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Dynamics of Radical Pair Reactions in Micelles

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Abstract: The time-resolved behavior of *sec*-phenethyl, cumyl, and diphenylmethyl radicals as radical pairs solubilized in micelles has been observed using pulsed laser photolysis. The decay of the micellized radical pairs consists of a fast component (20–2000 $\times 10^{-9}$ s), attributed to reaction within the geminate radical pair, and a slow component ($>2000 \times 10^{-9}$ s), attributed to reactions from random encounters of radicals. The extent of geminate pair reaction (micellar cage reaction) depends upon the competition between the rate constants for reaction and diffusive separation. The rate constants for the reaction and diffusion processes are determined and the nature of these processes is discussed. A correlation is found between the extent of fast decay observed in the time-resolved experiments and the extent of cage reaction determined from steady-state photolysis.

A considerable number of examples of the effect of external magnetic fields on the chemistry of radical pairs and radical ion pairs have been reported.[1-6] The influence of an external magnetic field on singlet radical ion pair recombination efficiencies has been investigated using both time-resolved and steady-state techniques.[1] It has been observed that the yield and decay kinetics of the radical ion pairs, monitored using time-resolved absorption spectroscopy, correlate with the intensity of the appropriate exciplex fluorescence, and with the growth of the delayed monomer fluorescence and monomer triplet absorption.[1] In general, a predictable relationship exists between the time-resolved (radical ion and triplet yield) and steady-state (exciplex and monomer fluorescence) observables in these systems. For reactions of triplet radical pairs in micellar solutions, the corresponding observables are the reaction dynamics of the intermediate radicals, which may be monitored by time-resolved absorption spectroscopy, and the steady-state product distributions. Although the time-resolved absorption kinetics of several micellized triplet radical pairs have been reported,[3-6a] no detailed and systematic correlations, of kinetic behavior with steady-state product distributions have been described. Indeed the nature of the processes which contribute to the overall time-resolved radical absorption decay is not well established.[3-6a] Additionally no systematic study of the effect of radical structure on the reaction dynamics has been reported.

Dibenzyl ketone (DBK) has been particularly useful as a triplet radical pair precursor in product studies which have demonstrated magnetic field and magnetic isotope effects in radical pair chemistry.[6] However, this ketone is less suitable as a radical pair precursor in time-resolved studies since decarbonylation of the initially formed phenacetyl radical occurs within 250 ns to yield a benzyl radical.[7] Thus contributions from two radical pair systems have to be considered simultaneously when analyzing the reaction dynamics. In the present study we have examined the time-resolved absorption dynamics of several benzylic radical pairs in which decarbonylation is either much faster or much slower than the rates of intramicellar reaction of the radicals. In particular, the effects of systematic changes in radical hydrophobicity, radical partner, micelle structure, and external magnetic field on the reaction dynamics have been investigated. Additionally the steady-state product distributions for some systems have been compared with the data obtained using the time-resolved techniques. The results provide information concerning the nature of the processes which are influenced by external magnetic fields

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[1] (a) Schulten, K.; Staerk, H.; Weller, A.; Werner, H. J.; Nickel, B. *Z. Phys. Chem. (Frankfort am Main)* **1976**, *101*, 371. (b) Michel-Beyerle, M. E.; Kruger, H. W.; Huberhorn, R.; Seidlitz, H. *Chem. Phys.* **1979**, *42*, 441. (c) Nalting, F.; Staerk H.; Weller, A. *Chem. Phys. Lett.* **1982**, *88*, 523. (d) Weller, A.; Nolting, F.; Staerk, H. *Ibid.* **1983**, *96*, 24.

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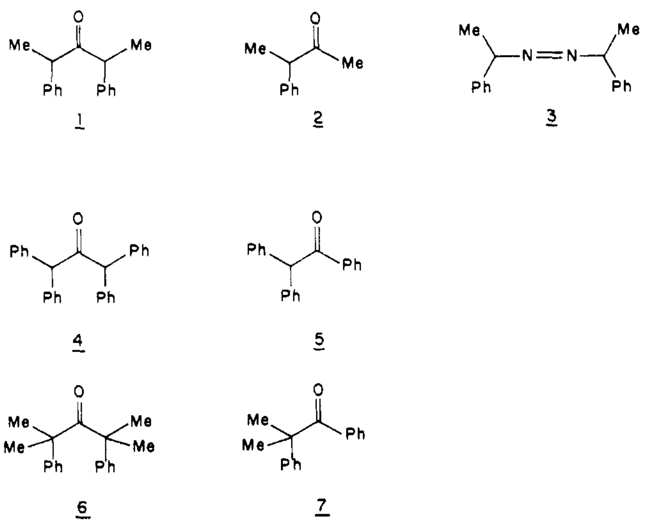
Scheme I. Compounds Used in the Present Study



and those which result in the increased probability of geminate combinations. In this work geminate radicals are defined as those which are derived from the same molecule.

Experimental Section

Transient absorption experiments were performed using a Lambda Physik excimer laser (EMG 101, 248 nm, ca. 100 mJ, 15 ns) in a conventional manner.[8] A 450-W xenon lamp, together with a PRA 301 power supply and PRA 305 pulser unit, was used as the analyzing source. Transient spectra were recorded using right angle detection; decay analysis was performed using an off-axis alignment of exitation and analyzing beams to accomodate either a 2.5 kG permanent magnet or a home-built variable field (up to 2 kG) electromagnet. Transmitted light intensities were monitored using six dynodes of an RCA 4840 photomultiplier tube, the output of which was passed through an automatic backoff unit and terminated into a 50-Ω load resistor. The backoff unit operated such that only deflections from the signal level 40 μs before the laser pulse were transmitted to a Tektronix 7912 AD digitizer.

The concentrations of the ketone radical precursors were adjusted so that solutions of optical density of ca. 0.7 at the excitation wavelength (248 nm) were obtained (10^{-4}–10^{-3} M). The concentrations of the surfactants sodium dodecyl sulfate (SDS, Biorad, used as received) and hexadecyltrimethylammonium chloride (HDTCl, Kodak, recrystallized twice from ethanol/ether) were 0.05 M for all experiments. Ketones (Scheme I) **1**,[6f] **4**,[9a] **5**,[9b] **7**,[6g] and azo compound **3**[9c] were synthesized according to literature procedures. Ketone **6** was obtained by refluxing dibenzyl ketone in THF with an excess of sodium hydride (5 equiv) and methyl iodide (8 equiv). Pure ketone **6** was obtained by recrystallization (four times) from hexane/ether solution (mp 110–115 °C (dec)). Ketone **2** was obtained by addition of benzyl methyl ketone to 1 equiv of potassium hydride in THF at 0 °C. The solution was slowly added to methyl iodide (1.1 equiv) in THF at 0 °C. Pure ketone **2** was obtained by distillation.

Steady-state product distributions for ketones **4** and **6** were obtained by irradiating ca. 10^{-3} M ketone in 0.05 M HDTCl and 25 mM $CuCl_2$ at 300 nm. Analysis of products was by GLC.[6f,g]

Results

1. Time-Resolved Absorption Spectroscopy. (i) *sec*-Phenethyl Radical. Pulsed laser photolysis of argon-purged acetonitrile or isooctane solutions of ketones **1** or **2** or the azo compound **3**, leads to transient absorption signals due to *sec*-phenethyl radicals. The absorption spectrum shows a maximum at 322 nm,[10] and the signals appear within the laser pulse.[11] In degassed solutions, clean second-order decay of radical absorption is observed in each case.

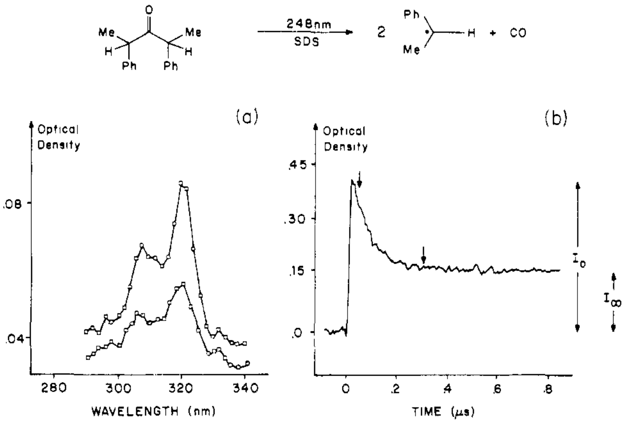


Figure 1. (a) Transient absorption spectra observed upon photolysis of ketone **1** in SDS. The two spectra were recorded at two times after the laser pulse as shown by the arrows on the typical time-resolved absorption trace (b) which was recorded at 322 nm. The yield of radicals which escape the geminate pair (see text) is given by I_∞/I_0.

Table I. Observed Rate and Intensity Ratio Parameters for Radical Pair Fast Decay

radical pair (λ_{obsd})[a]	micelle	$k_{obsd} \times 10^{-6}$ s^{-1} [b]	I_∞/I_0[b,c]	radical source
sec-phenethyl–*sec*-phenethyl (322)	SDS	12.0	0.40 (0.63)	1
	HDTCl	4.9	0.33 (0.66)	1
diphenylmethyl–diphenylmethyl (332)	SDS	6.5	0.20 (0.76)	4
	HDTCl	2.8	0.07 (0.73)	4
diphenylmethyl–benzoyl (332)	SDS	9.0	0.40 (0.58)	5
	HDTCl	6.4	0.37 (0.46)	5
cumyl–cumyl (324)	HDTCl	5.5	0.20 (0.73)	6
cumyl–benzoyl (324)	SDS	12.0	0.42 (0.54)	7

[a] Wavelength (nm) at which radical pair was monitored. [b] Errors are ±10%. [c] Numbers in parentheses are those determined in the presence of a 2.5-kG magnetic field.

In argon-purged SDS or HDTCl micellar solution photolysis of **1** leads to a nonexponential decay of transient absorption, which is resolvable into fast and slow components (Figure 1). The fast decays in each micelle can be analyzed via first-order kinetics, and the corresponding rate constants are given in Table I.

The transient absorption spectra observed for photolysis of **1** in SDS and HDTCl indicate that at longer times species other than *sec*-phenethyl radicals are absorbing in the region of interest (Figure 1). However, the absorptions at the wavelength of maximum radical absorption (322 nm) are mostly due to the *sec*-phenethyl radical since its characteristic sharp absorption band at this wavelength is clearly resolved even at the end of the fast decay. The ratio of the amount of absorption at the end of the fast decay to that at the beginning (I_∞/I_0 in Figure 1, Table I) is a measure of the number of radicals which do not recombine during the fast decay.[12] In oxygen-free solution half-lives of ca. 25 μs are observed for the slow decays in SDS and HDTCl although these do not obey first-order kinetics. In the presence of air, clean first-order lifetimes of 950 and 900 ns are observed in HDTCl and SDS. For all of the slow decays, approximately 10% of the total signal remains as a residual absorption.

An external magnetic field effect is observed on the fast decay in both SDS and HDTCl. In each case the ratio I_∞/I_0 increases when the experiment is performed in the presence of a 2.5-kG permanent magnet (Table I).

For ketone **2** no fast decay of radical absorption is observed in micellar solution; only a slow decay of half-life ca. 25 μs is

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[8] Turro, N. J.; Aikawa, M.; Butcher, J. A. *J. Quant. Electronics* **1980**, *QE-16*, 1218.

[9] (a) Dean, D. O.; Dikinson, W. B.; Quayle, O. R.; Lester, C. T. *J. Am. Chem. Soc.* **1950**, *72*, 1740. (b) Koelsh, C. F. *Ibid.* **1932**, *54*, 2049. (c) Cohen, S. G.; Groszos, S. J.; Sparrow, D. B. *Ibid.* **1950**, *72*, 3947.

[10] Porter, G.; Strachan, E. *Trans. Faraday Soc.* **1958**, *34*, 1595.

[11] Photolysis of **1** leads initially to a *sec*-phenethyl radical and a 2-phenylpropionyl radical which decarbonylates to form a second *sec*-phenethyl radical within 15 ns at room temperature. Similarly decarbonylation of the primary phenyldimethylacetyl radical, formed upon photolysis of ketone **6**, occurs within 7 ns at room temp (ref 7a).

[12] For all of the ketones studied we observed a laser power intensity effect on the ratio of I_∞/I_0, presumably due to photochemistry of the radicals which absorb laser light within the 15-ns excitation pulse. Each of the values of I_∞/I_0 reported in Table I were determined at sufficiently low laser powers that these effects were unimportant.

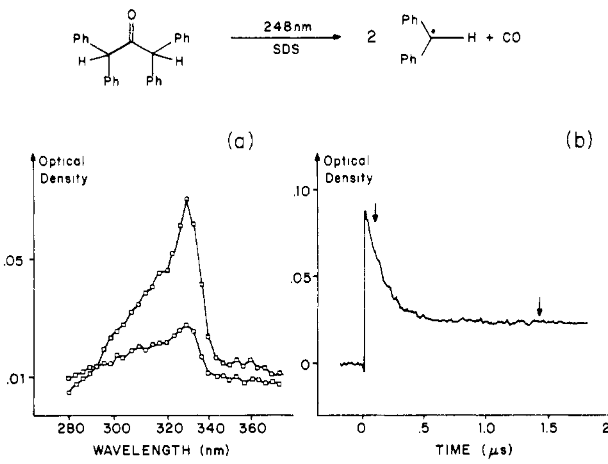

Figure 2. (a) Transient absorption spectra observed upon photolysis of ketone **4** in SDS. The two spectra were recorded at two times after the laser pulse as shown by the arrows on the typical time-resolved absorption trace (b) which was recorded at 332 nm.

observed. For the azo compound **3** only very weak transient absorptions are observed in SDS micelles. Analysis of the transient absorption spectrum indicated that no signals due to *sec*-phenethyl radicals are observed upon photolysis of this compound in SDS micelles.

(ii) Diphenylmethyl Radical. Pulsed laser photolysis of ketones **4** and **5** in argon-purged isooctane solution yields very strong transient absorptions. The transient spectra show absorption maxima at 332 nm which is characteristic of the diphenylmethyl radical.[10] The transient signals appear within the laser pulse.[13] For photolysis of **4** in HDTCl solution, 93% of the absorption decay monitored at 322 nm decays with a first-order constant of 2.8×10^6 s^{-1} (Table I). In SDS 75% of the absorption decays with a first-order constant of 6.6×10^6 s^{-1} (Figure 2, Table I). The remaining absorption decays with a half-life of ca. 0.5 ms. In the presence of air the remaining slow decay has a first-order lifetime of 1.5 μs, and the absorption signal decays to within 5% of the prepulse level. Transient absorption spectra recorded as a function of time indicate that in SDS most of the absorptions at the end of the fast decay are due to diphenylmethyl radicals (Figure 2).

Photolysis of **5** in SDS or HDTCl leads to fast and slow decays as for ketone **1**. The appropriate first-order constants and I_∞/I_0 ratios are given in Table I. Transient absorption spectra as a function of time for this ketone are similar to those shown in Figure 2 for ketone **4** and indicate that most of the absorptions monitored at 322 nm are due to the diphenylmethyl radical. In each micelle the half-lives of the slow decays are ca. 15 μs in argon-purged solution, and ca. 1 μs in air-saturated solution. For both **4** and **5** in the presence of an external 2.5-kG magnetic field, an increase in the ratio I_∞/I_0 is observed (Table I).

(iii) Cumyl Radical. Pulsed laser photolysis of ketones **6** and **7** in argon-purged isooctane solution results in transient absorption spectra with maximum absorption at 324 nm, which are characteristic of cumyl radicals.[10] In each case the radical absorptions appear within the laser pulse.[11] In HDTCl photolysis of **6** leads to fast and slow decay of radical absorption (Figure 3). From time-resolved transient absorption spectra we observe that most of the absorption observed at 324 nm at the end of the fast decay is due to the cumyl radical. Photolysis of **7** in SDS also results in fast and slow decay behavior (Table I). The slow decay has a half-life of ca. 20 μs in argon-purged solution and ca 1 μs in air-saturated solution.

2. Steady-State Photochemistry. It has been shown that irradiation of DBK in HDTCl micelles in the presence of Cu(II) solubilized in the aqueous phase leads to scavenging of only a portion of the benzyl radicals.[14a,b] Furthermore, it was shown that the amount of diphenylethane product which remained was directly related to the extent of geminate radical combination, which is substantially increased compared with homogeneous solution.[14c] The extent of increase of geminate radical pair combination in micellar relative to homogeneous solution is termed the micellar cage effect.[6] Thus, we expect that similar analysis of the quenching of the photoproduct from irradiation of **4** or **6** in HDTCl micelles should yield the extent of micellar cage reaction for these radical pair systems. It is found that when using concentrations of Cu(II) of up to 0.025 M, no change in the amount of photoproduct can be detected for ketone **4**, and only a small change is found for ketone **6**. These results indicate that a large percentage of the radical reactions for these ketones, solubilized within HDTCl micelles, are not scavengeable by water-solubilized Cu(II) ions.

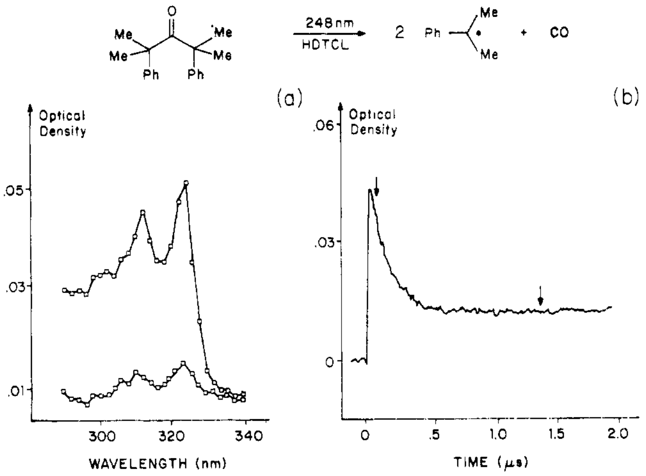

Figure 3. (a) Transient absorption spectra observed upon photolysis of ketone **6** in HDTCl. The two spectra were recorded at two times after the laser pulse as shown by the arrows on the typical time-resolved absorption trace (b) which was recorded at 324 nm.

Discussion

1. Singlet vs. Triplet Radical Pairs. Pulsed laser photolysis of both the ketone **1** and azo compound **3** results in strong transient radical absorption signals in homogeneous solution, but no absorptions due to radicals can be detected from photolysis of **3** in SDS. Photolysis of azo compounds such as **3** results in homolytic cleavage mainly from the first excited singlet state,[15a] and thus in the micelle a singlet radical pair is produced. For a singlet radical pair no spin barrier exists for recombination reactions and product formation. Evidently within the micelle a sufficiently large barrier to diffusive separation exists so that singlet geminate pair combination is completely efficient. The geminate singlet radical pair is too short lived to be resolved using the present technique.[15b] The ketones which have been examined in the present study cleave in the first excited triplet state,[16] and thus the geminate triplet radical pair must undergo intersystem crossing to a singlet radical pair before reaction can occur. It is the intersystem crossing requirement which enables the observation of longer lived radical absorptions from the micellized ketone precursors.

2. Influence of Radical Partner on Reaction Dynamics. For each of the radicals monitored in the present study, the dynamics

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(13) Decarbonylation of the primary diphenylacetyl radical occurs within 7 ns at room temperature (I. R. Gould, unpublished results, determined as described in ref 7a).

(14) (a) Turro, N. J.; Cherry, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 7431. (b) Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Weed, G. C.; Kraeutler, B. *Ibid.* **1980**, *102*, 4845. (c) Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Weed, G. C. *Ibid.* **1979**, *101*, 2227.

(15) (a) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99. (b) Strictly speaking the micelle result does not distinguish between very fast radical reaction, or no radical production. We consider it unlikely that the first excited singlet state of **3** does not cleave inside the micelle since this would require that either the cleavage reaction rate is drastically reduced or that the rates of other deexcitation mechanisms for the micellized azo excited singlet state are increased by at least an order of magnitude compared with rates in homogeneous solution.

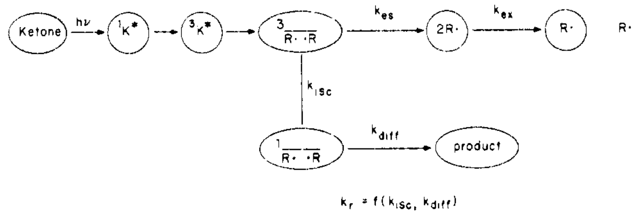
(16) Turro, N. J.; "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA., 1978; p 530.

Table II. Rate Constants for Reaction and Escape for Radical Pairs in Micelles

radical pair	micelle	$k_r \times 10^{-6}$ (s^{-1})^a	$k_{es} \times 10^{-6}$ (s^{-1})^a	B(G)^b
sec-phenethyl–	SDS	7.2	4.8	31
sec-phenethyl	HDTCl	3.3	1.6	
diphenylmethyl–	SDS	5.2	1.3	15
diphenylmethyl	HDTCl	2.6	0.20	
diphenylmethyl–	SDS	5.4	3.6	8
benzoyl	HDTCl	4.0	2.4	
cumyl–cumyl	HDTCl	4.4	1.1	36
cumyl–benzoyl	SDS	7.0	5.0	19

^{a}Errors are ±15%. ^{b}Calculated using eq 4 and 5 (see text).

Scheme II. Schematic Illustration of the Escape and Reaction Processes for Micellized Triplet Radical Pairs



of the reactions of the radical pair depends upon the identity of each radical. In general the smaller the hydrophobicity of either radical, the smaller the amount of fast decay which is observed. For example, radical pairs containing the benzoyl radical (from ketones **5** and **7**) have larger I_∞/I_0 values than the corresponding pairs with more hydrophobic radicals (from ketones **4** and **6**). The extreme case is that of the *sec*-phenethyl–acetyl radical pair (from ketone **2**) which shows no fast decay at all. These effects are attributable to the known ability of micelles to provide a barrier to diffusive separation of radicals within a pair.[6] The barrier to separation of the radicals and exit from the micelle into the water phase is larger for the more hydrophobic radicals, which results in a greater amount of cage reaction.[6] In the present study an increase in the amount of fast decay is observed. Evidently a very small barrier exists for the acetyl radical and thus no fast decay (and presumably no micellar cage reaction) is observed.[17]

3. Kinetic Analysis of the Fast Decay. From the above discussion and from the observed magnetic field effects (vide infra) it is reasonable to assign the fast transient decays to reaction from the initially triplet geminate (benzyl or substituted benzyl) radical pair. Scaiano[4] has described a method of analysis of the kinetic scheme (eq 1) region of interest, and k_1 and k_2 are the rates at

$$B \xleftarrow{k_1} A \xrightarrow{k_2} C \qquad (1)$$

which B and C are formed. The observed rate constant for decay of the transient absorption is given by $k_{obsd} = k_1 + k_2$ when the "baseline" is chosen as the transmitted light level at the end of the fast decay. In the present case A corresponds to at least one component of the triplet geminate radical pair; B represents the appropriate reaction products and C the radicals which escape from the geminate pair A. In the present system the process A → B corresponds to reaction of the primary triplet pair via intersystem crossing to a singlet pair followed by diffusive reencounter within the micelle to form a product, i.e., $k_1 = k_r$. The process A → C is thus assigned to a process in which one radical escapes from the pair via diffusion, i.e., $k_2 = k_{es}$. The rate constants k_r and k_{es} are related to the experimental observables by the following simple equations:

$$k_{obsd} = k_r + k_{es} \qquad (2)$$

$$I_\infty/I_0 = k_{es}/(k_r + k_{es}) \qquad (3)$$

An analysis of this sort requires that the species B be optically transparent at the wavelength of observation. The transient absorption spectra shown in Figures 1–3 indicate that although this requirement is not strictly met in all of the present systems, most of the optical absorptions at the end of the fast decay are due to the radical transients, especially when the decays are monitored at the wavelength of maximum absorption of these species. Thus good estimates of the values of k_r and k_{es} can be obtained using the data of Table I and eq 2 and 3 (Table II). Any absorptions due to species other than radicals will result in calculated values of k_r which are too small, and those of k_{es} which are too large.

The values of k_r for either micelle are remarkably independent of the radical pair (3–7 × 10^6 s^{-1} for SDS and 2–4 × 10^6 s^{-1} for HDTCl). The reaction process results in product formation, and previously it has been assumed that the rate-determining step is intersystem crossing to a singlet radical pair, which then rapidly reacts to form product.[3-5,6a] Certainly the observation of very fast reaction of the singlet radical pair from **3** suggests that singlet geminate radical pairs are very short lived. However, the singlet pair which is formed upon intersystem crossing from the triplet manifold must have a different spatial separation and orientation than the geminate radical pair formed upon cleavage of the azo compound. The intersystem crossing process requires spatial separation of the radicals so that exchange interactions are minimized and the singlet and triplet states becomes degenerate.[18] Subsequent reaction of radical pairs which acquire singlet character under these conditions requires a diffusive reencounter step.

By analogy with the CIDNP phenomenon[18] and from an examination of magnetic field and magnetic isotope effect upon steady-state micellar radical pair reactions,[6] it has been concluded that the triplet to singlet intersystem crossing processes in these systems are due to the hyperfine interactions between the electron and nuclear spin moments. As a result of these hyperfine interactions, pure triplet radial pairs develop singlet-state character,[18] and thus reactions can occur upon reencounter of the radical pair partners. If the reaction rate constants reflect rate-determining intersystem crossing, then there should be a correlation between the values of these constants and the extent of the hyperfine coupling that the electron on the radicals in the pair experience. In their studies of magnetic field effects on radicals ion pair reactions, Weller et al.[1d] have used the B value (eq 4 and 5) to

$$B = 1/2(B_1 + B_2) \qquad (4)$$

$$B_{1,2} = (\textstyle\sum a_k^2 I_k(I_k + 1))^{1/2} \qquad (5)$$

quantify the extent of hyperfine interaction within a radical pair. B is given by the arithmetic mean of the sums of the hyperfine interactions B_1 and B_2 for each radical, which are calculated using eq 5, in which a_k represents the hyperfine coupling of nucleus k, and $I = {}^1/_2$ for the hydrogen atom. Values of B for each of the radical pairs are given in Table II. For the benzylic radical pairs from ketones **1**, **4**, and **6**, we observe that the values of k_r do indeed increase with increasing B in HDTCl. However unexpectedly high values of k_r are found for those radical pairs containing the benzoyl radical (from ketones **5** and **7**). Additionally we observe that the k_r rate constants are higher in SDS than HDTCl for each of the radical pairs studied in each micelle. These observations suggest that while hyperfine interactions are clearly important in determining the rate of reaction of triplet radical pairs in micelles, other processes may have to be taken into account.[19] For example,

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[17] (a) Scaiano[17b] has shown that acetone triplets exit SDS micelles with a rate constant of >10^8 s^{-1}. (b) Leigh, W. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5652.

[18] (a) Adrain, F. J. In "Chemically Induced Magnetic Polarization"; Muus, L. P.; Ed.; Reidel: Dordrecht, Holland, 1969. (b) Lawler, R. G. *Prog. Nucl. Magn. Reson. Spectrosc.* **1973**, *9*, 147. (c) Buchachenko, A. L. *Russ. Chem. Rev.* **1976**, *45*, 375.

[19] (a) From a quantitative analysis of the effect of magnetic field on the yield of escaped radicals formed in the electron-transfer reaction between thionine triplets and aniline in reversed micelles, Schlenker et al.[19b] have concluded that the rate-determining step for recombination within the reversed micelle consists of contributions from both the intersystem crossing process and the diffusion dynamics of the radical pair, although individual rate constants were not obtained. (b) Schlenker, W.; Ulrich, T.; Steiner, U. E. *Chem. Phys. Lett.* **1983**, *103*, 118. (c) Experimental and theoretical estimates of the rates of diffusion-controlled intramicellar reactions range from 0.5–5.0 × 10^7 s^{-1} depending upon the probe and micelle size: Hatlee, M. D.; Kozak, J. J. *J. Chem. Phys.* **1980**, *72*, 4358.

different micelles may influence the extent of diffusive separation of the radicals, which affects the reduction of exchange interactions, and thereby alter the energies of the important T_0, $T_\pm$, and S radical pair states. The radicals might experience different rates of diffusional motion within different micelles.[19] In this case k_r would have components from both intersystem crossing and diffusion within the micelle, and thus would be a function of the rates of both of these processes (Scheme II). Additionally the benzoyl radical may be able to undergo rapid electron spin relaxation via an alternate mechanism.[20]

Unlike the reaction rate constants, considerable differences are observed among the escape rate constants observed for the different radical pairs ($1-5 \times 10^6$ s^{-1} in SDS and $2-24 \times 10^5$ s^{-1} in HDTCl). In a previous study it was found that for the diphenylketyl–cyclohexadienyl radical pair in SDS, the escape rate constant corresponded to the rate constant for exit (k_{ex}) of the latter radical from the micelle into the water phase.[4] Certainly the escape constants in the present system are related to the expected extent of radical hydrophobicity within the pair. For example, k_{es} decreases in the order *sec*-phenethyl > cumyl > diphenylmethyl in HDTCl, and k_{es} is greater for radical pairs containing the benzoyl radical (Table II). The rate constants for exit into the water phase of a series of benzylic radicals from SDS micelles have recently been reported.[21] The results of the study indicated that the exit rate constant for any radical species is similar to the exit rate constant for the equivalent fully saturated molecule. Thus the directly determined value of k_{ex} for *sec*-phenethyl radicals (3.0×10^5 s^{-1})[21] and the estimated value for biphenyl (1.0×10^4 s^{-1})[22] in SDS can be compared with the values of k_{es} for *sec*-phenethyl, cumyl, and diphenylmethyl radicals in SDS (Table II). If k_{es} were determined solely by radical exit, then k_{es} would equal the sum of the radical exit constants (k_{ex}) for both radicals in the pair. In each case the values of k_{es} are larger than the values determined, or expected, for k_{ex}. Clearly for these radicals the process which results in escape from the geminate radical pair need not involve exit of the radical into the water phase. Although the measured values of k_{es} do not reveal the nature of the escape process, the data can be accomodated in terms of a model in which diffusive separation of the radicals results in the formation of two micellized, spatially separated radicals. Further reactions are not determined by k_r and must compete with exit of either radical into the water phase (k_{ex}) (Scheme II).

4. Magnetic Field Effects. For all the radical pairs examined in this and other studies,[2-6a] a significant external magnetic field effect is observed on the fast decay. In general an increase in the ratio I_∞/I_0 is observed in the presence of a 2.5-kG external field. This effect has been attributed to the Zeeman splitting of the three sublevels of the triplet radical pair which increases as a function of the applied field.[2-6] At 0 G the three sublevels of the triplet radical pair are isoenergetic and behave identically.[18] In the absence of both significant exchange interactions and an external magnetic field, the singlet and triplet states of the radical pair have similar energies, and intersystem crossing from the triplet to the singlet can be described by a single rate constant. In the presence of an external field, the T_+ and T_- sublevels are raised and lowered in energy with respect to both T_0 and S. The T $\rightleftharpoons$ S hyperfine induced intersystem crossing mechanism requires a near degeneracy of these states, and thus as the energy gap increases as a function of the applied field, the intersystem crossing rate from $T_\pm \rightarrow S$ is reduced. When the external field is much stronger than the hyperfine interactions, then the hyperfine induced intersystem crossing from $T_\pm$ is effectively shut off.

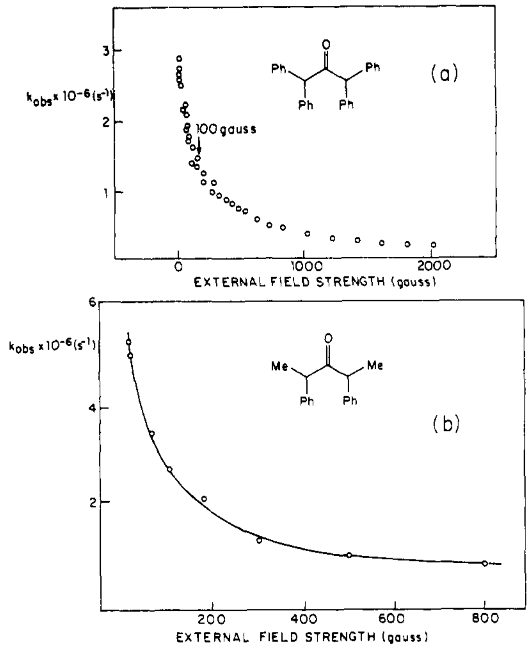

Figure 4. Plot of the variable field part of k_{obsd} vs. external field strength for photolysis of (a) ketone **4** and (b) ketone **1** in HDTCl (see text).

The magnetic field effect was examined in more detail for photolysis of ketones **1** and **4** in HDTCl using a variable field electromagnet. In each case at low field strengths (≤700 G) a steady decrease in the first-order rate constant for the fast decay was observed as a function of the applied field. At greater fields the fast decays in each case were resolvable into two components. It is clear from the data that only one part of each fast decay is affected by the application of a field. Plots of the first-order rate constants for *that part of the decay which slowed upon application of the field* are in Figure 4. Although these rate constants can only be viewed as approximate, since in the presence of the field the decays consist of at least three components, the qualitative effect of the magnetic field is beyond doubt.[23] In each case the effect of the magnetic field is monotonic in direction, with no "inflections" which would be characteristic of a T_-/S level crossing.[24] In each radical pair the largest changes occur below 100 G[25] and are thus qualitatively consistent with the hyperfine mechanism for intersystem crossing, since these fields represent the orders of magnitude of the hyperfine coupling. However, the

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[20] (a) For example, acyl radicals, but not benzyl radicals, possess an anisotropy in their *g* factors, which is the origin of a mechanism for relaxation between the three triplet sublevels (ref 20b). Fischer (ref 20c) has provided evidence that such relaxation is more facile for these radicals, since saturation of the ESR signal from the benzyl radical fragment formed upon photolysis of dibenzyl ketone is much easier than saturation of its phenacyl radical partner. (b) Poole, C. P., Jr.; Farach, H. A. "Relaxation in Magnetic Resonance"; Academic Press: New York, 1971; p 76. (c) Paul, H.; Fischer, H. *Helv. Chim. Acta* **1973**, *56*, 1575.

[21] (a) Turro, N. J.; Zimmt, M. B.; Gould, I. R. *J. Am. Chem. Soc.* **1983**, *105*, 6347. (b) The value for k_{ex} of 3.0×10^6 s^{-1} for *p*-methyl benzyl radical which was originally reported in ref 21a was a typographical error which has been corrected to its true value of 3.0×10^5 s^{-1}. (c) Turro, N. J.; Zimmt, M. B.; Gould, I. R., *J. Am. Chem. Soc.* **1983**, *105*, 7475.

[22] Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 279.

[23] The decay rates measured at the highest fields were 8×10^5 and 2×10^5 s^{-1} for radical pairs derived from ketones **1** and **4**, respectively. As pointed out by a referee, this rate of decay of radical pairs derived from ketone **1** is smaller than the value of k_{es} in the earth's field, a mechanistically impossible result. We feel this discrepancy is due to either the inherent uncertainty in the rate of the fast decay in the presence of the field (due its multicomponent nature) or in k_{es}, whose value may be inaccurate because of residual absorption after the fast decay (vide supra for discussion).

[24] (a) If a significant energy difference exists between T_0 and S at zero field and S is lower in energy than T_0, then as a function of the field the T_- state will become closer in energy to S, will then become degenerate at a certain specific field, and then decrease in energy with respect to S as the field is increased further. At the point of degeneracy $T_- \rightleftharpoons S$ intersystem crossing will be maximized and thus a maximum in triplet radical pair reaction rate could be observed. This effect has recently been observed in CIDNP signals produced upon photolysis of dibenzyl ketone in SDS (ref 22b). A maximum was found at 300 G for this system. However, it should be emphasized that these CIDNP experiments relied upon the presence of a large ^{13}C hyperfine interaction for the observation of a signal. The rates of k_{obsd} measured here reflect only the rates at which the radicals react. (b) Zimmt, M. B.; Doubleday, C. Jr.; Turro, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 3363.

[25] Similar data have been presented by Scaiano[4] and Schenlker et al.[19] for the magnetic field effect on the yield of escaped radicals, and by Tanimoto[5b] for rate constants of reaction of micellized triplet radical pairs. Hayashi, H.; Nagakura, S. Bull. *Chem. Soc. Jpn.* **1984**, *57*, 322.

Table III. Cage Values for Radical Pair Reactions in HDTCl Micelles

radical pair	field (kG)	$\text{cage}_{\text{min}}{}^{a}$	$\text{cage}_{\text{actual}}{}^{b}$
sec-phenethyl–*sec*-phenethyl	0	66	67^{c}
	2.5	34	23^{c}
diphenylmethyl–diphenylmethyl	0	93	100
	2.5	27	100
cumyl–cumyl	0	80	95
	2.5	27	74

[a] Determined using eq 7. Errors are ±10%. [b] Errors are ±5%. [c] Reference 6f.

fields at which half of the rate change is observed (ca. 100 G for both radical pairs) are significantly larger than the B values given in Table II (15 and 31 G, respectively) (cf. ref 19b). The observations support the assignment of the magnetic field effects of the Zeeman effect. The $T_\pm \rightleftharpoons S$ intersystem crossing processes are affected by the field whereas the $T_0 \rightleftharpoons S$ process is not affected at these field strengths. When the $T_\pm$ intersystem crossing rates become sufficiently slow we observe the part of the fast decay (assigned to reaction from T_0) which is unaffected by the field. At high fields the observed fast decay is from T_0 only. The extent of intersystem crossing from this state may be estimated by comparing the I_∞/I_0 ratios at 0 and 2.5 kG (Table I). We find that for the *sec*-phenethyl–*sec*-phenethyl radical pair in HDTCl, 50% of the fast decay is unaffected by the field, and for the diphenylmethyl–diphenylmethyl radical pair 29% is unaffected. For an equal distribution of radical pairs among the three triplet sublevels, 33% of the decay should be unaffected. Although the reason for the different sizes of the field effects are not revealed by the data, one possible reason is that some fraction of electron spin polarization is generated in the ketone triplet state and is carried over to the radical pair, so that in the presence of an applied field T_+, T_- and T_0 are not initiatially populated with equal probability.[26]

5. Correlation between Time-Resolved and Steady-State Photochemistry. Steady-state irradiation of benzyl radical precursors in HDTCl micelles in the presence of a sufficient concentration of Cu(II) as an aqueous phase radical scavenger leads to a decrease in the yield of the recombination products.[6,14] The extent of micellar cage reaction under these conditions is given by eq 6 in which $[\text{products}]_{\text{US}}$ and $[\text{ketone}]_{\text{R}}$ represent the concentrations

$$\%\ \text{cage} = 100[\text{products}]_{\text{US}}/[\text{ketone}]_{\text{R}} \qquad (6)$$

of unscavengeable radical product and reacted ketone. The Cu(II) ion has been shown to scavenge *sec*-phenethyl and cumyl radicals,[6f,g] and thus by extention we assume that this species can trap the diphenylmethyl radical. We can thus apply eq 6 to determine the extent of micellar cage reaction for photolysis of ketones **1**, **4**, and **7** in HDTCl micelles. The results are summarized in Table III and indicate that for ketones **4** and **7** substantial micellar cage reaction occurs even in the presence of an external magnetic field. The extent of micellar cage reaction can also be estimated from the time-resolved experiments. According to the analysis of the data given in the previous sections, a minimum value for cage reaction is given by the amount of radicals which undergo fast decay vs. the total number of radicals:

$$\%\ \text{cage}_{(\text{minimum})} = 100(1 - I_\infty/I_0) \qquad (7)$$

A comparison of the cage values from steady-state analysis with the minimum cage values from eq 7 (Table III) reveals that within experimental error the two values are the same at zero field. The results also support the conclusion that the time-resolved data can be correlated with steady-state cage data, and that the fast decay does represent reaction of the geminate radical pair. In the presence of the magnetic field the data for the cumyl–cumyl and diphenylmethyl–diphenylmethyl radical pairs suggest that substantial geminate recombination reaction occurs after the fast decay. This result shows that although intersystem crossing from $T_\pm \rightarrow S$ is significantly slowed in the presence of the field, the reduced intersystem crossing rates still result in some cage reaction. The small values of k_{ex} for these radicals allow other, slower nonhyperfine induced intersystem crossing mechanisms to produce reactive singlet radical pairs.

6. Slow Radical Decays. The slow radical decays have not been quantitatively analyzed in detail because they do not obey clean first-order kinetics, having first half-lives which are laser-power dependent. Additionally in no case does the transient absorption decay totally to the prepulse level. However, the slow absorption decays can be assigned to radical reactions on the basis of transient absorption spectra and oxygen quenching effects (see Results). The slow radical reactions do not lead to cage products and so correspond to recombination or disproportionation reactions of radicals which are not necessarily geminate. Thus the rate of slow decay will be determined by the rate at which random encounters of radicals from different micelles occur. In turn this will depend upon the rates of radical micellar exit and reentry, and their rates of reactions in the micellar and aqueous phases. The slow decays will represent a complex combination of each of the above rate processes. As an illustration of this point we can compare the first half-lives for the slow decay of the diphenylmethyl–diphenylmethyl radical pair (ca. 500 μs) with that of the diphenylmethyl–benzoyl radical pair (ca. 15 μs) in SDS. In the former the hydrophobic diphenylmethyl radicals are essentially isolated in the micelles and thus are "protected" from recombination reactions. In the latter case the more mobile benzoyl radicals can "seek out" the diphenylmethyl radicals and thus faster reactions are observed.

Conclusions

The reactions of initially triplet geminate radical pairs in micelles can be observed directly on a nanosecond time scale. The decay rates of initially singlet radical pairs are too fast to be measured using the present technique. From the determination of the rate constants for reaction and escape for a series of triplet radical pairs we can draw two conclusions which are illustrated in Scheme II: (i) reaction is controlled by a combination of processes which probably involve hyperfine induced intersystem crossing and radical diffusion; (ii) escape of either partner from the geminate radical pair within the micelle need not involve total exit of the radical into the water phase. The fast radical decay which is observed for triplet pairs can be correlated with steady-state cage effects in the absence of an applied magnetic field.

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Registry No. 1, 33500-61-7; **2**, 769-59-5; **3**, 5661-68-7; **4**, 7476-11-1; **5**, 1733-63-7; **6**, 71254-82-5; **7**, 13740-70-0; $\text{Ph}\dot{\text{C}}\text{HCH}_3$, 2348-51-8; $\text{Ph}_2\text{CH}\cdot$, 4471-17-4; cumyl radical, 4794-07-4.

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[26] This phenomenon is due to spin sublevel selective intersystem crossing from S_1 to T_1 and is termed the triplet mechanism of spin polarization: K. A. McLauchlan In "Chemically Induced Magnetic Polarization", Eds. Muus, L. P., et al.; Reidel: Dordrect, Holland, 1977, p 151.