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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[1−6] such as radical pairs (e.g., **1**, **RP−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 (k_{exit}) of the micellized radical pair fragments have been determined for the latter,[1] quantitative determination of k_{exit} by TRESR was not possible due to complications arising from spin−lattice relaxation (T_{1e}) of the polarized radical signals. We report a direct and quantitative evaluation of k_{exit} 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 λ_{max} at ~355 nm ($\epsilon \approx 150$)[8] and ketyl radicals, λ_{max} at ~300 nm ($\epsilon \approx 750$).[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 photolyses of products produced by the reactions of free pairs that are produced in the primary photolysis.[8,10−12] However, this interferent to benzoyl absorbance in micellar systems is minimized by the use of a flow cell and the scavenging of radicals exiting the micelle. Because of electrostatic repulsion, the ionic radical scavenger **7** cannot enter anionic micelles,[13] so only radicals that exit from the micelle are scavenged by **7**. At sufficiently high concentration of **7**, the decay of the exiting radicals becomes dominated by scavenging by **7**; i.e., the radical absorption decay follows pseudo-first-order kinetics and can be characterized by a pseudo-first-order rate constant, k_{obs}, for each radical. Concentration of the radical scavenger leads to a domain wherein each exiting radical is scavenged, so that the rate of micellar exit, k_{exit}, determines the observed radical lifetime. Under this condition, $k_{exit} = k_{obs}$.[12]

Chart 1

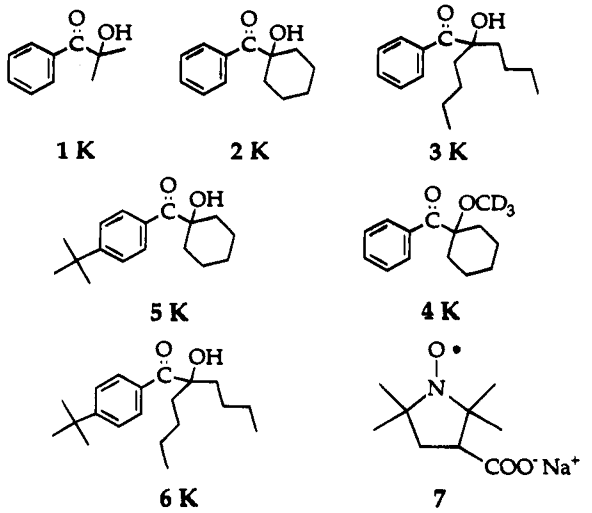

Figure 1a shows a plot of k_{obs} for the SDS micellized benzoyl/ketyl radical pairs (**2RP**) as a function of [**7**].[12,14] At [**7**] = 30 mM, the values of k_{obs} for both the benzoyl (monitored at 355 nm) and ketyl (monitored at 300 nm) radicals approach nearly the same "plateau" value. Thus, for these concentrations of **7**, $k_{exit} = k_{obs}$.[12] For the pair **2RP**, the values of k_{exit} of both benzoyl and ketyl radicals from the SDS micelle (at [**7**] = 50 mM) are similar, $(1.7 \pm 0.3) \times 10^6$ and $(1.9 \pm 0.3) \times 10^6$ s^{-1}, respectively. On the other hand (Figure 1b), the value of k_{exit} for the benzoyl radical and ketyl radicals derived from the radical pair **3RP** and the value for exit of the benzoyl radical (~1.7×10^6 s^{-1}) are considerably faster than those for the companion ketyl radical (~3.5×10^4 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 ~1.7×10^6 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., ~2×10^6 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

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[1] Wu, C.-H.; Jenks, W. S.; Koptyug, I. V.; Ghatlia, N. D.; Lipson, M.; Tarasov, V. F.; Turro, N. J. *J. Am. Chem. Soc.* **1993**, *115*, 9583. Jenks, W. S.; Turro, N. J. *J. Am. Chem. Soc.* **1990**, *112*, 9009.

[2] For an excellent discussion and review of the ideas of supramolecular systems, see: (a) Lehn, J. M. *Supramolecular Chemistry*; VCH: New York, 1995. (b) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89. Lehn, J.-M. *Science* **1985**, *227*, 849.

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[4] Buckley, C. D.; Hunter, D. A.; Horp, P. J.; McLauchlan, K. A. *Chem. Phys. Lett.* **1987**, *135*, 307.

[5] Turro, N. J.; Zimmt, M. B.; Lei, X. G.; Gould, I. R.; Nitsche, K. S.; Cha, Y. *J. Phys. Chem.* **1987**, *91*, 4544.

[6] Thurnauer, M. C.; Meisel, D. *J. Am. Chem. Soc.* **1983**, *105*, 3729.

[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, depending on the concentration of added **7**. Excitation source is the 308 nm excimer laser (~30 mJ/pulse). The flow cell is used with the flow rate ≈ 2 mL/min. The λ_{max} of the alkoxy radical from **4RP** is ~293 nm. However, we still monitored its kinetic absorption decay 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.

[8] Fisher, H.; Baer, R.; Hany, R.; Verhoolen, I.; Walbiner, M. *J. Chem. Soc., Perkin Trans. 2* **1990**, 787−798.

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

[10] Neville, A. G.; Brown, C. E.; Rayner, D. M.; Lusztyk, D. M.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 1869−1870.

[11] Weir, D.; Ajayaghosh, A.; Muneer, M.; George, M. V. *J. Photochem. Photobiol. A: Chem.* **1990**, *52*, 425.

[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), disintigration 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 T_1 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. 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.

[13] Gao, Z.; Wasylishen, R. E.; Kwak, J. C. T. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 947−948.

[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 k_q of **7** is ~1.7×10^8 s^{-1} to benzoyl radical and ~2.1×10^8 s^{-1} to the ketyl radical.

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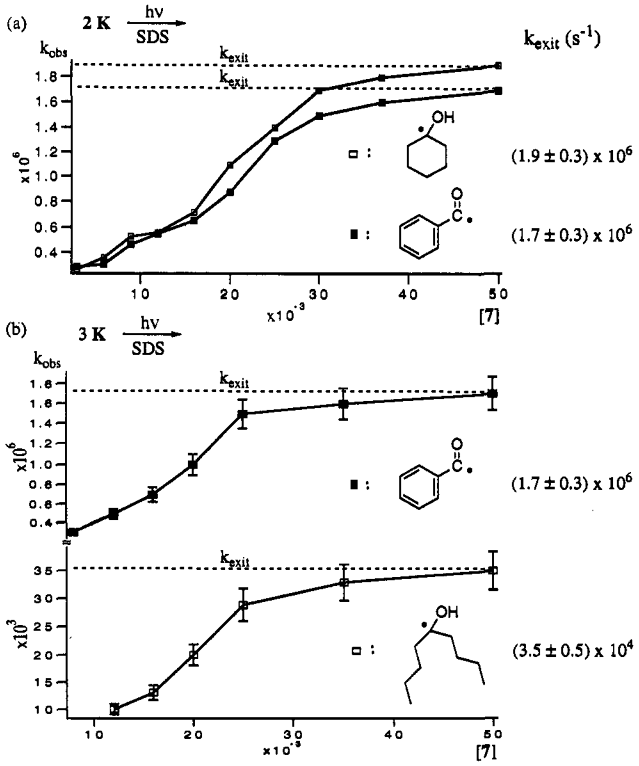
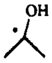
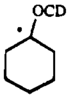
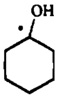
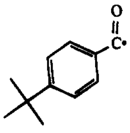
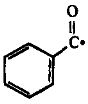
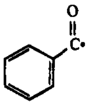
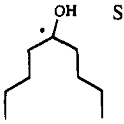
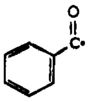


Figure 1. Plots of the rate of decay (k_{obs}) of benzoyl/ketyl radical pair (a) **2RP** and (b) **3RP** absorption in SDS as a function of added radical scavenger **7**. At the plateau of each curve, $k_{obs} = k_{exit}$.

Table 1

radical	micelle	[Na$^+$] (mM)	k_{exit} ($\times 10^{-4}$ s) ± 15%	radical	micelle	[Na$^+$] (mM)	k_{exit} ($\times 10^{-4}$ s) ± 15%
	SDS	50[a]	(too fast)		SDS	50	1
	SDS	50	190		SDS	50	0.8
	SDS	50	170		SDeS	50	260
	SDS	50	3.5		SDS	250[b]	100

[a] Only those sodium ions besides those associated with the individual surfactant molecules are reported here. [b] With additional 200 mM NaCl.

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 (C_{12}) micelles at a slower rate than from the smaller sodium decyl sulfate (SDeS, C_{10}) micelles (Table 1).

The fraction of radical pairs undergoing geminate recombination (cage effect) and the associated fraction of exiting radicals are important parameters in the quantitative theory of radical pairs in micelles.[15,16] Information on these parameters is available from examination of the overall decay of radicals in the presence and absence of the aqueous scavenger **7**. The decays of the benzoyl radical absorption derived from **3RP** in SDS micellar solution, both with and without 50 mM scavenger **7**, follow the same kinetics as those observed from **2RP**, a pair that possesses a more hydrophilic and more rapidly exiting ketyl radical. For the more hydrophobic ketyl radical, while the addition of the scavenger **7** modifies the absorption decay somewhat, the presence of scavenger does not shorten the overall time scale of ketyl radical decay (~80 μs).

For the very hydrophilic isopropyl ketyl radical (from **1RP**), k_{exit} from SDS micelles is too fast to be measured using the above technique. The ketyl radical absorption vanishes within 400 ns in the presence of 50 mM **7**, implying that k_{exit} is comparable to the rate of the micellar geminate cage reaction, k_{rxn}.[15,17] The measured values of k_{exit} of the SDS micellized radicals can be ranked according to the extent of their supramolecular hydrophobic interactions, as shown in Table 1.[18] These results are consistent with the prediction that the exit rate of micellized radicals decreases as the micelle size increases, i.e., as the length of the surfactant increases.[1] Micelle size can also be manipulated by varying ionic strength, with an increase in ionic strength leading to an increase in micelle size.[5,19] Table 1 shows that for **2RP** generated in a micelle, k_{exit} of the benzoyl radical is (2.6 ± 0.4) × 10^6 s^{-1} from SDeS micelle, (1.7 ± 0.5) × 10^6 s^{-1} for a SDS micellar solution, and (1.0 ± 0.3) × 10^6 s^{-1} from a SDS micellar solution containing 250 mM Na$^+$. Thus, benzoyl radicals will exit micelles at differing rates dependong 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.[2]

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_{rxn}; (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 $k_{exit} = k_{obs}$. 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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(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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