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A Time-Resolved Electron Spin Resonance and Laser Flash Spectroscopy Investigation of the Photolysis of Benzaldehyde and Benzoin in Homogeneous Solvents and Micellar Solutions

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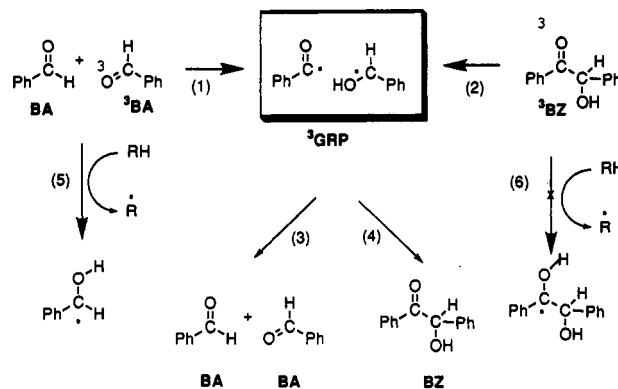
Both photochemical α -cleavage of triplet benzoin (BZ) and hydrogen abstraction by triplet benzaldehyde (BA) from ground-state benzaldehyde produce geminate radical pairs of identical chemical structure. A search for "memory effects" in the chemically identical geminate radical pairs generated from different photochemical pathways was examined using the techniques of time-resolved electron spin resonance (TRESR) and time-resolved optical absorption spectroscopy. Photolysis of BZ in homogeneous organic solvents and in sodium dodecyl sulfate (SDS) micellar solutions leads to chemically induced dynamic electron polarization (CIDEP) of benzoyl and α -hydroxybenzyl radicals consisting of a strong emission (E) due to the triplet mechanism (TM) in the generation of electron polarization. Photolysis of BA in hydrogen-donating organic solvents results in a E/A (or E*/A) CIDEP pattern of α -hydroxybenzyl radicals due to the radical pair mechanism (RPM). In solvents which are poor hydrogen donors (benzene, acetonitrile) and/or at relatively high concentrations of BA, the photoreduction of triplet BA by ground-state BA generates benzoyl and α -hydroxybenzyl radicals, which manifest an E/A CIDEP spectrum assigned to RPM. Photoreduction of BA by KCNS in aqueous acetonitrile results in absorptive (A) CIDEP of α -hydroxybenzyl radicals, assigned to a rare case of RPM for which the g factor difference overwhelms the hyperfine interactions of the pertinent radical pair (the α -hydroxybenzyl and the $(\text{CNS})_2^{\cdot-}$ radical). Computer simulation allows the estimation of the g factor of this inorganic polarized radical to be in the range $2.015 < g < 2.03$. Under conditions of low occupancy number of BA, the photolysis of BA in SDS micellar solution displayed CIDEP spectra assigned to a spin-correlated geminate radical pair (SCRIP) consisting of α -hydroxybenzyl and alkyl radicals of SDS. At a higher occupancy number, a different SCRIP spectrum is observed and is assigned to a polarized α -hydroxybenzyl and benzoyl radical pair. Computer simulation confirms all of the proposed assignments. Measurements of the decay kinetics of the α -hydroxybenzyl radical, observed by time-resolved absorption spectroscopy, show that the application of an external magnetic field of 0.30 T leads to a decrease in the rate of micellized geminate recombination in the photoreduction of micellized BA and to an increase in the rate of radical escape. No significant magnetic field effect was found on the decay of the α -hydroxybenzyl radicals produced from BZ. These results imply that radicals formed by α -cleavage of triplet BZ escape from micelles faster than the chemically identical geminate pair generated by the photoreduction of triplet BA by ground-state BA.

1. Introduction

The photochemistry of benzaldehyde (BA) and benzoin (BZ) has been the subject of a number of investigations.^{1–13} In addition to product analysis,^{1–4} the mechanism of the photolysis of BA and BZ in a variety of solvents has been investigated by the techniques of CIDEP,^{4–6} CIDNP,^{3,6–10} lamp,¹¹ and laser^{12–14} flash spectroscopy employing optical detection. In general, the photochemistry of BA and BZ is solvent and conversion dependent. For the case where hydrogen-donating solvents are employed, photolysis is limited to low conversion to avoid secondary photolysis. The photochemistry of BA and BZ is consistent with the working paradigm shown in Scheme I, where it is assumed that triplet benzaldehyde (^3BA) and triplet benzoin (^3BZ) are the species involved in the primary photochemical events. An interesting aspect of the mechanism shown in Scheme I is the formation of a common primary triplet geminate radical pair (^3GRP) that can be generated in two ways: (1) from the hydrogen abstraction reaction of ^3BA from ground-state BA and (2) from the α -cleavage of ^3BZ . The putative ^3GRP is expected, for example, to collapse to the same set of products (disproportionation to form BA and combination to form BZ, steps 3 and 4 in the Scheme I), independent of the origin of generation. In addition to these primary photochemical processes, ^3BA may abstract a hydrogen from a hydrogen-donating solvent,⁶ step 5, as may ^3BZ .

BA is an important product of the photochemistry of BZ, and BZ is formed as a product of the photolysis of BA under conditions

SCHEME I



that hydrogen abstraction is dominant as a primary process,^{1–4} as suggested in Scheme I. In a pioneering study, Closs and Paulson¹⁰ showed that the CIDNP spectra of BA and BZ are essentially identical, a result consistent with the involvement of a common ^3GRP . Despite these similarities, immediately after their creation, the radical pair may be different in certain measurable ways because of their different origins. Let us term the radical pair produced (Scheme I) in the elementary step of hydrogen abstraction by ^3BA (step 1) as $^3\text{GRP}_{\text{BA}}$ and the radical pair produced by the elementary step of α -cleavage of ^3BZ (step 2) as $^3\text{GRP}_{\text{BZ}}$. It is conceivable that one may observe measurable differences in the spin properties of $^3\text{GRP}_{\text{BA}}$ and $^3\text{GRP}_{\text{BZ}}$. It is clear that, for any "memory" of different origins to remain, one

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must interrogate $^3\text{GRP}_{\text{BA}}$ and $^3\text{GRP}_{\text{BZ}}$ at very early times after their formation or make measurements which contain evidence of the "memory" and which is "slowly relaxing". It occurred to us that another magnetic resonance technique, time-resolved ESR (TRESR) of geminate radical pairs in micelles, might be suitable to search for memory effects in $^3\text{GRP}_{\text{BA}}$ and $^3\text{GRP}_{\text{BZ}}$. Important contributions to the mechanistic use of TRESR were also made by Closs,¹⁵ particularly in the area of probing electron exchange interactions in geminate radical pairs. Recent developments in TR ESR have provided insight into the relationships between reaction dynamics in micelles and magnetic parameters.¹⁶

In this report, we have examined and compared the *molecular* photochemistry of BA and BZ in homogeneous solutions and the *supramolecular* photochemistry of BA and BZ in sodium dodecyl sulfate (SDS) micellar solutions. The motivation for the study was to determine whether the micellized geminate radical pairs generated by hydrogen abstraction (step 1 in Scheme I) and by α -cleavage (step 2 in Scheme I) can be modeled as a *supramolecular system* consisting of a *guest geminate radical pair in a host micellar supercage*. We have employed TR ESR as a direct structural probe of the magnetic features of the radical pairs and have employed (nanosecond and picosecond) time-resolved optical laser spectroscopy and magnetic field effects as a probe of the photochemical dynamics.

2. Experimental Section

A. Instruments. A detailed description of the TR ESR instrument is given elsewhere.^{17,18} The instrument consists of a Bruker ER 100 D spectrometer, a PAR Model 4402 digital boxcar integrator, a Quanta Ray DCR 2A Nd:YAG laser (third [λ 355 nm] or fourth [λ 266 nm] harmonic, 8-ns fwhm, typical laser energy 10–15 mJ/pulse at 20 Hz), and a Bruker broad-band preamplifier with response time of 60 ns. An excimer laser (described below) was also used for photoexcitation of the solutions. Typical sampling gates were 100–500 ns, and the sampling was started at 100–500 ns after the laser pulse. The earliest time at which reliable data can be obtained is estimated to be *ca.* 200 ns. The experiments were run with a flow system consisting of a flat (0.5 mm) quartz cell. Flow rates were chosen in the range 2–5 mL/min.

The nanosecond flash photolysis system employs a Lambda Physik EMG 101 excimer laser (Xe/HCl gas mixture, λ 308 nm, \approx 20-ns pulses, <25 mJ/pulse) for excitation. Experiments were carried out using a 1×1 cm² quartz cell. A pulsed xenon lamp, combined with an ISA H10 monochromator, serves as the monitoring system. The signals from a Hamamatsu R928 photomultiplier tube were terminated into 93 Ω and into a Gould Biomation 4500 digital oscilloscope. This scope was controlled along with other aspects of the experiment (shutters, pulser, etc.) through a GPIB interface (National Instruments) using an Apple Macintosh IIfx computer with Labview 2 software. The data were processed and stored also using the Macintosh and Labview software. Typically 10–15 laser pulses were averaged to produce each experimental trace. Quartz cells having cross sections of 1×1 and 1×0.1 cm² were used. The latter cell was used for solutions of high concentration of BA (see below). In this case the laser pulse entered the sample at a small angle (17°) with respect to the probe beam. Flash photolysis in an external magnetic field was carried out as described elsewhere;¹⁹ i.e., the reaction cell was positioned between the poles of a permanent magnet ($B = 0.30$ T). The short-lived components of the kinetic traces have been measured in separate additional experiments with the accumulation of *ca.* 128 points.

For the picosecond system¹⁸ a typical pump/probe setup²⁰ with monochromatic detection was employed. The output from an actively-passively mode-locked Quantel YG 501 C Nd:YAG laser (λ 1064 nm, fwhm \approx 40 ps, 75 mJ/pulse) was frequency-doubled to produce 532-nm pulses which were divided into two equal

portions. Half of the green light was passed along with the residual fundamental through a KDP crystal to produce the third harmonic, 355-nm pulses (\approx 7 mJ/pulse, fwhm \approx 30 ps), while the second half, reflected at right angles, was passed out a hole cut in the laser cover and directed with a dichroic mirror through a second frequency-doubling crystal to produce 266-nm light (2–4 mJ/pulse, fwhm \approx 26 ps). The residual green left after fourth harmonic generation (\approx 6 mJ/pulse, fwhm 36 ± 4 ps) was also available, after appropriate attenuation of the power to be used as a probe beam. All decay kinetics reported here which correspond to the decay of the triplet-triplet absorption of the BZ employed 355-nm pulses attenuated to less than 1 mJ/pulse as the probe light and either 266- or 355-nm pulses, concentrated to a 2-mm diameter for excitation of the samples. Pump and probe beams entered the cell at a small angle with the diameter of the probe beam being centered within and smaller than the pump beam. The probe beam was passed along a variable delay such that it could arrive at the sample at a delay time between -1000 and +15 000 ps with respect to the pump beam. Data collection, shutter control, and delay line position were automatically controlled via an Apple Macintosh IIfx computer using Labview 2 software which also provided data processing, storage, and hard copy output.

B. Reagents and Solutions. BA and BZ (both from Aldrich) were used as received. Solvents (benzene, 1,4-dioxane, acetonitrile, alcohols, formamide, cyclohexanol, glycerol, *N*-methylformamide, *N,N*-dimethylformamide, benzene, benzyl acetate) were from Aldrich. Potassium thiocyanate (KCNS) was from Baker. Deionized water was used. A binary mixture of acetonitrile/water (1:3 v/v) was also used in experiments with KCNS. For preparation of micellar solutions the following detergents were dissolved in aqueous solutions with subsequent sonication: sodium 1-dodecyl sulfate (SDS, Bio-Rad Laboratories), hexadecyltrimethylammonium chloride (HDTCl, Kodak), sodium salts of 1-hexadecanesulfonic acid, 1-decanesulfonic acid, both from Kodak, and Triton X-100 (Aldrich). The concentration of micelles was estimated²¹ to be *ca.* 2.0×10^{-4} – 5×10^{-3} M, and the aggregation numbers were taken for aqueous solutions containing only corresponding surfactants. The stock solution of SDS micelles (0.33 M) with concentration of micelles of 5×10^{-3} M was used. This solution dissolves large amounts of BA.²² Solutions which contained occupancy numbers ($\langle n \rangle$) of up to 50 molecules of BA²³ were prepared. (The occupancy number ($\langle n \rangle$) is defined as the number of additive molecules per micelle.²¹) BZ and BA were dissolved in solutions in concentration of 5×10^{-3} – 5×10^{-2} M in homogeneous solvents for TR ESR experiments. For laser flash photolysis experiments, the concentration of reagents was adjusted such that an optical density (OD) of about 0.3 at the wavelength of photoexcitation in a 1-cm cell. In the picosecond experiments (λ 355 nm) the OD was much higher, 0.2–0.3 in a 0.2-cm cell. All solutions were deoxygenated by argon bubbling and were maintained at room temperature.

3. Results

A. TRESR Study. Benzoin in Homogeneous Solutions. Laser flash photoexcitation (λ 355 or 308 nm) of BZ in various solvents (1,4-dioxane, *n*-hexadecane, formamide, *N*-methylformamide, *N,N*-dimethylformamide, methanol, 1-propanol, 2-propanol, 1,4-dioxane, acetonitrile, cyclohexanol, glycerol) led to almost identical TRESR spectra (Figure 1). The experimental spectrum is in total emission and consists of a triplet due to the benzoyl radical (lines indicated by the asterisk in the spectrum) and a complex pattern due to the α -hydroxybenzyl radical. Computer simulation (see Results section 3 below) of the benzoyl and α -hydroxybenzyl radical (Figure 1b) shows that that major mechanism of polarization is the triplet mechanism (TM), which leads to single-phase polarization of both radicals.²⁴ No ESR signals of radicals derived from hydrogen abstraction from the solvent were observed.

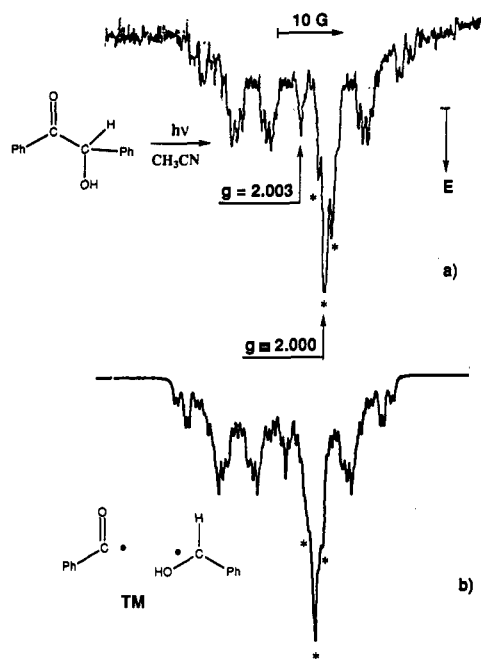


Figure 1. (a) TRESR spectrum of BZ in acetonitrile taken 300 ns after excitation at 308 nm. (b) Computer simulation of the CIDEP spectrum assuming the polarized radicals are the benzoyl and α -hydroxybenzyl and that the mechanism of polarization is TM. See text for discussion.

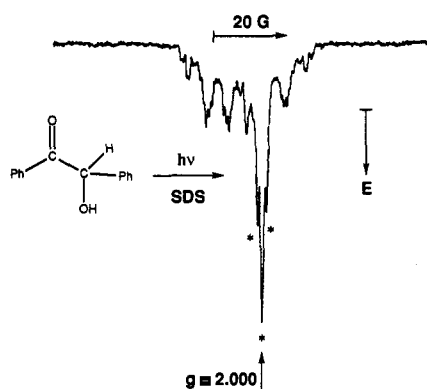


Figure 2. TRESR spectrum of BZ in SDS micelles taken 300 ns after excitation at 308 nm. The peaks labeled with an asterisk are due to the $\text{C}_6\text{H}_5\text{C}=\text{O}$ radical. The remaining peaks are assigned to the $\text{C}_6\text{H}_5\text{C}^{\bullet}\text{-HOH}$ radical, as in refs 4 and 5.

Benzoin in Micelles. A typical TRESR spectrum produced by the laser flash photoexcitation (λ 355 or 308 nm) of BZ in SDS micelles is shown in Figure 2. Spectra with similar features but exhibiting poorer resolution were observed in other micelles. A comparison of Figure 1 and Figure 2 shows that the spectrum produced by the photolysis of BZ in SDS micellar solution is essentially identical to that produced in acetonitrile, so that the carriers of the polarization observed in Figure 1 are safely assigned to the benzoyl and α -hydroxybenzyl radicals. Addition of "inert" molecules such as benzene or benzyl acetate to solutions of SDS (in concentrations formally corresponding to $\langle n \rangle = 50$ molecules of inert additive²³) does not change the form of TRESR spectra produced by photolysis of BZ in micellar solution (Figure 2).

The TRESR spectrum of BZ in SDS micelles with the two central ^{13}C atoms demonstrates the E pattern; hyperfine coupling constant $a_{\text{H}} = 130$ G for benzoyl radical.²⁵

Benzaldehyde in Homogeneous Solutions. Laser photoexcitation (λ 355 or 308 nm) of BA (0.05 M) in acetonitrile or benzene leads to a TRESR spectrum presented in Figure 3a. The photoexcitation of BA ($[\text{BA}] < 10^{-2}$ M) in hydrogen-donating solvents, i.e., alcohols, formamides and substituted formamides, 1,4-dioxane, leads to TRESR spectra of the corresponding free radicals derived from hydrogen abstraction from the solvents.

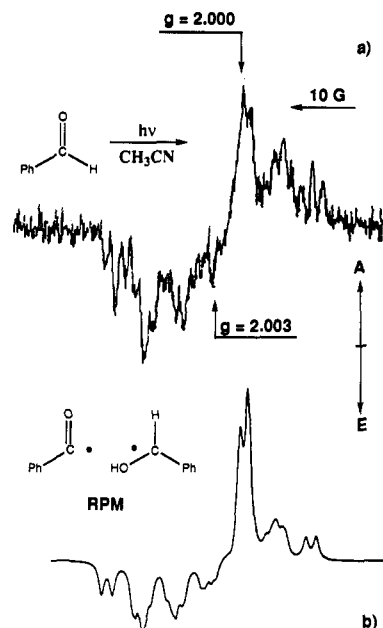


Figure 3. (a) TRESR spectrum of BA in acetonitrile taken 300 ns after excitation at 355 nm. (b) Computer simulation of the CIDEP spectrum assuming the polarized radicals are the benzoyl and α -hydroxybenzyl and that the mechanism of polarization is RPM. See text for discussion.

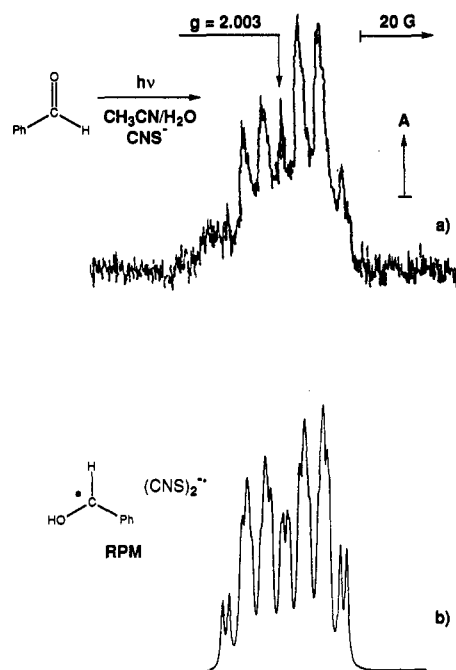


Figure 4. TRESR spectrum of BA in aqueous acetonitrile in the presence of KCNS (0.05 M) taken 300 ns after excitation with λ 355 nm. (b) Computer-simulated CIDEP of α -hydroxybenzyl radical generated by photoreduction of BA by KCNS. For the simulation, the g factor of the $(\text{CNS})_2^{\bullet-}$ radical is taken to be 2.020. See text for discussion.

The carriers of the polarization are again the benzoyl and α -hydroxybenzyl radicals, as demonstrated by computer simulation (Figure 3b; see section 3C) which assumes that the origin of the observed polarization is dominantly the radical pair mechanism (RPM, hyperfine-dependent polarization²⁴).

The photoexcitation of BA in aqueous acetonitrile in the presence of KCNS (0.05 M) leads to the TRESR spectrum presented in Figure 4. The TR ESR spectrum of BA in the presence of KCNS also exhibits a short-lived, poorly resolved emissive component at higher field relative to the spectrum of Figure 4. This component can be observed only at times not longer than 50–100 ns after excitation. Computer simulation (Figure 4b) allows the assignment of the observed polarization

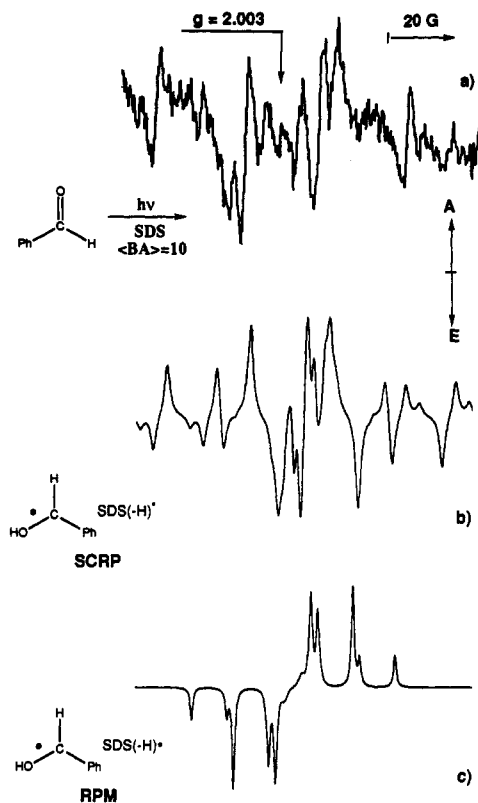


Figure 5. (a) TRESR spectrum of BA in SDS micelles (10 molecules of BA per micelle) taken 200 ns after excitation at 308 nm. (b) Computer simulation of the CIDEP spectrum assuming the polarized radicals are the α -hydroxybenzyl and a radical derived from hydrogen abstraction from SDS and that the mechanism of polarization is SCRIP. For the simulation shown, the exchange interaction is assumed to be $J = -2$ G. See text for discussion. (c) Computer simulation of the CIDEP spectrum assuming the polarized radicals are the α -hydroxybenzyl and a radical derived from hydrogen abstraction from SDS and that the mechanism of polarization is RPM. See text for discussion.

to the α -hydroxybenzyl radical under the assumption that the (unobserved) $(\text{CNS})_2^{\cdot-}$ radical is involved in the generation of the polarization by the RPM (see section 4A).

Photoexcitation of BA at 266 nm in homogeneous or micellar solutions did not lead to significant TRESR signals.²⁶ Only the photolysis of BA in 2-propanol displayed a CIDEP spectrum expected from radicals derived from hydrogen abstraction of the solvent.

Photolysis of Benzaldehyde in Micelles. The TRESR spectrum produced by laser excitation of BA in SDS micelles depends upon the concentration of BA relative to SDS; cf. Figures 5 and 6. We subdivide the observed TRESR spectra into two extreme types, i.e., (i) those obtained under relatively low (formal) occupancy number of BA (up to $\langle n \rangle = 10$ BA molecules,²³ Figure 5) and (ii) those obtained under relatively high (formal) $\langle n \rangle$ (up to $\langle n \rangle = 50$ molecules of BA, Figure 6). We emphasize that the occupancy number indicates a qualitative "swelling of micelles" as the number of additive molecules is increased,^{21c} but we do not attribute a quantitative aspect to $\langle n \rangle$.²³ The TRESR spectrum of BA in SDS micelles changes gradually from one extreme case to the other when the $\langle n \rangle$ of BA is varied between 10 and 50. The use of lower concentration of BA leads to a decrease of signal-to-noise ratio, most likely due to a lower OD of BA at the wavelengths of laser excitation, 308 or 355 nm. (The extinction coefficient of BA is *ca.* $30\text{--}50\text{ M}^{-1}\text{ cm}^{-1}$ depending upon solvent at both wavelengths.²⁷ The extinction coefficient of BA is much higher at 266 nm,²⁷ but as mentioned above, we did not obtain signals with acceptable signal to noise when this wavelength was employed.

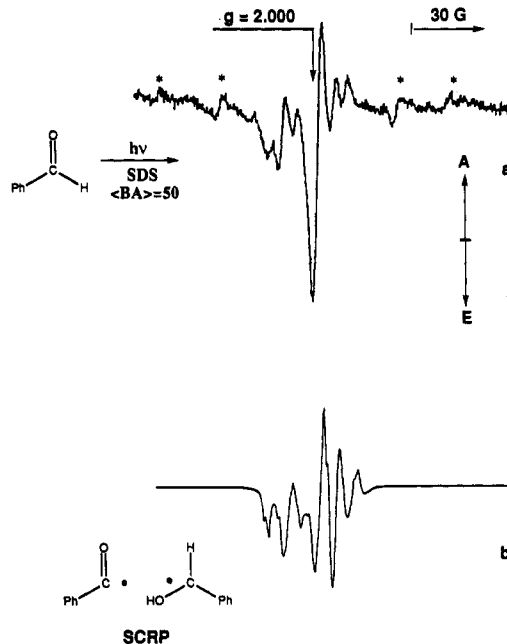


Figure 6. (a) TRESR spectrum of BA in SDS micelles (50 molecules of BA per micelle) taken 200 ns after excitation at 308 nm. Asterisks mark several weak signals of $\text{SDS}(-\text{H})^{\cdot}$. (b) Computer simulation of the CIDEP spectrum assuming the polarized radicals are the α -hydroxybenzyl and a radical derived from hydrogen abstraction from SDS and that the mechanism of polarization is SCRIP. For the simulation shown, the exchange interaction is assumed to be $J = -2$ G. See text for discussion.

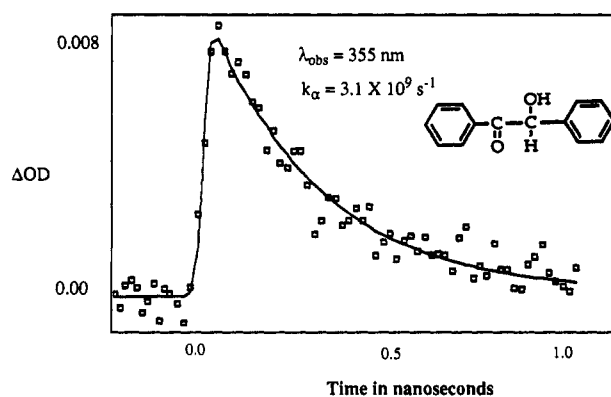


Figure 7. Transient absorption kinetics obtained with the picosecond pump-probe apparatus (pump, λ 355 nm; probe, λ 355 nm) and assigned ^3BZ decay. Obtained under photolysis of BZ in benzene.

The experiments with BA and BZ in other micelles (the detergents are listed in section 2B) lead to results similar to those obtained in SDS solutions (see this section above).

B. Kinetics of Primary Reactions under Benzoin and Benzaldehyde Photolysis. Solutions of BZ in acetonitrile were examined for optical absorption at 355 nm by picosecond pump-probe experiments. A transient absorption appears with a measurable growth of *ca.* 30 ps and decays to base line within a few nanoseconds. We assign the absorption to the triplet state of BA based on the following: (1) the triplet-triplet spectra of similar arylalkyl ketones (e.g., acetophenone²⁸ and β -phenylpropionophenone²⁹) exhibit a broad, structureless absorption in the region 300–400 nm; (2) the growth of the transient absorption is appreciably slower in appearance than that expected for a singlet state of an arylalkyl ketone, which is generally faster;³⁰ (3) the rate constant for decay of the transient is in agreement with that measured by Stern-Volmer quenching.² We therefore assign the decay of triplet BZ (Scheme 1) to the α -cleavage and compute a rate constant $k_d = (3.1 \pm 0.5) \times 10^9\text{ s}^{-1}$.

When BA ($C < 10^{-2}\text{ M}$) in aqueous/acetonitrile or benzene solutions was excited with 308-nm pulses from an excimer laser,

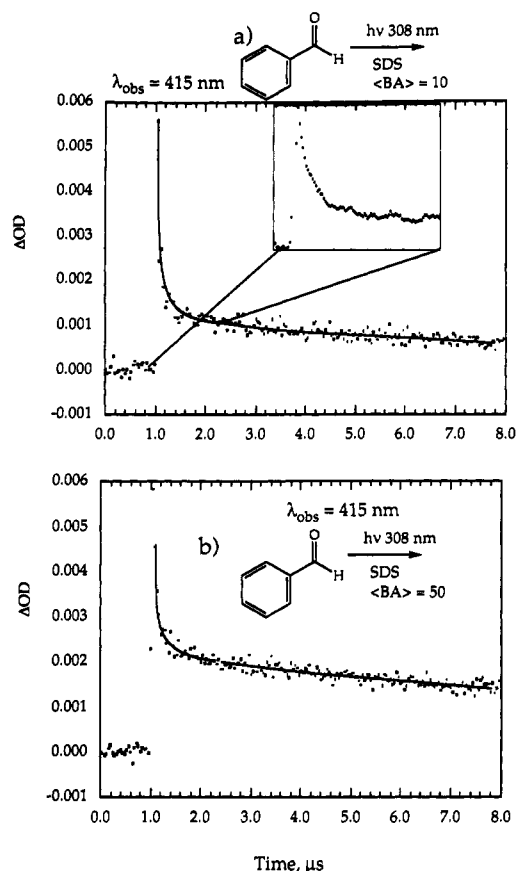


Figure 8. Kinetic traces at λ 415 nm obtained by nanosecond laser photolysis of BA in SDS micelles. The calculated occupancy number of BA molecules was (a) $\langle n \rangle = 10$ and (b) $\langle n \rangle = 50$. The insert displays the fast component of the decay kinetics collected on a shorter time scale following the laser pulse. The data presented on longer time scales are intended to be illustrative of the two-component kinetics. The reported kinetic values of this paper are computed from short-time scale data where appropriate; see section 2A).

a relatively structureless transient absorption in the region 350–450 nm was noted. This absorption was assigned to the triplet state of BA based on the following: (1) the triplet state of BA has been assigned a similar absorption;¹² (2) at high concentration of BA ($C > 10^{-2}$ M) or in the presence of hydrogen-donating reagents or (co)solvents, the absorption is replaced by a different weak but long-lived transient absorption whose spectrum^{11,13} and decay behavior (*vide infra*) are consistent with those of the α -hydroxybenzyl free radical^{11,13} and which were observed on short time scales (or first 2–300 ns) after the laser flash. Excitation of BA in the presence of KCNS produces a strong absorption at λ_{\max} 500 nm, assigned to $(\text{CNS})_2^-$.^{12,31}

When BA and BZ in SDS micelles were excited at 308 nm, a transient absorption of the α -hydroxybenzyl free radical (*vide supra*) is observed, and its decay fits a biexponential. We assign the faster component of the decay to the geminate recombination of the micellized benzoyl/ α -hydroxybenzyl RP and assign the slower component of the decay to reactions of α -hydroxybenzyl radicals which have escaped into the solvent bulk (Figure 8). Application of an external magnetic field leads to a decrease in the portion of the decay assigned to geminate recombination and to an increase in the fraction of the decay assigned to the recombination of α -hydroxybenzyl radicals in the solvent bulk. The latter is consistent with a greater fraction of escape of radicals into the solvent bulk (or a decrease of the cage effect). The results of the magnetic field experiments are summarized in Table I and are discussed below. We note here that the cage escape seems to be larger in the photolysis of BZ for which a clear portion of the decay associated with geminate recombination could not be observed (Figure 9a). The use of benzene or methyl benzoate

TABLE I: Rate Constants,^a Escape Values, and Magnetic Field Effects for the Photolysis of Benzaldehyde and Benzoin in SDS^b Micelles

solution	k_{obs}	k_d	k_r	$e, \%$	field, T	magnetic field effect, %
BA (0.1 M)	22	5	17	25 ± 10	0	
BA (0.1 M)	12	4	8	35 ± 10	0.30	60 ± 15
BZ (5×10^{-3} M), benzene (0.1 M)	18	13	5	70 ± 10	0	
BZ (5×10^{-3} M), benzene (0.1 M)	17	12	5	70 ± 10	0.30	0 ± 15

^a In 10^6 s^{-1} . Determination error: k_{obs} , 15%; k_d and k_r , 20%. ^b Detergent concentration 0.33 M, calculated occupancy number of BA and benzene was $\langle n \rangle \approx 50$ molecules; see section 2.

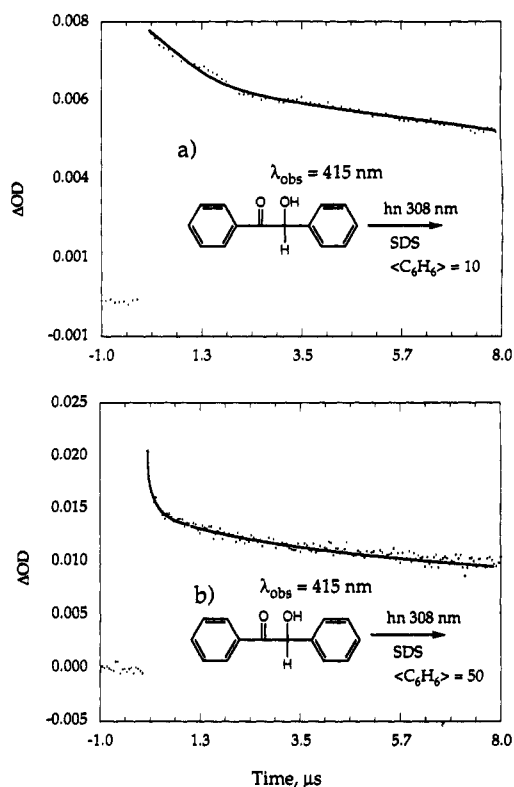


Figure 9. Kinetic traces at λ 415 nm obtained by nanosecond laser photolysis of BZ (5×10^{-3} M) in SDS micelles: (a) micelles did not have other additives; (b) micelles contained sufficient benzene molecules to correspond to an occupancy number of $\langle n \rangle = 50$. For comments to the fast components of kinetic curves see the caption to Figure 8.

to increase the occupancy number of "inert" additives results in an increase in the cage effect (Figure 9b). Within the experimental error (10–15%) there was no magnetic field effect in all experiments with BZ including experiments in micelles with high occupancy number of inert compounds.

C. Computer Simulation of CIDEP Spectra. We simulated the experimental TR ESR spectra based on literature models.^{15,24a} The observed TR ESR spectrum is assumed to be a superposition of two or three spectra, generated by different mechanisms.^{24a} The relative contribution of each mechanism was varied empirically for the best visual match between experimental and simulated spectra.^{15,24a} The HFC constants and g factors of α -hydroxybenzyl, benzoyl, and alkyl radicals of SDS, SDS($-\text{H}$), are literature values.^{4,15}

4. Discussion

A. Photolysis of Benzaldehyde and Benzoin in Homogeneous Solutions. TRESR spectra produced by the photolysis of BZ in acetonitrile and other homogeneous solvents (Figure 1a) agree well with the spectra previously reported in the literature.^{4,5} They

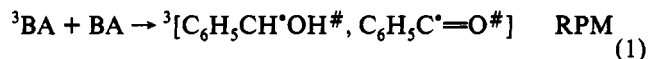
are assigned to the electron polarization in two "free" radicals, $\text{C}_6\text{H}_5\text{CH}^*\text{OH}\#$ and $\text{C}_6\text{H}_5\text{C}^*=\text{O}\#$, under the assumption that the observed spectrum is composed only of polarization due to these two radicals. The ESR spectra of these two radicals are well established, and all of the hyperfine coupling parameters are available in standard references.⁴ Computer simulation (Figure 1b) shows that the observed spectrum is well described as arising mainly from polarization due to TM (E). Thus, the TRESR spectra can be readily understood based on the standard paradigm for the photolysis of a ketone which undergoes intersystem crossing from S_1 to selectively populate the highest energy T_1 sublevel, and which then undergoes α -cleavage faster than triplet sublevel spin-lattice relaxation. For the photolysis of BZ, this sequence produces a geminate pair of emissively polarized $\text{C}_6\text{H}_5\text{CH}^*\text{OH}\#$ and $\text{C}_6\text{H}_5\text{C}^*=\text{O}\#$ radicals (the peaks due to the $\text{C}_6\text{H}_5\text{C}^*=\text{O}\#$ radicals appear to be a triplet, due to hyperfine coupling with the two meta hydrogens of the phenyl ring) which occur close to $g = 2.000$. These absorptions are indicated by the asterisks in Figure 1a. Although TM polarization clearly dominates, a small contribution of RPM (*ca.* 5%)³² manifests itself as a slightly stronger emission of low-field components of α -hydroxybenzyl radical compared to the corresponding symmetrically-related high-field components of the radical. Such a RPM (E/A pattern) is an expected characteristic for a triplet precursor of the observed radicals.²⁴

For TM polarization to be observed α -cleavage must compete with T_1 spin-lattice relaxation (*ca.* $3 \times 10^9 \text{ s}^{-1}$). The lifetime of triplet BZ measured in this work corresponds to a rate constant of α -cleavage (k_a) of *ca.* 10^9 s^{-1} , a value consistent with the requirement for the effective operation of TM. We note that for BZ values for k_a of $1.1 \times 10^8 \text{ s}^{-1}$ ^{14a} and of $1.2 \times 10^9 \text{ s}^{-1}$ ² (both for benzene) have been reported. The former value was derived from laser flash photolysis, and the latter value was derived from Stern-Volmer analysis of the quenching of reaction and the assumption of diffusion-controlled quenching of ^3BZ . Our value agrees well with the value obtained from the quenching results. Moreover, a value of *ca.* 10^8 s^{-1} for decay of ^3BZ would appear to be too slow to compete with T_1 spin-lattice relaxation. We therefore prefer the value of k_a of *ca.* 10^9 s^{-1} .

Carbonyl compounds possessing lowest-lying or thermally accessible triplet n, π^* states are effective hydrogen atom abstractors from a variety of hydrogen-donating solvents.³³ CIDEP, assigned to alkyl and other carbon-centered radicals of solvents resulting from hydrogen abstraction reactions of triplet ketones, is commonly observed.^{16a,34} However, we do not observe CIDEP from such radicals even when BZ is photolyzed in excellent hydrogen-donating solvents such as 2-propanol. This result supports the conclusion of a very high rate of α -cleavage of triplet BZ, as is readily demonstrated from a simple kinetic argument. The rate constants of hydrogen atom abstraction by typical n, π^* triplet states of carbonyl compounds from good hydrogen donors are in the range *ca.* $1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (e.g., photoreduction of triplet benzophenone by 2-propanol)³³ so that in a neat solvent (*ca.* 10 M) the pseudo-first-order rate constant for hydrogen abstraction will be of the order of 10^7 s^{-1} . From the measured rate of triplet deactivation of BZ (10^9 s^{-1}), the rate of hydrogen atom abstraction is expected to be about 2 orders of magnitude slower than α -cleavage and will not be able to compete successfully with photodissociation, a result consistent with the TR ESR results.

Although the lowest triplet state of BA is thought to be π, π^* in character,¹³ the rate constant for hydrogen abstraction by ^3BA from hydrocarbons has been reported to be *ca.* $4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. This fast rate may be due to favorable steric factors, electronic factors, or a low-lying reactive n, π^* state. The rate constant for self-quenching of ^3BA by ground-state BA is apparently very solvent dependent, as deduced from self-quenching studies: $k_1 \approx 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in *n*-hexane^{6,35} and $k_1 \leq 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile.¹³ From these considerations, the abstraction of a

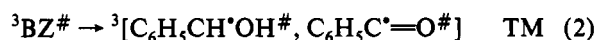
hydrogen atom by ^3BA from a ground-state BA is expected to occur at sufficiently high concentration of BA and to produce the same triplet geminate radical pair as is produced by the α -cleavage of ^3BZ (Scheme I). Indeed, in investigations of the ^1H CIDNP produced by either photolysis of BZ or BA, similar CIDNP spectra were observed for both systems.¹⁰ However, the TRESR spectra (Figure 3a) observed when that ^3BA abstracts a hydrogen atom from ground-state BA (eq 1 of Scheme I) are clearly different from that observed by the photolysis



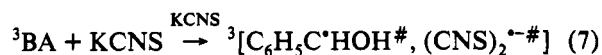
of BZ (Figure 1a) and is of the E/A pattern that is typical of CIDEP produced by the RPM. (The symbol # designates an electron polarized intermediate.) The simulation of the CIDEP spectrum expected from "pure" RPM involving the $\text{C}_6\text{H}_5\text{CH}^*\text{OH}$, $\text{C}_6\text{H}_5\text{C}^*=\text{O}$ radical pair (Figure 3b) is in reasonable agreement with the experimental spectrum (Figure 3a). The contribution of TM to the observed spectrum is estimated to be less than 5%.

When the concentration of the BA in solution is low and is in solvents that have readily abstractable hydrogen atoms, CIDEP signals associated with radicals produced by hydrogen abstraction are observed. In acetonitrile, a poor hydrogen-donating solvent for carbonyl triplets, even at relatively low [BA] of the order of 0.05–0.1 M, ^3BA is photoreduced only by BA ground-state molecules.

The CIDEP spectra produced by the photolysis of BZ (Figure 1a)



and BA (Figure 3a) in homogeneous (nonreactive) organic solvents display the E and E/A patterns expected from conventional TM and RPM polarization, respectively. The main features of these spectra derive from the hyperfine lines of the α -hydroxybenzyl radical. However, a third, and rather unusual, CIDEP spectrum consisting of an essentially total absorptive pattern was observed when BA was photolyzed in aqueous acetonitrile solutions containing KCNS (Figure 3c). The spectrum is interpreted as resulting from RPM after the electron abstraction from CNS $^-$ by ^3BA as the primary photochemical step (eq 7). According to the literature¹² and our own laser flash photolysis results, ^3BA is very reactive toward KCNS. After the elementary act of electron transfer,¹² the primary radical anion formed is $\text{C}_6\text{H}_5\text{CHO}^{\cdot-}$, a species that is expected to be rapidly protonated in aqueous acetonitrile to form the α -hydroxybenzyl radical ($\text{p}K_a = 10.5$ ¹¹). Under high concentrations of KCNS used in the experiments (0.05–0.1 M) the CNS $^-$ counter radical is rapidly replaced by $(\text{CNS})_2^{\cdot-}$ counter radical during the cage lifetime.³¹



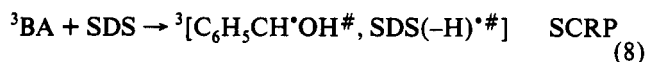
With this mechanism as a model, we now consider how the observed absorptive CIDEP spectrum could result. Although we have not been able to locate the magnetic parameters for $(\text{CNS})_2^{\cdot-}$ in the literature, it is expected that significant spin-orbit coupling in this radical ion will cause an electronic relaxation time that is smaller and a g factor that is larger than the respective parameters of the α -hydroxybenzyl radical. With these assumptions, we simulated the spectrum of α -hydroxybenzyl radical (Figure 4a) according to the operation of the RPM (Figure 4b) with $(\text{CNS})_2^{\cdot-}$ as the second radical of the pair. From the simulation, reasonable agreement with the observed spectrum was obtained if the g factor of the $(\text{CNS})_2^{\cdot-}$ is assumed to be in the range $2.015 < g < 2.03$. It appears that the observed spectrum in Figure 4a corresponds to a rare example of RPM, where the contribution of the Δg term to the rate of S–T interconversion is considerably larger than that of HFC term.

Such a situation leads to an A (E) pattern of CIDEP of a radical with smaller (larger) g factor for a triplet-derived RP, rather than the more usual E/A (A/E) pattern when the hyperfine term is dominant. In this unusual case, the observed polarization will only weakly depend upon hyperfine states of the radicals involved. Although only one phase of polarization is observed, it is emphasized that it is produced by RPM and should not be confused with single-pulse polarization produced by TM.

B. Photolysis of Benzaldehyde and Benzoin in SDS Micelles. The micellar effects on TRESR spectra produced by the photolysis of BZ and BA are shown in Figures 2 and 5a, respectively. The TR ESR spectrum of BZ in SDS micelles does not differ substantially (except for signal-to-noise considerations) from that observed in homogeneous solution (Figure 1a), so that the polarization is clearly dominated by TM. Nor does the spectrum change significantly when substantial amounts of benzene are added to the micellar solutions of BZ. (The rationale for this experiment will be apparent after the results with BA are discussed.)

In contrast to the similarity of the TRESR spectra observed from photolysis of BZ in homogeneous or SDS micellar solution and its lack of a dependence on occupancy number, the photolysis of BA in micellar SDS solutions led to CIDEP spectra (Figures 5a and 6a), which differ markedly in form from those obtained for photolysis of BA in homogeneous solvents (Figure 3). The pattern observed (biphasic hyperfine lines) has been shown to be characteristic of radical pairs possessing a significant spin-spin coupling through the electron-exchange (J) interaction and is typical of the CIDEP observed for RPs in media with restricted molecular mobility, i.e., biradicals and micellized radical pairs.^{15,16} Radical pairs displaying such spectra have been termed as spin-correlated radical pairs (SCRPs).^{15,16,24a}

Interestingly, the results depend on the ratio of BA to surfactant employed. Occupancy numbers of $n = \langle 10 \rangle$ and $n = \langle 50 \rangle$ were employed to obtain the spectra shown in Figures 5a and 6a and are termed "low" loading and "high" loading of BA, respectively. The spectrum obtained in the case of low loading of micelles is not of good quality from the standpoint of signal to noise (Figure 5a), but from computer simulation (Figure 5b), the spectrum observed can reasonably be assigned as arising mainly from a spin-correlated radical pair (SCRPs) consisting of an α -hydroxybenzyl and an alkyl radical of SDS, i.e., $^3[\text{C}_6\text{H}_5\text{CH}^*\text{OH}\cdot, \text{SDS}(-\text{H})^*\cdot]$, and does not arise from RPM of the same pair, as found in homogeneous solvents (Figure 5c).³⁶ Such a SCRPs radical pair is expected to result from hydrogen atom abstraction from SDS by ^3BA (eq 8).



Indeed, among the first examples of SCRPs were those produced when triplet benzophenone abstracted hydrogen from SDS micelles.¹⁵

At high loading of BA ($\langle n \rangle = 50$), a different TRESR spectrum from that observed at low loading was found (Figure 6a). The spectrum observed at high loading is clearly recognizable through computer simulation (Figure 6b) as dominantly derived from the SCRPs derived from hydrogen abstraction by ^3BA from ground-state BA, i.e., $[\text{C}_6\text{H}_5\text{C}^*=\text{O}\cdot, \text{C}_6\text{H}_5\text{C}^*\text{HOH}\cdot]$, with a contribution from the pair derived from hydrogen abstraction by ^3BA from SDS. The TRESR spectrum of the latter RP, polarized according to RPM or SCRPs mechanism, is spread much wider due to the larger HFC of the alkyl free radical (21 and 25 G)¹⁵ compared to α -hydroxybenzyl and benzoyl radicals (compare Figures 3 and 5). Evidently, even at high loading the photoreduction by SDS occurs to a small extent and manifests itself in the existence of several weak signals of $\text{SDS}(-\text{H})^*\cdot$ in the outer part of the spectrum (noted by asterisks in Figure 6a).³⁷

Now we seek a supramolecular structural basis to explain the

basis for the difference in the results on TRESR spectra of the "same" ^3GRP , $^3[\text{C}_6\text{H}_5\text{CH}^*\text{OH}\cdot, \text{C}_6\text{H}_5\text{C}^*=\text{O}\cdot]$, obtained in SDS micelles by two different pathways: by photoreduction of BA and by photodissociation of BZ. We emphasize that the conditions required to produce the pair from micellized BA require high loadings, so that a comparison with the results for micellized BZ was performed with the addition of sufficient benzene to make the occupancy number *ca.* 50, thereby mimicking the system of BA in SDS at high loading. For photoreduction of micellized BA, a SCRPs spectrum was observed, whereas for the photodissociation of BZ, a SCRPs spectrum was not observed. Among the possible sources for this difference between the two systems is a difference in the initial mutual orientation of the ^3GRP , $^3[\text{C}_6\text{H}_5\text{C}^*\text{HOH}\cdot, \text{C}_6\text{H}_5\text{C}^*=\text{O}\cdot]$, produced by photoreduction compared to that produced by α -cleavage. Such an initial stereochemical difference would be expected based on the stereoelectronic requirements of the primary photochemical processes.^{33c} An initial difference in the structure of the micellized RP could lead to a difference in the reactivity and the molecular dynamics of the pairs, i.e., the dynamics determining the competition between recombination reactions and escape from the micelle into the bulk aqueous phase. However, hydrophobic micellized organic $^3\text{GRPs}$ often undergo a large number of collisions and reencounters in micelles before escaping into the aqueous phase.³⁸ These repetitive contacts and reencounters are the source of the enhanced cage effects observed for $^3\text{GRPs}$ in micelles and for the existence of large magnetic field effects on the reactions of micellized radical pairs.³⁸ Such repetitive contacts would be expected eventually to average out the effects of possible different initial mutual orientations of the radicals comprising the two $^3\text{GRPs}$ at the time of observation by TRESR (*ca.* 300 ns after creation of the pair). Recently, we have shown that the hydrophobicity of radical pairs, which extends their lifetime in micelles, is essential for observation of SCRPs.³⁹ However, hydrophobicity *per se* is not an obvious feature that would lead to different behavior of two *chemically identical* $^3\text{GRPs}$ which happen to be generated from different precursors.

We now consider the kinetic data obtained from nanosecond laser flash spectroscopy to obtain further insight into the possible sources of the different behavior of the $[\text{C}_6\text{H}_5\text{C}^*\text{HOH}\cdot, \text{C}_6\text{H}_5\text{C}^*=\text{O}\cdot]$ pair produced from photolysis of micellized BA and BZ. Inspection of Figures 8 and 9 reveals clear differences in the decay of the $\text{C}_6\text{H}_5\text{C}^*\text{HOH}$ radical in SDS micelles depending on whether the precursor is BA or BZ. In both cases a nonexponential decay is observed. We shall employ a simple kinetic treatment of geminate recombination⁴⁰ in which all processes are described as first-order reactions. The data in Figures 8 and 9 can be described as consisting of two first-order processes termed "fast" decay and "slow" decay.

The fast initial decay is assigned to geminate recombination of micellized pairs and may be described by a first-order rate constant, k_{obs} . It is convenient to define $k_{\text{obs}} = k_r + k_d$, where k_r is the rate constant of recombination within the micelle and k_d is the rate constant of irreversible escape from micelle to form free radicals. The fraction of escape is defined as $e = k_d/k_{\text{obs}}$.⁴⁰ Such treatment allows the estimation of the parameters k_d , k_r , and e , and the estimated values of these parameters are summarized in Table I. Note that in comparing the results the SDS micelles containing BZ were loaded with benzene to mimic the high loading condition of BA (Table I).

The influence of a magnetic field on the measurable parameters of radical pairs in micelles has been an important mechanistic tool for understanding of behavior of the pair.⁴⁰ The magnetic field effect A on the "cage" reaction of radical pairs in micelles is defined as $A = (e_B - e_0)/e_0$, where e_B and e_0 are the fractions of micelle escape in the external magnetic field B and in the earth's field, respectively. The validity of such a description is supported by the observation that k_d , the value of the escape rate

of radicals from micelles, for experiments with BA does not depend, within the experimental error of its estimation, upon an external magnetic field (Table I) as one might have expected.^{40a}

Within the accuracy of the data of Table I and the validity of our assumptions in treating the data, it appears that k_r for BZ is comparable to or smaller than corresponding constants for BA and that k_d is clearly larger for BZ compared to that for BA. In addition, the escape efficiency for BZ (70%) is twice as large as that for BA (35%). Thus, the conclusions from Table I are that the $\text{C}_6\text{H}_5\text{CH}\cdot\text{OH}$ radical escapes faster from "highly loaded" SDS micelles when this radical is prepared from BZ (compared to preparation from BA) and that the fraction of escape is greater for this radical from "highly loaded" SDS micelles when it is prepared from BZ (compared to preparation from BA).

The conclusions derived from the independent laser spectroscopy experiments allow an understanding of the results of the TR ESR experiments. An enhanced rate and efficiency of escape from a micelle are expected to lead to weak or absent SCRPs signals,¹⁵ because a fast or efficient escape will cause the number of SCRPs to be small or absent at the earliest time of TR ESR observation. In experiments involving the photoreduction of benzophenone in different micelles, the absence of CIDEP signals ascribable to SCRPs in the small 1-octyl sulfate micelles was due to a large fraction of (or fast) escape.¹⁵ Other possibilities include a smaller value of k_r for radical pairs derived from BZ (cf. Table I) as well as an overwhelming polarization due to TM for this system.

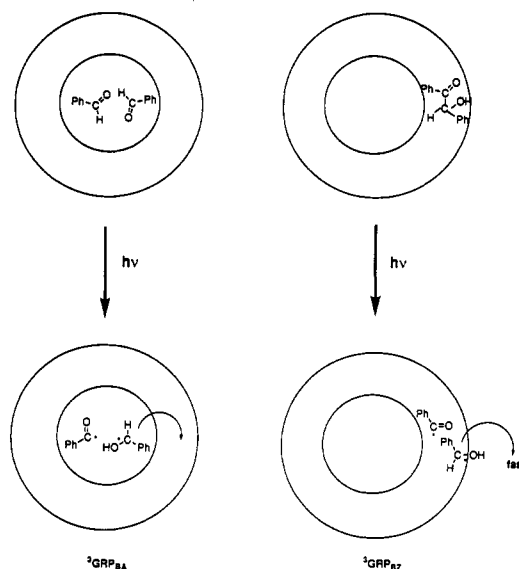
Thus, both the results of TRESR and laser spectroscopic measurements are consistent with the conclusion that α -hydroxybenzyl radicals produced in the photolysis of BZ escape faster and more efficiently from SDS micelles than the same radicals produced in the photoreduction of ^3BA by ground-state BA. The question now arises as to whether such a conclusion is in turn consistent with conventional supramolecular paradigms of the structure of radical pairs in micellar systems or whether a paradigm modification is required.

It is becoming increasingly clear that micellized radical pairs are an example of guest-host supramolecular systems for which the properties of the guest cannot be treated independently of the properties of the host. In this regard, many of the structural features associated with molecules can be considered as appropriate to describe the structures of supramolecular systems. In molecular terms, if two systems have identical compositions but measurably different properties, they are considered to be isomeric. We therefore anticipate isomeric supramolecular systems.

Let us consider the supramolecular system of two radical pairs that are identical in composition (host = SDS micelle, guest = $[\text{C}_6\text{H}_5\text{C}\cdot\text{HOH}, \text{C}_6\text{H}_5\text{C}\cdot=\text{O}]$ geminate radical pair) but which differ in terms of their initial connectivity. By connectivity we mean the location of the pair at its moment of birth depending on whether it was formed by the α -cleavage of ^3BZ or the hydrogen abstraction by ^3BA from ground-state BA. It is reasonable that BZ is sited, on the average, with the hydrophilic hydroxy group near or protruding into the Stern layer at the very hydrophilic micelle water interface, with the benzoyl group pointing toward the hydrophobic micellar core.⁴¹ If this model has validity, upon photolysis of BZ, the geminate $\text{C}_6\text{H}_5\text{C}\cdot\text{HOH}, \text{C}_6\text{H}_5\text{C}\cdot=\text{O}$ radical pair will be "born" with the $\text{C}_6\text{H}_5\text{C}\cdot\text{HOH}$ radical close to or in the hydrophilic micellar Stern layer and the $\text{C}_6\text{H}_5\text{C}\cdot=\text{O}$ will be "born" close to or within the hydrophobic micellar core (shown in Scheme II).

Now let us consider the situation for BA. This molecule is probably more hydrophobic than BZ, at the instant of photolysis; it should be located closer to the hydrophobic core, on the average, than BZ, so that when hydrogen abstraction occurs, the $[\text{C}_6\text{H}_5\text{C}\cdot\text{HOH}, \text{C}_6\text{H}_5\text{C}\cdot=\text{O}]$ pair from the photolysis of BA will be produced more within the hydrophobic core than is the case for the identical pair from the photolysis of BN. From these

SCHEME II



considerations we have initially two isomeric supramolecular structures: $^3\text{GRP}_{\text{BA}}$ and $^3\text{GRP}_{\text{BZ}}$, produced from photolysis of BA and BZ, respectively, in SDS micelles (Scheme II). At some point in time these two supramolecular structures will equilibrate, and the differences in the measurable properties of $^3\text{GRP}_{\text{BA}}$ and $^3\text{GRP}_{\text{BZ}}$ will "relax" or merge into the properties of a common pair, GRP. The time scale for this relaxation is not known, but it may be that the observable properties related to polarization may be dominated by the early time behavior of the "unrelaxed" pair. In any case, within this admittedly speculative model the $\text{C}_6\text{H}_5\text{C}\cdot\text{HOH}$ partner of $^3\text{GRP}_{\text{BZ}}$ is hypothesized to display a faster escape rate into the aqueous phase than the $\text{C}_6\text{H}_5\text{C}\cdot\text{HOH}$ partner of $^3\text{GRP}_{\text{BA}}$, thereby rationalizing the following: (1) the observation of a SCRPs TR ESR spectrum for RP_{BA} and its absence for $^3\text{GRP}_{\text{BZ}}$, (2) the faster rate constant for escape for the $\text{C}_6\text{H}_5\text{C}\cdot\text{HOH}$ radical derived from $^3\text{GRP}_{\text{BZ}}$ from laser flash spectroscopic kinetics, (3) the higher yield of escape for the $\text{C}_6\text{H}_5\text{C}\cdot\text{HOH}$ radical from $^3\text{GRP}_{\text{BZ}}$, (4) the significant magnetic field effect observed on the escape of $\text{C}_6\text{H}_5\text{C}\cdot\text{HOH}$ for $^3\text{GRP}_{\text{BA}}$ and the negligible magnetic field effect observed on the escape of $\text{C}_6\text{H}_5\text{C}\cdot\text{HOH}$.

5. Conclusions

A TR ESR investigation of the photolysis of BZ and BA in homogeneous solvents allows the observation of three distinct polarization patterns of the α -hydroxybenzyl radical: E (under α -cleavage of BN, TM), E/A (under photoreduction of BA by BA, RPM), and A (under photoreduction of BA by KCNS, RPM with the dominant contribution of Δg mechanism into the S-T evolution). The latter result is quite unexpected, and conditions for its occurrence are rarely met in practice. In view of the general interest in inorganic compounds as reducing agents for triplet states (halides, carbonates, formates, nitrites, azides),^{31,42} the application of TRESR to study mechanisms of such reactions seems promising. From computer simulations, the g factor of the radical anion $(\text{CNS})_2^{\cdot-}$ was estimated to be in the range $2.015 < g < 2.03$, and its paramagnetic relaxation was estimated to be $T_{1,2} \leq 10^{-7}$ s. The difference between the TRESR pattern for BZ and BA in homogeneous solutions is explained as follows. The intersystem crossing from ^1BZ to ^3BZ leads to polarized triplet,^{4,5,24} and the polarized triplet undergoes a very fast (*ca.* 10^9 s⁻¹) α -cleavage to produce a radical pair possessing emissive polarization, i.e., TM polarization results. The hydrogen abstraction by ^3BA from ground-state BA is too slow to compete with triplet spin-lattice relaxation, and RPM produces the observed polarization.

The photolysis of BZ in SDS micellar solution leads to a TR ESR spectrum similar to that observed in homogeneous solvents

(TM), even when the micelles were "swollen" with an inert hydrophobic additive (benzene). In contrast, the TR ESR spectra observed during the photolysis of BA in SDS micellar solutions were completely different from those observed in homogeneous solution. The photolysis of BA under high loading conditions resulted in a SCRIP spectrum due to the $[C_6H_5C^{\bullet}HOH^{\bullet}, C_6H_5C^{\bullet}=O^{\bullet}]$ geminate radical pair. The explanation for the absence of SCRIP in the case of BZ and for its presence in the case of BA (Scheme II) is based on the possibility of different initial isomeric supramolecular structures which are produced by the photolysis of BA and BZ, which are expected to possess different average locations in the micelle. This model leads to the expectation that the pair generated from BZ will be situated relatively close to the Stern layer, which facilitates the exit of radicals from the micelle as the random motions of the pair explore the restricted space of the micelle. The relatively high escape fraction (and rate of escape) of radicals produced in the BZ photolysis from SDS micelles is the main reason for the absence of SCRIP in this model.

Work is currently in progress to establish the sites of BZ and BA in SDS by the use of spectroscopic techniques such as NMR and IR.

In conclusion, to rationalize the TR ESR and flash photolysis results, the molecular photochemistry of BA and BZ (Scheme I) must be supplemented by some supramolecular photochemical features (Scheme II). Micellar supercages not only are excellent hosts for prolonging the lifetimes of reactive species such as triplet geminate radical pairs but also can provide novel significant supramolecular features which are not observed in nonviscous homogeneous solvents.

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- (36) An experimental CIDEP spectrum similar to the calculated one (Figure 5c, RPM) was observed during the photolysis of BA in n -hexadecane.
- (37) In practice, bimolecular photochemical reactions in micelles between species which are very reactive in homogeneous solutions (reaction 1 in our case) may be slower than expected on the basis of a high local concentration of one of the reagents in the micelle; for example, see ref 19. Thus, reaction 8 can compete with reaction 1 even in micelles heavily loaded with BA.
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