Laser Flash Spectroscopic Investigation of Micellized Radical Pairs. Direct Measurement of the Exit Rates of Micellized Radicals

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Time-resolved electron spin resonance (TRESR) has proven to be a valuable technique for the investigation of supramolecular systems such as radical pairs (e.g., 1RP–6RP) derived from the Norrish type I photocleavage of ketones (e.g., 1K–6K, Chart 1)1 adsorbed in variously sized micelles. Although the relative exit rates (kexit) of the micellized radical pair fragments have been determined for the latter,1 quantitative determination of kexit by TRESR was not possible due to complications arising from spin–lattice relaxation (T1) of the polarized radical signals. We report a direct and quantitative evaluation of kexit of the micellized 1RP–6RP employing time-resolved laser flash photolysis with optical detection of both radicals of the pair.

Radical pairs 1RP–6RP were produced in sodium dodecyl sulfate (SDS) solutions in the presence and absence of an aqueous phase efficient radical scavenger,7,7 Under these conditions, both radicals can be detected: benzoyl radicals, maximum absorption Amax at ~355 nm (ε ~150) and ketyl radicals, Amax at ~300 nm (ε ~750).9 The kinetics of benzoyl radicals are difficult to monitor in homogeneous solutions by transient absorption at 355 nm due to interference from the absorption of secondary photolysis products of producers by

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(7) All micellar solutions in this work contain 1 mM micelle and 1.5–2.5 mM ketone, with solution OD ~0.3–0.4 at 308 nm. Unless otherwise stated, the concentration of added ketone is 30.8 nm excimer laser (~30 mJ/pulse). The flow cell is used with the flow rate ~2 mL/min. The Amax of the alkoxyl radical from 4RP is ~293 nm. However, we still monitored its kinetic absorption at 300 nm for a better S/N ratio. Although the scavenger absorbs slightly at 308 nm, this absorption does not contribute to the observed decays, since the scavenger is in large excess and does not significantly decay itself as the result of reaction.


(9) The AD at 300 nm (~0.03) is ~5 times larger than that at 355 nm.


(12) (a) Turro, N. J.; Zimmt, M. B.; Gould, I. R. J. Am. Chem. Soc. 1983, 105, 6347. (b) A referee has suggested that at short times (~1 μs), electronic relaxation may be contributing to the observed rate and that at long times (~1 μs), disintegration of the micelles may be contributing to the observed rates. We believe that both possibilities are plausible and should be pursued in other cases but are probably not dominant in the systems reported here. The relaxation of the benzoyl radical in micelles has been noted in earlier investigations to occur on a time scale of a microsecond or less,1 so we do not believe that contributions from T1 contribute significantly to the fastest exit rates reported in Table 1. If micelle disintegration were important, a common value of exit for the radicals would be reached. However, this situation, in fact, may be approached for the most hydrophobic radicals listed in Table 1. We thank the referee for commenting on these important issues.


(14) From a quenching study of 7 to 2RP in an aqueous solution containing 4 mM SDS surfactant (still below the CMC), the quenching rate kq of 7 is ~1.7 × 108 s−1 to benzoyl radical and ~2.1 × 106 s−1 to the ketyl radical.

Figure 1a shows a plot of kexit for the SDS micellized benzoyl/ketyl radical pairs (2RP) as a function of [7].12 At [7] = 30 mM, the values of kexit for both benzoyl (monitored at 355 nm) and ketyl (monitored at 300 nm) radicals approach nearly the same "plateau" value. Thus, for these concentrations of 7, kexit = kobs.12 For the pair 2RP, the values of kexit of both benzoyl and ketyl radicals from the SDS micelle (at [7] = 5 mM) are similar, (1.7 ± 0.3) × 106 and (1.9 ± 0.3) × 105 s−1, respectively. On the other hand (Figure 1b), the value of kexit for the benzoyl radical and ketyl radicals derived from the radical pair 3RP and the value for exit of the benzoyl radical (~1.7 × 106 s−1) are considerably faster than those for the companion ketyl radical (~3.5 × 104 s−1). From the results summarized in Table 1, the exit rate of a radical from a given micelle is seen to be independent of the structure of the radical precursor; i.e., the exit rate of the benzoyl radical is ~1.7 × 106 s−1 whether it is generated from flash photolysis of 1K, 2K, 3K, or 4K. Similarly, the exit rates of the cyclohexyl ketyl radical generated from the flash photolysis of 2K or 5K were the same, i.e., ~2 × 106 s−1.

The results support a previous assumption made in the analysis of a quantitative theory of the behavior of micellized radical pairs, namely that any differences in hydrophobicity or initial spatial distribution of the radicals in the micelle are averaged out and that micellar diffusion and equilibrium occur before exit.15 The measured exit rates summarized in Table 1 clearly depend on both the guest and host properties, especially
the hydrophobic properties of both the guest and host. For example, the rate of exit of a benzoyl radical clearly depends not only on its own "inherent" hydrophobicity but also on the "inherent" hydrophobicity of the micelle; e.g., benzoyl radicals exit from the larger SDS "inherent" hydrophobicity of the micelle; e.g., benzoyl radicals from a SDS micellar solution containing 250 mM Na+.

Thus, benzoyl radicals will exit micelles at differing rates depending on not only its hydrophilic character but also the hydrophilic character of the micelle in which it is adsorbed; i.e., the radical pair/micelle behaves as a supramolecular system.20 In conclusion, we envision three different radical pair reaction pathways for systems in which micellized radical pairs are generated by α-cleavage of micellized ketones: (1) primary cage reactions between geminate radical partners, characterized by a first-order rate constant, \( k_{\text{gem}} \); (2) secondary, nongeminate reactions of the benzoyl radicals that have escaped rapidly and have reentered the same or different micelles containing other radicals, characterized by a second-order rate constant and may be determined by the long time portion of radical decay; and (3) free radical reactions of exiting radicals in the aqueous phase that become a dominant process when an aqueous free radical scavenger is present in sufficiently high concentration, characterized by \( k_{\text{exit}} \) and \( k_{\text{obs}} \). The addition of 50 mM scavenger 7 effectively eliminates the contributions of pathways 2 and 3. These results support the emerging supramolecular description of a radical pair in a micelle; i.e., the exit rate of a radical from a micelle is a "supramolecular" property of the micellized radical pair and cannot be understood by consideration of the "molecular" properties of the host or guest alone.20 For example, the exit rates of benzoyl or ketyl radicals depend not only on their own molecular structure and inherent hydrophobicity but also on the hydrophobicity of the micellar host with which they are associated.

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**Table 1**

<table>
<thead>
<tr>
<th>Radical</th>
<th>( [\text{Na}^+] ) (mM) ( \pm 15% )</th>
<th>( k_{\text{gem}} ) (10^-6 s)</th>
<th>Radical</th>
<th>( [\text{Na}^+] ) (mM) ( \pm 15% )</th>
<th>( k_{\text{exit}} ) (10^-6 s)</th>
</tr>
</thead>
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<tr>
<td>OH</td>
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<td></td>
<td>OCH_3</td>
<td>SDS 50</td>
<td></td>
</tr>
<tr>
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<td>0.8</td>
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<tr>
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<td>260</td>
<td>SDeS</td>
<td>SDeS 50 260</td>
<td>100</td>
</tr>
<tr>
<td>O</td>
<td>SDS 50 3.5</td>
<td>100</td>
<td>SDeS</td>
<td>SDeS 50 260</td>
<td>100</td>
</tr>
</tbody>
</table>

*Only those sodium ions besides those associated with the individual surfactant molecules are reported here.*

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(18) Comparison of the hydrophobicity should only be made among those radical fragments having the same functional group; see ref 1.


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**Figure 1.** Plots of the rate of decay \( (k_{\text{obs}}) \) of benzoyl/ketyl radical pair (a) 2RP and (b) 3RP absorption in SDS as a function of added radical scavenger 7. At the plateau of each curve, \( k_{\text{obs}} = k_{\text{exit}} \).