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# A Comparative Study of Magnetic Field Effects on the Dynamics of Geminate and Random Radical Pair Processes in Micelles

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**Abstract:** Magnetic field effects on the dynamics of random radical–radical reactions in micellar systems are reported for the self-reaction of benzyl radicals in sodium dodecyl sulfate (SDS) and cetyltrimethylammonium chloride (CTAC) micelles. The self-reaction rate constants ($2k_t$) determined using laser flash photolysis techniques are reduced by 44% (SDS) and 35% (CTAC) by application of moderate fields. One-half of the maximum magnetic field effect can be achieved with as little as 200 and 120 G in SDS and CTAC micelles, respectively. The results are discussed in terms of a single kinetic model where 75% of random encounters lead to micellized triplet radical pairs where micellar escape and intersystem crossing are competitive processes. The implications of these observations in biological chemistry are briefly discussed. The benzyl radicals were produced from dibenzyl ketone. In short time scales the geminate radical pairs involve benzyl and phenylacetyl radical pairs. The dynamics of this widely studied system were examined in detail. For example, for the SDS system, it is estimated that phenylacetyl exit occurs with a rate constant of $\sim 6.6 \times 10^6$ s$^{-1}$ (compared with $1.4 \times 10^6$ s$^{-1}$ reported for benzyl), and geminate reaction with $k_{\text{gem}} = 1.2 \times 10^7$ s$^{-1}$. Of the initial benzyl–phenylacetyl geminate radical pairs, approximately 23% decarbonylate, 31% separate, and 46% undergo geminate reaction.

Magnetic fields are well established to have extensive influence on the behavior of geminate radical pairs in organized systems.[1-8] Numerous reports have been concerned with triplet-derived radical pairs in micellar solutions, although occasionally there have been reports on singlet-derived pairs,[9] as well as on other microheterogeneous systems, such as microemulsions,[10] reversed micelles,[11] and vesicles.[12] In principle, one should also anticipate magnetic field effects on the behavior of *random* radical pairs, but to the best of our knowledge, such effects have not been demonstrated experimentally in organized systems, although evidence has been reported in viscous media.[13] One may anticipate that these effects could be of considerable relevance in biological chemistry, since most radical–radical reactions *in vivo* are likely to involve random encounters of free radicals.

Among the radical-forming reactions employed in studies of this type, the photoreduction of carbonyl compounds[6] and the Norrish type I photocleavage (Scheme I)[4] have played a prominent role.

In this work we have employed the photolysis of dibenzyl ketone (DBK) as a free radical source in micellar solution. The system is undoubtedly one of the most extensively studied, yet our knowledge of a number of details on the dynamics of intramicellar geminate processes is incomplete. Laser flash photolysis has been employed in the study of DBK in micelles,[14] but more recent detailed studies of several ketones[15] exclude DBK, probably recognizing that the relatively slow decarbonylation of phenylacetyl radicals complicates the time-resolved work.

Phenylacetyl radicals decarbonylate with solvent-dependent rate constants in the $5 \times 10^6$ to $1 \times 10^7$ s$^{-1}$ range.[16,17] Thus, early phenomena, predominantly of a geminate nature, should involve the benzyl–phenylacetyl radical pair, while in the microsecond time scale one can anticipate that the phenylacetyl radical will be largely absent from the system.

In our experiments we have used nanosecond laser flash photolysis techniques employing an excimer laser at 308 nm for sample irradiation. Our work, in cationic and anionic micellar systems, provides direct kinetic evidence on the effect of external magnetic fields on random encounters between benzyl radicals. Our results also provide a much improved understanding of the dynamics of geminate radical pairs. Further, we provide the first rate constants for the decarbonylation of phenylacetyl radicals in micellar and aqueous solutions.

## Experimental Section

Dibenzyl ketone (Aldrich) was recrystallized from methanol prior to use. Sodium dodecyl sulfate (SDS) was obtained in a "specially pure" grade from BDH and used as received. Cetyltrimethylammonium chloride (CTAC) was obtained in a 50% solution from K & K Laboratories and precipitated with acetone/methanol. The precipitate was washed with ether and dried under vacuum. Aqueous solutions of SDS and CTAC were prepared using Millipore purified water.

The samples, usually 2.5 mL, were contained in 7 × 7 mm$^2$ cells made of Suprasil quartz tubing. The micellar solutions were typically 0.1 M SDS or 0.05 M CTAC. The CTAC micellar solutions were sonicated briefly (5 min). Dibenzyl ketone was added to the micellar solutions to

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(5) Closs, G. L.; Forbes, M. D. E.; Norris, J. R., Jr. *J. Phys. Chem.* **1987**, *91*, 3592.

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(14) Turro, N. J.; Chow, M. F.; Chung, C. J.; Tanimoto, Y.; Weed, G. C. *J. Am. Chem. Soc.* **1981**, *103*, 4574.

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(16) Lunazzi, L.; Ingold, K. U.; Scaiano, J. C. *J. Phys. Chem.* **1983**, *87*, 529.

(17) Turro, N. J.; Gould, I. R.; Baretz, B. H. *J. Phys. Chem.* **1983**, *87*, 531.

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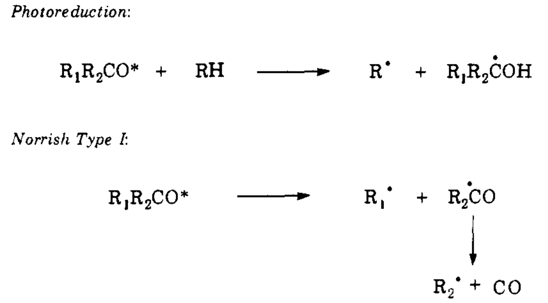
**Scheme I**



$$R_1R_2CO^* + RH \longrightarrow R^{\bullet} + R_1R_2\dot{C}OH$$

$$R_1R_2CO^* \longrightarrow R_1^{\bullet} + R_2\dot{C}O \downarrow R_2^{\bullet} + CO$$

obtain an absorbance at 308 nm of ≈0.3. The absorbance at 308 nm after photolysis was >90% of that before photolysis, indicating that only minor sample depletion occurred during the course of the experiments. Absorbance measurements were made with a Hewlett-Packard 8451 diode array spectrometer. Each sample was purged with oxygen-free nitrogen for 20 min prior to photolysis. In the experiments where the concentration of SDS was varied, the ionic strength of the solutions was kept constant at 0.4 M with sodium chloride.

The samples were irradiated with pulses (308 nm, ~5 ns, ≤30 mJ/pulse) from a Lumonics TE-510 excimer laser operating with Xe–HCl–He mixtures. Transient decay traces were averages of 5–10 shots monitored at 316 nm. Front face irradiation was used with a ca. 20° angle with respect to the monitoring beam. The excitation beam in some cases was attenuated with neutral density filters in order to achieve transient optical densities within desirable limits. Transient absorptions were captured with a Tektronix 2440 transient digitizer and transferred to a Macintosh IIci computer which controls the experiments and provides suitable processing facilities through the use of a home-developed program using LabVIEW-2 software. Further details have been reported elsewhere.[18]

The external magnetic field source was a "homemade" magnet which can achieve fields of up to 2500 G.[19] Continuous variation in the magnetic field from 20 to 1500 G was possible through the use of a Hewlett-Packard 6282A DC power supply.

## Results and Discussion

The choice of the free radical precursor to be used in this work is a very important one. We reasoned that a source of two identical radicals should be preferred over one giving two different species, as illustrated in the photoreduction path of Scheme I. In this way random radical–radical processes involve only one reaction, rather than three. A symmetrically substituted ketone capable of giving the Norrish type I (i.e. $R_1 = R_2$) reaction is an ideal choice, provided that the decarbonylation of $R_2CO^{\bullet}$ (see Scheme I) is complete in the time scale in which random radical processes are monitored.

The mobility of the radicals involved is another important parameter that needs to be taken into consideration. For magnetic fields to exert significant control over the outcome of free radical reactions, the radicals must remain in the micelle for a sufficiently long time for spin evolution to take place. Studies of several radical systems in micellar solution suggest that for carbon-centered radical pairs spin evolution typically occurs with rate constants in the $10^6$–$10^7$ $s^{-1}$ range in the absence of an external magnetic field.[2,14,15,20-24] The benzyl radical has been reported to exit micelles of sodium dodecyl sulfate (SDS) with a rate constant of $1.4 \times 10^6$ $s^{-1}$ at room temperature, thus leading to the expectation that exit and spin evolution should be competitive processes.[15,22]

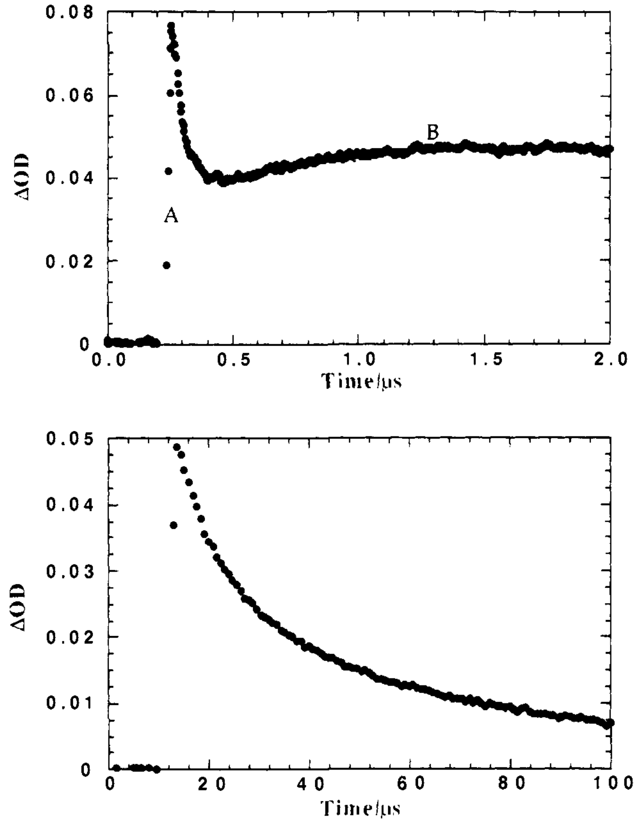


**Figure 1.** Transient decay traces at 316 nm generated upon 308-nm laser photolysis of dibenzyl ketone in 0.1 M SDS: (top) 2.0-µs total time scale; (bottom) 100-µs total time scale.

It is important to understand the reasons why too slow an exit would not be desirable. For example, exit of diphenylmethyl radicals from common micelles is a very slow process and their decay in the absence of an external field occurs exclusively via intramicellar geminate processes.[24] Radicals are usually generated in pairs from relatively hydrophobic precursors;[25] thus, if their exit is extremely slow, no, or very few, radicals would survive the initial geminate decay. As a result, random encounters would rely only on the very few surviving radicals, which would be difficult to examine as a result of the weak signals and long times involved.

The choice of dibenzyl ketone reflects an adequate balance between the rates for exit and spin evolution for at least the benzyl-benzyl radical pair. While we could not find any reports of exit rate constants for the phenylacetyl radical, one can expect it to exit more rapidly than benzyl, given the increased hydrophilicity of the former. Our results (*vide infra*) confirm these expectations.

Figure 1 illustrates representative decay traces recorded upon 308-nm laser irradiation of DBK in a 0.1 M solution of SDS. The concentration of DBK was adjusted to achieve an absorbance of ~0.3 at the laser wavelength. Radical processes are monitored at 316 nm, the absorption maximum for benzyl radicals.[26] Note that in short time scales (Figure 1, top) the initial fast decay is followed by a limited but readily detectable growth. This characteristic of the DBK/SDS traces has been noted before.[27] Figure 2 shows an enlargement of this growth in SDS micellar solution. We attribute this growth to the decarbonylation of phenylacetyl radicals according to reaction 2.

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[22] Turro, N. J.; Zimmt, M. B.; Gould, I. R. *J. Am. Chem. Soc.* **1983**, *105*, 6347.

[23] Turro, N. J.; Zimmt, M. B.; Lei, X. G.; Gould, I. R.; Nitsche, K. S.; Cha, Y. *J. Phys. Chem.* **1987**, *91*, 4544.

[24] Scaiano, J. C.; Shi, J. L. *Chem. Phys. Lett.* **1990**, *173*, 271.

[25] For example, diphenylmethyl radicals are usually generated from 1,1,3,3-tetraphenylacetone, and photodecomposition as well as radical–radical reactions occur within the original micelle.[24]

[26] Chatgilialoglu, C. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II, p 3.

[27] Scaiano, J. C.; Leigh, W. J.; Ferraudi, G. *Can. J. Chem.* **1984**, *62*, 2355.

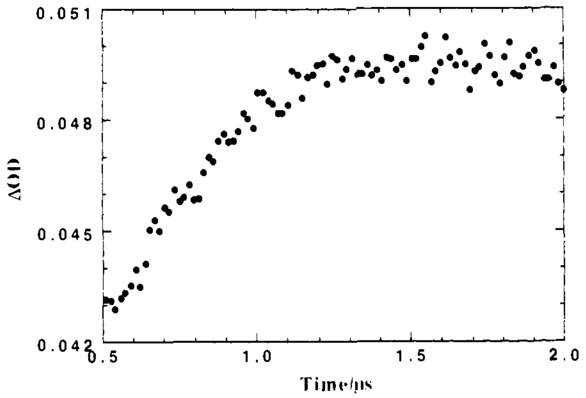

**Figure 2.** Enlargement of the growth at 316 nm observed upon 308-nm laser photolysis of dibenzyl ketone in 0.1 M SDS. The horizontal time scale can be compared directly with that in Figure 1 (top).

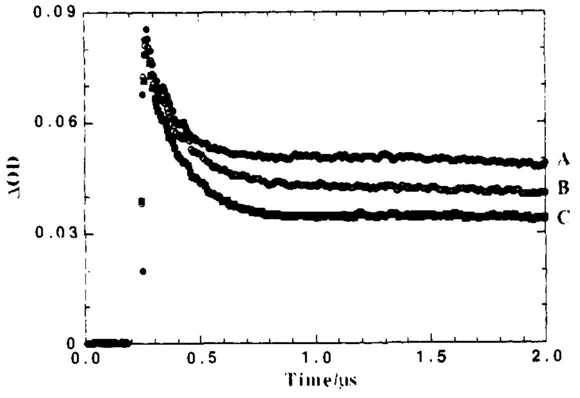

**Figure 3.** Magnetic field effect on the transient decay traces at 316 nm upon 308-nm laser photolysis of dibenzyl ketone in 0.05 M CTAC: (A) $H = 1400$ G; (B) $H = 150$ G; (C) $H = 0$ G.

$$\mathrm{PhCH_2COCH_2Ph} \xrightarrow{h\nu} \mathrm{PhCH_2C^{\bullet}O + PhCH_2^{\bullet}} \tag{1}$$

$$\mathrm{PhCH_2C^{\bullet}O} \xrightarrow{k_{\mathrm{CO}}} \mathrm{PhCH_2^{\bullet} + CO} \tag{2}$$

The growth of $\mathrm{PhCH_2^{\bullet}}$ in Figure 2 can be adequately fitted with a monoexponential function and leads to a rate constant of $\sim 3.5 \times 10^6$ s$^{-1}$ in 0.1 M SDS micellar solution. Within experimental error the same value was obtained in CTAC micellar solution, although we note that this measurement was less accurate due to the decreased importance of this process in CTAC. Decarbonylation rate constants for phenylacetyl are well established in homogeneous solution.[16,17] The values of $k_{\mathrm{CO}}$ are solvent dependent, being $9.1 \times 10^6$, $\sim 7 \times 10^6$, and $5.2 \times 10^6$ s$^{-1}$ (300 K) in isooctane, tetrahydrofuran, and methanol, respectively.[16] The decreased rate constants in polar media are presumably a reflection of stabilization of $\mathrm{PhCH_2CO^{\bullet}}$ relative to $\mathrm{PhCH_2^{\bullet}}$ in these media. Thus, the slow rate constant ($\sim 3.5 \times 10^6$ s$^{-1}$) obtained in micellar systems suggests that this process occurs in an environment that is more polar than methanol. While water is well-known to penetrate the micelles, the resulting environment is very unlikely to exceed the polarity of neat methanol. The simplest explanation is that the growth observed in Figure 1 (top) and Figure 2 reflects the occurrence of reaction 2 in the aqueous phase. Note that this does not imply that decarbonylation does not occur in the micelles, but simply that the slow process monitored occurs in the aqueous phase. We will show below that this is consistent with the nature and kinetics of geminate processes.

Experiments performed in water containing 2% methanol led to a growth lifetime for $\mathrm{PhCH_2^{\bullet}}$ of 345 ns, in full agreement with the value given above. It therefore appears reasonable to assume that the decarbonylation of Figures 1 and 2 occurs in the aqueous phase.

The mechanism of reactions 1 and 2 would lead to 50% of the benzyl radicals being formed "instantly" (i.e. <10 ns)[28,29] and the other half being formed through reaction 2. An extrapolation of the growth segment of the curve to the time of laser excitation for the SDS sample leads to ~37% of the final radicals formed through the slow growth (based on points A and B in Figure 1, top). In fact this must be an overestimate, given that micellar exit is not instantaneous.[30] The observation can be readily rationalized by the occurrence of geminate decarbonylation (prior to radical exit), which is hardly surprising given the extensive studies by Turro's group which demonstrate the importance of cage processes in the self-reaction of benzyl radicals in micelles.[1,23,31]

In the case of CTAC micelles ≤15% of the radicals detected after 2 μs result from the slow growth discussed above.

At long times the decay of benzyl radicals followed remarkably clean second-order kinetics. These processes were typically monitored for 100 μs, a time scale sufficiently long that geminate processes, as well as reaction 2, should be complete. Figure 1 (bottom) illustrates a representative trace in SDS micellar solution,

The following sections discuss in detail geminate and nongeminate processes. While our paper centers on the latter, our data provide a detailed understanding of the former as well. In fact, our results show clearly the dominance of benzyl–phenylacetyl processes (reaction or separation) in the decay of the geminate radical pair from DBK in SDS micelles.[32]

**Geminate Processes in the Absence of a Field.** The decay part of the trace in Figure 1 (top) shows clearly that geminate phenomena occur during the first 500 ns following excitation. Similar data for the DBK/CTAC system are shown in Figure 3. The fast decays can be adequately fitted with first-order kinetics and lead to lifetimes of 50 and 155 ns, for SDS and CTAC micelles, respectively. It is important to establish if these processes involve the benzyl–benzyl or the benzyl–phenylacetyl radical pairs, i.e. whether they precede or follow decarbonylation (reaction 2). We note that the slow rate for reaction 2 measured from the growth kinetics (*vide supra*) cannot be used to rule out intramicellar geminate decarbonylation. Not only would this be contrary to all the cage data mentioned above,[1,23,31] but in addition, one should expect a relatively faster decarbonylation in the micelles, given the known solvent effects on $k_{\mathrm{CO}}$.[16]

A simple interpretation of the fast decay according to the model suggested in earlier work would view the decay kinetics ($k_{\mathrm{decay}}$) as a composite of geminate decay ($k_{\mathrm{gem}}$) and micellar exit ($k_-$) processes, such that

$$k_{\mathrm{decay}} = k_{\mathrm{gem}} + k_- \tag{3}$$

$$\frac{\text{residual } \Delta\mathrm{OD}}{\max \Delta\mathrm{OD}} = \frac{k_-}{k_{\mathrm{gem}} + k_-} \tag{4}$$

where "residual ΔOD" is the transient absorbance following the fast geminate decay. This residual is 48% of the "max ΔOD" if one uses the minimum in the experimental curve (Figure 1, top) and 37% if one extrapolates the delayed growth to the time of laser excitation. Taking ~40% as an intermediate estimate one calculates $k_{\mathrm{gem}} \sim 1.2 \times 10^7$ s$^{-1}$ and $k_- \sim 8 \times 10^6$ s$^{-1}$ in SDS

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[28] Engel, P. S. *J. Am. Chem. Soc.* **1970**, *92*, 6074.

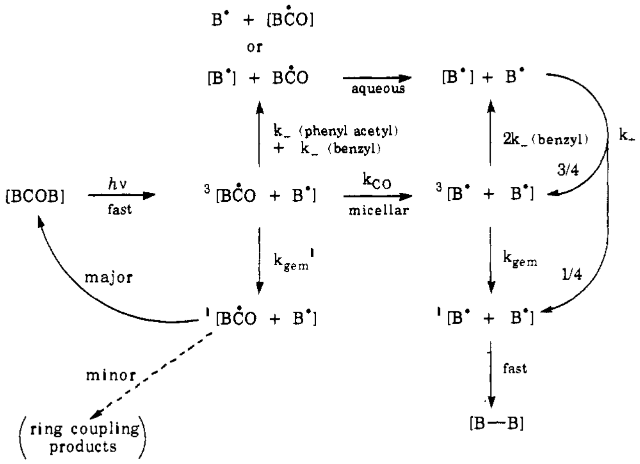
[29] Arbour, C.; Atkinson, G. H. *Chem. Phys. Lett.* **1989**, *159*, 520.

[30] Thus, the "zero time" for the aqueous growth is in reality somewhat displaced with respect to the point of laser excitation; i.e. the true position of point A in Figure 1 should be displaced slightly to the right.

[31] (a) Turro, N. J.; Cherry, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 7431. (b) Turro, N. J.; Weed, G. C. *J. Am. Chem. Soc.* **1983**, *105*, 1861.

[32] Turro, N., Jr.; Paczkowski, M. A.; Zimmt, M. B.; Wan, J. K. S. *Chem. Phys. Lett.* **1985**, *114*, 561.

**Scheme II**[a]



[a] B = $PhCH_2$; micellar incorporation is shown by square brackets; superscripts show spin configuration.

micelles, and a similar analysis leads to $k_{gem} \sim 3.8 \times 10^6$ s$^{-1}$ and $k_- \sim 2.6 \times 10^6$ s$^{-1}$ in CTAC (errors ca. ± 20%). That is, both $k_-$ and $k_{gem}$ decrease with increasing micellar size as already observed in other systems.[15,21,22,33,34] The values of $k_{gem}$ are somewhat higher than those observed for closely related benzylic radicals[15] or free radicals derived from benzophenone photoreduction.[20,21]

The results in the DBK system are however somewhat more complex than those for systems (e.g. dicumyl ketone)[15] where decarbonylation is a very fast process. While early results on DBK[14,35] were interpreted in terms of a fast decarbonylation ($k_{CO}$), results from Turro's and our group establish unequivocally that this process is not as rapid as suggested by early work.[16,17] Further, the delayed growth of benzyl radicals already discussed shows that many phenylacetyl radicals survive the geminate decay and exit into the aqueous phase. Thus, we suggest that $k_{gem}$ represents predominantly (but not exclusively) the reaction between benzyl and phenylacetyl where the main path leads to the starting material, DBK.[36] Scheme II shows a general mechanism for the decomposition of DBK in micelles and follows closely that used by Turro's group in many reports.[1,23] The mechanism shown is a close approximation, although it does not take into account explicitly that diffusion and spin evolution are coupled processes; this has been discussed in detail elsewhere.[5,34,37,38] Note on the right of Scheme II that benzyl radical reentry, $k_+$, has been assumed to lead to a statistical distribution of singlet and triplet encounters. These random processes will be discussed later.

The relatively high values of $k_{gem}$ observed are consistent with the fast decay being dominated by benzyl–phenylacetyl processes. Radical pairs can formally be regarded as biradicals where the ends are prevented from separation by a phase boundary rather than the molecular framework.[4] Indeed, acyl–alkyl biradicals are unusually short-lived[39] when compared with typical lifetimes for carbon-centered biradicals.[40] The short lifetimes of these biradicals and related radical pairs are probably due to the presence of a $\sigma$ radical center.

In SDS micelles we estimated an overall value for $k_-$ of $\sim 8 \times 10^6$ s$^{-1}$, which corresponds to the sum of rate constants for all exit processes. Given the value of $1.4 \times 10^6$ s$^{-1}$ reported for benzyl, one estimates that for phenylacetyl the rate constant for exit from SDS micelles is about $6.6 \times 10^6$ s$^{-1}$. Thus, phenylacetyl is more hydrophilic than benzyl, as expected. The observation is consistent with the solvent dependency of $k_{CO}$ (*vide supra*) that suggests that phenylacetyl is stabilized in polar media. We could not find in the literature a value for the rate of exit of benzyl from CTAC micelles, but assuming that these are usually around one-third of the rates for SDS,[15,21] we estimate that $k_-$ values are $\sim 0.5 \times 10^6$ s$^{-1}$ for benzyl and $\sim 2.1 \times 10^6$ s$^{-1}$ for phenylacetyl exit from CTAC micelles. Thus, the contribution of radical exit to loss of geminate character is largely due (5/1) to exit of phenylacetyl.

The value of $k_{CO}$ in micelles is likely to be faster than the value estimated in the aqueous phase. If we assume a polarity intermediate between methanol and tetrahydrofuran, we can estimate $k_{CO}$ (micelles) at $\sim 6 \times 10^6$ s$^{-1}$. This would imply that, of the original radical pairs in SDS, approximately 23% decarbonylate, 31% separate, and 46% undergo geminate reaction; these numbers should only be taken as a rough estimate, since a fraction (probably 25–50%)[31b] of the benzyl radicals produced via decarbonylation (23%) also contribute to geminate processes, leading to an overall error around ±10%.

A similar calculation for CTAC would be subject to considerably more error given that $k_{CO}$ and $k_{gem}$ are probably about equal. Thus, about 50% of the primary radical pairs should lead to geminate benzyl–benzyl pairs as a result of decarbonylation. As a result of the increased relevance of intramicellar decarbonylation in the case of CTAC, one detects only a very small slow growth of benzyl, consistent with the reduced importance of decarbonylation in the aqueous phase.

**Effect of a Magnetic Field on Processes Occurring on Short Time Scales.** Figure 3 shows decay traces in the DBK/CTAC system at several applied magnetic fields. The main feature is a significant increase in the residual absorption and an apparent slowdown of the decay kinetics. While detailed kinetic analysis of the proposed mechanism would suggest that at least at intermediate fields the rapid decay should not follow simple first-order kinetics, the reality is that once an allowance is made (i.e. base-line shifts) for the residual absorption, all the fast components of the traces can be adequately fitted with first-order kinetics. Figure 4 shows the dependence of $k_{decay}$ with the magnetic field applied for both CTAC (top) and SDS (bottom) micellar solutions; the shape is typical of systems of this type.[33] A simple interpretation is based on the assumption that as a moderate field is applied, triplet–singlet crossing from $T_+$ and $T_-$ is slowed down, while the $T_0 \rightarrow S$ process remains largely unchanged. The experimental $k_{decay}$ is a composite of all these values and as a result decreases in an applied field. At high fields intersystem crossing from $T_+$ and $T_-$ are for practical purposes completely shut off; as a result, the only decay observed is from $T_0 \rightarrow S$, which has the same kinetics as at zero field. Thus, at high fields $T_+$ and $T_-$ contribute to the residual absorption but do not affect the fast decay kinetics. We note that the shape of Figure 4 is characteristic of systems with a slow interconversion between the triplet sublevels. The shape is different for systems involving fast interconversion or equilibration between triplet sublevels.[37]

The residual absorption due to benzyl radicals increases in the presence of a field (see Figure 3) and levels off between 1.0 and 1.5 kG (Figure 5). The yield of residual $PhCH_2^\bullet$ increases by 28% and 33% in SDS and CTAC, respectively. Interestingly, 50% of the maximum effect is achieved with less than 150 G.

**Slow Decay in the Absence of an Applied Field.** The slow decay of benzyl radicals was typically monitored for times up to 100 μs and fitted in the 2-μs to up to 100-μs time window. This decay followed clean second-order kinetics, as illustrated in Figure 6, which includes a conventional second-order fit as well as a

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(33) Evans, C.; Ingold, K. U.; Scaiano, J. C. *J. Phys. Chem.* **1988**, *92*, 1257.

(34) Evans, C. H.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 140.

(35) Turro, N. J.; Okubo, T.; Chung, C. J. *J. Am. Chem. Soc.* **1982**, *104*, 1789.

(36) In addition these radicals react by ring coupling at the ortho and para positions.

(37) Evans, C. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 2694.

(38) Closs, G. L.; Forbes, M. D. E.; Piotrowiak, P. *J. Am. Chem. Soc.* **1992**, *114*, 3285.

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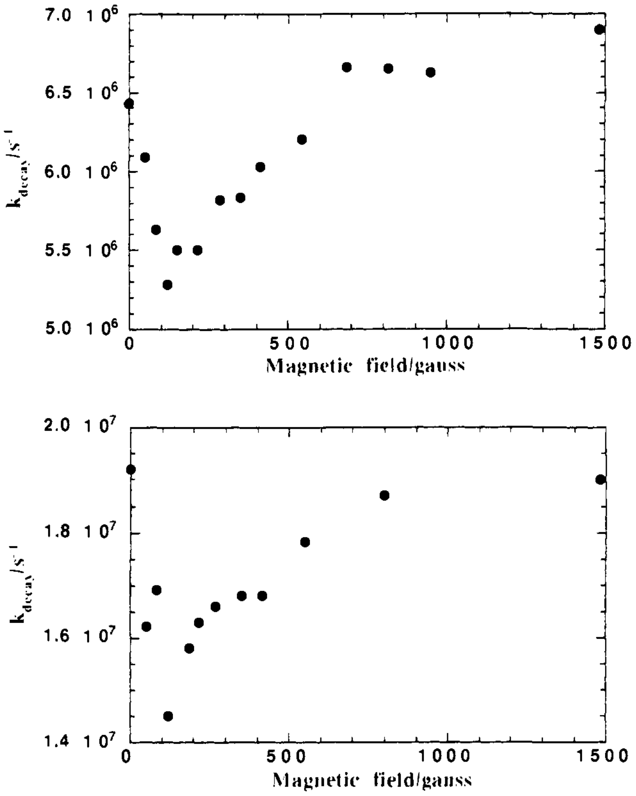

**Figure 4.** Variation of the first-order rate constant ($k_{decay}$) with magnetic field strength for the benzyl–phenylacetyl radical pair: (top) 0.05 M CTAC; (bottom) 0.1 M SDS. Rate constants are reproducible within ±5%, except in SDS at very low fields where errors approach 10%.

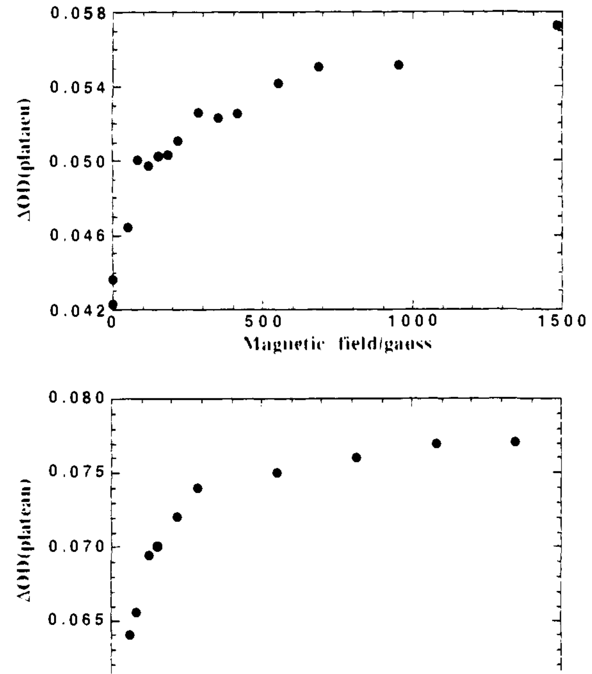

**Figure 5.** Magnitude of the optical density of the benzyl radicals 2 μs after the laser flash as a function of the applied magnetic field: (top) 0.05 M CTAC; (bottom) 0.1 M SDS.

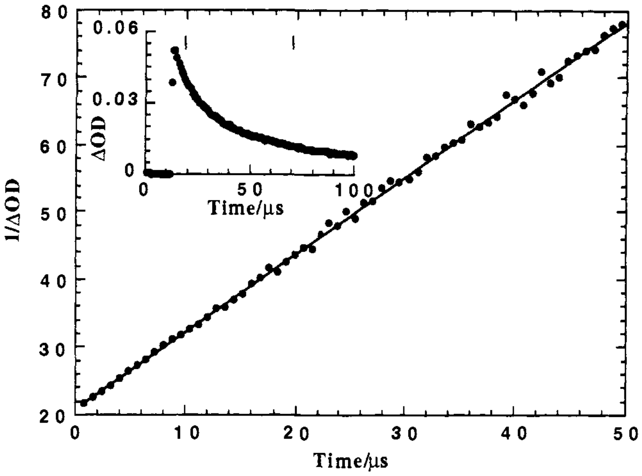

**Figure 6.** Plot of 1/ΔOD as a function of time for the decay of the escaped benzyl radials in 0.1 M SDS. The insert shows the corresponding transient second-order decay trace at 316 nm, and the vertical markers indicate the segment of the trace fitted in the main part of the figure.

representative (insert) decay trace. A plot of the reciprocal of the absorbance against time yields, from the slope, the ratio $2k_t/\epsilon l$, where $2k_t$ is the rate constant for self-reaction of the radicals, $\epsilon$ their extinction coefficient at the monitoring wavelength, and $l$ the optical path employed in the laser experiment. We have shown earlier that for small angle front face irradiation the effective optical path is about 75% of the true one.[41] Thus, an optical path of 0.7 cm leads to an effective path of ca. 0.5 cm. Reported extinction coefficients for benzyl are 8800 and 5500 $M^{-1}$ $cm^{-1}$ in cyclohexane and water, respectively.[42] We employ an intermediate value of 7200 $M^{-1}$ $cm^{-1}$ at 316 nm in our calculations, reflecting the intermediate polarity of the micellar environment. In our experiments (see Figure 6) we obtained $2k_t/\epsilon l$ values of $1.3 \times 10^6$ and $2.0 \times 10^6$ $s^{-1}$ in 0.1 M SDS and 0.05 M CTAC, respectively.[43] For comparison, benzyl undergoes self-reaction with a rate constant of $4.1 \times 10^9$ $M^{-1}$ $s^{-1}$ (298 K) in cyclohexane,[44] while reported values in water are between $3.1 \times 10^9$ and $5.1 \times 10^9$ $M^{-1}$ $s^{-1}$.[45,46]

The rate of self-reaction in micelles can be estimated as

$$-\frac{d[B]}{dt} = k_+[BM][B]_{aq}p_r + 2k_t[B]_{aq}^2 \qquad (5)$$

where the first term on the right corresponds to micellar reaction and the second one to the contribution in the aqueous phase, and $p_r$ is the probability that a radical pair in a micelle resulting from a random encounter will undergo reaction. This value should be between 0.25 and 1.0.[47] BM are the micellized benzyl radicals, and $[B]_{aq}$ represents the aqueous equilibrium concentration of the radicals. [BM] and $[B]_{aq}$ are related through the equilibrium constant for benzyl association with the micelles, M:

$$B_{aq} + M \rightleftarrows BM \qquad (6)$$

The micellar concentrations, [M], can in turn be readily calculated from the well-known aggregation numbers and critical micelle concentrations.[48] For 0.1 M SDS and 0.05 M CTAC, the molar concentrations of micelles are $\sim 1.5 \times 10^{-3}$ and $\sim 6 \times 10^{-4}$ M, respectively. The equilibrium constant for eq 6 is related to the entry ($k_+$) and exit ($k_-$) rate constants according to eq 7.

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(41) Bohne, C.; Abuin, E. B.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 4226.

(42) Chattopadhyay, N.; Dutta, R.; Chowdhury, M. *J. Photochem. Photobiol., A* **1989**, *47*, 249.

(43) These lead to $2k_t$ values of $4.7 \times 10^9$ and $\sim 7 \times 10^9$ $M^{-1}$ $s^{-1}$ in 0.1 M SDS and 0.05 M CTAC, respectively.

(44) Lusztyk, J.; Kanabus-Kaminska, J. M. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. 2, p 177.

(45) Christensen, H. C.; Sehested, K.; Hart, E. J. *J. Phys. Chem.* **1973**, *77*, 983.

(46) Mittal, J. P.; Hayon, E. *J. Phys. Chem.* **1974**, *78*, 1790.

(47) On the assumption that singlet encounters (25%) lead to reaction.

(48) Leigh, W. J.; Johnston, L. J. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II, p 401.

$$K_{eq} = \frac{k_+}{k_-} \tag{7}$$

If we assume diffusion-controlled entry into the micelles ($\sim 10^{10}$ $M^{-1}$ $s^{-1}$), then for both systems about 90% of the radicals will be contained in the micelle. We note that the lower micellar concentration in the case of CTAC can be expected to be approximately compensated by the proportionally lower value of $k_-$. In addition, since $k_+$ and $2k_t$ will have comparable magnitudes, the last term in eq 5 will be small ($\sim$10%) compared with the term related to micellar termination. In a first approximation we neglect the last term in eq 5, leading to

$$-\frac{d[B]}{dt} \sim k_+[BM][B]_{aq}p_r \tag{8}$$

Further we assume that

$$[BM] \approx [B]_{total} \tag{9}$$

and

$$[B]_{aq} \approx \frac{[B]_{total}}{K_{eq}[M]} \tag{9a}$$

from which

$$-\frac{d[B]}{dt} \approx \frac{k_+p_r}{K_{eq}[M]}[B]_{total}^2 \tag{10}$$

and

$$-\frac{d[B]}{dt} \approx \frac{k_-p_r}{[M]}[B]_{total}^2 \tag{11}$$

Equation 11 can also be readily derived by assuming that every radical that exits a micelle will reenter another one (i.e. no aqueous reaction) where it has a probability $p_r$ of reacting. Thus, in a micellar system

$$2k_t \approx \frac{k_-p_r}{[M]} \tag{12}$$

Estimates based on our data lead to estimation of the right term in eq 12 of about $1 \times 10^9 p_r$ $M^{-1}$ $s^{-1}$, which is somewhat lower than the value of $4.7 \times 10^9$ $M^{-1}$ $s^{-1}$ estimated for $2k_t$ in micelles. This may suggest that entry ($k_+$) is not diffusion controlled (i.e. lower than $10^{10}$ $M^{-1}$ $s^{-1}$) and/or that the extinction coefficient for benzyl is closer to the aqueous value than our estimate of 7200 $M^{-1}$ $cm^{-1}$. In any event, given the many approximations involved and the combined errors in $\epsilon$, $k_+$, and $k_-$, it is reassuring that the two sides of eq 12 are of comparable magnitude. The data obtained in the presence of magnetic fields leaves no doubt (*vide infra*) that a large fraction of the self-reaction occurs in the micelles, as opposed to the aqueous phase. Equation 12 predicts that $2k_t$ should have an inverse dependence with the micellar concentration, [M]. In order to test this prediction we carried out a series of measurements for SDS concentrations ranging from 0.1 to 0.4 M; in these experiments the ionic strength was kept constant at 0.4 M using the appropriate concentration of NaCl, in order to minimize variations in micellar size. The values of $2k_t$ follow the expected dependence with [M], as illustrated in Figure 7, which shows decay traces for various micellar concentrations, as well as a plot of $2k_t$ against the reciprocal of [M]. Values of [M] are based on literature data for SDS aggregation.[49]

To end this section it is worth noting that we have also neglected the fact that the benzyl radicals monitored include also those

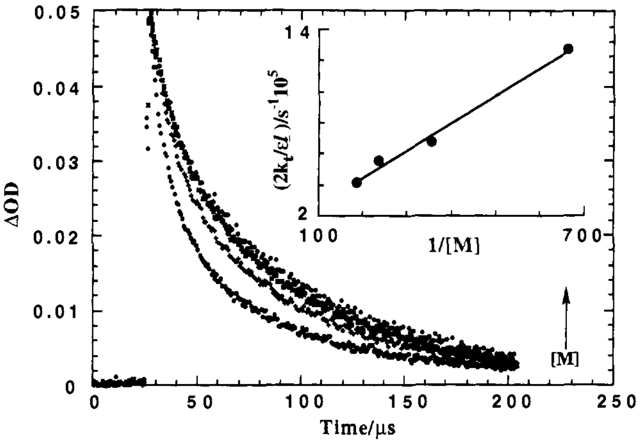

**Figure 7.** Influence on $2k_t/\epsilon l$ for benzyl radicals in SDS micellar solution at SDS concentrations of 0.1, 0.2, 0.3, and 0.4 M. Ionic strength was maintained at 0.4 M by the addition of appropriate amounts of NaCl. Neutral density filters were used to obtain comparable initial optical densities. The insert shows a plot of $2k_t/\epsilon l$ as a function of 1/[SDS micelle].

pairs which at any given time are undergoing a competition between exit and geminate reaction, i.e. those that determine the value of $p_r$. Given that these pairs will have submicrosecond lifetimes, then their steady-state concentration is unlikely to be more than 2% of the total radical concentration. Overall, it is not the error introduced by individual assumptions, but rather the number of assumptions that make the equality of eq 12 a rather soft parameter.

**Magnetic Field Effects on the Slow Decay of Benzyl Radicals in Micellar Solution.** To the best of our knowledge magnetic field effects have not been observed before on the random, nongeminate decay of free radicals in micelles. The only mention of these processes we could find is contained in a 1982 report by Turro.[4] The minor differences observed were within the experimental error, and the author concluded that "the application of a weak magnetic field does not significantly change the rate of slow decaying benzyl radicals." [4] A decade later, with improved laser techniques and an improved understanding of radical processes in micelles, it is clear that Turro's conclusion needs to be revised. The differences we have recorded do reflect the magnetic field effects on these processes.

Figure 8 (top) illustrates radical decay traces in the presence and absence of a magnetic field. Kinetic analysis leads to values of $1.3 \times 10^6$ and $7.3 \times 10^5$ $s^{-1}$ for $2k_t/\epsilon l$ in 0.1 M SDS solution at zero field and for an applied field of 1.4 kG.

Application of a field induces an increase in the radical concentrations as a result of magnetic field effects on the early geminate processes (*vide supra*). We were concerned with the fact that changes in rate constants could reflect changes in the errors of the evaluation, reflecting these concentration changes. In order to explore this possibility we used neutral density filters to attenuate the laser beam in order to match the concentration of radicals in the presence and absence of a field. Figure 8 (bottom) shows an example in which both concentrations have been matched by use of a 65% neutral density filter. The differences are now even more evident. Use of the filter had no effect on the calculated second-order rate constant, although it did affect the half-life, as expected. The effects are very reproducible and readily observable in both micellar systems examined. The effect of the field on the magnitude of $2k_t/\epsilon l$ is shown in Figure 9 for both CTAC (top) and SDS (bottom) micelles. In both systems the rate constant levels off at the higher fields employed, leading to ratios for $2k_t$ in the presence and absence of a field of 0.56 and 0.65 for SDS (0.1 M) and CTAC (0.05 M), respectively.

Since $k_-$ and [M] are independent of the field applied (see eq

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[49] Croonen, Y.; Geladé, E.; Van der Zegel, M.; Van der Auweraer, M.; Vandendriessche, H.; de Schryver, F. C.; Almgren, M. *J. Phys. Chem.* **1983**, *87*, 1426.

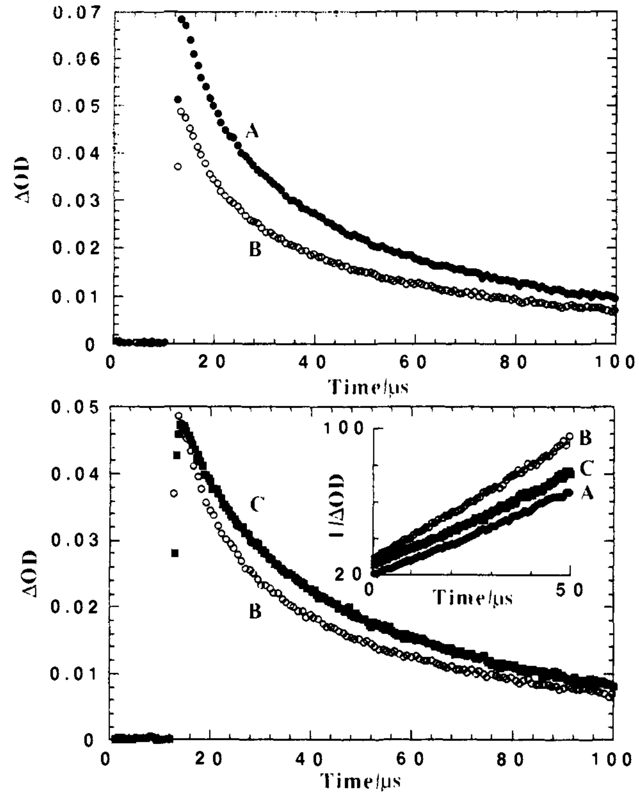

**Figure 8.** Second-order decay traces for the random encounter of benzyl radicals in 0.1 M SDS in the presence (A and C) of an applied magnetic field of 1400 G and (B) in the absence of a magnetic field: (top) A and B generated using full laser dose; (bottom) B generated using full laser dose, C generated after attenuation of the laser dose to 65%. The insert shows a plot of 1/ΔOD as a function of time for the three different traces shown. Note that A and C are parallel, as expected.

12), it is reasonable to assume that the ratios given above are simply ratios for $p_r$ values in the presence and absence of a field, $p_r^H/p_r^\circ$. These ratios should be rather accurate values, in spite of our earlier comments about eq 12 being a "soft" relationship. Most of the errors are systematic and apply equally in the presence or absence of a field. Only the contribution from self-reaction in the aqueous phase is likely to gain slightly in relative importance as the field increases.

The values of $p_r$ can be estimated according to eq 13:

$$p_r = 0.25 + 0.75 p_r^{\text{triplet}} \tag{13}$$

where the value of 0.25 reflects the assumption that 100% of the singlet pairs will undergo reaction (see Scheme II). A similar approach has been employed in highly viscous solvents.[13] We can further expand the triplet component, $p_r^{\text{triplet}}$, in terms of the contribution from the individual triplet sublevels, i.e.

$$p_r = 0.25(1 + p_r^{T_+} + p_r^{T_-} + p_r^{T_0}) \tag{14}$$

If we further assume that in the absence of an applied field the $p_r$ values for the three triplet sublevels are equal, that $p_r^{T_0}$ is unchanged by the field, and that at sufficiently high fields the reactive channels from $T_+$ and $T_-$ can be shut off completely,[50] then the value of $p_r$ triplet can be estimated explicitly, i.e.

$$p_r^{\text{triplet}} = \frac{1 - (p_r^H/p_r^\circ)}{3(p_r^H/p_r^\circ) - 1} \tag{15}$$

which corresponds to reaction probabilities for triplet pairs of ca. 0.4 for CTAC and 0.65 for SDS. Once corrected for singlet contributions, the fractions of triplets that undergo reaction at $H = 0$ are 0.65 and ~0.90 for CTAC and SDS, respectively. This type of analysis also predicts that the minimum value possible for $p_r^H/p_r^\circ$ should be 0.50.

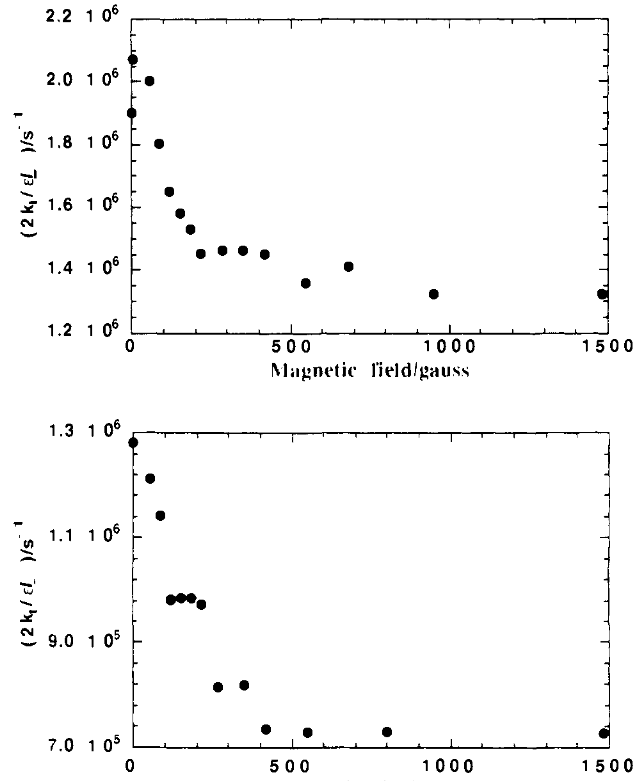

**Figure 9.** Variation in $2k_t/\epsilon l$ for the random encounter of benzyl radicals as a function of the applied magnetic field: (top) 0.05 M CTAC; (bottom) 0.1 M SDS.

In the case of SDS micelles, where exit rate constants are experimentally known,[22] it is possible to use the value of $p_r^{\text{triplet}}$ to estimate a value for the rate constant for intramicellar reaction by the triplet correlated radical pairs which are formed in 75% of the encounters. These radical pairs are essentially indistinguishable from the original triplet geminate pairs (ignoring differences in triplet sublevel populations). Thus, for these geminate-like pairs we also use $k_{\text{gem}}$, acknowledging that in spite of their different origins they should behave like triplet correlated pairs. Thus,

$$p_r^{\text{triplet}} = \frac{k_{\text{gem}}}{k_{\text{gem}} + 2k_-} \tag{16}$$

Note the use of $2k_-$. This reflects the presence of two benzyl radicals in the micelle. Exit of either one prevents self-reaction on any given encounter. The technique employed by Turro et al.[22] measured $k_-$, rather than $2k_-$.[51]

Thus, for SDS we estimate $k_{\text{gem}} = 5.2 \times 10^6\ \text{s}^{-1}$, based on a value of $k_-$ of $1.4 \times 10^6\ \text{s}^{-1}$. This value of $k_{\text{gem}}$ should be compared with that of $1.2 \times 10^7\ \text{s}^{-1}$ estimated earlier for the fast geminate processes. The difference reflects the fact that the initial fast processes are dominated by reaction of benzyl–phenylacetyl pairs, rather than benzyl–benzyl pairs. The latter undergo slower geminate processes, which is in accordance with our suggestion that fast processes in the benzyl–phenylacetyl pair reflect the presence of a $\sigma$ radical site (*vide supra*).

Finally, we note that 50% of the maximum effects (see Figure 9) can be achieved with just ~200 and 120 G in SDS and CTAC micelles, respectively. The results follow the rather common

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[50] Note that the fields used are around an order of magnitude higher than those required to achieve 50% of the maximum effect.

[51] The technique relies on trapping of excited radicals by Fremy's salt and measures *all* forms of radical decay. In the time scale of the measurement only radicals that lost their phenylacetyl partner will be monitored.[22]

observation that smaller fields are required in the larger aggregates. Note also that the fields given above are comparable in magnitude with those from typical laboratory stirring magnets.

**Comparison of Micellized Triplet Radical Pairs of Geminate and Random Origin.** If one could generate a triplet benzyl–benzyl radical pair instantaneously in SDS micelles, one would expect $k_{\mathrm{gem}} \sim 5.2 \times 10^6$ s$^{-1}$, $k_- = 1.4 \times 10^6$ s$^{-1}$,[22] $k_{\mathrm{decay}} \sim 8 \times 10^6$ s$^{-1}$, and 35% residual absorption. The values are in line with those reported for cumyl and *sec*-phenethyl radicals in SDS micelles,[15] except for the unusual observation that the exit ($k_-$) of these radicals is faster than that of benzyl.[15,22,52]

Our analysis of $k_{\mathrm{gem}}$ (see also Scheme II) assumes that triplet radical pairs are identical regardless of whether they are formed from a triplet precursor, or via random encounters of free radicals in the long time scales that characterize the previous two sections of this report. We believe that the only likely difference between pairs from these two origins may be in the relative population of the $T_+$, $T_-$, and $T_0$ sublevels. Random encounters in long time scales should produce essentially equal populations in the absence of a field, while this is not necessarily true of excited triplet-derived radical pairs. In the presence of a field, random encounters may not involve identical populations since intramicellar processes will deplete $T_0$ encounters more rapidly than $T_+$ and $T_-$. Spin relaxation times and reentry probabilities will undoubtedly have an effect; our data does not provide information on these questions.

**Biological Implications.** Earlier studies of magnetic field effects on radical processes in organized assemblies had concentrated on the chemistry of geminate pairs, usually of triplet origin, and exceptionally from singlet precursors.[53] Perhaps as a result of this, these studies have largely escaped the attention of researchers in the biological and health-related sciences.[54] Clearly most biological free radical processes do not involve triplet geminate pairs, which have been the preferred subject on much work. It is, however, worth noting that biologically generated triplet carbonyl compounds, such as acetone,[55-57] may indeed decay through the generation of triplet radical pairs via the photoreduction pathway of Scheme I.

Whatever radical–molecule processes may take place in biological systems, the radical concentrations will be ultimately regulated by radical–radical processes which remove free radicals from the system. Our results show that such radical processes should be the subject of magnetic field effects, and that small fields are sufficient to cause significant effects. Further, a simple model (see eqs 13–15) predicts that the combined singlet/triplet reaction probability could be reduced by as much as 50% and experimental observations lead to reductions in $2k_t$ of 44% and 35% for SDS and CTAC micelles, respectively. Given that magnetic field effects have been observed in a wide range of organized systems in addition to micelles, it would be rather surprising if such effects were absent in biological systems.

## Conclusion

Our results demonstrate unequivocally that magnetic field effects can have a strong influence on the dynamics of radical–radical reactions resulting from random encounters of free radicals in micellar systems. The effects parallel closely those which are well established in radical pairs derived from excited triplet precursors, except that they influence 75% rather than 100% of the radical pairs, the difference reflecting the importance of singlet radical pairs (25%) which are assumed to react with a probability of 1 when sequestered in the same micelle.

Our results also show that fast geminate processes in the DBK system in SDS micelles are dominated by reactions and escape of the benzyl–phenylacetyl pair. These are faster than frequently observed for carbon-centered pairs, reflecting the presence of a σ radical center in $PhCH_2CO^{\bullet}$.

Phenylacetyl radicals are quite hydrophilic and escape rapidly into the aqueous phase (e.g. $k_- = 6.6 \times 10^6$ s$^{-1}$ for SDS) where they undergo decarbonylation with a lifetime of ca. 350 ns. This process is slower than that in organic solvents and presumably the micellar phase as a result of solvent effects that reflect stabilization of $PhCH_2CO^{\bullet}$ in polar media.

The effect of magnetic fields on random processes is also influenced by the competition between spin evolution and radical escape, which determine not only the degree to which a magnetic field influences a reaction, but also the fraction of radicals that escape the fast geminate processes that follow their formation and thus become available for random radical reactions.

**Acknowledgment.** This work has been supported by an operating grant from the Natural Sciences and Engineering Council of Canada.

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[52] Note that the technique used in this case measures $2k_-$.[15]

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[57] Silva, E.; Cilento, G. *Photochem. Photobiol.* **1989**, *50*, 259.