For 1% tritium mixtures, the percent differences we predict in the T_2O production by eq 13 are small, differing by only 0.6% approximately 10^5 s after mixing. This is mainly because the initial [T] to [T_2] ratio is not as large in the 1% mixtures as in the 10^{-4}% mixtures.

Summary

Self-radiolysis products present in tritium gas at the time of mixing with oxygen can have a significant effect on the mechanism, rate, and concentration of T_2O, but only in the early stages of the reaction. This early stage lasts up to 0.1 s for 1% initial tritium, 100 s for 0.01% tritium, and 1000 s for 10^{-4}% tritium. Certain pathways to water formation can, however, be affected in their relative importance later, but the total T_2O concentration, in the 10^3–10^6 time scale, where most of it is formed, is unaffected by the early self-radiolysis in the tritium.

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Registry No. T_2, 10028-17-8; O_2, 7782-44-7; T_2O, 14940-65-9; T atomic, 15086-10-9; T^+, 98499-70-8; T_2^+, 12597-41-0; T_3^+, 71587-35-4.

Magnetic Field and Isotope Dependence of the Reaction Rates of Micellized Triplet Radical Pairs

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Nanosecond time resolved optical absorption studies of the isotopic dependence of the magnetic field effect on geminate triplet benzylic radical pair reaction dynamics in micelles of HDTCl are reported. The isotopic susceptibilities of the $T_\pm$ radical pair reaction rate constants in small (<50 G) and intermediate (100–500 G) fields are substantially different. The magnitude and field dependences of the isotopic effects are discussed in terms of the mechanisms of radical pair spin evolution (intersystem crossing) in the presence of magnetic fields.

Introduction

The dynamics of geminate radical and radical ion pairs in solution are strongly modulated by the radicals' hyperfine couplings and by externally applied magnetic fields.[1] Theoretical models have been developed which describe the dependences of the geminate pair reaction kinetics and product yields on the size of the radicals' hyperfine couplings and on the strength of the external magnetic fields.[2,3] These models are applicable in the limit $\tau < 1/A$, where A is the appropriate hyperfine interaction (s^{-1}) and τ is the effective lifetime of the geminate radical pair. In nonviscous solution, this condition is satisfied since diffusive separation of the radicals is rapid compared to the time scales for hyperfine-induced changes in the spin character of the radical pair. According to these models, magnetic isotope effects result from the influence of A, which alters the time dependence of the interconversion between the radical pair triplet (T) and singlet (S) states. Magnetic field effects arise from the Zeeman-induced splitting of the energies of the T_+ and T_- radical pair states, from the nearly degenerate T_0 and S states. Hyperfine-induced transitions (intersystem crossing) between the T_+ and T_- states and the S state are substantially retarded by the field-induced energy splitting and cannot compete with the diffusive separation of the pair. In the presence of sufficiently high magnetic fields, intersystem crossing occurs only between the T_0 state and the S state, which is assumed to be the only state from which the pair can react.

If the radical (ion) pair is produced within a solution "supercage" (micelle, inverse micelle, or microemulsion) the geminate correlation of the pair may be preserved for microseconds. Under these conditions, $\tau \gg 1/A$. The theoretical models mentioned above are not applicable in this regime. The diffusive behavior of the radical pairs and the frequency of reencounters within the supercage are determined by the latter's size and internal order. The drastically decreased rate of diffusive separation in supercage environments allows contributions from reaction pathways which are too slow to be important in homogeneous solution. In contrast to homogeneous solution dynamics, the interplay of singlet–triplet evolution and diffusion in determining radical pair chemistry and dynamics within supercage environments is poorly understood.

Magnetic field and isotope effects have been observed in a variety of supercage systems. The product distributions from reactions of geminate triplet radical pairs in micelles are sensitive to isotopic substitution and to magnetic fields ranging from 0 to 100 kG.[4] The decay kinetics of micellar benzylic radical pair reactions were observed to be strongly influenced by magnetic fields.[5] Both the product and kinetic effects were interpreted primarily in terms of the magnetic field and isotopic dependence of the intersystem crossing process in the $T_\pm$ radical pairs.

Steiner et al.[6] reported the decay kinetics of thionine–aniline radical ion pairs in reverse micelles in the microsecond and na-

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nosecond time range. The radical pair decay rate constants were sensitive to magnetic fields well above 100 G. The authors attributed transient absorption decays observed under these conditions to reactions of the $T_\pm$ radical ion pairs.

It is clear that supercage environments retard diffusive separation sufficiently that substantial intersystem crossing and reaction of $T_\pm$ radical pairs can occur even in the presence of magnetic fields. The identity of the dominant ISC mechanism under these conditions, however, is not clear. In addition to hyperfine-induced ISC, which dominates homogeneous solution spin dynamics, Hayashi[7] has developed an extension of Brocklehurst's proposal[8] of anisotropy-induced electron spin relaxation as a mechanism for inducing $T_\pm$ to S ISC. Steiner et al.[6] interpreted their results in terms of this spin relaxation mechanism.

In this paper, we report our studies on the isotopic dependence of the magnetic field effect on triplet benzylic radical pair reaction kinetics in micelles of hexadecyltrimethylammonium chloride (HDTCl). The isotopic susceptibilities of the reaction rate constants in small (<50 G) and intermediate (100–500 G) fields are substantially different. The magnitude and field dependences of the isotope effects are discussed in terms of the $T_\pm$ to S ISC mechanisms mentioned above.

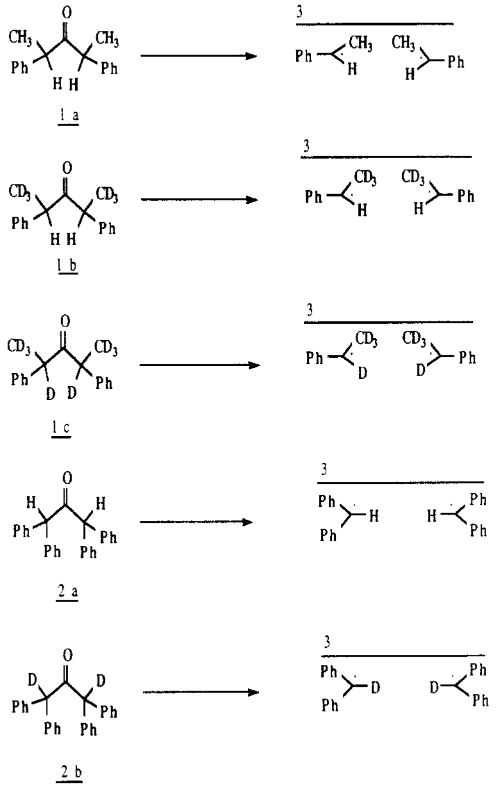
Experimental Section

The magnetic field dependent transient absorption experiments were performed as previously described.[5] Briefly, an HDTCl solution containing the radical pair precursor was photolyzed in a 1-cm^2 quartz cuvette held between the poles of a home-built electromagnet. The laser energy (Excimer EMG 101, 308 nm, 20 ns) was strongly attenuated to minimize contributions from second-order decays (vide infra). The excitation beam was approximately 30° off the analysis direction in order to accommodate the magnet. The change in transmittance at the analyzing wavelength (322 or 331 nm) was recorded by means of a monochromator, RCA 4840 photomultiplier tube, and Biomation 4500 transient waveform recorder. A minimum of four averages were performed for each data set and five data sets were collected at each field for each isotopic compound. The reported uncertainties represent two standard deviations. The data were not collected in any specific order of field strength. The concentrations of the ketones were adjusted to give an optical density of 0.2–0.4 at 308 nm, the laser wavelength. The solutions were degassed with argon for 10 min prior to photolysis and mixed between the laser shots.

2,4-Diphenylpentan-3-one (**1a**, Scheme I) and 1,1,3,3-tetraphenylpropan-2-one (**2a**) were synthesized according to literature procedures.[9] 1,1,1,5,5,5-Hexadeuterio-2,4-diphenylpentan-3-one (**1b**) was synthesized according to the literature procedure for the protio compound[9] except that iodomethane-d_3 (Merck, Sharpe and Dohme >98% D) was used instead of methyl iodide. 1,1,1,2,4,5,5,5-Octadeuterio-2,4-diphenylpentan-3-one (**1c**) and 1,3-dideuterio-1,1,3,3-tetraphenylpropan-2-one (**2b**) were converted from the corresponding α-protonated ketones by using phase-transfer catalysis. Hundred milligrams of Ketone, 1 mL of anhydrous benzene, and 400 mg of benzyltriethylammonium chloride were added to 1 mL of 1 M NaOD (Na + D_2O) at 40 °C and stirred vigorously for 30 min. The NaOD solution was replaced and an additional 50 mg of phase-transfer catalyst was added. The latter step was repeated at least twice. The solutions were then diluted to 25 mL with D_2O, extracted with ether, and flash chromatographed on silica (5% ether in hexane). ^{1}H NMR (Varian XL-200) indicated that better than 95% deuterium incorporation was achieved.

In the absence of magnetic fields, the radical absorption decays consist of a fast component and a slow component. The fast component obeys first-order kinetics, (<1 μs) and is attributed to the intramicellar recombination of geminate radical pairs.[5] The slow component, occurring on time scales extending beyond 50 μs, obeys second-order kinetics and is attributed to bulk recombinations of nongeminate radicals. In this work, the contribution of the second-order process to the decay kinetics observed on time scales <10 μs was made negligible by attenuating the laser power.

SCHEME I: Structures of Ketones and Radical Pairs Studied in Present Work



In the presence of magnetic fields of less than 1 kG, the fast component is observed as a single-exponential decay which decreases in rate as a function of the applied field strength. At fields greater than 1 kG the fast component becomes nonexponential but can be analyzed as a biexponential decay. Under these conditions, ca. 20–30% of the total fast component decays with a rate which is identical with that observed in the absence of a field and is attributed to the dynamics of the T_0 radical pairs. The decay rate of the main part of the fast component continually decreases upon application of the field and is attributed to the dynamics of the $T_\pm$ radical pairs.[5] Presumably, at fields less than 1 kG the decay kinetics of the $T_\pm$ and the T_0 pairs are sufficiently similar that the absorption decay curves fit reasonably well to a single exponential. In the present work the decrease in the rate of decay of triplet geminate radical pairs in micelles is examined as a function of applied field. The dynamics of the T_0 radical pairs do not depend upon the applied field strength. To minimize the contributions of these pairs, analyses were performed on the latter portions of the observed decays, i.e., those parts of the radical pair decays which varied with the applied field. No attempt was made to fit the data to a biexponential function. The rates of decay which are reported thus represent the dependences of the dynamics of the $T_\pm$ radical pairs upon the external magnetic field.

Results and Discussion

The structures of the ketones studied in the present work, together with the radical pairs which are formed upon photolysis of these ketones, are shown in Scheme I. The relevant aspects of the photochemistry of these ketones in micellar solution are shown in Scheme II.[4,5] Photolysis of the ketones results in rapid intersystem crossing from the excited singlet to triplet states, followed by homolytic α-cleavage, within the time scale of the laser pulse, to form a phenacyl:benzylic radical pair. The phenacyl radicals undergo rapid decarbonylation, also within the time scale of the laser pulse, to produce a geminate triplet benzylic:benzylic radical pair.[5,10] The ketones **1** form *sec*-phenethyl:*sec*-phenethyl

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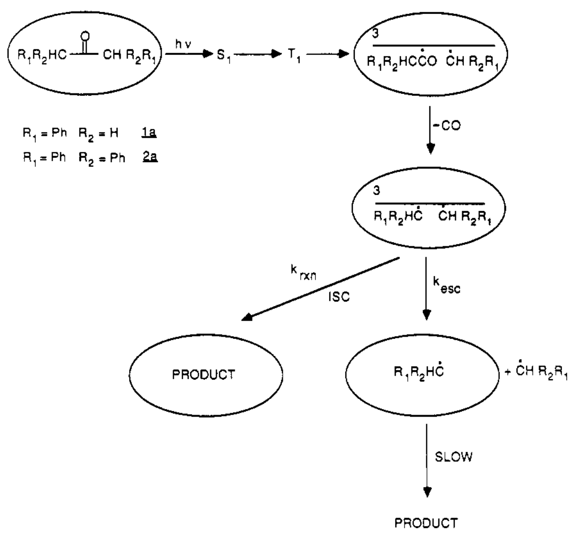
(7) Hayashi, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 322.
(8) Brocklehurst, B. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1869.
(9) Turro, N. J.; Baretz, B. H. *J. Am. Chem. Soc.* **1983**, *105*, 1309.

SCHEME II: Photochemistry of Dibenzyl Ketones in Micelles



radical pairs, whose dynamics were monitored at 322 nm,[5] and the ketones **2** form diphenylmethyl:diphenylmethyl radical pairs whose dynamics were monitored at 331 nm.[5] The observed fast radical absorption decays were due to reactions of the geminate benzylic:benzylic radical pairs only.

The magnetic field dependence of the radical pair decay rate constants, k_{obsd}, determined for the isotopically substituted *sec*-phenethyl radical pairs in 50 mM HDTCl micellar solution are shown in Figure 1 (see experimental for details of the kinetic analysis). In zero field, the methyne and methyl deuteriated pair, D_8 (from ketone **1c**), decays with a rate constant of $(6.31 \pm 0.30) \times 10^6\ \mathrm{s}^{-1}$. The decay rate constant decreases monotonically with applied magnetic field. In fields of 0 and 12.5 G, the decay rates of the methyl deuteriated pair, D_6 (from ketone **1b**), are the same, $(6.47 \pm 0.32) \times 10^6\ \mathrm{s}^{-1}$. Larger magnetic fields induce a monotonic decrease in the decay rate. In all fields less than 1 kG, the D_6 pair decays more rapidly than the D_8 pair. The field dependence of the rate constants for the nondeuteriated radical pair, H_8 (from ketone **1a**), exhibits a maximum at 12.5 G. Higher magnetic fields induce a monotonic decrease in k_{obsd}. Throughout the 0–500 G range, the H_8 rate constants are 10–40% greater than the D_6 and D_8 rate constants. In fields greater than 800 G, all three decay rates are the same within experimental error. It is important to note that the isotopic dependence of the rate constants is observed at 0 G; $k_{\mathrm{obsd}}(H_8) = (7.14 \pm 0.38) \times 10^6\ \mathrm{s}^{-1}$.

The magnetic field dependences of the decay rates for the nondeuteriated, H_2 (from ketone **2a**), and methyne deuteriated, D_2 (from ketone **2b**), diphenylmethyl radical pairs are also shown in Figure 1. The observed rates decrease monotonically with increasing magnetic field strength. The zero field rates exhibit a small isotopic dependence; $k_{\mathrm{obsd}}(H_2) = (2.63 \pm 0.15) \times 10^6\ \mathrm{s}^{-1}$, $k_{\mathrm{obsd}}(D_2) = (2.49 \pm 0.11) \times 10^6\ \mathrm{s}^{-1}$. Larger isotope effects are observed in fields less than 2 kG.

Scaiano[11] has proposed an analysis of micellar pair decay kinetics that divides k_{obsd} into the sum of two parts. The first, k_{rxn}, reflects the kinetics of the geminate radical pair reaction. The second, k_{esc}, is associated with the nonreactive destruction of the geminate correlation of the radical pair (Scheme II). The sum of the two radicals' micellar exit rate constants sets a lower limit on k_{esc}.

Magnetic fields between 0 and 2 kG have no effect on the micellar structure, or on the nonmagnetic interactions of the radicals with the micelle. Deuteriation should have a negligible effect on the radicals' diffusive and hydrophobic characteristics.

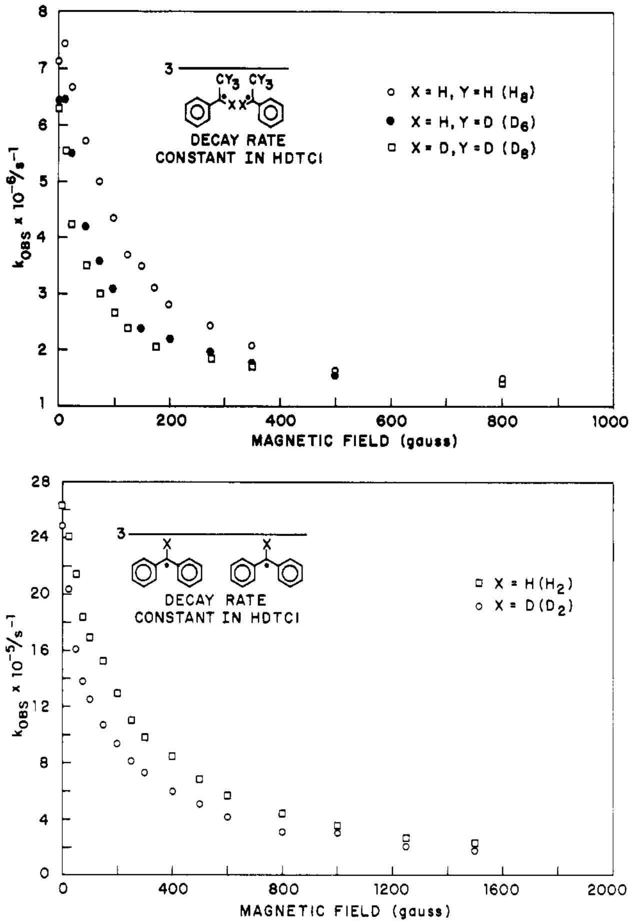


Figure 1. Decay rate constants of triplet geminate radical pairs in micelles of HDTCl as a function of magnetic field strength and isotopic substitution: (a, top) *sec*-phenethyl radical pairs; (b, bottom) diphenylmethyl radical pairs.

Thus, we expect k_{esc} to be independent of isotopic substitution and of magnetic field. The entire isotopic and magnetic field dependences of k_{obsd} are contained within k_{rxn}. In order to evaluate k_{rxn} as a function of field and isotope, k_{esc} must be determined. According to Scaiano's analysis,[11] the ratio $k_{\mathrm{esc}}/k_{\mathrm{obsd}}$ is the fraction of the geminate radical pairs that do not react within the micelle. After the fast geminate decay, these radicals are observed as the slowly decaying species. The ratio of the transient absorption signal following, I_{inf}, and prior, I_0, to the geminate decay is thus equal to $k_{\mathrm{esc}}/k_{\mathrm{obsd}}$. In zero field, we obtain $k_{\mathrm{esc}} = (2.1 \pm 0.2) \times 10^6\ \mathrm{s}^{-1}$ for *sec*-phenethyl pairs and $(2.0 \pm 0.3) \times 10^5\ \mathrm{s}^{-1}$ for diphenylmethyl pairs.[5] This analysis can only place an upper limit on k_{esc}. Interference from fluorescence and geminate reaction products that absorb at the detection wavelength serve to decrease I_0 and increase I_{inf}, respectively.[5] Transient absorption spectra recorded as a function of time during the decay indeed exhibit absorptions not attributable to the radicals,[5] although, for both *sec*-phenethyl and diphenylmethyl radical pairs, the observed spectra at all times are dominated by the characteristic radical spectra.

In the limit that k_{rxn} approaches zero, as occurs for $T_{\pm}$ radical pairs upon application of high external fields, k_{obsd} approaches k_{esc} and becomes independent of isotopic substitution. Extrapolation of the experimental k_{obsd} values to field strengths where they are independent of isotopic substitution provides an estimate of k_{esc}. This procedure leads to $k_{\mathrm{esc}} = (1.4 \pm 0.2) \times 10^6\ \mathrm{s}^{-1}$ for *sec*-phenethyl and $k_{\mathrm{esc}} = (1.0 \pm 0.1) \times 10^5\ \mathrm{s}^{-1}$ for diphenylmethyl pairs. These values are $^2/_3$ and $^1/_2$, respectively, of k_{esc} determined by the previous analysis, consistent with the interfering absorption in our spectra. In the following, we will employ the latter determined values of k_{esc}.

Ratios of k_{rxn} for the deuteriated–undeuteriated pairs as a function of magnetic field are plotted in Figures 2 and 3 for the

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[10] (a) Lunnazzi, L.; Ingold, K. U.; Scaiano, J. *J. Phys. Chem.* **1983**, *87*, 529. (b) Turro, N. J.; Gould, I. R.; Baretz, B. H. *J. Phys. Chem.* **1983**, *87*, 531. (c) Gould, I. R.; Baretz, B. H.; Turro, N. J. *J. Phys. Chem.* **1987**, *91*, 925.

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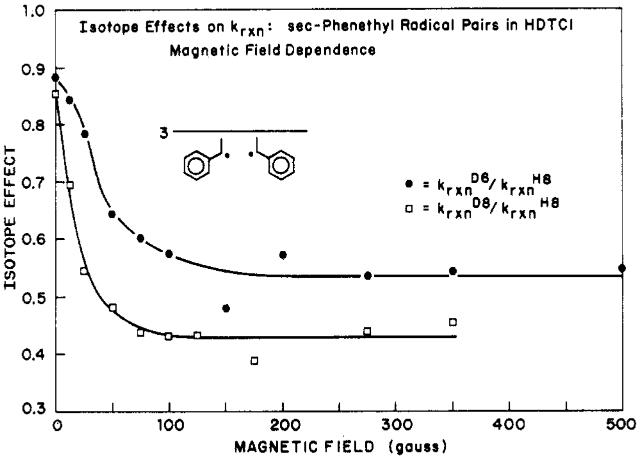

Figure 2. Magnetic field effect on the k_{rxn} ratio for isotopically substituted *sec*-phenethyl radical pairs in HDTCl micelles.

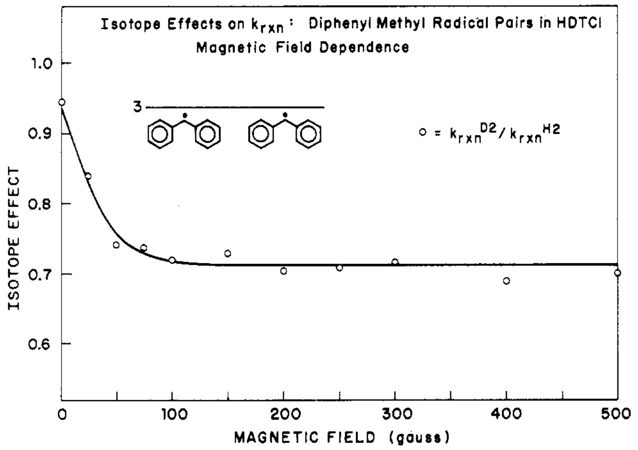

Figure 3. Magnetic field effect on the k_{rxn} ratio for isotopically substituted diphenylmethyl radical pairs in HDTCl micelles.

TABLE I: Reaction Ratios ($R = k_{rxn}(D_n)/k_{rxn}(H_n)$) for Isotopically Substituted Radical Pairs at Two External Field Strengths in HDTCl Micelles

ketones	radical pairs	R (0 G)	R (100–500 G)
2b and **2a**	D_2/H_2	0.94	0.72
1b and **1a**	D_6/H_8	0.88	0.57
1c and **1a**	D_8/H_8	0.86	0.44

sec-phenethyl and diphenylmethyl radical pairs, respectively. In each case, the k_{rxn} ratio, $R = k_{rxn}(D_n)/k_{rxn}(H_n)$, decreases significantly in the presence of fields less than 50 G but maintains a nearly constant value between 100 and 500 G. Values of R at zero field and in the plateau region are summarized in Table I. Within the magnetic field region defined by the plateau (100–500 G), k_{obsd} decreases by 30 to 60% of the total 0–2 kG rate change. The magnetic field strongly modulates k_{rxn} throughout this magnetic field region, but the ratio $k_{rxn}(D_n)/k_{rxn}(H_n)$ does not change. Clearly, the interplay of the radical pair diffusion dynamics and singlet–triplet evolution in fields less than 100 G is much less sensitive to isotopic composition than in the 100–500-G fields.

In a series of studies, Nagakura[12] has reported that isotopic composition has no effect on the decay rate constant of the benzophenone ketyl–surfactant radical pair in fields less than 100 G. However, Scaiano[11] has shown that the optical density changes observed in this system reflect a mixture of benzophenone triplet and ketyl reactions. Precise determinations of the radical pair reaction dynamics of this system in small fields are, thus, difficult and unreliable.

Cage effects from the photolyses of unlabeled, ^{13}C and D labeled dibenzyl ketone in HDTCl micelles[4] have been reported. Ignoring contributions from the primary phenacyl–benzyl radical pair, the observed cage effect should be equal to $1 - (k_{esc}/(k_{esc} + k_{rxn}))$. The cage effects determined at 0 G from the nondeuteriated, cage(H_4) = 0.32, and methylene deuteriated, cage(D_4) = 0.29, yield a k_{rxn} ratio, $R(D_4/H_4) = 0.87$, comparable to the ratios which are obtained from the current kinetic study.

Small Field Region (<100 G). In terms of the analysis advanced by Schulten[3] and employed by Steiner,[6] kinetic isotope effects may be observed if $\tau_r < \tau_H < \tau_D$ or if $\tau_H < \tau_r < \tau_D$, where τ_r is the average time between pair reencounters, and τ_H and τ_D are the times required to achieve a quasi-spin equilibrium between the S and T spin states of the nondeuteriated and deuteriated radical pairs, respectively. Steiner's zero field analysis indicated that in inverse micelles larger than 25 Å, diffusion controls the observed kinetics, i.e., $\tau_H < \tau_r$.[6] Reaction rates in smaller micelles were less than those predicted by diffusion, presumably because $\tau_r < \tau_H$.

The radii of HDTCl micelles are approximately 17 Å, which is within the range where both spin dynamics and diffusion would be predicted to control the reaction rate in Steiner's system at zero field.[6] If $\tau_r < \tau_{H,D}$ then diffusion is the rate-determining step for reaction, and no isotope effect would be observed. If $\tau_{H,D} > \tau_r$, i.e., spin interconversion is the rate-determining step, then based upon the predictions of Schulten for pyrene radical anion/hole pairs,[13] k_{rxn} ratios as small as 0.25 might be expected. The observation of k_{rxn} ratios of ca. 0.85–0.95 from both micellar product distributions[4] and reaction kinetics (Figures 2 and 3) in the absence of magnetic fields indicates that $\tau_r \approx \tau_{H,D}$ for benzylic radical pairs in HDTCl.[18] These results suggest that isotopic substitution in Steiner's system should have kinetic consequences in the smaller micelles. The effect should diminish with increasing micellar size.

The reason for the rate maximum in the H_8 *sec*-phenethyl radical pair at 12.5 G (and presumably for the D_6 pair at fields between 0 and 12.5 G) is not clear. Magnetic field dependent CIDNP studies of radical pair reactions in SDS micelles provided evidence for nonzero average exchange interactions for the radical pair.[14] Application of the appropriate strength field (75–300 G for ^{13}C studies) induced a T_-/S level crossing. The magnitude of the field required for degeneracy depends on the radical pairs' hyperfine couplings. Kinetic studies of biradical reactions have demonstrated, conclusively, that field-induced T_-/S level crossings increase triplet biradical decay rates.[15]

However, a second explanation for the maximum in the rate can be found in the theoretical analyses of Schulten[3] and Salikhov[16] which suggest that the rate and the amount of ISC should increase in small fields relative to those in zero field. These predictions do not depend upon T_-/S level crossings. However, these predictions are only valid for homogeneous solution dynamics, i.e., rapid destruction of the pairs' geminate correlation.

In magnetic fields less than 50 G, hyperfine-induced intersystem crossing is accepted as the major pathway for $T_\pm,T_0$ to S interconversion and reaction of triplet radical pairs.[4,16] The observation of small isotope effects in the kinetics and product distributions of radical pair reactions in the micelles in the absence of magnetic fields indicates that $\tau_{H,D} \approx \tau_r$.[18] Magnetic fields slow the hyperfine induced ISC from $T_\pm$ to S and cause $\tau_{H,D} > \tau_r$. The increasing magnitude of the isotope effects in the 0–100-G region is consistent with the development of ISC as the rate-limiting process for k_{rxn} of the $T_\pm$ radical pairs. The different field dependences of the reaction rate constants, as manifested in the R values which drop rapidly in the field range 0–100 G, are also consistent with an isotropic hyperfine coupling mechanism for intersystem crossing

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[12] (a) Sakaguchi, Y.; Nagakura, S.; Minoh, A.; Hayashi, H. *Chem. Phys. Lett.* **1981**, *82*, 213. (b) Sakaguchi, Y.; Hayashi, H.; Nagakura, S. *J. Phys. Chem.* **1982**, *86*, 3177.

[13] Werner, H.-J.; Schulten, Z.; Schulten, K. *J. Chem. Phys.* **1977**, *67*, 646.

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[15] Zimmt, M. B.; Doubleday, C. Jr.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 6726.

[16] Salikhov, K. M.; Molin, Y. N.; Sagdeev, R. Z.; Buchachenko, A. L. *Spin Polarization and Magnetic Field Effects in Radical Reactions*; Elsevier: Amsterdam, 1984.

in the small field region. For this mechanism the strength of the applied field required to reduce the efficiency of isotropic hyperfine-induced intersystem crossing decreases with increasing deuteration of the radical pair. Above 50–100 G the extent of isotropic hyperfine coupling induced intersystem crossing between the $T_\pm$ and S states of the radical pair diminishes rapidly,[16] and other mechanisms, which may have different isotopic and field dependences, must be considered. In the applied field range of ca. 50–100 G both the isotropic hyperfine and the other mechanisms must contribute to the reaction rates, and the field dependence of R will reflect the change in the mechanism of intersystem crossing.

Intermediate Field Region (100–500 G). The experimentally determined reaction rate constants within this field range exhibit a strong dependence on magnetic field. The rate constant ratios R depend on the isotopic composition but are independent of the magnetic field strength. Previously it was suggested that the spin relaxation mechanism, which applies in the limit $\tau_r < \tau_{H,D}$, could account for the behavior of micellized radical pairs in magnetic fields greater than 100 G.[6–8]

The hyperfine interactions mix the zero-field triplet and singlet radical pair states. In large magnetic fields, the Zeeman effect splits the $T_\pm$ state energies away from T_0 and S. Under these conditions, the hyperfine interaction can only mix the T_0 and S states. However, according to the spin relaxation mechanism, the anisotropies of the nuclear hyperfine and **g** tensors cause relaxation of the individual radical's electron spins as they tumble in solution.[16,17] This individual relaxation serves to interconvert $T_\pm$ states with T_0 and S.[7,8] The rate of relaxation is described in the equation

$$k_{\rm rel} \propto \langle {\rm Wa}^2 \rangle (\tau/(1 + (g\beta H\tau)^2)) \qquad (1)$$

in which τ is the correlation time of the motion which causes relaxation, g is the isotropic magnetogyric ratio, β is the electronic Bohr magneton, H is the magnetic field strength, and $\langle {\rm Wa}^2 \rangle$ depends upon the anisotropy of the hyperfine tensors.[17] The functional form of the relaxation model separates the isotopic dependence, $\langle {\rm Wa}^2 \rangle$, from the magnetic field dependence, $\tau/(1 + (g\beta H\tau)^2)$, of the ISC rate. Isotopically substituted radical pairs are predicted to have identical field dependences; the absolute rates differing by the ratios of the $\langle {\rm Wa}^2 \rangle$. Radical pairs of differing structures may have different field dependences, provided the correlation times, τ, of the motions inducing relaxation are different.

The four main experimental observations for applied fields > 100 G are (1) the values of $k_{\rm rxn}$ continue to decrease as a function of field; (2) the field dependence in this region is different for the two sets of radical pairs (the decay rates of the diphenylmethyl radical pairs decrease more slowly than those of the *sec*-phenethyl radical pairs, Figure 1); (3) the R values above 100 G are independent of the applied field; (4) the R values depend upon the isotopic composition of the radical pairs. All of these observations can be explained in terms of the relaxation model. The field dependences of the *sec*-phenethyl and diphenylmethyl radical pairs can be fitted according to the relation described in eq 1. The correlation times, τ, necessary to achieve the best fits are different for the two radical pairs, but in both cases are less than 1 ns. As previously indicated the dependence of R upon isotopic composition and the independence of R upon applied field are predicted by eq 1.

The ability of the relaxation model to explain these observations provides qualitative evidence that this mechanism is active for $T_\pm$ to S intersystem crossing for benzylic radical pairs in micelles. Independent evaluation of the radical reorientation correlation times within the micelles, or determination of R values via analysis of the anisotropic hyperfine couplings in the radicals, would provide more quantitative evidence for the importance of the relaxation mechanism in micellar radical pair reactions.

Conclusion

The effect of deuteration on the decay rates of geminate triplet radical pairs in HDTCl micelles has been examined as a function of magnetic field. In fields between 0 and 1 kG, deuteration decreases the radical pair decay rate. The magnitude of the kinetic isotope effect increases significantly between 0 and 100 G. Between 100 and 500 G, the kinetic isotope effect is constant and is determined by the chemical structure of the pair and by the extent of deuteration. The results indicate that both diffusion- and hyperfine-induced triplet–singlet evolution affect the decay kinetics of $T_\pm$ radical pairs in fields between 0 and 100 G. Above 100 G, triplet–singlet evolution determines the kinetics of reaction of $T_\pm$ radical pairs. The relaxation mechanism appears to be the predominant ISC pathway. The results underline the need for proper theoretical analysis of coupled spin evolution and diffusion in a finite volume space. Such an analysis is necessary in order to understand the rate constants of intramicellar reactions and for confirming the identity of the active ISC mechanisms in the various field regimes.

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Registry No. **1a**, 33500-61-7; **1c**, 111743-39-6; **2a**, 7476-11-1; **2b**, 111743-40-9; HDTCl, 112-02-7; D_2, 7782-39-0; $Ph(CH_3)CH^\bullet$, 2348-51-8; $Ph_2CH^\bullet$, 4471-17-4.

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[17] Poole, C. P. Jr.; Farach, H. A. *Relaxation in Magnetic Resonance*; Academic: New York, 1971.

[18] The observation of zero-field isotope effects is particularly interesting since calculations of benzyl:alkyl radical pair spin dynamics indicate that equivalent spin equilibration is attained within 10^{-8} s for both deuteriated and nondeuteriated pairs (ref 16); however, diffusive reencounter times within micelles are estimated to be an order of magnitude larger (ref 19).

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