

THE OBSERVATION OF CIDEP FROM THE PHOTODECOMPOSITION OF DIBENZYL KETONE IN MICELLAR SOLUTION

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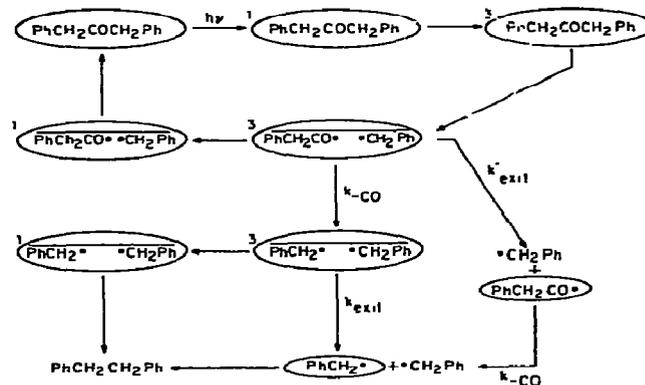
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The photolysis of dibenzyl ketone (DBK) in sodium dodecyl sulfate micellar solution was studied using time-resolved ESR techniques. The CIDEP spectra observed are consistent with phenacyl-benzyl radical pair interactions with little, if any contribution from benzyl-benzyl radical pair interactions. There is a marked contrast in the CIDEP observed in homogeneous and micellar solution which cannot be explained simply by viscosity arguments.

1. Introduction

Our interest in the spin and molecular dynamics of radicals and radical pairs in heterogeneous solution has prompted us to employ time-resolved ESR as a means of gaining further kinetic and mechanistic information. In particular, we have been interested in the photodecomposition of dibenzyl ketone, DBK, and other benzyl radical precursors in ionic and polymeric micelles (scheme 1) [1-5][‡]. In homogeneous solvents, a primary geminate triplet radical pair ($\text{PhCH}_2\text{CO}^\bullet \text{ } ^\bullet\text{CH}_2\text{Ph}$) is produced by homolytic cleavage of the triplet ketone and a secondary triplet ($\text{PhCH}_2^\bullet \text{ } ^\bullet\text{CH}_2\text{Ph}$) geminate pair is produced by decarbonylation. The amount of cage recombination of either the primary or secondary geminate pairs is $\approx 0\%$ in homogeneous solution because of the relatively rapid diffusional separation. The amount of cage reaction of both geminate pairs increases to $\approx 50\%$ within the micelle environment due to the entrapment of the geminate radical pairs within the micelle for a time



Scheme 1.

comparable to that required for intersystem crossing and reactions to occur. The predominant mechanism of intersystem crossing has been demonstrated to be due to a hyperfine induced mixing of the singlet and triplet levels of the radical pair [1].

Most of the information presently available on radical pair reactions in micellar solution has been obtained using time-resolved optical techniques [1-3], steady state chemically induced dynamic nuclear polarization (CIDNP) studies [4], and time-resolved CIDNP studies

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[‡] For reviews of photochemistry in micelles, see ref. [1].

[5]. In CIDNP, one measures the nuclear polarization produced in the diamagnetic products as a result of radical pair interactions within the solvent cage. In time-resolved ESR, one observes the electron polarization produced in the radicals which have escaped the solvent cage. The information obtained from chemically induced dynamic electron polarization (CIDEP) studies provides an integrated account of the pairwise interaction of radicals. The combination of these various techniques provides us with the unique opportunity to obtain mechanistic information concerning radicals from their creation as pairs through their reactions as pairs.

In this communication, we wish to report on our investigations of the photodecomposition of DBK in homogeneous and micellar solutions. Our steady state and time-resolved results reveal some interesting aspects about the interaction of radicals in micellar environment.

2. Experimental

Dibenzyl ketone (Aldrich) was recrystallized from ether at dry ice temperatures. Dibenzylsulfone (Parish), and the surfactant sodium dodecyl sulfate, SDS (Biorad), was used as supplied. All samples were deoxygenated by bubbling with either argon or nitrogen before and during photolysis. Typical solutions contained ≤ 5 mM of either DBK or DBS in 80 mM of surfactant. The solutions were flowed at a rate of ≈ 2 ml/min through a 0.25 mm thick thermostatted fused silica cell.

Our experimental apparatus consisted of a Bruker-IBM ER-100D ESR spectrometer interfaced with a Princeton Applied Research model 440 boxcar averager and signal processor. The signals were detected directly from the diode and were amplified first through a pre-amplifier (6.5 MHz bandwidth) and then through a Corcom video amplifier (500 MHz bandwidth) before being fed into the boxcar.

For the time-resolved experiments, a frequency quadrupled (266 nm) Quanta Ray DCR-2A Nd:YAG laser operating at 20 Hz was used as the excitation source. The laser was synchronized with the gate on the boxcar, and the boxcar was operated either in a static gate mode at a fixed delay time (to give time-resolved polarization spectra) or in a waveform mode

(to supply the decay of the polarization at a fixed magnetic field). Gate widths of 10–20 ns gave the most satisfactory signal-to-noise. Typical laser energies were approximately 5 mJ per pulse (2.5 mJ/cm^2) and the pulse width was 5–10 ns fwhm.

In the steady state mode, the sample was photolysed with a 1000 W Hg–Xe lamp using a NiSO_4 solution filter to isolate the near UV region of the spectra.

3. Results and discussion

For DBK, we have observed marked differences in the steady state ESR spectra of benzyl radicals in homogeneous and micellar solutions at room temperature (fig. 1). The qualitative differences in the spectra are that benzyl radicals in cyclohexanol show a *decrease* in the intensity of the low-field resonances (fig. 1a) while benzyl radicals in micellar solution show a *decrease* in the intensity of the high-field resonances (fig. 1b) in comparison to the calculated spectrum

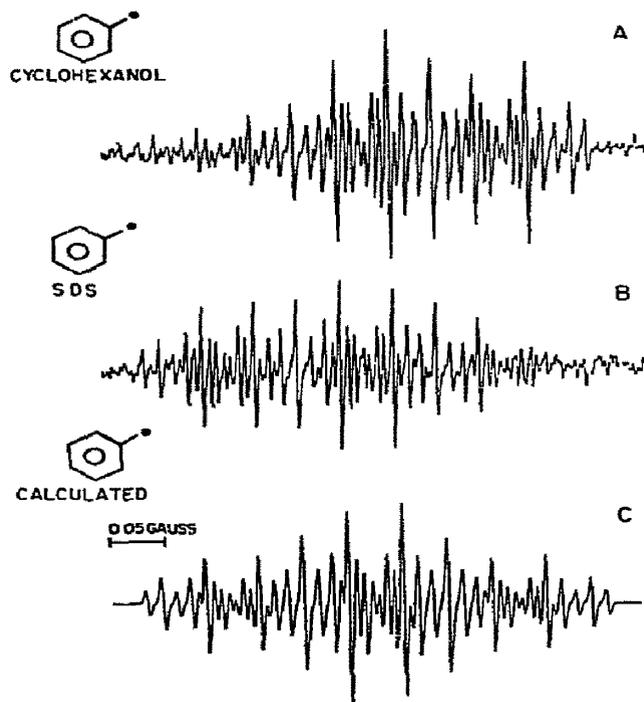


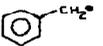
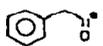
Fig. 1. Steady state ESR spectra of benzyl radicals from the photolysis of DBK in (A) cyclohexanol and (B) SDS micellar solution. For comparison, (C) is the calculated spectrum.

(fig. 1c). The result in cyclohexanol is easily understandable in light of radical pair theory. The spectrum consists of the thermal absorption spectrum and an emission/absorption (E/A) contribution from the interactions of triplet pairs and F pairs. The result in micellar solution, however, is unexpected since a decrease in the intensity in the high-field resonances would suggest the existence of an A/E profile added to the thermalized absorption spectrum. In radical pair theory involving normal $S-T_0$ behavior, this can be possible only if the triplet energy falls *below* the singlet surface in the radical pair ($J > 0$). This possibility has been suggested in at least two instances [6,7].

Table 1 lists the predicted polarizations of the escaped radicals in the photodecomposition of DBK from triplet mechanism (TM) and radical pair mechanism (RPM). The TM polarization predictions are derived from experimental data of McLauchlan et al. [8]. The RPM predictions are made with the assumption that all singlet radical pairs generate products. In the RPM, there are two possible interactions of triplet pairs: benzyl-benzyl (multiplet effect) and benzyl-phenacyl (net effect). The observed CIDEP can have contributions from both TM and RPM.

The time-resolved ESR spectra of benzyl radicals in the photolysis of DBK in isopropanol (fig. 2a) exhibit absorptive polarizations as early as 500 ns after the flash. At longer delay times (figs. 2b, 2c), the spectra develop E/A* polarizations (where the A* indicates net absorption). McLauchlan and co-workers

Table 1
Possible CIDEP signals produced in the photolysis of DBK

Mechanism	Polarization a)		
			
triplet c)	A	A	A d)
RPM			
benzyl-benzyl	E/A	-	E/A
phenacyl-benzyl	E*/A	A	A d)

a) A = absorption; E = emission; E* = net emission.

b) Benzyl radical produced after decarbonylation.

c) The polarizations show here are the observed polarizations seen in the photolysis of DBK in isopropanol.

d) Predicted in the transfer of polarization from the phenacyl radical to the benzyl radical through decarbonylation in the absence of re-encounters.

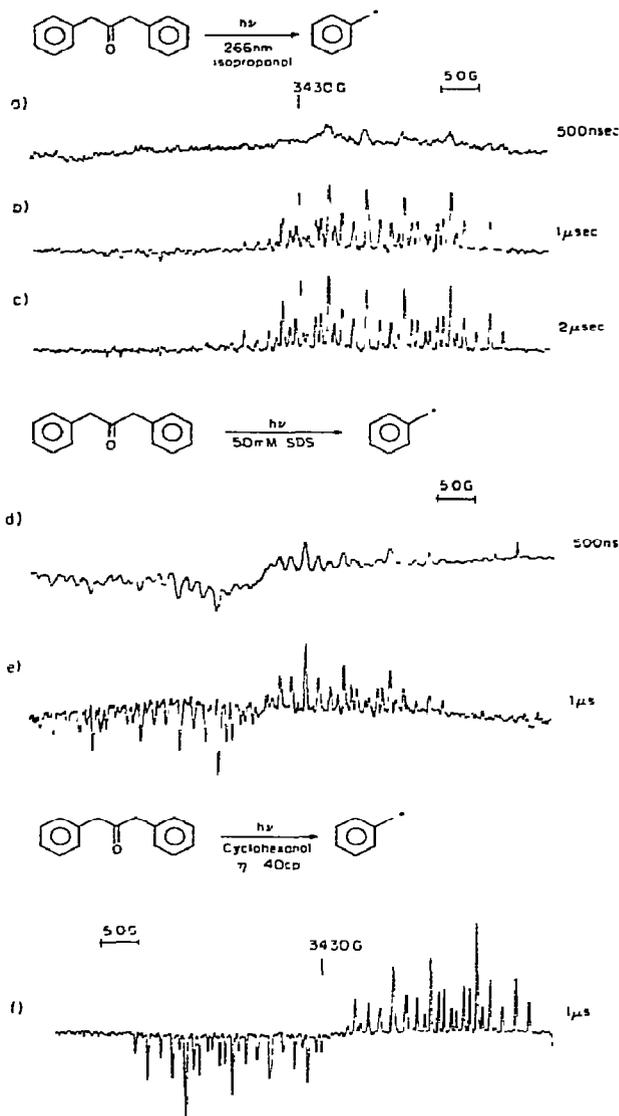


Fig. 2. CIDEP spectra of benzyl radicals from the photolytic decomposition of DBK in (a) isopropanol at 500 ns, (b) isopropanol at 1 s, (c) isopropanol at 2 s, (d) 50 mM SDS at 500 ns, (e) 50 mM SDS at 1 s, (f) cyclohexanol at 1 s.

[8] have reported that the zero-field splitting parameter, D , for triplet DBK is positive which corresponds to absorptive CIDEP due to the TM. The spectral development is attributed to the generation of E/A polarization by RPM in benzyl-benzyl pairs. The observed CIDEP in the benzyl radicals generated from

the photolysis of DBK in micellar solution is remarkably different (figs. 2d and 2e). Even at the shortest time intervals achievable in our system, ≈ 500 ns, the spectrum exhibits E^*/A polarization (RPM net effect). This is an intriguing results since we expected to see more multiplet RPM contribution in light of the high cage value for benzyl–benzyl pairs ($\approx 20\%$) at 3 kG [9].

We have simulated CIDEP spectra based on the RPM formalism of Adrian [10] and find that the majority of the polarization in the experimental spectra can be attributed to $\text{PhCH}_2\text{CO}^{\cdot}\text{CH}_2\text{Ph}$ interactions (fig. 3). The discrepancy between the relative intensities of the observed and calculated spectra, especially in the outer lines, is due to the omission of reactivity terms in our simulation program. The observed spectra contain less than 10% of an absorptive contribution which can arise from three different mechanisms: (1) TM which results in absorption in homogeneous solution; (2) secondary polarization of the benzyl radical from decarbonylation of the phenacyl radical; (3) multiplet effect (up to 20%). Secondary polarizations

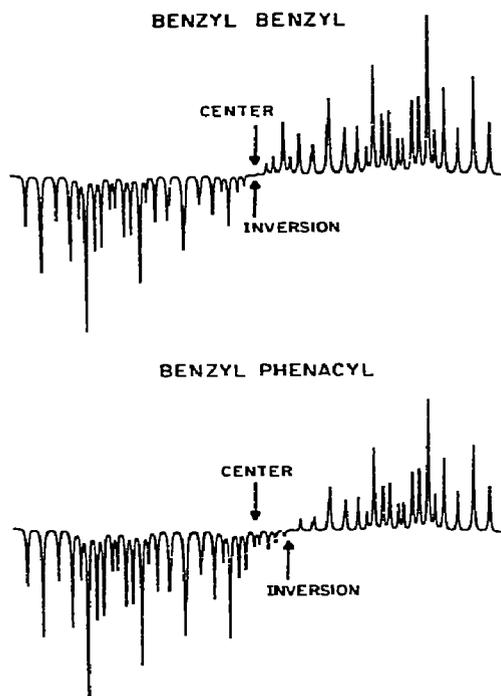


Fig 3. Theoretically calculated spectra of RPM multiplet effect for benzyl–benzyl radical pairs and of RPM net effect for benzyl–phenacyl radical pairs.

can occur if the $k_{-\text{CO}} \gg 1/T_1$ of the phenacyl radical. The polarization of the phenacyl radical from either TM or RPM is absorptive, which would lead to absorptively polarized benzyl radicals assuming no further interactions. The extent of the contribution from each of these mechanisms to the observed spectra is unknown.

In an attempt to differentiate among these three mechanisms, we have studied the photolysis of DBK under a number of conditions. The photolysis of DBK in cyclohexanol (10 mM) gives the CIDEP spectrum illustrated in fig. 2f. The high viscosity leads to a smaller rate of diffusion and therefore an increase in the contribution of RPM to the observed polarization. The center of inversion is to the high-field side of the center of the spectrum (see fig. 3 for comparison) which implies RPM net effect. The observed spectrum can be simulated by adding an absorptive contribution (TM) to the net effect. In an additional experiment, the irradiation of a 10 mM solution of DBK in ethanol cooled to 180 K gave polarization in the resulting benzyl radicals which is consistent with *pure net effect*. This is reasonable since the rate of decarbonylation is slowed to $6.3 \times 10^3 \text{ s}^{-1}$ [11] which leads to more phenacyl–benzyl re-encounters. An intriguing observation is that CIDEP in the phenacyl radical is not observed under these conditions. We suspect that the relaxation rate of the phenacyl radical is too fast to be observed. In steady state experiments, microwave power dependence studies indicate that the benzyl radical resonances are easily saturated while the phenacyl radical resonance only broadens slightly [12]. A crude estimate of the relative relaxation times of the benzyl and phenacyl radicals based on this study indicates that the T_1 of the phenacyl radical is at least an order of magnitude shorter. The observed decay of the benzyl radical polarization in micellar solutions at low microwave power (0.18 mW) fit to a single exponential gives a rate of $\approx 2.3 \times 10^5 \text{ s}^{-1}$. This value is near the reported value of $1.2 \times 10^5 \text{ s}^{-1}$ [13]^{‡‡}. If this is the T_1 of the benzyl radical, then relaxation of the phenacyl radical is faster than the response time of our system.

We can provide a rationalization of the spectra we see for benzyl radicals in micellar solution in light of

^{‡‡} We thank Professor H. Fischer for bringing these results to our attention.

these results. Since the exit rate of the benzyl radicals ($\approx 2 \times 10^6 \text{ s}^{-1}$) [14] and the relaxation rate of the phenacyl radical are of similar magnitude, we are observing polarization in only one of the benzyl radicals. The benzyl radical which results from the decarbonylation of the phenacyl fragment will be thermalized if cleavage occurs after relaxation ($k_{\text{CO}} < 1/T_1$), or absorptively polarized if cleavage occurs before relaxation ($k_{\text{CO}} \geq 1/T_1$) (assuming no subsequent re-encounters). The small multiplet RPM contribution can arise if the radicals remain at a non-zero J for too long a period of time [10]. The radicals' spin can become thermalized by spin exchange.

The rates of polarization decay for the benzyl radical are similar for the high- and low-field lines (within experimental error). These values are $2.3 \times 10^5 \text{ s}^{-1}$ for the high-field line, and $2.8 \times 10^5 \text{ s}^{-1}$ for the low-field line. Comparable decay rates suggest that we are observing polarization decay due to only one species and subsequent F pair encounters do not generate significant CIDEP in micellar solutions.

4. Conclusions

Time-resolved CIDEP spectra of benzyl radicals resulting from irradiation of DBK in micellar solutions illustrate the dramatic effect that the micellar environment has on the interaction of radical pairs. The effects cannot be explained by viscosity alone. The micelle must be acting as a "super cage" which allows strong interactions of both the initial and subsequent geminate radical pairs.

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