barrier to hydrogen bond formation was examined through temperature studies. No enthalpy of activation was found, $\Delta H^\ddagger = 1.0 \pm 1.0$ kcal/mol; the rate of sep-

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ation was found to be controlled by an entropy of activation, $\Delta S^\ddagger = -20 \pm 2$ eu.³²

The Special Salt Effect

The influence of alkali cations on the reduction of carbonyl compounds had been the subject of extensive investigation.³⁴ The effect of added salt on reaction rates is usually discussed in terms of either the normal salt effect or the special salt effect.³⁵ The normal salt effect can be accounted for by considering the changes in polarity of the solvating media upon the addition of salt. The special salt effect, on the other hand, requires a molecular interpretation. Based on studies of the effect of added lithium perchlorate on the rate of solvolysis of alkyl arenesulfonates, Winstein concluded that the salt accelerated the rate by undergoing an ion-pair exchange with the solvent-separated ion pair formed by heterolysis of the sulfonate. Such an exchange prevents the initially formed solvent-separated ion pair from returning to the sulfonate precursor.³⁶ Although Winstein concluded that the exchange reaction involved the solvent-separated ion pair, ion-pair exchange could occur, in principal, with either the contact or solvent-separated form³⁷ (Scheme II). One would expect that the mechanism of exchange, as well as the rate of exchange, would depend not only on the types of ion pairs involved but also on the specific interaction that exists between the ion and the surrounding solvent molecules.

The ion-pair intermediates resulting from the photolysis of both DMABB and benzophenone-diethylaniline system in acetonitrile can be used to elucidate the microdynamics of ion-pair exchange. The salts NaClO₄ and NaI were chosen because of their propensity to form solvent-separated ion pairs (>99%)³⁸ and contact ion pairs (>90%),³⁹ respectively, in acetonitrile. Our studies revealed that the rate of exchange is indeed sensitive to the ion-pair structure. The rate of exchange between two contact ion pairs, NaI and

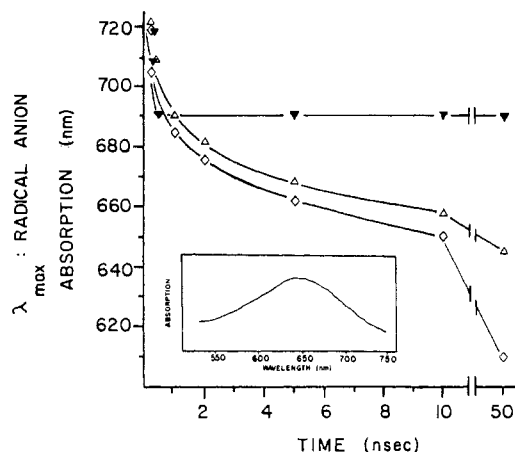


Figure 2. Time evolution of the absorption maximum of the radical anion of benzophenone in acetonitrile salt solutions: \blacktriangledown , no salt; Δ , 0.1 M NaClO₄; \diamond , 0.1 M LiClO₄. Insert: transient absorption spectrum of the sodium-benzophenone radical anion contact ion pair in acetonitrile.

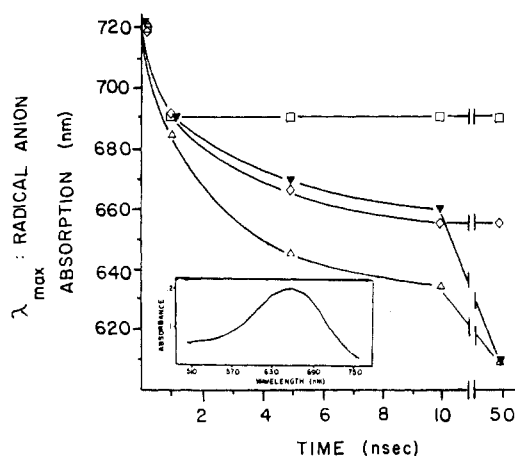


Figure 3. Time evolution of the radical anion of benzophenone absorption maximum in 1,2-dimethoxyethane salt solution: \square , no salt; \diamond , 0.1–1.0 M NaClO₄, \blacktriangledown , 0.1 M LiClO₄, Δ , 0.5 M LiClO₄. Insert: transient absorption spectrum of the sodium-benzophenone radical anion contact ion pair in dimethoxyethane.

benzophenone-diethylaniline, is identical with the rate of exchange involving two solvent-separated ion pairs, NaClO₄ and DMABB, $k_{\text{exchange}} = (7.3 \pm 0.7) \times 10^8$ mol⁻¹ s⁻¹. However, exchange between a contact and solvent-separated ion pair, NaI and DMABB, was found to be slower by over 1 order of magnitude. Thus the rate of ion-pair exchange is sensitive to the ion-pair structure with a maximum rate occurring between ion pairs of the same structure.

Solvent Effects on Ion-Pair Exchange

Ideally, one would like to examine the exchange process in solvents of both high and low dielectric, possessing both weak and strong affinities for cations and anions. In an attempt to elucidate the role of solvent interaction in the exchange mechanism, we have studied the dynamics of exchange between the intermolecular benzophenone-diethylaniline system and NaClO₄ and LiClO₄ in acetonitrile, 1,2 dimethoxyethane, and dimethyl sulfoxide. The pertinent results are shown in Figures 2 and 3. Raman,⁴⁰ NMR^{40,41} and

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dielectric relaxation⁴² studies clearly demonstrate that both salts exist predominantly (>95%) in the solvent-separated form in the solvents studied. On the basis of the rates of ion-pair exchange presented above, these salts will undergo preferential exchange with the solvent-separated ion pair benzophenone radical anion–diethylaniline radical cation. Thus for all of the reactions examined, we can assume that $k_3 \gg k_2$ (Scheme II). The change in dynamics observed for the two salts must be due to changes in the rates k_1 , k_{-1} , and k_3 .

For the acetonitrile studies, the observed bimolecular rate of exchange with Na^+ (<1 M) indicates that $k_3[\text{NaClO}_4] < k_{-1}$.^{40a} Furthermore, the rate of exchange is slower in the case of Li^+ . The difference in rate observed for the two salts can be accounted for by the difference in solvation energy. Raman studies indicate that lithium interacts more strongly than sodium with acetonitrile solvent molecules.^{40a} 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, k_{-1} , but the desolvation of the alkali cation.

Comparing exchange rates of Li^+ and Na^+ in dimethoxyethane, the rate of exchange is independent of the concentration of Na^+ but dependent on Li^+ concentration.^{40a} The change in relative ordering of the exchange rate in dimethoxyethane and acetonitrile is due to one or both of the following: $k_{-1}(\text{dimethoxyethane}) < k_{-1}(\text{acetonitrile})$ or the rate of sodium desolvation is faster in dimethoxyethane than in acetonitrile, $k_3[\text{NaClO}_4](\text{dimethoxyethane}) > k_3[\text{NaClO}_4](\text{acetonitrile})$.

In dimethyl sulfoxide, no exchange is observed between NaClO_4 and the amine–ketone ion pair. Al-

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though dimethyl sulfoxide is similar in donor number to dimethoxyethane, the above results indicate that the exchange process is also sensitive to the polarity of the solvating media.^{40a}

The importance of ion-pair reactions in organic chemistry necessitates an understanding of these processes on the molecular level. The above studies have enabled us to begin examining the effect of solvation on ion-pair dynamics. However, we still cannot accurately relate the measured kinetic data to specific solvent interactions. All of the data discussed in this Account clearly demonstrate that *molecular interactions* between solvent and reacting molecules influence the energetics and kinetics of molecular transformations. Further picosecond studies are required in order to more fully understand the “microdynamics” of chemical processes.

Concluding Remarks

The experimental studies described above demonstrate that picosecond spectroscopic techniques can result in a better understanding of the molecular details associated with organic photoreactions. However, a complete understanding of chemical transformations on the microscopic level rests on advances in both picosecond kinetic techniques as well as in the theory of reaction processes. While, in principle, theoretical approaches are capable of providing a complete picture of the molecular motions in reaction dynamics, only experiment can sufficiently test and give us confidence in these theoretical predictions. Accompanying further improvements in picosecond technology and spectroscopies, a better understanding of the molecular details of chemical reactions is sure to emerge.

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Flash Photolysis Studies of Carbenes and Their Reaction Kinetics¹

D. GRILLER,* A. S. NAZRAN, and J. C. SCAIANO*

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

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The basic principles of carbene chemistry were established in the 1950s by ingenious studies of their reaction products.² However, measurements of abso-

David Griller was born in 1948 and received his B.Sc. and Ph.D. degrees from University College London. He is a research officer at the Division of Chemistry of the National Research Council of Canada. His research interests focus on reactive intermediates and EPR spectroscopy.

A. S. Nazran was born in India in 1948. He received his B.Sc. and Ph.D. degrees at Queen Elizabeth College, University of London. He is presently a Research Associate at the National Research Council of Canada, and his research interests focus on free radical and carbene chemistry.

J. C. Scaliano was born in Buenos Aires, Argentina, in 1945 and received his B.Sc. from the University of Buenos Aires and his Ph.D. from the University of Chile. He is a research officer at the Division of Chemistry of the National Research Council of Canada. His research interests focus on kinetic studies of photochemical and free radical processes.

lute rate constants for carbene reactions followed very much later. In 1976, Closs and Rabinow³ measured the first absolute rate constants for the reaction of a carbene in solution by using conventional flash photolysis. With this technique, the measurements were restricted to microsecond time resolution. However, with the advent of the laser flash photolysis technique, nanosecond time resolution became widely available and caused a resurgence of interest in the kinetics of carbene reactions.

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