solvent in vacuo, chromatography of the red oil on a column (basic alumina, 6-cm diameter, 50-cm length) with *n*-pentane yielded in the first fraction small amounts of **4**. The following red fraction contained after removal of the solvent 350 mg (0.59 mmol, 40%) of **7** as red glass: mp 73–78 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19/1.19/1.20/1.20/1.23/1.24/1.28/1.28/1.29 (9 s, 36 H, *t*-Bu), 2.11/2.13/2.16/2.16 (4 s, 3 H, $-CH_3$), 2.48 (s, 3 H, $-CH_3$), 4.20–4.63 (m, 6 H, 2-H, 2′-H, 4-H, 4′-H, 5-H, 5′-H), 6.04–6.22 (m, 2 H, 3″-H, 3‴-H), 6.41–6.55 (m, 4 H, 1″-H, 1‴-H, 4″-H, 4‴-H); MS (70 eV), *m*/*e* (rel intensity) 540 (M^+, 100), 57 (*t*-Bu, 29); UV (*n*-hexane), λ_{max} (ϵ) (nm) 287 sh (16 000), 324 (31 800), 343 sh (28 500), 423 (4410), 488 (3270); IR (KBr), ν (cm^{-1}) 2900 (s, C–H), 1590 (s, C═C), 1350 (s, C–H). Anal. Calcd for $C_{40}H_{54}Fe$: C, 81.33; H, 9.21; Found: C, 81.88; H, 9.40.

3,3′-Di-*tert*-butyl-1,1′-bis(*Z*-2-*tert*-butyl-6-methyl-6-pentafulvenyl)ferrocene (7a). Chromatography of **7** on basic alumina (6-cm diameter, 80-cm length) with *n*-pentane allowed the separation of a small red zone behind the main fraction. After removal of the solvent 50 mg (0.08 mmol, 6%) were obtained as red crystals (mp 129–134 °C (2-propanol)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (s, 18 H, 2″-*t*-Bu, 2‴-*t*-Bu), 1.21 (s, 18 H, 3-*t*-Bu, 3′-*t*-Bu), 2.46 (s, 6 H,$-CH_3$), 4.32 (dd, J_1 = 1.5 Hz, J_2 = 2.6 Hz, 2 H, 5-H, 5′-H), 4.37 (dd, J_1 = 1.5 Hz, J_2 = 2.6 Hz, 2 H, 4-H, 4′-H), 4.44 (t, J = 1.5 Hz, 2 H, 2-H, 2′-H), 6.20 (m, 2 H, 3″-H, 3‴-H), 6.54 (m, 2 H, 1″-H, 1‴-H), 6.55 (m, 2 H, 4″-H, 4‴-H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.1 (6″-CH_3, 6‴-CH_3), 29.7 [2″-$C(\mathit{C}H_3)_3$, 2‴-$C(\mathit{C}H_3)_3$], 30.8 [$-\mathit{C}(CH_3)_3$], 31.5 [3-$C(\mathit{C}H_3)_3$, 3′-$C(\mathit{C}H_3)_3$], 32.2 [$-\mathit{C}(CH_3)_3$], 67.7 (C-2, -2′), 68.8 (C-4, -4′), 71.8 (C-5, -5′), 85.8/105.4 (C-1, -1′, -3, -3′), 112.7 (C-3″, -3‴), 122.1/129.6 (C-1″, -1‴, -4″, -4‴), 142.2/145.3/156.8 (C-2″, -2‴, -5″, -5‴, -6″, -6‴).

Lithium 3,3′-Di-*tert*-butylferrocenylene-1,1′-bis[1-(3-*tert*-butylcyclopentadienido)vinylidene]lithiate (8) (0.1 M Solution in THF-*d*$_8$). Similar to the preparation of **5**, **8** was prepared from 0.60 mL (0.36 mmol) of a 0.6 M solution of ^{6}Li-enriched *n*-propyllithium in *n*-hexane, 60 mg (0.43 mmol) of 2,2,6,6-tetramethylpiperidine, 60 mg (0.10 mmol) of **7a**, and 1.0 mL of THF-d_8: ^{1}H NMR (300 MHz, 313K, THF-d_8) (The numbering is according to Figure 1 and does not correspond to nomenclature.) δ 1.25 (s, 18 H, 10-*t*-Bu, 10′-*t*-Bu), 1.29 (s, 18 H, 3-*t*-Bu, 3′-*t*-Bu), 3.96 (br s, 2 H, 4-H, 4′-H), 4.23 (br s, 2 H, 5-H, 5′-H), 4.43 (br s, 2 H, 2-H, 2′-H), 4.69 (d, J = 2.9 Hz, 2 H, trans-7-H, -7′-H), 4.76 (d, J = 2.9 Hz, 2 H, cis-7-H, -7′-H), 5.39 (m, 2 H, 11-H, 11′-H), 5.61 (m, 4 H, 9-H, 9′-H, 12-H, 12′-H); ^{13}C NMR (75.5 MHz, 313 K, THF-d_8) δ 31.7/32.5 [$-\mathit{C}(CH_3)_3$], 32.8 [3-$C(\mathit{C}H_3)_3$, 3′-$C(\mathit{C}H_3)_3$], 33.7 [10-$C(\mathit{C}H_3)_3$, 10′-$C(\mathit{C}H_3)_3$], 66.6 (C-4, -4′), 86.3 (C-1, -1′ or C-3, -3′), 100.8 (br, C-7, -7′, invisible in DEPT experiment), 101.7 (C-11, -11′), 102.4/102.5 (C-9, -9′, -12, -12′), 119.8 (C-8, -8′), 131.6 (C-10, -10′), 146.6 (C-6, -6′). One signal belonging to either C-1, -1′ or C-3, -3′ could not be identified and was supposed to be hidden at $\delta \approx 102$ (from comparison with **7a**).

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Supplementary Material Available: Additional spectroscopic data of **7a** and **8** (NOE and COSY) (2 pages). Ordering information is given on any current masthead page.

Influence of Micellar Size on the Decay of Triplet-Derived Radical Pairs in Micelles[†]

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Abstract: The photoreduction of butyrophenone by α-tocopherol in anionic micelles has been examined by laser flash photolysis. The reaction leads to a triplet-derived radical pair that decays by a competition of escape processes and geminate reactions. The dependence of both processes on the surfactant's chain length, the addition of electrolytes, and the temperature were examined in detail. The rate constants for radical exit from the micelles (k_-) follow Arrhenius-type behavior; for example, the exit from sodium dodecyl sulfate micelles occurs with an activation energy of 6.5 kcal/mol and log (A/s^{-1}) = 10.7. The results suggest that entropy plays an important role in determining the dynamics of escape processes. The rate constants for geminate reaction (k_{gem}) are largely determined by the size of the micelles. Both spin evolution and the frequency of reencounters are important in controlling geminate processes. For the radical pair examined, spin evolution is believed to be controlled by hyperfine couplings, while the frequency of reencounters depends upon micellar size and intramicellar diffusion dynamics.

Introduction

The impact of organized media on the kinetics of chemical reactions is now widely recognized.[1] In particular, triplet-derived geminate radical pairs or radical ion pairs sequestered in a micellar environment can often retain their geminate character for sufficiently long times that the radical pair can access the singlet surface, ultimately leading to closed shell products.[2-6] This is due to compartmentalization of the radical pair by the micelle and is in contrast to homogeneous solution where radical separation is so rapid that geminate reaction is generally a very minor process for triplet-derived neutral radical pairs[7-9] as well as some radical cation–radical anion pairs.[10]

Time-resolved studies of micellized, neutral triplet-derived radical pairs have concentrated mainly on carbon-centered species,[6]

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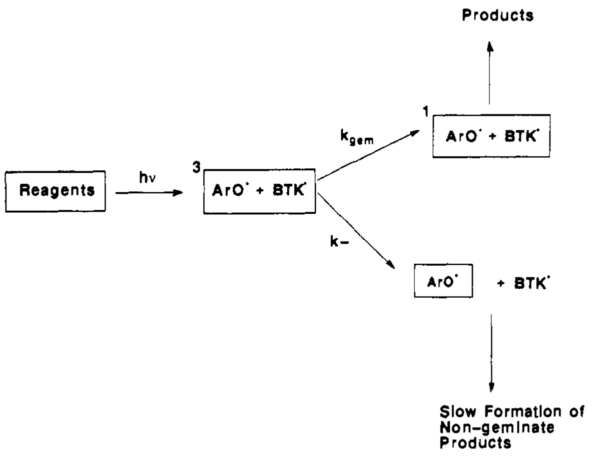
Scheme I



but a few recent reports have dealt with radicals centered on group IV elements other than carbon[11-13] as well as on phosphorus,[14] sulfur,[15] and oxygen.[16] There have also been several time-resolved studies of micellized radical ion pairs (see the review by Steiner[6] for examples). The kinetic behavior of the majority of these systems has been analyzed in terms of a model resembling that shown in Scheme I for the decay of aryloxyl-butyrophenone ketyl triplet-derived radical pairs in sodium dodecyl sulfate (SDS) micelles.[17] These radical pairs were formed via hydrogen abstraction from the phenol, ArOH, by triplet *n*-butyrophenone, leading to formation of the phenoxyl ($ArO^\bullet$) and the butyrophenone ketyl ($BTK^\bullet$).

$$PhCOC_3H_7{}^* + ArOH \rightarrow ArO^\bullet + \underset{(BTK^\bullet)}{PhC^\bullet(OH)C_3H_7} \qquad (1)$$

In the model of Scheme I k_{gem} represents the geminate reaction rate constant of the radical pair in the micelle in which it originates (the boxes represent micelles). k_{gem} is generally believed to be intersystem crossing (ISC) controlled. k_- represents the sum of rate constants for exit of the radical pair partners from the micelle in which reaction 1 occurs. In fact k_- is not necessarily associated with the actual exit of radicals from the micellar environment but includes all processes which cause the radical pair to lose its geminate character.

A number of time-resolved studies of triplet-derived radical pairs in micelles suggest that k_{gem} and k_- as well as the efficiency of geminate reaction are influenced by micellar size.[16-20] Of these, the effect of micellar dimensions has been studied in a systematic way only for k_- and for the efficiency of geminate reaction,[19,20] the micellar volume having been controlled by altering the surfactant chain length and by adding an electrolyte such as sodium chloride or an alcohol. A recent theoretical study of radical pairs in micelles emphasizes the lack of sufficient data and the need for studies of the temperature and micellar size dependence of geminate processes.[21]

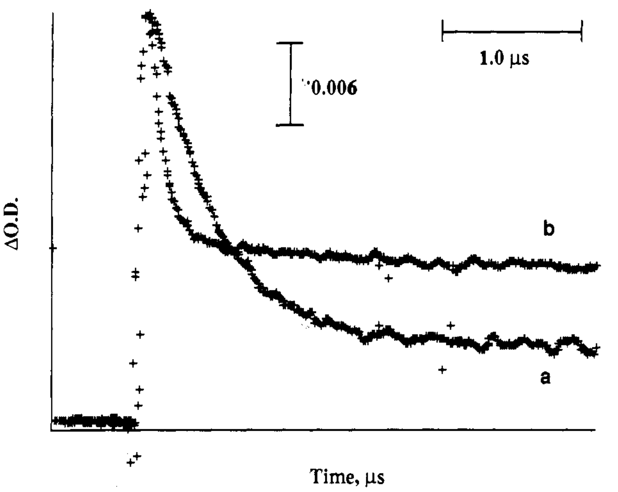


Figure 1. Kinetic traces for the decay of the Vitamin E phenoxyl radical at 425 nm recorded in SDS at 6 °C (a) and 69 °C (b). [EOH] = 2.5 mM, [butyrophenone] = 0.021 M, [SDS] = 0.15 M.

Although the size dependence of the geminate rate constant, k_{gem}, has not been examined in detail in the studies noted above, there is ample evidence to suggest that it is also influenced by micellar dimensions. For example, the value of k_{gem} for the benzophenone ketyl–cyclohexadienyl radical pair in cetyltrimethylammonium chloride (CTAC) is 1.7×10^6 s^{-1} [17] compared to 5.8×10^6 s^{-1} in the smaller SDS micelle.[18] Similarly, for the Vitamin E phenoxyl (EO)–butyrophenone ketyl ($BTK^\bullet$) radical pair $k_{gem} = 0.94 \times 10^6$ s^{-1} in CTAC and 3.3×10^6 s^{-1} in the smaller dodecyltrimethylammonium chloride micelles.[16] The geminate reaction kinetics of the triplet-derived thionine radical–aniline radical cation pair in reversed micelles also depends on the size of the water pool.[22] Very recently the geminate rate constant for the radical pair formed upon hydrogen abstraction from surfactant molecules by triplet 9-fluorenylidene was shown to depend on micellar size[23] as was the value of k_{gem} for α-terthienyl/methyl viologen radical cation pairs in anionic micelles.[24]

In this paper we report a systematic study of the influence of micellar dimensions on the geminate reaction kinetics and on the exit kinetics of a triplet-derived radical pair in the absence of applied magnetic fields. The system we have chosen for study is the EO–$BTK^\bullet$ pair in SDS and in its smaller analogue sodium decyl sulfate (SDecS). In this radical pair the extremely hydrophobic[25] Vitamin E phenoxyl radical is readily detectable and is expected to be associated exclusively with the micellar environment. Furthermore, the kinetic behavior of this pair in several different surfactants at room temperature has recently been reported.[16] In order to change the state of micellar aggregation we have added sodium chloride and varied the temperature of the system. To the best of our knowledge this is the first detailed study of the effect of temperature on the decay behavior of a triplet-derived radical pair in micelles.

Experimental Section

Vitamin E (EOH, (2*R*,4′*R*,8′*R*)-α-tocopherol) was a high-purity Eastman Kodak product and was used as received. *n*-Butyrophenone (Aldrich) was vacuum distilled prior to use. Sodium dodecyl sulfate (SDS) was a "specially pure" grade from BDH and was used without further purification. Sodium decyl sulfate (SDecS, Lancaster Synthesis) was recrystallized from ethanol. Water was of conductivity grade (>18 MΩ/cm^2).

Nitrogen-saturated samples of 2.5×10^{-3} M EOH and 2.1×10^{-2} M butyrophenone were prepared in 0.15 M aqueous solutions of SDS or 0.25 M SDecS. The samples were contained in 7 × 7 mm^2 cells made of Suprasil quartz tubing which typically held 2 mL of solution. If sodium chloride was to be included, it was added prior to injection of the organic reagents. Temperature was controlled by flowing N_2 gas through a copper heat exchange coil which could either be warmed electrically

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Table I. Values of k_{gem}, k_-, and $1000/N$ under Various Conditions of Micellar Aggregation

		$10^{-6}k_{gem}$, s^{-1}		$1000/N^a$	$10^{-6}k_-$, s^{-1}	
surfactant	[NaCl], M	20 °C	80 °C	20 °C	20 °C	80 °C
SDecS	0.0	3.4	6.2	25	1.1	6.2
	0.25	2.9	6.3		0.75	6.3
	0.50	2.2	6.2		0.64	4.5
SDS	0.0	2.5	5.6	15	0.72	5.2
	0.25	1.6	5.3	8.7	0.43	4.5
	0.5	0.31	5.6	5.4	0.27	4.9

[a] Data taken from refs 30 and 36.

or cooled by immersion in liquid nitrogen. The sample cells, which were surrounded by a quartz vacuum jacket, were allowed to equilibrate for 5–10 min once the desired temperature had been reached. The temperature was monitored with a Pt thermometer.

The samples were irradiated with the pulses (337.1 nm, ~8 ns, ≤10 mJ/pulse) from a Molectron UV-24 nitrogen laser. The transient decay signals, initially captured by a Tektronix R-7912 transient digitizer, were then transferred to a PDP 11/23$^+$ computer that controlled the experiment and provided suitable data storage, processing, and hardcopy facilities. Further details have been reported elsewhere.[26,27]

Measurements of surfactant critical micelle temperature (cmt) were carried out by FTIR by monitoring the symmetric $-CH_2-$ stretch of the surfactant's alkyl chain as a function of temperature at about 2855 cm^{-1}. These experiments were kindly performed by Dr. H. Casal, and details of the method are available elsewhere.[28]

Results

(1) Decay Traces and Their Analysis. The primary data collected in this study are transient absorption decay traces obtained in surfactant solution and recorded at 425 nm, the λ_{max} of the absorption spectrum of the Vitamin E phenoxyl radical (EO$^\bullet$). Figure 1 shows two such traces, one obtained at 6 °C and the other at 69 °C in SDS. In experiments of this type it is important to establish that radical pair generation is a fast process relative to its geminate lifetime.[17] We have already shown that for the radical pairs examined here this criterion is met at room temperature[16] and the same applies to all the experiments in this report. As indicated earlier,[16] the short lifetime of triplet butyrophenone greatly facilitates meeting the criterion of short formation lifetime.

The traces in Figure 1 consist of two kinetic components: a rapid initial decay followed by a relatively low intensity, long-lived residual absorption. As in other systems involving micellar reactions of radical pairs, we attribute the fraction of fast kinetic contribution to the sum of geminate decay and radical exit.[17] The residual absorption reflects that fraction of radical pairs that have undergone escape from the micellar environment. The fast component, which behaves monoexponentially under our experimental conditions, corresponds to the sum of the rate constants for geminate and escape processes.[17,18]

$$k_{decay} = k_{gem} + k_- \quad (2)$$

k_{gem} and k_- are as defined in Scheme I. The fraction of escape, as determined by the ratio of residual absorption (ΔOD_∞) to the maximum absorption before significant decay takes place (ΔOD_0), is given by eq 3.[17,18]

$$\%\ \text{escape} = 100\left(\frac{k_-}{k_{gem} + k_-}\right) = 100\left(\frac{\Delta OD_\infty}{\Delta OD_0}\right) \quad (3)$$

Thus, from the experimental data it is possible to obtain k_{gem} and k_- using eqs 2 and 3. In order to fit the experimental traces we have employed a biexponential function. This procedure, which has been described in greater detail elsewhere,[16] led to k_{decay} and % escape from which values of the desired rate constants could be calculated. Finally, we note that good fits were obtained for all of our data using this approach as judged by the random distribution of weighed residuals as well as by visual inspection.

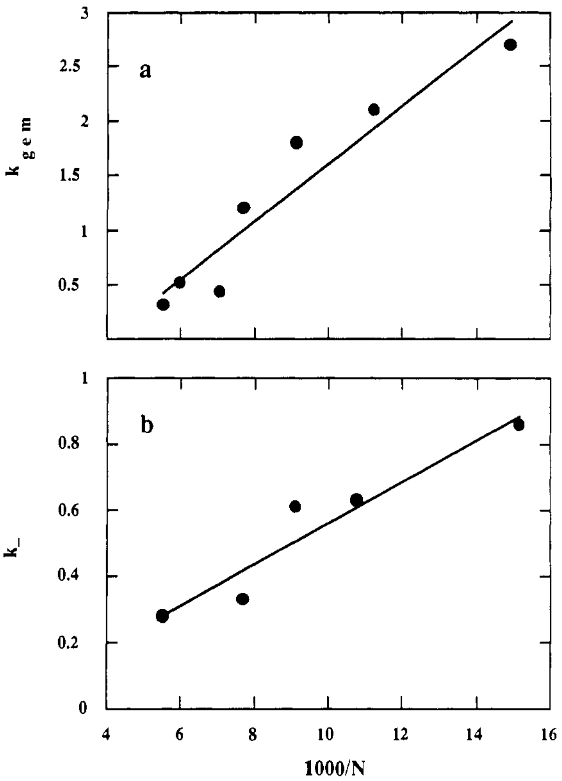

Figure 2. Variation in k_{gem} (a) and k_- (b) (in units of 10^6 s^{-1}) with the reciprocal of SDS aggregation number for the Vitamin E phenoxyl–butyrophenone ketyl radical pair at room temperature. The points represent different NaCl concentrations between 0 and 0.6 M; [EOH] = 2.5 mM, [butyrophenone] = 0.021 M, and [SDS] = 0.15 M.

Table II. Activation Parameters for BTK$^\bullet$ Exit Processes from SDS and SDecS Micelles

surfactant	[NaCl], M	E_a, kcal/mol	log (A/s^{-1})
SDecS	0.0	5.5 ± 0.8	10.2 ± 0.6
	0.25	6.1 ± 1.2	10.5 ± 1.0
	0.50	5.9 ± 0.6	10.3 ± 0.4
SDS	0.0	6.5 ± 1.8	10.7 ± 1.2
	0.25	7.0 ± 1.0	10.9 ± 0.8
	0.50	8.4 ± 1.4	11.7 ± 1.0

(2) Effect of Added Electrolyte. It is a well-known characteristic of SDS and its analogues that the micellar aggregation number (N) and micellar volume increase upon addition of counter ions.[1,29] Figure 2a shows a plot of k_{gem} versus $1/N$ at room temperature for the EO$^\bullet$/BTK$^\bullet$ system where N is the aggregation number for SDS. Each point represents a different sodium chloride concentration between 0 and 0.6 M. The N data were taken from the literature.[30-36] There is a good correlation between the two sets of data. Figure 2b shows a similar plot of k_- versus $1/N$.

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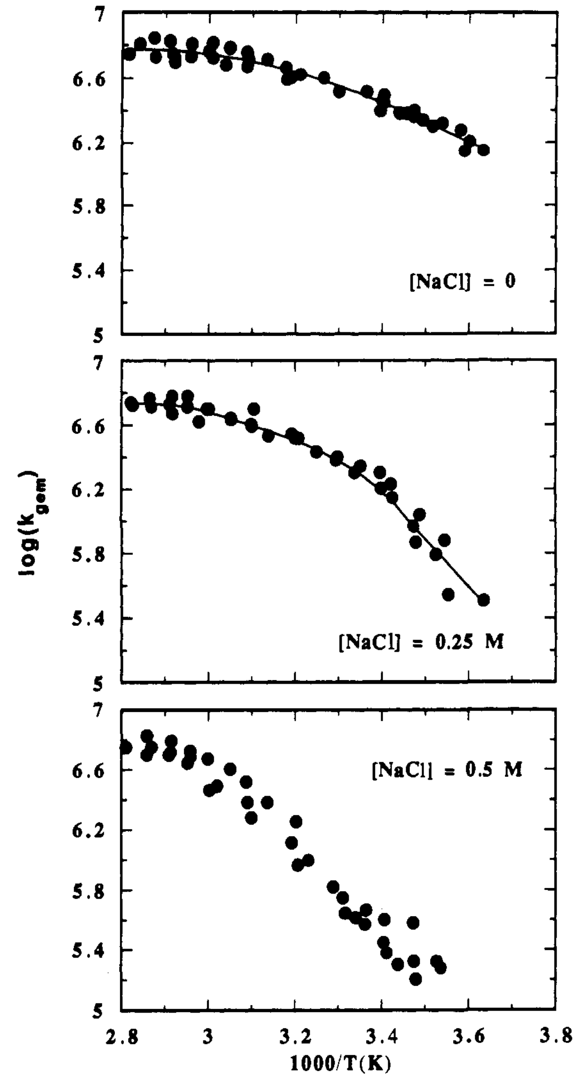

Figure 3. Temperature dependence of k_{gem} for the $\mathrm{EO}^{\bullet}$/BTK radical pair in 0.15 M SDS at various concentrations of NaCl.

Table I shows selected values of k_{gem} and k_- at various sodium chloride concentrations in both SDS and SDecS. These data also illustrate the inverse relationship between the rate constants and micellar size.

(3) Effect of Surfactant Chain Length. The length of the surfactant's hydrocarbon tail, C_9 for SDecS and C_{11} for SDS, has an effect on k_{gem} and k_- which parallels the influence of other variables (i.e., electrolytes and temperature) which also alter the micellar size. This is also illustrated in Table I. In fact, the effect of surfactant chain length on the dynamics of radical pairs in micelles is the only one among the variables studied in this work for which the size effect was already established in the literature (vide supra).

(4) Effect of Temperature. (a) Exit Rate Constant. In the Earth's magnetic field the decay of the $\mathrm{EO}^{\bullet}/\mathrm{BTK}^{\bullet}$ system in SDS and in SDecS shows a pronounced temperature dependance (Figure 1). This dependance is influenced by the addition of sodium chloride, and in the range of temperatures (5–85 °C) and sodium chloride concentrations (0–0.5 M) examined we were able to determine values of k_{gem} and k_-. Arrhenius plots based on k_- were linear over this temperature range at 0, 0.25, and 0.5 M sodium chloride for both SDS and SDecS. Table II presents the Arrhenius parameters for exit processes involving the $\mathrm{EO}^{\bullet}/\mathrm{BTK}^{\bullet}$ radical pair.

(b) Geminate Rate Constant. Figure 3 shows Arrhenius plots based on k_{gem} for the $\mathrm{EO}^{\bullet}/\mathrm{BTK}^{\bullet}$ pair in SDS at three different concentrations of sodium chloride. Similar plots in SDecS show qualitatively similar behavior. In contrast to the k_- data, the k_{gem} Arrhenius plots are curved. k_{gem} becomes largely temperature independent at higher temperatures, reaching a limiting value of log (k_{gem}) of about 6.8 for all salt concentrations.

Attempts to correlate the values of temperature at which this "plateau" behavior begins with values of the critical micelle temperatures (cmt) were carried out. The cmt values for SDS at various salt concentrations were obtained from literature sources[37] as well as from our own FTIR measurements (see Experimental Section). It was hoped that finding such a correlation, or not, would help decide if the curvature observed in the plots of Figure 3 was due to a phase change of the micelle. Unfortunately the curvature is so broad that it was not possible to define a temperature at which the plateau behavior commenced.

Discussion

(1) Interpretation of Exit Rates. (a) Influence of Added Electrolyte and Surfactant Chain Length. Turro and co-workers[19,20] have examined the effect of adding alkali chlorides to SDS on the exit rate constants for benzyl radicals. They concluded that k_- varied inversely with the surfactant aggregation number (a parameter reflecting micellar volume). Our k_- data support this view (see Table I). Similar conclusions have been reached by Steiner[22] in studies of the decay of triplet-derived thionine radical/aniline radical cation pairs in reversed micelles and by Scaiano on the benzophenone/1,4-cyclohexadiene system[17,18] and on the α-terthienyl/methyl viologen system.[24] In all of these cases exit rate constants varied inversely with micellar dimensions, although only Turro's work[19,20] involved changes induced by salt addition.

In a similar fashion k_- decreases as the surfactant's alkyl chain length increases (see Table I). Turro has reported the same type of behavior for exit of the benzyl radical from sodium *n*-alkyl sulfate micelles.[19,20]

(b) Influence of Temperature. In the absence of NaCl the activation energies for exit of the $\mathrm{EO}^{\bullet}/\mathrm{BTK}^{\bullet}$ pair are 6.5 ± 1.8 and 5.5 ± 0.8 kcal/mol for SDS and SDecS, respectively. These values compare well with DeSchryver's report of a value of 5.7 kcal/mol for exit of *m*-dicyanobenzene from SDS micelles.[31]

Exit of the ketyl radical into the bulk aqueous phase is the most likely escape process for the $\mathrm{EO}^{\bullet}/\mathrm{BTK}^{\bullet}$ pair. Other possible intermicelle reagent exchange mechanisms such as collision/exchange[38,39] or fragmentation/coagulation[40,41] which would also result in radical pair separation can be ruled out since they are known to be accelerated at higher salt concentrations. Both phenols[42,43] and ketones[44,45] reside near the micellar Stern layer, and if diffusion across the Stern layer controls the exit process, one may interpret the E_a values in terms of an enthalpy barrier to the ketyl radical's crossing of the micelle–water interface.

The log *A* data of Table II clearly show that exit is associated with a *decrease* in entropy. We attribute this to the hydrophobic effect.[46,47] Solubilization of a hydrocarbon in water requires an initial disruption of water structure followed by a substantial increase in the structure of the water surrounding the hydrocarbon molecule, with a corresponding decrease in entropy. Our log *A* data suggest that such water ordering is highly developed when $\mathrm{BTK}^{\bullet}$ achieves the transition state for exit. Thus, this must be a late transition state with the ketyl radical largely in an aqueous environment. This is consistent with the observation that rate constants for entry of hydrophobic species into micelles are generally close to diffusion controlled,[1] consistent with an early transition state for entry.

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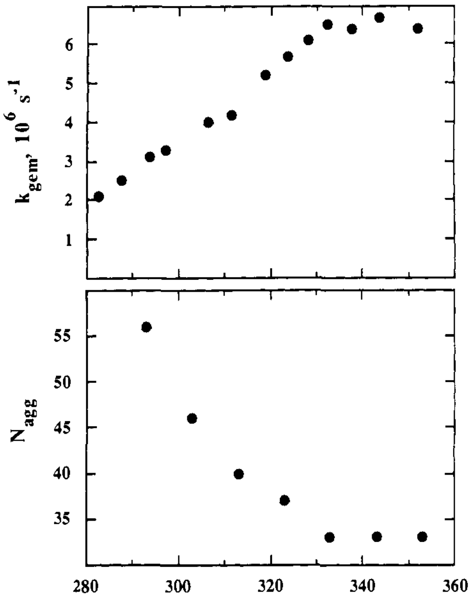

Figure 4. Variation of k_{gem} and SDS aggregation number with temperature in the absence of added electrolyte; [EOH] = 2.5 mM, [butyrophenone] = 0.021 M, [SDS] = 0.15 M.

One can calculate $\Delta S^{\ddagger}$ values for the EO$^{\bullet}$/BTK$^{\bullet}$/SDS system from the log A values of Table II. These may be compared with that for the separation of a reaction pair in the absence of the hydrophobic effect. For example, $\Delta S^{\ddagger}$ for the dissociation of pyrene excimer in cyclohexane is +15 gibbs/mol[48] as compared to −12 to −9 gibbs/mol for radical exit from the micelles studied here. The large difference and the negative values of $\Delta S^{\ddagger}$ in micelles are attributed to entropic requirements related to the hydrophobic effect.[47]

(2) Geminate Rate Constant. The most important observation made here is the inverse dependance of k_{gem} on the micellar size. One way in which size can be changed is by modification of the surfactant's chain length. For example, Table I shows that the value of k_{gem} for EO$^{\bullet}$/BTK$^{\bullet}$ is about twice as large in SDecS as in SDS at 0.25 M sodium chloride at 20 °C.

Temperature variation also causes the aggregation number of micelles to change.[30,34,36,49–52] They achieve a minimal, spherical configuration at high temperatures and grow as the temperature decreases. The growth effect is more pronounced at higher salt concentrations. Our k_{gem} values for SDS show a behavior that parallels temperature-induced changes in micellar size (see Table I and Figure 3). Similar behavior was observed in SDecS micelles. To illustrate further the relationship between k_{gem} and micellar volume with temperature we have plotted values of the aggregation number[30,36] and k_{gem} as a function of temperature. Figure 4 shows a complementary relationship between these sets of data for the EO$^{\bullet}$/BTK$^{\bullet}$/SDS system. Similar relationships were observed at 0.25 and 0.5 M NaCl.

The activation energy determined from the linear, low-temperature portion of the k_{gem} Arrhenius plot of Figure 3 in the absence of sodium chloride is about 4 kcal/mol. If, as we propose, the variation in k_{gem} with salt concentration, surfactant chain length, and temperature is due mainly to changes in micellar volume with these parameters, the activation energy calculated from Figure 3 is in fact a composite activation energy which incorporates changes in micellar size as the temperature is varied.[53–55] We may apply a "scaling factor" to k_{gem} in order to take into account micellar volume changes. The appropriate scaling factor is the aggregation number,[53] N, a parameter which is available in the literature.[30,36] Values of log (Nk_{gem}) in the absence of sodium chloride are plotted against $1/T$ in Figure 5. The resulting activation energy is just 0.9 ± 0.4 kcal/mol. At 0.25 and 0.5 M sodium chloride E_a values are 1.9 ± 1.6 and 2.5 ± 1.1 kcal/mol, respectively. Errors associated with these activation energies may be greater than the statistical errors given due to the narrow temperature range studied and the fact that the N values were obtained under somewhat different experimental conditions than those used here.

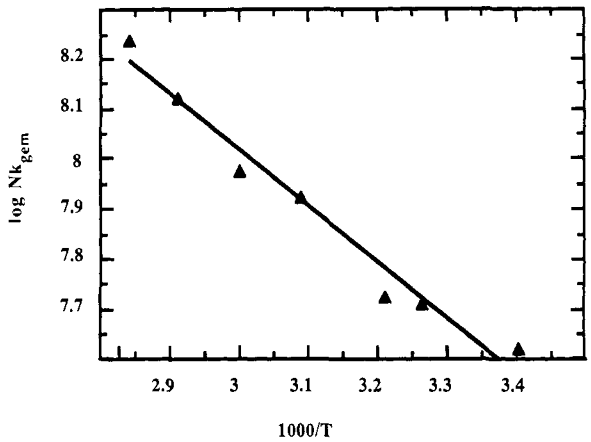

Figure 5. Arrhenius plot based on values of the product Nk_{gem} recorded for the Vitamin E phenoxyl–butyrophenone ketyl radical pair in 0.15 M SDS in the absence of NaCl.

Distance-related effects have also been observed for the lifetimes of triplet 1,n-biradicals[56–61] in which the maximum separation is controlled by the molecular structure (i.e., by n), rather than by a phase boundary. Most lifetimes of triplet 1,n-biradicals appear to be ISC controlled.[60,62,63] However, chain dynamics may become important for large values of n.[58,60,64]

Two factors may be responsible for the dependence of k_{gem} on micellar dimensions, viz., diffusional motion and spin evolution. In the past, the zero-field value of k_{gem} has generally been associated with spin evolution, i.e. with ISC.[2–6,17,18,65–69] However, some recent reports suggest that diffusional motion of the radicals within the micelle may be important.[21,70] In most cases where the value of k_{gem} was associated with ISC, spin evolution was attributed to hyperfine coupling interactions. This suggests that if k_{gem} was determined solely by the rate of hfc-induced ISC its value should, if anything, have increased in the larger micelles

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which is contrary to our observations. As an alternative, one might therefore imagine that k_{gem} was controlled by ISC and that spin evolution was determined by spin–orbit coupling since the rate of spin–orbit coupling is known to decrease as the separation between the unpaired electrons increases.[71] While spin–orbit coupling mediated ISC would qualitatively explain the variation of k_{gem} with micellar size, it would be inconsistent with the fact that the EO$^•$/BTK$^•$ system exhibits a pronounced magnetic field effect.[16] This is because spin–orbit coupling mediated processes are at best only weakly magnetic field dependent.[6]

Theoretical models of intramicellar diffusion controlled reactions predict that their rate constants will decrease in large micelles.[72-76] Further, a large magnetic field effect is not precluded as long as k_{gem} is only diffusion controlled in the absence of an external field. The most compelling evidence to rule out diffusion *as the sole parameter* determining k_{gem} is provided by a recent study of the benzophenone ketyl–$C_6H_5S^•$ radical pair in SDS.[77] In this system the value of k_{gem} is 5×10^7 s^{-1}, no magnetic field was observed, and the decay is believed to be diffusion controlled due to rapid relaxation induced by the thiophenoxyl radical. Since these radicals are rather similar to those studied here one must conclude that our comparatively small values of k_{gem} (see Table I) cannot reflect solely diffusion.

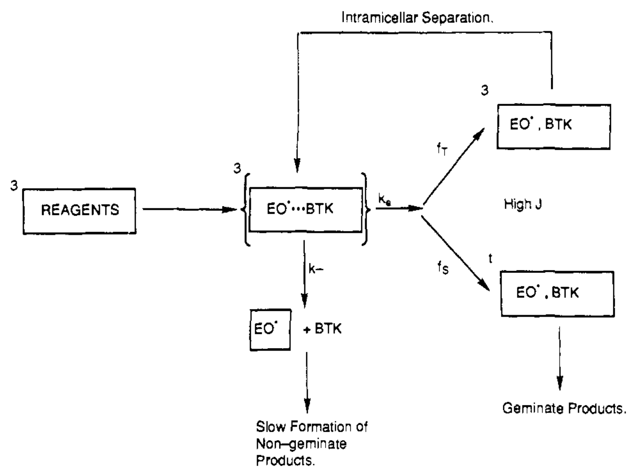
A final problem with identifying k_{gem} with a solely diffusion controlled rate constant is the numerous examples of magnetic isotope effects on the decay of triplet-derived radical pairs in micelles.[6] These effects arise because of an increased rate of geminate reaction in systems labeled with a radical (such as ^{13}C) which has a greater hfc than do the protons for the unlabeled (i.e. ^{12}C) radicals. Such an isotope effect could not possibly be explained on the basis of a diffusional model, since isotope substitution will not affect diffusion rates.

The explanation given below follows closely our recent model used to rationalize the influence of micellar size and of heavy atom substitution on the geminate rate constants for radical cation pairs.[24] We suggest that identifying the zero-field value of k_{gem} with *either* a diffusion controlled *or* an ISC controlled process is an oversimplification. This reflects the tendency to view $T_\pm$, T_0, and S as pure, unmixed spin states. In fact, while triplet-born radical pairs will indeed be formed in pure triplet $T_\pm$, T_0 states, these will mix with the S state when the exchange interaction energy, $2J$, has been reduced to the level of hfc energies via intramicellar radical separation (i.e., $T_\pm$, T_0, and S are nearly degenerate).[6,61,78] This mixing occurs at about 10^8 s^{-1},[79] which is faster than the rate of geminate decay. This means that at zero field a "triplet" radical pair should be viewed as predominantly triplet with some degree of singlet character[6,78] rather than as a pure triplet.

Radical pairs must achieve an encounter in order to undergo (geminate) reactions since radical–radical reaction is a contact process. Only that fraction of (mixed) radical pairs which can access the singlet surface during the contact encounter (where $2J$ is large due to the proximity) will lead to closed shell geminate products. Thus, the partners of a given mixed, but largely triplet, radical pair may have to undergo numerous collisions before one leading to singlet character occurs. Thus, the experimental geminate rate constant, k_{gem}, is related to the product of the frequency of reencounter of the geminate partners within the micelle (k_e) and the fraction of singlet character in the mixed radical pair (f_s), eq 4.

$$k_{gem} \propto k_e f_s \tag{4}$$

Scheme II



Micellar size effects on k_{gem} arise because of the k_e term, which is predicted to depend inversely on micellar size,[72,73] while magnetic environment effects (such as magnetic isotope effects) influence k_{gem} through the f_s term. This model is also compatible with observation of magnetic field effects; these are due to inhibition of hfc-mediated spin-state mixing induced by Zeeman splitting of the triplet sublevels. The values of f_s, which here are determined by hfc interactions, should increase in larger micelles. Thus, the observed changes of k_{gem} with micellar size are dominated by the k_e term.

Our model requires mixing of the triplet and singlet sublevels at zero field due to the hfc interaction. This will only be possible if the exchange energy is small. There is excellent experimental evidence that this is the case from time-resolved ESR data for the benzophenone ketyl–surfactant radical pairs in SDS and SDecS.[78] This work shows that $2J_{av}$ (the average exchange energy) is 3.8 G in SDecS and just 2.4 G in SDS. A recent elegant contribution on biradicals by Closs and Forbes[61] presents a detailed analysis of the parameters that control these interactions and their relative role.

Scheme I must be revised in order to reflect the mixed spin nature of triplet-derived radical pairs in micelles. Scheme II presents an alternative view which is more realistic. The curly braces emphasize the mixed nature of the geminate radical pair spin states. The use of the superscript 3 in conjunction with the curly braces indicates the predominant spin character. The extended dots (i.e. EO$^•$···BTK$^•$) represent a situation where the radicals are sufficiently separated that the exchange interaction is low. When the radicals are at contact separation (i.e., EO$^•$, BTK$^•$) the exchange interaction is high. Only those collisions (the frequency of which is governed by k_e) in which the singlet character is expressed can lead to geminate products. The fraction of collisions in which singlet character is expressed is determined by the fraction of singlet character, f_s, in the low J (i.e. mixed, large separation) radical pair. Furthermore, since no spin evolution can occur when J is high, pairs which have undergone "triplet collisions" will eventually undergo diffusive separation and return to the low J regime where spin evolution can occur.

Finally, two recent articles have addressed the problem of size effects on the decay of micellized phenoxyl–ketyl radical pairs.[80,81] They report Arrhenius plots based on the observed rate constant (k_{decay} in eq 2) which are linear, giving an activation energy of 4–5 kcal/mol, and conclude that geminate reaction is therefore diffusion controlled. However, the authors do not appear to have

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taken into account that up to 30% of the initial radical pairs undergo exit at room temperature in their system. We plotted our values of k_{decay} in the Arrhenius fashion and also found that no curvature was detectable. Thus, failure to take the exit fraction into account may give misleading information regarding the geminate reaction, especially at high temperatures where the escape can be much greater than 30%.

Conclusion

In summary, the geminate and exit rate constants for decay of triplet-derived radical pairs in micelles are strongly influenced by micellar size. Our k_- data suggest that the loss of geminate character by the EO$^•$/BTK$^•$ neutral radical pair is due to exit of the ketyl radical from the micelles into the bulk aqueous environment. The activation energy for this process is around 6–7 kcal/mol and should probably be interpreted as representing the enthalpic barrier due to crossing of the micelle–water interface. In addition, the large negative entropy of activation for exit gives some insight into the nature of the transition state and provides an illustration of the hydrophobic effect, suggesting that entropy plays a significant role in holding the ketyl radical in the micellar environment. Thus, the free energy barrier to ketyl exit also has a large entropic contribution.

The rate constant for geminate reaction, k_{gem}, is also controlled by the micellar size which has been changed by modifying the surfactant's structure, by addition of salts, and by changing the temperature. The values of k_{gem} are interpreted as depending on the product of the degree of singlet character (f_s) and the frequency of reencounter of the geminate radical partners (k_e). While chemical reaction requires singlet character and contact distances, spin evolution requires large separations so that exchange interactions can become comparable or smaller than hfc interactions; as a result, diffusion and spin evolution are coupled processes. The values of k_{gem} are largely dependent on the interplay of these parameters.

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Registry No. EOH, 59-02-9; EO$^•$, 109954-22-5; SDS, 151-21-3; SDecS, 142-87-0; butyrophenone, 495-40-9; sodium chloride, 7647-14-5.

Living Ring-Opening Metathesis Polymerization of Cyclobutene: The Thermodynamic Effect of a Reversibly Binding Ligand

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Abstract: Trimethylphosphine, PMe_3, is shown to bind reversibly to the alkylidene complex W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (**1**, Ar = 2,6-diisopropylphenyl), and the binding constants at several temperatures are measured ($\Delta H^\circ = -15.7$ kcal/mol, $\Delta S^\circ = -40.7$ eu). In the presence of PMe_3, **1** catalyzes the living ring-opening metathesis polymerization (ROMP) of cyclobutene to yield polybutadiene with a polydispersity index (PDI) as low as 1.03, based on gel permeation chromatography versus polystyrene standards. The polymerization in the presence of PMe_3 is first order in monomer and catalyst concentrations with $\Delta\Delta G^\ddagger_{273\mathrm{K}} = 19.8$ kcal/mol, $\Delta\Delta H^\ddagger_{(\mathrm{p})} = 20.8$ kcal/mol, and $\Delta\Delta S^\ddagger_{(\mathrm{p})} = 4$ eu. The observed rate of initiation of the polymerization is much greater than the rate of propagation. In the absence of trimethylphosphine, the polydispersity of the polymer produced with **1** is broader (PDI > 2) due to the rate of propagation being much greater than that of initiation and the existence of chain termination. This difference is attributed to the fact that PMe_3 binds more strongly to the propagating alkylidene complex than to the more sterically bulky initiating neopentylidene.

Introduction

Living polymerizations provide control of polymer properties on a molecular level, thus enabling the facile preparation of block copolymers.[1] The recent syntheses of a number of well-defined transition-metal alkylidene and metallacyclobutane complexes have resulted in the living ring-opening metathesis polymerization (ROMP) of norbornene and some of its derivatives to give essentially monodispersed polymers.[2] Since relief of ring strain is the driving force for these polymerizations,[3] it should be possible to ring open other highly strained olefins, such as cyclobutene, under the proper conditions to obtain polymers of low polydispersity. Perfectly linear, monodispersed polybutadiene (ring-opened polycyclobutene) is needed as a source of linear, monodispersed polyethylene. Presently, polyethylene of low polydispersity is produced by the hydrogenation of 1,4-polybutadiene prepared by the anionic polymerization of 1,3-butadiene. This approach results in branched polyethylene, since the polybutadiene produced by this technique contains C_2 branches as a result of low levels of 1,2-polymerization of the butadiene. Linear, low polydispersity polyethylene is an extremely important synthetic goal and provides the challenge of preparing essentially monodispersed, linear polybutadiene by the ROMP of cyclobutene.

In previous efforts to polymerize cyclobutene using well-defined titanium and tungsten metathesis catalysts, we obtained linear polybutadiene with broad polydispersities and high molecular weights which were much greater than expected from the monomer-to-catalyst ratio.[4] During the polymerization, only a small

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