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Solvent Effects on the Picosecond Dynamics of the Photoreduction of Benzophenone by Aromatic Amines

John D. Simon and Kevin S. Peters*

Contribution from the Department of Chemistry,
Harvard University, Cambridge, Massachusetts 02138. *Received January 13, 1981.*
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Abstract: Solvent effects on the primary processes in the photoreduction of benzophenone by *N,N*-dimethylaniline and *N,N*-diethylaniline have been studied by using picosecond absorption spectroscopy. It has been found that the photoreduction proceeds by rapid electron transfer to form the solvent-separated ion pair. This is followed by diffusion to form a contact ion pair. Subsequent to contact ion-pair formation, proton transfer is observed. Solvent effects on the ion-pair intermediate indicated a dielectric dependent equilibrium between the contact ion pair and the ketyl radical.

Since Menschutkin's[1] initial observations, the role of the solvent in the dynamics of organic reactions has been an area of active research. This has resulted in the development of an extensive literature probing solvent effects both experimentally and theoretically.[2] But even today our understanding of solvent effects on organic reaction mechanisms is only qualititative. Due to our inability to isolate the many intermediates in a given reaction sequence, only net solvent effects upon the dynamics and product distribution are observed. An ideal approach to the study of medium effects is the resolution of each component of the chemical reaction, enabling one to investigate the solvent dependence of each species separately. In this paper we employ picosecond absorption spectroscopy to examine solvent effects on the dynamics of the photoreduction of benzophenone by *N,N*-dimethylaniline and *N,N*-diethylaniline. The time resolution of our experiment enables us to resolve and study each intermediate in the reduction process.

During the past 15 years the mechanism for the photoreduction of benzophenone by aliphatic and aromatic amines has been an active area of research. Based upon photoreduction quantum yields and fluorescence quenching studies, Cohen[3] and Wagner[4] first proposed that the photoreduction of aromatic ketones by amines proceeds by rapid formation of a charge-transfer complex followed by a proton transfer to generate the benzhydrol and amine radicals. This proposal has received substantial support. We have recently reported[5] the direct observation of electron transfer followed by proton transfer for the photoreduction of benzophenone by 3.0 M triethylamine.

Though the basic mechanism for the photoreduction of aromatic ketones by amines has been established, many significant questions remain unanswered. It is not known whether a specific spatial relationship between the ketone and the amine is necessary for electron transfer to occur. The question of first or second solvent shell electron transfer has also not been adequately addressed; nor have the dynamics of the proton transfer been examined. If electron transfer does occur from an amine not directly involved in solvating the carbonyl moiety of the ketone, can the proton transfer directly or is it necessary for a contact ion pair to form between the radical anion and the amine cation prior to transfer? In this paper we will address these questions.

Experimental Section

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

Table I. Dielectric (ϵ) Dependence of K_{eq}[a]

solvent	K_{eq}- (DMA)[b]	K_{eq}- (DEA)[b]	ϵ
acetonitrile	2.7	0.1	34.5
propionitrile	5.4	0.7	27.8
butyronitrile	7.3	1.7	23.2
hexanenitrile	10.8	2.7	17.3
acetonitrile[c]	2.6	1.8	34.5

[a] K_{eq} = (ketyl radical/radical anion). [b] Error in measurement ±0.2. [c] [amine] = 5.0 M, K_{eq} determined 14.2 ns after photolysis.

Freshly distilled *N,N*-dimethylaniline (Fisher) and *N,N*-diethylaniline (Aldrich) were used. Benzophenone (MCB) was recrystallized from ethanol. 1,4-Diazabicyclo[2.2.2]octane (Aldrich) was purified by sublimation. Acetonitrile (Mallinckrodt), propionitrile (Aldrich), butyronitrile (Aldrich), and hexanenitrile (Aldrich) were used without further purification.

Results

Transient absorption spectra for the photoreduction of benzophenone by 1.0 M *N,N*-diethylaniline (DEA) and 1.0 M *N,N*-dimethylaniline (DMA) are shown in Figure 1. Upon photolysis of 0.25 M benzophenone and 1.0 M DEA (DMA) we observe concomitant with the decay of triplet benzophenone (λ_{max} = 525 nm), the rapid transfer of the electron to form the radical anion of benzophenone (λ_{max} = 715 nm). For photoreduction by 1.0 M DMA and 1.0 M DEA, the rate of electron transfer is 3.6×10^{10} and 4.2×10^{10} s^{-1}, respectively. Subsequent to electron transfer, proton transfer to form the ketyl radical (λ_{max} = 545 nm) is observed. The rate of proton transfer for photoreduction by 1.0 M DMA is 2.0×10^9 s^{-1} (k_h). The transient absorption spectrum does not change from 2 to 10 ns following photolysis, indicating that an equilibrium between the ketyl radical and radical anion has been achieved in both systems. The equilibrium between the ketyl radical and radical anion for photoreduction by 1.0 M DEA lies strongly in favor of the radical anion and prevents us from determining the rate of proton transfer in this system (Table I).

Examination of the photoreduction of benzophenone by 5.0 M DEA (DMA), we observe a greater rate of electron transfer relative to that found for photoreduction by 1.0 M amine. At 35 ps after photolysis only the radical anion of benzophenone is observed in solution. The absorption maximum of this species is found to be red-shifted (λ_{max} = 725 nm) from that observed for 1.0 M amine. In addition the rate of proton transfer for 5.0 M DMA is found to be slower by a factor of 4, $k_h = 5.0 \times 10^8$ s^{-1}. For photoreduction by 5.0 M DEA we observe a shift in the ketyl radical/radical anion equilibrium in favor of the ketyl radical (Table I). For photoreduction by both 5.0 M DEA and 5.0 M

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(1) Menschutkin, N. *Z. Phys. Chem.* **1890**, *5*, 589.

(2) Reichardt, C. "Solvent Effects in Organic Chemsitry"; Verlag Chemie: New York, 1979.

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

(4) (a) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1. (b) Wagner, P. J.; Leavitt, R. A. *J. Am. Chem. Soc.* 1973, *95*, 3669. (c) Wagner, P. J.; Lam, H. M. H. *Ibid.* **1980**, *102*, 7566.

(5) Shaefer, C. G.; Peters, K. S. *J. Am. Chem. Soc.* **1980**, *102*, 7566.

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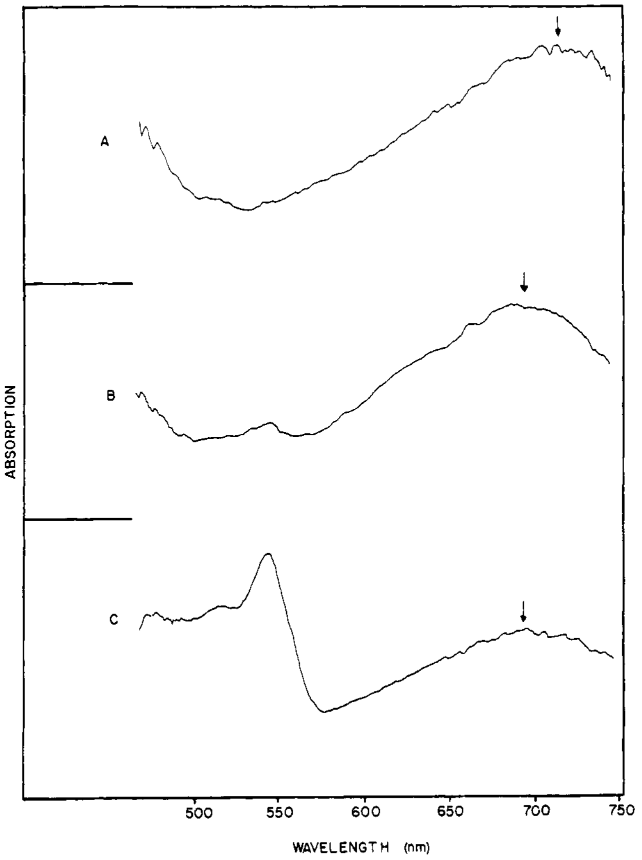

Figure 1. Transient absorption spectra for the photoreduction of benzophenone by DMA and DEA: A, 0.25 M benzophenone/1.0 M DEA in acetonitrile at 35 ps after photolysis; B, 0.25 M benzophenone/1.0 M DEA in acetonitrile at 300 ps after photolysis; C, 0.25 M benzophenone/1.0 M DMA in acetonitrile at 2 ns after photolysis.

DMA we observe a decay ($k = 5 \times 10^8$ s^{-1}) in the absorption intensity of the radical anion to 50% of its initial intensity.

In order to determine the above rate constants, we determined the relative extinction coefficients of the transients species. The extinction coefficient of triplet benzophenone was taken to be 7630 M^{-1} cm^{-1}. We have previously reported[5] that the ratio of the extinction coefficient of the triplet absorption to that of the ketyl radical is approximately 2.4:1 resulting in an extinction coefficient of 3220 M^{-1} cm^{-1} for the ketyl radical. To determine the relative extinction coefficient of the radical anion, we compared transient absorption spectra obtained at 2 ns after photolysis for solutions of 0.25 M benzophenone and 0.25 M benzophenone/1.0 M 1,4-diazabicyclo[2.2.2]octane [Dabco] in acetonitrile.[6] We observe equal intensities for the triplet and radical anion absorptions which, assuming a quantum yield of 1.0 for anion formation, indicate a similar extinction coefficient for these two species. With use of these extinction coefficients the transient absorption spectra were deconvoluted to obtain the relative concentrations of the transient species. These concentrations were then fitted to a series of first-order reactions in order to obtain the rate constants for the electron- and proton-transfer processes.

For photoreduction of benzophenone by 1.0 M DEA (DMA) we observe a blue shift in the absorption maximum of the radical anion from 715 to 690 nm with a half-life of 200 ± 50 ps (Figure 1A,B). This shift of 490 cm^{-1} is indicative of contact ion-pair formation between the radical anion of benzophenone and the amine cation. Similarly, a blue shift from 725 to 690 nm is observed in the absorption maximum of the radical anion for photoreduction by 5.0 M DEA (DMA). The observed shift has a half-life of 800 ± 200 ps.

Table II. Electron-Transfer Rates for the Dabco/Benzophenone System

solvent	ϵ	$10^{10}k_{et}$[a]
benzene	2.28	1.3
chloroform	4.81	.37
THF	7.58	1.1
butyronitrile	23.2	1.3
propionitrile	27.8	1.1
acetonitrile	34.5	1.7
Me_2SO	46.7	0.95

[a] Error in measurement ±10%.

Solvent effects on the equilibrium between the ketyl radical and radical anion were also investigated. The equilibrium constants obtained at 2 ns after photolysis for a series of nitriles are tabulated in Table I. We find that ketyl radical formation is favored as the dielectric constant of the medium is decreased.

The rate of electron transfer in a variety of solvents was examined by using Dabco as the electron donor. These rates are summarized in Table II. We find that when the solvent is changed from benzene ($\epsilon = 2.3$) to Me_2SO ($\epsilon = 46.7$), the rate of electron transfer, k_{et}, changes by a factor of only 4. No correlation with dielectric constant is observed (Table II). For all solvents examined, we observed a blue shift (half-life of 100 ps) in the absorption maximum of the radical anion of benzophenone similar to that observed in the DEA (DMA) system.[7]

Discussion

It is currently accepted that the primary processes in the mechanism of the photoreduction of aromtic ketones by amines involves two steps.[3,4] The first step is an electron transfer generating the radical anion of the ketone and the radical cation of the amine. This, in turn, is followed by proton transfer resulting in the formation of the benzhydrol and amine radicals. Although the overall mechanism has been established, little is known about either the dynamics of the various steps or the solvent dependence of the reactive intermediates. The spectral changes observed in our study of the photoreduction of benzophenone by 1.0 and 5.0 M DEA (DMA) support this general mechanism. In addition, our ability to resolve the reactive intermediates enables us both to probe the solvent dependences of these species and to observe directly the dynamics of each step in the reaction.

From fluorescence quenching studies, Weller[8] concluded that electrons can transfer over an average encounter distance of 7 Å. Hence, it is probable that a solvent molecule is situated between the two reaction sites. The subsequent electron transfer would result in the formation of the solvent-separated ion pair.[9] In addition, if the electron-transfer step of the photoreduction of ketones by amines involves an amine not involved in solvating the carbonyl moiety of the ketone, then we would expect that diffusion to form a contact ion pair to be important in the dynamics of the proton transfer. However, it is also possible that such a mechanism might compete with long-range proton transfer.[10]

Spectral changes resulting from the diffusion of cations and anions to form ion pairs in solution have been extensively studied.[11]

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(6) Peters, K. S.; Freilich, S. C.; Shaefer, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 5701. We have previously reported that for the photoreduction of benzophenone by Dabco the radical anion of benzophenone is formed within 60 ps and persists beyond 2 ns without decay in the absorption maximum.

(7) We previously reported[6] that for the photoreduction of benzophenone by Dabco, the radical anion had an absorption maximum at 675 nm which was constant in time. An accurate determination of the absorption maximum was not obtained due to the limits of our interrogation range. However, with the extension of the interrogation light to 800 nm and an enhanced signal to noise ratio, a spectral shift in the absorption maximum is observed.

(8) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(9) Winstein, S.; Robinson, G. C. *J. Am. Chem. Soc.* **1958**, *80*, 169.

(10) Masuhara, H.; Maeda, Y.; Mataga, N.; Tomita, K.; Tatemitsu, H.; Sakata, Y.; Misumi, S. *Chem. Phys. Lett.* **1980**, *69*, 182.

(11) (a) Szwarc, M. *Acc. Chem. Res.* **1969**, *2*, 87. (b) Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1966**, *88*, 307. (c) T. E. Hogen-Esch and J. Smid[11b] reported the absorption maximum for the fluorenyl-Na^+ ion pair in THF and pyridine as 356 and 373 nm, respectively. The absorption maximum at 356 nm as assigned the contact ion pair while the maximum at 373 nm was assigned to the solvent-separated ion pair. For the benzophenone radical anion, the corresponding absorption maxima in THF and pyridine are 677 nm (contact ion pair) and 711 nm (solvent-separated ion pair), respectively. See: Garst, J. F.; Walmsley, D.; Hewitt, C.; Richards, W. R. Zabolotny, E. R. *J. Am. Chem. Soc.*, **1964**, *86*, 412.

For the photoreduction of benzophenone by 1.0 M DEA (DMA) and 5.0 M DEA (DMA) we observe blue shifts in the absorption maximum of the radical anion of benzophenone of 490 and 700 cm^{-1}, respectively, before any significant concentration of ketyl radical is observed. This spectral shift is in close agreement with hypsochromatic shifts observed for contact ion-pair formation between the fluorenyl anion and alkali metals.[11b,c] The observed spectral shift could result from two effects: contact ion-pair formation or vibrational energy relaxation[12] of the radical anion following the exothermic electron-transfer event. If the latter effect were responsible for inducing the shift, we would expect to see similar rates for the shift observed for the photoreduction by 1.0 M DEA (DMA) and 5.0 M DEA (DMA). The fact that the time dependence and the magnitude of the spectral shift differ by a factor of 4 for these two cases indicates that the shift is not caused by vibrational relaxation. This suggests that the observed spectral shift results from contact ion-pair formation between the radical anion of benzophenone and the amine cation. In addition, we find that at 2 ns after photolysis the location of λ_{max} for the radical anion is independent of solvent dielectric. This is consistent with contact ion-pair formation in that the resulting structure would be expected to be insensitive to a lowering of dielectric.[11b]

For the photoreduction of benzophenone by 1.0 M Dabco and 1.0 M DEA (DMA), the diffusion processes leading to the formation of the contact ion pair have half-lives of 100 and 200 ps, respectively. The difference in rate of diffusion may result from any or all of the following effects: relative stability of the solvent separated ion pair, steric hindrance in the contact ion pair, or a mass effect on the diffusion rate.

Subsequent to the electron-transfer process, it is possible to observe proton transfer from both the solvent-separated ion pair and the contact ion pair. Intramolecular proton transfer has been observed[10] in molecules where contact ion-pair formation is inhibitied. However, for the photoreduction of benzophenone by both 1.0 M DMA and 1.0 M DEA no ketyl radical is observed prior to contact ion-pair formation. The equilibrium distribution between the contact ion pair and the ketyl radical is found to be dielectric dependent (Table I). We observe an increase in ketyl radical formation with a decrease in medium dielectric.

For high amine concentrations ([amine]) > 1.0 M), Cohen[3b] observed curvature in Stern–Volmer plots, indicating an apparently higher order dependence of quantum yield for reduction on the amine concentration. To account for this deviation, he proposed an amine-mediated transfer of the proton in the charge-transfer complex. We observe an increase in the rate of electron transfer upon increasing the DEA (DMA) concentration from 1.0 to 5.0 M. However, the rate of proton transfer decreases at high amine concentrations; from 1.0 to 5.0 M amine, a fourfold decrease in the rate of proton transfer is observed. The rate of shift of the absorption maximum of the radical anion of benzophenone from 715 to 690 nm is also found to be slower by a factor of 4. The origin of this decrease cannot be entirely accounted for by an increase in viscosity as the viscosities of the 1.0 and 5.0 M amine solutions differ only by a factor of 1.6.[13] In a 1.0 M amine solution there are 16 acetonitrile molecules for every amine molecule, while at 5.0 M this ratio has dropped to 1.3:1. Thus, at 5.0 M amine, approximately every other molecule in the solvent sphere of an amine is another amine. After the electron has been transferred, the solvent molecules reorient to stabilize the resulting charged species. Because DEA (DMA) is a better electron-pair donor[14] than acetonitrile, we propose that the decrease in the rate of formation of the contact ion pair observed at high amine concentration results from a stabilization of the amine cation by a neighboring amine. This stabilization of the solvent-separated form by specific interactions of neighboring amines results in an increase in the energy of activation for the diffusion process to form the contact ion pair. Since no proton transfer is observed from the solvent-separated ion pair, the decrease in the rate of diffusion will be manifested in a decrease in the observed proton-transfer rate.

The increase in the electron-transfer rate at high amine concentrations may result from either or both of the following effects: the standard concentration dependence observed for second-order reactions or an increase in the polarizability of the medium. From Marcus theory[15] the rate constant for electron transfer is expressed as

$$k = Z \exp[-(\Delta G_0 + \lambda_0)^2/4\lambda_0 kT]$$

where Z is the preexponential factor; ΔG_0, the free energy of the reaction; and λ_0, the energy necessary to repolarize the solvent to the most probable electron-transfer configuration. In this formalism the energy of activation for the electron-transfer process is a function of the repolarization energy, λ_0. This energy can be expressed as

$$\lambda_0 = \left(\frac{e^2}{2a_+} + \frac{e^2}{2a_-} - \frac{e^2}{D}\right)\left(\frac{1}{n^2} - \frac{1}{\epsilon_s}\right)$$

where n and ϵ_s are the index of refraction and the static dielectric constant of the medium, respectively. Under certain conditions an increase in polarizability can offset a decrease in dielectric constant resulting in a lowering of the repolarization energy. This would be manifested in a lower activation energy for the electron transfer and hence an increase in rate.

In our study of the quenching of the triplet state of benzophenone by 1.0 M Dabco, we observed only a fourfold decrease in the rate upon changing the solvent from acetonitrile to benzene (Table II). Partial charge transfer has been invoked to explain the insensitivity of electron-transfer rates to changes in solvent dielectric.[3a,4] Yet for all solvent systems examined, the absorption spectrum revealed the formation of the radical anion concomitant with the decay of the excited triplet. Thus we observed no evidence supporting partial charge transfer in this system. The apparent discrepancy between the insensitivity of the electron-transfer rate to changes in solvent dielectric and that predicted by Weller[16] can be resolved in light of recent observations in electron-transfer studies.[15b] When the reaction is exothermic by more than 10 kcal/mol, the rate of electron transfer approachs a limiting value. Thus solvent effects will be observed only when the exothermicity of the reaction is less than 10 kcal/mol.[17]

For the photoreduction of benzophenone by 5.0 M DEA (DMA) we observe a 50% decay in the absorption intensity of the radical anion during the first 400 ps following photolysis. This decay is not observed for the photoreduction of benzophenone by 1.0 M DEA (DMA). Upon photolysis, the benzophenone molecule is excited into its lowest singlet state, S_1. The excited molecule undergoes intersystem crossing to the $n\pi^*$ T_1 state in less than 10 ps. Thus depending on the electron-transfer rate, it is possible to create various distributions of singlet and triplet radical anion. We have previously reported that the triplet radical anion formed in the photoreduction of benzophenone by 1.0 M Dabco does not show any appreciable decay within 2 ns.[6] Based on these observations, we propose that for photoreduction of benzophenone by 5.0 M DMA and DEA the time-dependent decrease in intensity of the radical anion absorption results from the decay of the singlet radical anion. Our observations using 5.0 M DEA (DMA) indicate that the rate of electron transfer to the first excited singlet state is approximately equal to that of intersystem crossing. Both

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

(13) The viscosity of the mixture was calculated by using the expressions log $\eta^s = X_1 \log \eta^1 + X_2 \log \eta_2$ with the viscosity of the amine, η_1, and acetonitrile, η_2, taken to be 1.285 and 0.345, respectively. X_1 and X_2 are the respective mole fractions.

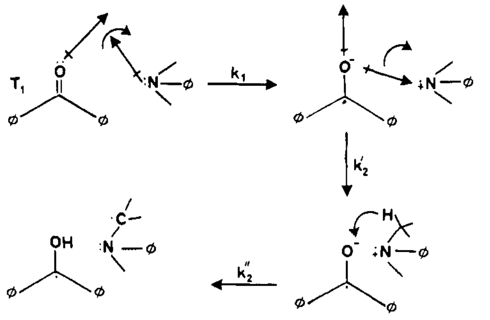
(14) V. Gutman, "The Donor-Acceptor Approach to Molecular Interactions"; Plenum Press: New York, 1978.

(15) (a) R. A. Marcus, *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 748.

(16) Weller[8] examined the quenching of perylene fluorescence by substituted anilines. He found that the rate decreased by a factor of 13 upon changing the solvent from acetonitrile to methylcyclohexane. Partial charge transfer is invoked when the quenching rate decreases by a factor less than 13 upon such a solvent change.

(17) We have previously reported[6] that the electron-transfer event for the Dabco/benzophenone system is exothermic by at least 15.0 kcal/mol.

Scheme I



events, however, occur too rapidly to be resolved by our experiment. The singlet radical anion decays with a rate constant of 5.0×10^8 s^{-1}.

At 10 ns after photolysis, the equilibrium constant for the ketyl radical/radical anion equilibrium is similar for the photoreduction by both 1.0 and 5.0 M DMA (Table I). However for the photoreduction by DEA we observe a shift in the equilibrium in favor of the ketyl radical upon an increase in amine concentration. An increase in amine concentration results in a decrease in the dielectric of the medium. This in turn destabilizes the ion pair with respect to the ketyl radical. Examining the equilibrium constants in Table I, we observe that the equilibrium constants for photoreduction by 1.0 M DEA are more sensitive to a lowering in dielectric than the corresponding values for 1.0 M DMA. The increased sensitivity of the ketyl radical/radical anion equilibrium in the DEA system can be explained within the Born continuum approximation[18] by postulating an increased internuclear separation in the contact ion pair. This increased separation results from the increased steric hindrance in the contact ion pair with an increase in alkyl chain length.

In summary (Scheme I) the dynamics and solvent dependences of the primary processes of the photoreduction of benzophenone by DMA and DEA have been elucidated by using picosecond absorption spectroscopy. The first step, k_1, involves electron transfer from an amine not directly involved in solvating the carbonyl moiety of the ketone. The resulting solvent-separated ion pair diffuses together, k_2', forming the contact ion pair from which the proton is then transferred, k_2''.

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(18) Denison, J. T.; Ramsey, J. B. *J. Am. Chem. Soc.* **1955**, *77*, 2615.

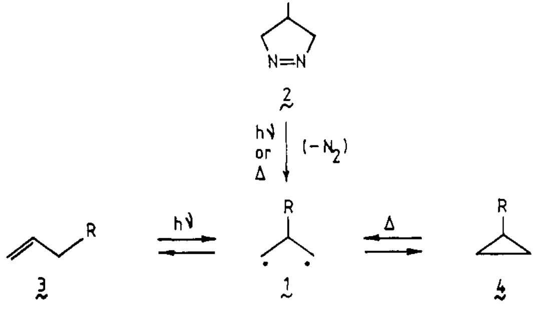
Thermolysis and Photolysis of the Azoalkane 2,3-Diazatricyclo[4.3.0.0^{4,9}]non-2-ene: Generation and Transformation of the Bicyclo[2.2.1]heptane-2,7-diyl Diradical

Waldemar Adam,* Nestor Carballeira,‡ and Ottorino De Lucchi

Contribution from the Department of Chemistry of the University of Puerto Rico, Rio Piedras, Puerto Rico 00931, and Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-8700 Würzburg, West Germany. *Received March 20, 1981*

Abstract: The trimethylene diradical bicyclo[2.2.1]heptane-2,7-diyl (**5**) was generated via denitrogenation of the azoalkane 2,3-diazatricyclo[4.3.0.0^{4,9}]non-2-ene (**6**) by means of vacuum flash pyrolysis, tetramethyl-1,2-dioxetane chemienergization, direct photolysis at 350 nm by excitation of the n,π* azo chromophore, and benzophenone sensitization. It is concluded that the thermally equilibrated singlet-state and triplet-state diradicals **5** exclusively cyclize into tricyclo[3.2.0.0^{4,6}]heptane (**7**). For the vibrationally excited ("hot") diradical (**5**), rearrangement into bicyclo[3.2.0]hept-2-ene (**10**) competes, although inefficiently, with cyclization. Fragmentation of **5** into 3-vinylcyclopentene (**8**) and rearrangement into norbornene (**9**) are not observed.

The behavior of 1,3-diradicals such as the trimethylenes **1** has been an active area of mechanistic research[1] during the last decades. These elusive reaction intermediates can be conveniently prepared via thermal or photochemical denitrogenation of the corresponding azoalkanes,[2,3] the pyrazolines **2** (eq 1). Although the rearrangement of the trimethylenes **1** into the alkenes **3** is according to thermochemical estimates[1f] by 8 kcal/mol more exothermic than cyclization into the cyclopropane **4**, the latter is kinetically the preferred process by 2 kcal/mol; in fact, matrix isolation work on the related 1,3-cyclopentanediyl diradical suggests that the activation energy for cyclization is <2 kcal/mol.[3] Alternatively the 1,3-diradical **1** can be generated photochemically[4]



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*Send correspondence to this author at the Würzburg address.

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