

and solved as described previously.  $|K_{el}|_{\max} = (C/A)^{1/2}$  contains a sum of terms of the same order of magnitude; for  $f \rightarrow 0$ ,  $|K_{el}|_{\max} \rightarrow 2/(S_0 L_0 \nu_{\max})$ .

### Appendix C

Here the quadratic eq 11 becomes

$$A = -0.25L_0^2 y^3 + 0.5S_0 L_0(1-2f)y^2 + S_0^2 f(1-f)y$$

$$B = 0.5L_0^2 y^3 - S_0 L_0(1-2f)y^2 + S_0(S_0 f^2 + S_0(1-f)^2 + L_0)y - S_0^2(1-2f)$$

$$C = A$$

The maximum rate was calculated from (11) with  $K_e = 1$

$$y_{\max} = (1-2f)/(1+L_0/S_0)$$

### Appendix D

For two substrates  $S_A$  and  $S_B$  in competitive exchange diffusion with  $S_2$ , eq 9 becomes

$$\frac{dS_{Aout}}{dt} = V_{\max} K_{eA} \frac{N}{D_1 D_2}$$

$$N = S_{Ain} S_{in} - S_{Aout} S_{out} + K_{eB}(S_{Ain} S_{Bout} - S_{Aout} S_{Bin})$$

$$D_1 = (K_{eA} S_{Ain} + K_{eB} S_{Bin} + S_{Aout} + S_{Bout})$$

$$D_2 = (K_{eA} S_{Aout} + K_{eB} S_{Bout} + S_{Ain} + S_{Bin})$$

with

$$S_{A(B)in} = S_0 - S_{A(B)out}$$

$$S_{In(out)} = S_{Ain(out)} = + S_{Bin(out)}$$

A similar equation holds for  $dS_{Bout}/dt$ , where subscripts A are exchanged for B and conversely. The coupled linear differential equations were solved numerically for a given set ( $S_0, V_{\max}, K_{eA}, K_{eB}$ ) with initial conditions  $S_{A(B)in} = 0.5S_{2out} = S_0$ . The concentrations  $S_{A(B)out}$  were plotted against time (Figure 9) and the selectivity  $S_{Aout}/S_{Bout}$  against  $f$  (Figure 8).

## Micellar Systems as Devices for Enhancing the Lifetimes and Concentrations of Free Radicals<sup>1</sup>

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Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. Received June 11, 1984

**Abstract:** Optical modulation spectroscopy was used to monitor the second-order decay kinetics of phenylthiyl (I) and mesitythiyl radicals (II) in both heptane and sodium dodecyl sulfate (SDS) solutions. The self-reactions of the thiyl radicals were found to be diffusion controlled in the hydrocarbon solvent. Little change was observed in the decay kinetics of I when the solvent was aqueous SDS (0.2 M), suggesting that the radical was not strongly partitioned into the micelles. However, enhancements of a factor of ca. 50 in both the lifetime and concentration of II were observed in 0.05 M SDS, implying that the larger radical was effectively caged within the micelles. Kinetic analysis led to a value of  $2 \times 10^3 \text{ s}^{-1}$  for the exit rate constant of II from SDS micelles.

The behavior of radical pairs formed photochemically in micelles has been the focus of extensive investigation.<sup>2-14</sup> Often the micelle functions as a temporary cage for the radical pair, in which case,

radical-radical encounters are frequent and reaction is only restricted if the radical pair is in the triplet state.<sup>2</sup> Even with this restriction, intersystem crossing to the singlet state and subsequent reaction normally occurs in the submicrosecond time scale.<sup>6,7</sup> Of course, micelles are not perfect jailors and escape by one of the radicals is an important process which forms the subject of this paper.

Once free of its partner, a given radical has two major pathways for decay. If there is no strong preference for the micellar environment, then the concentration of radicals in the aqueous phase will be relatively high so that radical-radical reaction in that phase will be the most important mode of decay. The decay kinetics will be second order and will hardly be perturbed by the presence of the micelles.

For a radical which shows a strong preference for the micellar environment, the radical concentration in the aqueous phase will be low. Decay will then occur by a mechanism in which the radical visits a number of micelles by repeated exit and entry until it finds one which contains another radical, when reaction will generally occur. In this instance decay may again follow second-order kinetics (vide infra) with the exit process being the rate-controlling step.

It is this second case which is intriguing, since it suggests the possibility that the rate constant for exit from the micelle can be measured by following the overall rate of radical decay. Moreover,

- (1) Issued as NRCC publication 23904.
- (2) Turro, N. J.; Kraeutler, B.; Anderson, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 7435.
- (3) Turro, N. J.; Kraeutler, B. *Acc. Chem. Res.* **1980**, *13*, 369.
- (4) Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Weed, G. C.; Kraeutler, B. *J. Am. Chem. Soc.* **1980**, *102*, 4843.
- (5) Lehr, G. F.; Turro, N. J. *Tetrahedron* **1981**, *37*, 3411.
- (6) Scaiano, J. C.; Abuin, E. B. *Chem. Phys. Lett.* **1981**, *81*, 209.
- (7) Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Tanimoto, Y.; Weed, G. C. *J. Am. Chem. Soc.* **1981**, *103*, 4574.
- (8) Equation 5 is based upon the assumption that reaction 3 proceeds with 100% efficiency. However, this assumption is not quantitatively correct since some escape from the micelle is likely to occur before radical-radical reaction takes place. Comparison with data for the micellar escape of triplet radical pairs<sup>6</sup> suggests that reaction 3 will proceed with an efficiency of ca. 70%. No correction was introduced to account for this effect since it is small with respect to the other experimental errors involved in this work.
- (9) Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Kraeutler, B. *J. Am. Chem. Soc.* **1981**, *103*, 3886. Turro, N. J.; Anderson, D. R.; Chow, M.-F.; Chung, C.-J.; Kraeutler, B. *J. Am. Chem. Soc.* **1981**, *103*, 3892.
- (10) Turro, N. J.; Mattay, J. *J. Am. Chem. Soc.* **1981**, *103*, 4200.
- (11) Scaiano, J. C.; Abuin, E. B.; Stewart, L. C. *J. Am. Chem. Soc.* **1982**, *104*, 5673.
- (12) Turro, N. J.; Weed, G. C. *J. Am. Chem. Soc.* **1983**, *105*, 1861.
- (13) Baretz, B. H.; Turro, N. J. *J. Am. Chem. Soc.* **1983**, *105*, 1309.
- (14) Thurnauer, M. C.; Meisel, D. *J. Am. Chem. Soc.* **1983**, *105*, 3729.

if the exit rate is very low for a suitably chosen radical, the use of micellar media might bring about dramatic enhancements in both its lifetime and concentration.

### Experimental Section

**Materials.** Phenyl disulfide was purified by triple recrystallization from warm hexane-ethanol solutions. Thiophenol was vacuum distilled and was stored under nitrogen in a freezer. Sodium dodecyl sulfate (electrophoresis grade), water, and heptane (liquid chromatography grade) were commercially available and were used as received. Mesityl disulfide<sup>15</sup> and mesitylthiol<sup>16</sup> were prepared by literature methods.

**Instruments.** The radicals examined in this work were monitored via their optical absorption spectra by using laser flash photolysis and modulation spectroscopy. Both of these techniques have been described in detail elsewhere.<sup>17,18</sup> Briefly, in the laser flash photolysis method, pulses (8 ns duration, 308 nm, 10 mJ) from an excimer laser were used to generate the radicals.<sup>17</sup> They were monitored with use of a standard detection system consisting of a xenon monitoring lamp, monochromator, and photomultiplier tube. The output of the tube was fed through a terminator to a transient digitizer for analog-to-digital conversion and then to a computer for data processing.

In the modulation spectrometer,<sup>18</sup> the photolysis source was a 1000W mercury-xenon lamp. The output of the lamp was filtered through a cobalt-nickel filter solution and then through a Pyrex filter, giving an effective wavelength range of 315 to 340 nm. The photolyzing light was modulated sinusoidally by using a mechanical light chopper fitted with appropriately shaped irises. The sample chamber was a standard fluorescence flow cell, and the radicals were monitored by using a system similar to that described for the laser flash photolysis apparatus. The detection system was arranged at right angles to the photolysis beam to reduce the problems associated with light scattering.

The signal from the photomultiplier tube detector consisted of a large dc signal,  $V$ , that reflected the overall optical absorption of the sample. Superimposed upon  $V$  was an ac signal,  $\Delta V$ , that reflected the modulated part of the optical absorption. The latter was analyzed with use of a lock-in amplifier. The ratio  $\Delta V/V$  defines the optical density and was obtained by dividing the two analog signals in a Franklin 1000 micro-computer fitted with an analog-to-digital converter (Interactive Microwave Adalab and Ada-Amp).

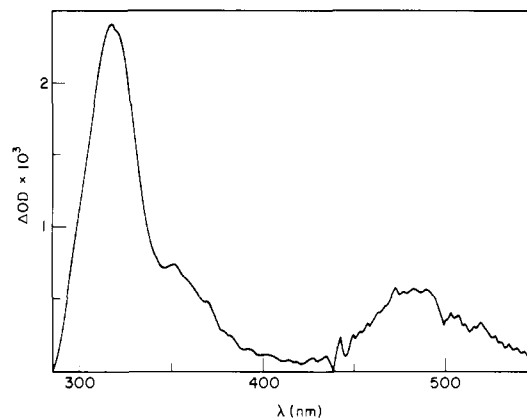
**Sample Preparation.** All of the solutions used in this work were carefully deoxygenated by nitrogen purging before use. They were flowed through the sample cells to eliminate problems associated with the disappearance of substrate and the accumulation of products. Those used in modulation spectroscopy were always optically dilute to ensure uniform radical distribution in the sample.

The preparation of sodium dodecyl sulfate solutions used in this work required special methods since the disulfides, in particular, dissolved extremely slowly in pure micellar solutions. In general, 10 mL of a pentane solution of the organic substrate ( $10^{-2}$  M) was added to 500 mL of sodium dodecyl sulfate solution which was then purged with nitrogen for 2 h to remove all of the pentane. Water was added to the solution to compensate for evaporation.

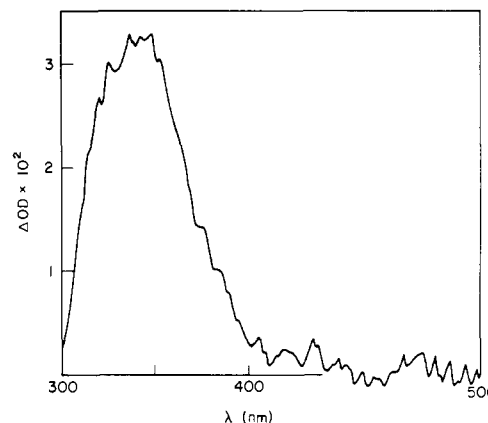
### Results and Discussion

**Kinetic Scheme.** The generation of radical pairs in micelles gives rise initially to intramicellar reactions such as recombination within the submicrosecond time scale.<sup>6,7</sup> A proportion of the radical pairs are destroyed when one member of the pair escapes the micelle and enters the aqueous phase. Once free of its partner, a radical will repeatedly enter and exit micelles until it encounters another radical either in the aqueous or micellar phases in which case reaction will generally occur. However, such processes will take place on very much longer time scales than the intramicellar reactions of the initial radical pairs.<sup>7</sup>

The decay of these free radicals is described by eq 1-4, where  $R_W$  and  $R_M$  represent the radicals in the water and in the micelles, respectively,  $k_+$  and  $k_-$  are the rate constants for their entry and

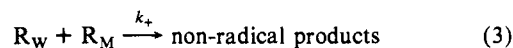
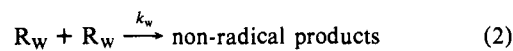
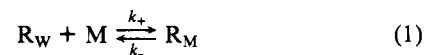


**Figure 1.** In-phase modulation spectrum of radical II recorded by modulated photolysis of  $8 \times 10^{-5}$  M II-II in heptane at 44 Hz. The amplitude of the out-of-phase spectrum was 0.7 that of the in-phase spectrum.



**Figure 2.** Out-of-phase modulation spectrum of radical II recorded by a modulated photolysis of  $2.5 \times 10^{-5}$  M II-II in 0.1 M SDS at a frequency of 44 Hz. No in-phase signal was detected at this frequency.

exit, and  $M$  represents the micelles themselves. Clearly, eq 2 describes radical-radical reactions which take place in the aqueous phase while eq 3 describes the reaction in which a radical enters an already occupied micelle and reacts with the radical in situ.



$$k_+/k_- = K = [R_M]/([R_W][M]) \quad (4)$$

If  $[R_T]$  is the total concentration of radicals in the system, then<sup>19</sup>

$$-d[R_T]/dt = \frac{[R_T]^2}{(1 + K[M])^2} \{2k_w + 2k_-K^2[M]\} \quad (5)$$

Moreover, when the radicals are predominantly in the micelles,  $K[M] \gg 1$  and  $[R_T] \approx [R_M]$ , and since  $2k_-K = k_+ \approx 2k_w$ ,<sup>20</sup> it follows that

$$-d[R_T]/dt = 2k_-[R_T]^2/[M] \quad (6)$$

For radicals which show a strong preference for the micellar environment and conform to this limit, eq 6 implies that their rates of bimolecular decay will be controlled by their exit rates from the micelle multiplied by the probability of entering a micelle

(15) Olah, G. A.; Narang, S. C.; Field, L. D.; Salem, G. F. *J. Org. Chem.* **1980**, *45*, 4792.

(16) Field, L.; Grunwald, F. A. *J. Org. Chem.* **1951**, *16*, 946.

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(19) A similar kinetic scheme has been described elsewhere.<sup>20</sup>

(20) Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 279.

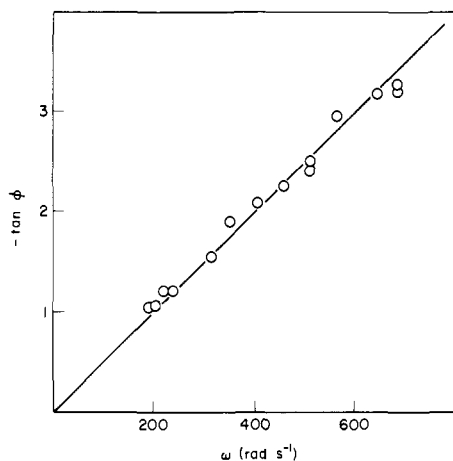
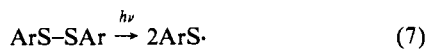


Figure 3. Frequency dependence of  $\phi$  for radical II in heptane.

which contains another radical. This raises the possibility that lifetimes of radicals could be substantially enhanced if their exit rates are so low that they are basically confined to the micellar medium.

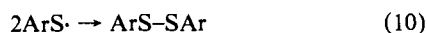
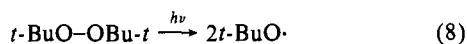
To probe these possibilities experimentally, we examined the decay kinetics of phenylthiyl and mesitylthiyl radicals in aqueous sodium dodecyl sulfate (SDS) and in heptane which was used as a standard for comparison.

**Assignments of Spectra.** Photolysis of phenyl or mesityl disulfide (ca.  $10^{-5}$  M) in heptane solvent was monitored both by modulation spectroscopy and by laser flash photolysis. Both techniques gave the same transient absorption spectra with photolysis of mesityl and phenyl disulfide giving maxima for the respective transients at 320 and 300 nm<sup>21</sup> (Figure 1), eq 7. In addition to the main



I, ArS· = phenylthiyl; II, ArS· = mesitylthiyl

absorption bands, broad and weaker bands were observed at 480 and 450 nm, respectively. The same spectra were observed when mixtures of di-*tert*-butyl peroxide and the corresponding thiols were photolyzed in heptane solvent and are therefore assigned to the corresponding thiyl radicals, eq 8–10.



As further evidence in support of these assignments, we note that in the laser flash experiments on phenyl disulfide, the transient absorption spectra had the same shape when recorded 30 ns and 5  $\mu$ s after the laser flash, indicating that the transients were produced in the initial photolysis and were not secondary products. Similarly, modulation spectra obtained from both disulfides had the same shape at low and high modulation frequencies (20 to 400 Hz).

Finally, the spectra were quenched by addition of thiyl radical scavengers such as di-*tert*-butyl nitroxide ( $10^{-3}$  M)<sup>22</sup> or tri-*n*-butylphosphine (0.5 M)<sup>23</sup> that were optically transparent at the photolysis wavelengths.

The spectra observed when similar photolyses were carried out in micellar solution were slightly different than those described above. The absorption bands were red shifted by 20–30 nm and

(21) Thyron, F. C. *J. Phys. Chem.* **1973**, *77*, 1478. Cf.: Ito, O.; Matsuda, M. *J. Org. Chem.* **1983**, *48*, 2410.

(22) Nakamura, M.; Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1980**, *102*, 698.

(23) The second-order rate constant for reaction of tri-*n*-butylphosphine and I is ca.  $10^6$ . Burkey, T. J.; Griller, D.; Nazran, A. S., unpublished results.

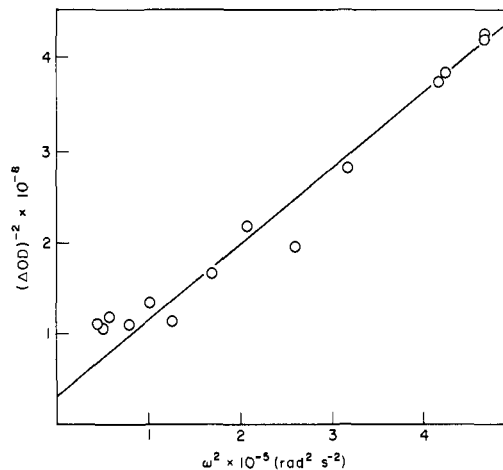


Figure 4. Frequency dependence of  $\Delta\text{OD}$  for radical II in heptane.

were much broader than those observed in heptane (Figure 2). We presume that these changes are due to the fact that the micelles are substantially impregnated with water particularly toward the micellar periphery and therefore afford a much more polar medium than heptane for solvation of the radicals. The broadening in the absorption bands may be due to the fact that the radicals are distributed through sites of varying polarity. Again laser flash photolysis experiments showed that the shape of the absorption spectra did not change with time.

The only significant complication that arose in the assignment of spectra was that the spectrum obtained during modulated photolysis of phenyl disulfide in heptane was dependent upon the concentration of the latter. At disulfide concentrations below  $3.5 \times 10^{-5}$  M the spectrum was clearly due to the thiyl radical with  $\lambda_{\text{max}}$  300 nm. However, at  $1 \times 10^{-4}$  M and above an additional species was present with  $\lambda_{\text{max}}$  340 nm. This spectrum was most probably due to an adduct formed by addition of the thiyl radical to the disulfide. To avoid complications from this source, all experiments were run at very low concentrations of phenyl disulfide.

**Kinetic Measurements.** All kinetic measurements for the second-order decay of the radicals examined in this work were made on the modulation spectrometer, the time scale of the laser flash photolysis system being too short for accurate kinetic analysis of the second order decay processes.

Changes in the phase angle,  $\phi$ , of the signal due to the radicals were monitored as a function of modulation frequency,  $\omega$ , and define the lifetime of the radical,  $\tau_{\text{R}}$ , according to eq 11 (Figure 3).

$$\tan \phi = -\omega\tau_{\text{R}} \quad (11)$$

In addition, changes in the modulation amplitude of the optical density,  $\Delta\text{OD}$ , were monitored as a function of  $\omega$ . Plots of  $(\Delta\text{OD})^{-2}$  vs.  $\omega^2$  gave straight lines of slope  $a$  and intercept  $b$  which are related to the parameters of interest by eq 12–14<sup>18</sup> (Figure 4). In these equations,  $\epsilon_{\text{R}}$  is the extinction coefficient of the

$$a = 4(\epsilon_{\text{R}}lI_0)^{-2} \quad (12)$$

$$b = 4(\epsilon_{\text{R}}lI_0\tau_{\text{R}})^{-2} \quad (13)$$

$$\tau_{\text{R}} = (4k_{\text{obsd}}I_0)^{-1/2} \quad (14)$$

radical,  $2k_{\text{obsd}}$  is the rate constant observed for its bimolecular decay,  $l$  is the path length of the cell in the direction of the monitoring beam, and  $I_0$  is the maximum light intensity during the modulation cycle. Clearly, the ratio of slope to intercept defines the lifetime of the radical which was checked for consistency against the measurements made by following the phase angle.

Rate constants for the bimolecular decay of I were measured relative to  $\epsilon_{\text{R}}$  in both heptane and SDS solutions (Table I). With the assumption that the extinction coefficient of I was not dras-

**Table I.** Data for the Recombination of Thiyl Radicals in Heptane and SDS Solutions

	heptane				[R] (10 <sup>8</sup> M)	SDS <sup>a</sup>			
	$2k_{10}/\epsilon$ (10 <sup>-5</sup> cm s <sup>-1</sup> )	$2k_{10}$ (10 <sup>-9</sup> M <sup>-1</sup> s <sup>-1</sup> )	$\epsilon$ (10 <sup>-4</sup> M <sup>-1</sup> cm <sup>-1</sup> )	$\tau$ (10 <sup>3</sup> s <sup>-1</sup> )		$2k_{\text{obsd}}/\epsilon$ (10 <sup>-2</sup> cm <sup>-1</sup> s <sup>-1</sup> )	$\tau$ (10 <sup>3</sup> s <sup>-1</sup> )	[R] (10 <sup>8</sup> M)	$2k_{-}$ (10 <sup>-3</sup> s <sup>-1</sup> )
I	5.0 <sup>b</sup>	5.5	1.1 <sup>b</sup>	2.9	3.1	1.4 × 10 <sup>4c</sup>	1.8	1.8	
II	2.8 <sup>d</sup>	6.4	2.3 <sup>d</sup>	5.1	1.5	1.3 <sup>e</sup> 3.9 <sup>f</sup>	230 250	73 22	2.0 1.7

<sup>a</sup> Micellar concentrations were calculated by using a critical micelle concentration of  $8.2 \times 10^{-3}$  and an aggregation number of 62; ref 20. <sup>b</sup>  $\lambda_{\text{max}}$  300 nm. <sup>c</sup>  $\lambda_{\text{max}}$  340 nm; 0.2 M SDS. <sup>d</sup>  $\lambda_{\text{max}}$  320 nm. <sup>e</sup>  $\lambda_{\text{max}}$  340 nm; 0.05 M SDS. <sup>f</sup> 0.02 M SDS.

tically affected by the change in solvent, the data show that there was little variation in the rate constant for decay, indicating that I could readily exit the micelles. This result is entirely consistent with measurements of the micelle-water partition coefficients for molecules which contain a similar number of heavy atoms. For example, benzene is partitioned 70%:30% between the aqueous and micellar phases of 0.1 M SDS.<sup>24</sup>

In an attempt to find a significant micellar effect, we examined the kinetic properties of II in hydrocarbon and SDS media to see if this increase in molecular weight would cause the radical to partition so strongly in favor of the micellar environment that it would be slow to exit and hence slow to undergo decay. The results reported in Table I show that the observed rate constant for second-order decay of II (relative to  $\epsilon$ ) was  $3 \times 10^3$  times less in 0.05 M SDS solution than in heptane.<sup>25</sup> This implies that the II has a strong preference for the micellar environment and that eq 6 describes the reaction kinetics, i.e.,  $2k_{\text{obsd}} = 2k_{-}/[M]$ . In support of this conclusion, we found that  $2k_{-}$  did not change significantly when the micelle concentration was changed by more than a factor of 3 (Table I).

To put these results on an absolute basis,  $2k_{10}$  was estimated for the radicals in heptane by using the von Schmoluchowski equation. When combined with the data in Table I this should yield  $\epsilon$  for the radical in heptane. With the assumption that this value is not substantially affected by a change to the micellar environment, the result can be combined with the value of  $2k_{\text{obsd}}/\epsilon$  to give the absolute value of the rate constant for exit from the micelle.

The von Schmoluchowski equation relates  $2k_{10}$  to the diffusion coefficient for an individual radical,  $D$ , the reaction diameter,  $\rho$ , Avogadro's number,  $N_L$ , and the spin statistical factor for the reaction,  $\sigma$ , eq 15.<sup>26-28</sup>

$$2k_{10} = (8 \times 10^{-3})\sigma\pi N_L D\rho \quad (15)$$

The reaction distances for I and II (5.5 and 6.3 Å) were calculated by using the molar volumes of the parent hydrides (I-H and II-H) as models.<sup>27b</sup> Similarly, the diffusion coefficients of their parent hydrides were measured on a Taylor Diffusion apparatus<sup>24,28</sup> and were both found to be  $2.7 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>. These values were assumed to be applicable to radicals I and II. The spin statistical factor for the reaction was taken to be  $1/4$ .<sup>29</sup> Combining these results in eq 15 gave the value of  $2k_{10}$  and hence the values of  $\epsilon$  and  $k_{-}$  reported in Table I.

It is difficult to make reliable error estimates for the kinetic data since they involve some assumptions<sup>8</sup> as well as experimental inaccuracies. Moreover, it was impossible to make an estimate of the change in  $\epsilon$  for these radicals on going from hydrocarbon to micellar media where the spectral bands were somewhat

broader. However, taking a cautious view, we suggest that the absolute values of  $2k_{10}$  are accurate to a factor of 2, whereas a factor of 5 applies to the absolute values of  $2k_{-}$ . Of course, the relative values of  $2k_{\text{obsd}}/\epsilon$  are substantially more reliable. These errors represent significant limitations in quantifying the micellar effect. Despite their magnitude, it has nevertheless been possible to establish the broad conditions under which the effect of micelles on radical lifetimes becomes dominant.

As stated above, the change in solvent from heptane to aqueous SDS had little effect on the concentration of I or its lifetime, indicating that the radical did not show a strong preference for the micellar environment. However, the use of aqueous SDS as solvent had a profound effect on the behavior of II, causing increases of a factor of ca. 50 in both its concentration and lifetime.<sup>30</sup>

The value of  $2k_{-}$  for II was somewhat smaller, but not grossly dissimilar, to the values reported by Almgren, Greiser, and Thomas for the exit from SDS micelles of organic molecules of similar size.<sup>20</sup> Those authors found that the values of  $\log k_{-}$  for simple organics were roughly proportional to their boiling points. Clearly, the correlation reflects molecular size and suggests that the decay kinetics for any nonpolar radical, which is similar in size to II, can be dramatically changed by the use of aqueous SDS as solvent. There is, of course, the obvious rider that the radical does not readily attack the micellar material.

The thiyl radicals described herein were generated as pairs in individual micelles. For mesitylthiyl radicals, which were slow to exit the micelles, a substantial proportion of these pairs must have recombined within the micelle in which they were formed. That is, recombination would have taken in the submicrosecond time scale, before one of the members of the pair had escaped the micelle. In the modulation experiments, radical concentrations were detected in the millisecond time scale and therefore reflect the diminution in overall quantum yield, caused by the initial intramicellar recombination described above, and the counterbalancing enhancement in concentration caused by the fact that, after escape, the radicals were effectively isolated in individual micelles and could not easily undergo recombination reactions.

The enhancements in lifetime and concentration for II imply that the latter effect was dominant. It therefore follows that the use of micellar media could be of general benefit in, for example, optical and electron spin resonance spectroscopies, where concentration is often a factor which limits the detectability of free radicals.

Finally, we note that the techniques described in the present work allow the measurement of exit rates from micelles by free radicals which are some 3 orders of magnitude less than those accessible to laser flash photolysis techniques and thus dramatically extend the range of molecules which can be investigated kinetically in micellar environments.

**Acknowledgment.** We thank Dr. A. S. Nazran for his help with the laser flash photolysis experiments and Dr. J. C. Scaiano for helpful discussions.

**Registry No.** I, 4985-62-0; II, 93255-32-4; phenyl disulfide, 882-33-7; mesityl disulfide, 1483-92-7.

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(25) The kinetic measurements were of  $2k_{10}/\epsilon$  and  $k_{\text{obsd}}/\epsilon$ . We assume that the extinction coefficient of the radical is the same in heptane as in the hydrocarbon-like interior of the micelle.

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(29) This assumption implies that triplet-to-singlet intersystem crossing for pairs of arylthiyl radicals is relatively inefficient so that only one-quarter of the diffusion-controlled encounters in homogeneous solution lead to reaction. Experiments are in progress to test this hypothesis. For further discussions concerning spin statistical factors see ref 27b.

(30) The same effect was observed for the 1-naphthylthiyl radical: for identical light intensities and concentrations of 1-naphthyl disulfide, the lifetime of the signal for the naphthylthiyl radical in SDS solution was also very long compared to that in heptane and this indicated escape from the micelle was the rate-limiting step for recombination. Rate data for this radical have not been reported since the presence of a second transient occurring in heptane (360 nm) precluded an accurate determination of  $\epsilon$ .