Preparation of Solutions of the Soluble Silver Complexes for NMR Analysis. (I) Equimolar, 2. To 0.5 cm^3 of 2 M KOH was added 10 mg (0.054 mmol) of ligand. To this solution 0.54 cm^3 of 0.1 N AgNO$_3$ (0.054 mmol) was added slowly with gentle stirring. The mixture was stirred until all of the Ag$_2$O formed dissolved. Precipitation of complex **3** sometimes occurs when this procedure is carried out. We found this could be prevented by the addition of the ligand to the silver solution. This clear, colorless solution was then added to a vigorously stirred solution of 100X absolute methanol. The resulting precipitate was washed with anhydrous methanol to neutral rinse, and the resulting solid was air dried: mp 220 °C dec. Anal. Calcd: C, 13.84, H, 2.32; S, 18.47; K, 11.26; Ag, 31.07. Found: C, 13.82; H 2.33; S, 18.39; K, 11.37; Ag, 30.92. The sample was kept in the dark to prevent silver photolysis.

(II) 2 mol of Ligand (DTT) to 1 mol of Silver, 3. The procedure for preparation of complex **3** was the same as that for **2** except that 0.28 cm^3 of 0.1 N AgNO$_3$ (0.0272 mmol) was used in this case and that the precipitate of complex **3** forms immediately after the solution is prepared: mp 240 °C dec.

Preparation of Crystals for X-ray Analysis, 3. An approximately 4% solution of DTT in 2 M KOH was prepared by simple addition of these two reagents followed by rigorous agitation. If after mixing undissolved material was still present, the solution was filtered. With rigorous agitation a slightly less than stoichiometric quantity of aqueous silver nitrate was then added. Precipitation of white crystalline **3** occurred after approximately 1/2 - 2/3 of the silver nitrate had been added. In practice, addition of a stoichiometric amount of silver resulted in formation of a small amount of silver oxide that could not be dissolved by further agitation. This was evidenced from visual observation of the dark brown silver oxide precipitate. When this occurred incremental addition of the disulfone was necessary until all of the silver oxide had dissolved.

The white precipitate was then suction filtered onto a sintered glass frit and washed with methanol until the wash was neutral to litmus. It was then recrystallized from water. In a test tube a saturated aqueous solution of the silver-disulfone complex was prepared at steam temperature. If any undissolved materials were observed, the solution was hot filtered into a second test tube. To prevent premature crystallization, all work was performed on a steam cone. At this point the steam was gradually reduced to zero over a 15-20-min period. The solution was then allowed to set undisturbed overnight. The crystals obtained were gathered onto a sintered glass frit and washed several times with methanol and air dried: mp 245 °C dec.

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Supplementary Material Available: Description, tables, and figures of X-ray data (33 pages). Ordering information is given on any current masthead page.

Photochemistry of Acetone in Surfactant Solutions[1]

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Abstract: Acetone triplets, generated predominantly in the aqueous pseudophase, are extremely mobile probes in micellar solution. Their exit and entry rates exceed 10^8 s^{-1} and 10^{10} M^{-1} s^{-1}, respectively. Exit is competitive even with fast (diffusion controlled) intramicellar processes, such as exothermic triplet energy transfer. Photoreduction by the surfactant plays an important role in the absence of added quenchers. While acetone triplets can be readily studied, experiments with other aliphatic carbonyl compounds are complicated by short lifetimes owing to self-quenching (aldehydes) and Norrish Type I and Type II reactions. This may provide insight into the reasons for nature's choice of acetone triplet as a species of biological importance.

Flash techniques have become widely used in the study of organized systems; among these, micelles have received considerable attention. Studies of this type lead to information on the behavior of short-lived reaction intermediates,[2-9] solubilization of added reagents,[10] as well as the properties of the aggregate itself,[11,12] such as polarity, critical micelle concentration (cmc), and aggregation number.

This study of acetone in several micellar systems has been mainly motivated by two reasons. First, flash studies of this type usually involve photoexcitation in the micellar pseudophase; in the case of acetone, one can expect light absorption to occur predominantly in the aqueous phase. We thought it would be desirable to understand better the effect of excitation site on the photoprocesses which follow.

Second, triplet acetone has been established to be an important intermediate in biological systems,[13] where it can be generated thermally through oxidation processes, involving particularly the

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(1) Issued as NRCC 21344.

(2) Scaiano, J. C.; Abuin, E. B.; Stewart, L. C. *J. Am. Chem. Soc.* **1982**, *104*, 5673-5679.

(3) Turro, N. J.; Chow, M. F.; Chung, C. J.; Tanimoto, Y.; Weed, G. C. *J. Am. Chem. Soc.* **1981**, *103*, 4574-4578.

(4) Atik, S. S.; Thomas, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 3550-3555.

(5) Brogger, P. A.; Infelta, P. P.; Braun, A. M.; Grätzel, M. *J. Am. Chem. Soc.* **1981**, *103*, 320-326.

(6) Hayashi, H.; Sakaguchi, Y.; Nagakura, S. *Chem. Lett.* **1980**, 1149-1152.

(7) Schmehl, R. H.; Whitten, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 1938-1941.

(8) Thomas, J. K. *Chem. Rev.* **1980**, *80*, 283-299.

(9) Grätzel, M.; Kalyanasudaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 7869-7874.

(10) Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 279-291.

(11) Atik, S. S.; Thomas, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4367-4371.

(12) Yekta, A.; Aikawa, M.; Turro, N. J. *Chem. Phys. Lett.* **1979**, *63*, 543-548.

(13) Kenten, R. H. *Biochem. J.* **1953**, *55*, 350-360.

0002-7863/83/1505-5652$01.50/0

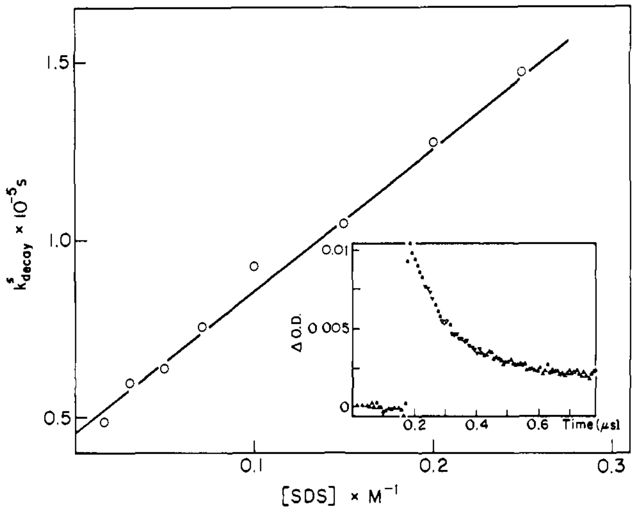

Figure 1. Quenching of acetone triplets by sodium dodecyl sulfate (SDS), according to eq 2, and (insert) representative decay trace monitored at 330 nm for [acetone] = 0.3 M, [SDS] = 0.15 M at 300 K.

cleavage of dioxetanes.[14] Cilento,[15] in a recent review, has pointed out the difficulties in assessing the role of the microenvironment on the behavior of acetone triplets, specifically, on their lifetimes and rate constants for quenching processes. While the difference in complexity between biological and micellar systems should not be underestimated, it is also clear that micelles can provide some insight into the effect of the microenvironment on excited-state behavior. Further, the relative simplicity of micelles offers the possibility of detailed kinetic analysis.

The aspects of the problem examined herein include the lifetime and pathways for decay of acetone triplets in cationic, anionic, and neutral micelles, a kinetic analysis of energy transfer to biphenyl, and a few exploratory experiments on the role played by molecular size on the dynamics of these processes. Our experiments lead us to conclude that triplet acetone is a remarkably mobile probe, resident largely in the aqueous phase, which usually follows homogeneous-like kinetics. With acceptors such as biphenyl and 4,4'-dimethylbiphenyl the overall rate constants for energy transfer are comparable with those in homogeneous solution.

Results

Most of our experiments have been carried out with the use of laser flash photolysis techniques, employing the pulses (308 nm, ~5 ns, up to 80 mJ) from a Xe-HCl excimer laser for excitation and a computerized system with nanosecond response to monitor the transient signals.[16] All experiments were performed under oxygen-free conditions.

The decay of triplet acetone can be monitored at 330 nm and, in detergent solutions, leads to decay traces (see insert in Figure 1) that do not return to the original (pre-pulse) level. This residual absorption is attributed to ketyl radicals, $(CH_3)_2\dot{C}OH$, expected from the photoreduction of acetone triplets by the surfactants, reaction 1.[17] This residual, long-lived absorption is absent in

$$(CH_3)_2CO^* + RH \rightarrow (CH_3)_2\dot{C}OH + R\cdot \qquad (1)$$

aqueous solutions in the absence of surfactant; our measured value of 4.2 μs for the acetone triplet lifetime in aqueous solution is in good agreement with previously reported values.[18,19] For acetone concentrations up to ca. 0.3 M and low (<20 mJ) excitation doses, the decay of triplet acetone (Ace*) in surfactant solutions follows clean first-order kinetics. At higher acetone concentrations (>0.3 M) and/or higher excitation intensities, this decay is complicated by contribution of a second-order component. This is presumably the result of triplet-triplet annihilation, which is expected to become more important under these conditions.

Table I. Lifetime of Acetone Triplets in Micellar Solution at 300 K[a,b]

surfactant	concn, M	τ_T, ns
none (H_2O)		4200 ± 500
SDS	0.03	1630 ± 100
	0.05	1430 ± 150
	0.07	1310 ± 100
	0.10	1080 ± 100
	0.15	950 ± 100
	0.20	780 ± 50
	0.25	680 ± 50
	0.30	670 ± 50
CTAC	0.01	1700 ± 100
	0.05	1240 ± 50
Brij-35	0.02	1000 ± 200

[a] [Acetone] = 0.33 M. [b] Monitoring T-T absorptions at 330 nm.

The lifetime of Ace* is dependent upon the surfactant concentration and, under conditions of low acetone concentrations and excitation intensities, follows the simple kinetic law of eq 2,

$$k^S{}_{decay} = k^0{}_{decay} + k_S[\text{surfactant}] \qquad (2)$$

in which the pseudo-first-order rate constant for decay of Ace* in the presence of surfactant ($k^S{}_{decay}$) is expressed in terms of the first order rate constant for Ace* decay ($k^0{}_{decay}$) and the second order term for quenching by the surfactant, k_S. For the acetone-sodium dodecyl sulfate (SDS) system, k_S was determined to be $(4.1 \pm 0.5) \times 10^6$ M^{-1} s^{-1} at 300 K (errors as $\pm 2\sigma$ throughout). The corresponding quenching plot is shown in Figure 1, where it should be noted that all SDS concentrations employed are well in excess of the cmc (8.1×10^{-3} M).[20] Neither the position nor the extinction coefficient of the n,π* band maximum in the UV absorption spectrum of acetone were changed (<1 nm) by the addition of up to 0.2 M SDS.

The lifetimes ($k^S{}_{decay} = \tau^{-1}$) of acetone triplets in several micellar systems have been summarized in Table I.

Biphenyl is well-known to be an efficient quencher of carbonyl triplets[21] and in studies of the type reported here has the advantage of being essentially transparent at the excitation wavelength (308 nm). Biphenyl quenches butyrophenone triplets with $k_q \sim 2 \times 10^9$ M^{-1} s^{-1} in benzene at room temperature,[21a] this value being about 2.5 times slower than that for naphthalene. This difference is believed to be due to energetic reasons, as well as an apparently inherent inefficiency in the process.[21a] In the case of acetone the rates can be expected to be closer to diffusion controlled, as a result of the high triplet energy of the ketone. Biphenyl is also known to reside predominantly in the micellar pseudophase.[10] When biphenyl was added to our acetone-containing samples, we observed the formation of triplet biphenyl, which was characterized by its strong T-T absorption spectrum (λ_{max} 365 nm in 0.2 M SDS) and was conveniently monitored at 375 nm, where overlap with the acetone triplet spectrum is minimal.

The buildup of triplet biphenyl followed pseudo-first-order kinetics; a representative trace is illustrated in the insert in Figure 2. There was no detectable "jump" preceding the buildup, indicating that triplet biphenyl is formed entirely via dynamic quenching processes (vide infra).

The quenching of acetone triplets can be expected to occur by the mechanism outlined in Scheme I, where M represents the micelles, Ace stands for acetone, and MAce* and MQ represent micelle-incorporated acetone triplets and quencher molecules, respectively.

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(14) Kopecky, K. R.; Munford, C. *Can. J. Chem.* **1969**, *47*, 709-711.
(15) Cilento, G. *Acc. Chem. Res.* **1980**, *13*, 225-230.
(16) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747-7753.
(17) Scaiano, J. C. *J. Photochem.* **1973/1974**, *2*, 81-118.
(18) Encinas, M. V.; Lissi, E. A.; Scaiano, J. C. *J. Phys. Chem.* **1980**, *84*, 948-951.
(19) Porter, G.; Dogra, S. K.; Loutfy, R. O.; Sugamori, S. E.; Yip, R. W. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 1462-1474.
(20) Mysels, K. J.; Princen, L. H. *J. Phys. Chem.* **1959**, *63*, 1696-1700.
(21) (a) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 2820-2825. (b) Beck, G.; Dobrowolski, G.; Kiwi, J.; Schnabel, W. *Macromolecules* **1975**, *8*, 9-11.

Scheme I

$$\mathrm{Ace^*} \rightarrow \mathrm{Ace\ or\ (AceH\cdot + S\cdot)}$$

$$\mathrm{MAce^*} \rightarrow \mathrm{MAce\ or\ (AceH\cdot + S\cdot)}$$

$$\mathrm{Ace^*} + \mathrm{M} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \mathrm{MAce^*}$$

$$\mathrm{MAce^*} + \mathrm{MQ} \xrightarrow{k_Q} \mathrm{MAce} + \mathrm{MQ^*}$$

The first two reactions in Scheme I represent the decay of aqueous and micelle-incorporated acetone triplets in the absence of quencher, respectively, and k^S_{decay} describes the composite of these two decay pathways. The third reaction in the scheme describes entry (k_+) and exit (k_-) of Ace* into and from the micelles. The last reaction represents intramicellar quenching of Ace* by the quencher molecules,[21] and could be alternatively written as:

$$\mathrm{M(Ace^* + Q)} \rightarrow \mathrm{M(Ace + Q^*)}$$

In this sense, k_Q should be interpreted as a first-order-rate constant, such that k_Q^{-1} would be the lifetime of an acetone triplet formally localized in a micelle containing a single quencher molecule, where all other modes of decay are ignored.

Acetone is predominantly resident in the aqueous phase (vide infra), and hence excitation is expected to mostly take place there. The decay of acetone triplets and the formation of biphenyl triplets are concurrent processes with an associated experimental pseudo-first-order rate constant, k_{exptl}, which can be related to the processes in Scheme I according to the equation

$$k_{exptl} = k^S_{decay} + \frac{k_+k_Q\bar{n}[\mathrm{M}]}{k_- + k_Q\bar{n}} \tag{3}$$

where $\bar{n}$ is the average occupancy number, i.e.[22]

$$\bar{n} = \frac{[\text{quencher}]}{[\mathrm{M}]_{total}} = \frac{[\mathrm{MQ}]}{[\mathrm{M}]_{total}} \tag{4}$$

Two limiting cases can be identified. In the limit of low quencher occupancy levels (i.e., $k_Q\bar{n} \ll k_-$), eq 3 can be reduced to eq 5, which predicts that the observed rate of acetone triplet

$$k_{exptl} \approx k^S_{decay} + K_{eq}k_Q[\mathrm{Q}];\ k_Q\bar{n} \ll k_- \tag{5}$$

decay should obey a linear dependence on [Q], the bulk quencher concentration, where K_{eq} ($=k_+/k_- = [\mathrm{MAce^*}]/[\mathrm{Ace^*}][\mathrm{M}]$) is the equilibrium constant describing the partitioning of acetone triplets between the aqueous and micellar phases.

In the limit of high occupancy levels (i.e., $k_Q\bar{n} \gg k_-$), eq 3 reduces to

$$k_{exptl} = k^S_{decay} + k_+[\mathrm{M}];\ k_Q\bar{n} \gg k_- \tag{6}$$

That is, at high occupancy levels k_{exptl} will be determined by the rate of entry into the micelles, and will depend only on the total micelle concentration [M], given by [M] = ([S] − cmc)/(aggregation number).

Thus, for a given surfactant/quencher combination, plots of k_{exptl} vs. [Q] at different surfactant concentrations and over a sufficiently wide range of micelle/quencher occupancy levels are expected to yield a series of curves with identical initial slopes ($=K_{eq}k_Q$) and which level off at high values of $\bar{n}$ at a value of k_{exptl} which depends on the micellar concentration and k_+.

Figure 2 shows a plot of k_{exptl} vs. [Q] for the acetone/0.2 M SDS system, showing the deviation from linearity which becomes apparent at higher quencher concentrations ($\bar{n} > 1$). Least squares analysis of the approximately linear portion of the curve below $\bar{n} \sim 0.3$ yields $K_{eq}k_Q = (4.7 \pm 0.4) \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$. Essentially the same result ($K_{eq}k_Q = (4.3 \pm 0.7) \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$) was obtained for 0.1 M SDS and the same quencher. For comparison, a similar measurement was carried out in homogeneous solution with use of 20% water in acetonitrile as solvent; this gave a quenching rate constant of $k_Q = (3.8 \pm 0.6) \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$, a value that is still somewhat lower than diffusion controlled.[21a]

Several measurements were also carried out with 4,4′-dimethylbiphenyl (DMB) as quencher, the triplet of which was characterized by its strong T–T absorption spectrum (λ_{max} 380 nm in 0.2 M SDS) and was monitored at 380 nm. The value of $K_{eq}k_Q$ obtained by least-squares analysis of the early portion of a plot of k_{exptl} vs. [Q] ($K_{eq}k_Q = (5.1 \pm 0.4) \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$) agrees fairly well with the value obtained with biphenyl as acceptor.

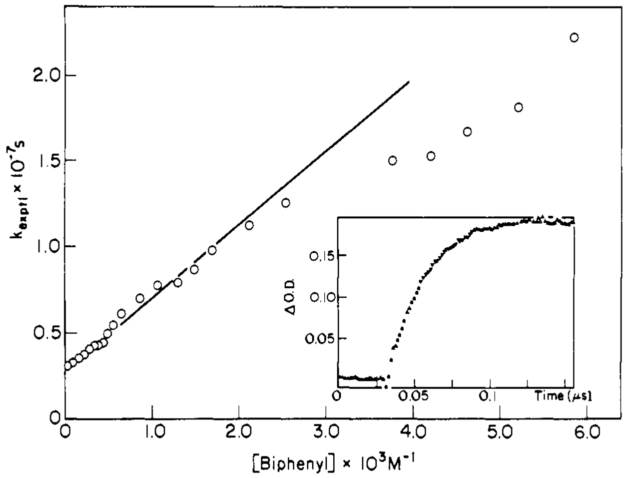

Figure 2. Quenching of acetone triplets in 0.2 M SDS solution by biphenyl plotted according to eq 5, and (insert) typical buildup trace for [biphenyl] = 4.4×10^{-4} M monitored at 375 nm. The trace has been corrected, subtracting the luminescence from the sample.

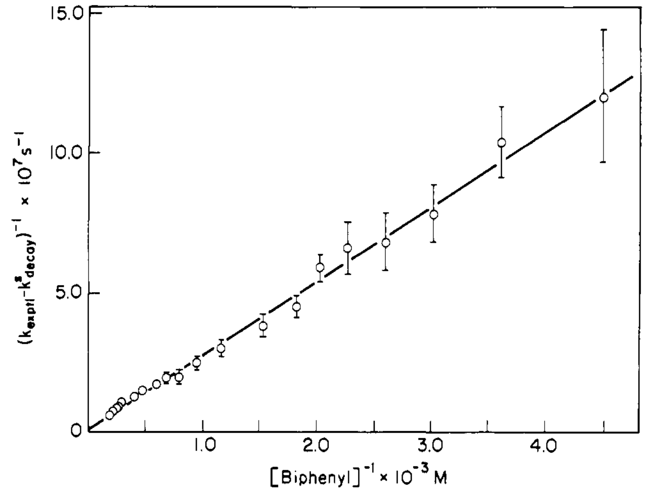

Figure 3. Quenching of acetone triplets by biphenyl in 0.2 M SDS solution, plotted according to eq 7.

A linear relation between k_{exptl} and [Q] can be obtained by rearrangement of the general expression for k_{exptl} given by eq 3.

$$\frac{1}{k_{exptl} - k^S_{decay}} = \frac{1}{k_+[\mathrm{M}]} + \frac{1}{K_{eq}k_Q[\mathrm{Q}]} \tag{7}$$

Figure 3 shows a representative plot, omitting the data at low quencher concentrations, where the error in ($k_{exptl} - k^S_{decay}$) is substantial. The values of $K_{eq}k_Q$ and k_+ obtained by using eq 5 and 7 have been summarized in Table II.

A few exploratory experiments were also carried out in the SDS system in order to test the effect of molecular size and solubility on the energy donor. The results for acetaldehyde and butanone, using biphenyl as acceptor, are summarized as well in Table II.

The equilibrium constant K_{eq} for the acetone (ground state)/SDS system was determined by the fluorescence quenching method recently reported by Encinas and Lissi.[23] The Stern–

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[22] The average quenching probability for an acetone triplet entering a micelle is given by:

$$P_Q = \frac{k_Q\bar{n}}{k_- + k_Q\bar{n}}$$

Table II. Triplet Quenching by Biphenyl and 4,4'-Dimethylbiphenyl at 300 K

substrate[a]	surfactant (concn)	quencher	$K_{eq}k_Q$[b] eq 5	$K_{eq}k_Q$[b] eq 7	k_+[c]	k^S_{decay}[d]
acetone	SDS (0.10)	biphenyl	4.3 ± 0.7			
	SDS (0.20)	biphenyl	4.7 ± 0.4	5.3 ± 0.4	1.0 ± 0.4	2.7 ± 0.2
	SDS (0.25)	biphenyl	3.6 ± 0.6	3.7 ± 0.6		1.5 ± 0.3
	SDS (0.30)	biphenyl	3.9 ± 0.7			1.5 ± 0.3
	SDS (0.10)	DMB[e]	4.7 ± 0.8	5.4 ± 1.3		1.6 ± 0.4
	SDS (0.20)	DMB	5.1 ± 0.4	6.6 ± 1.1		2.1 ± 0.3
acetone	CTAC (0.02)	biphenyl	7.3 ± 1.1	7.7 ± 1.1	4 ± 2	1.9 ± 0.1
	CTAC (0.05)	biphenyl	2.4 ± 0.5			
	CTAC (0.10)	biphenyl	1.4 ± 0.3			1.4 ± 0.5
	CTAC (0.01)	DMB	11.0 ± 0.9	14.4 ± 0.8	3.4 ± 0.5	1.1 ± 0.1
	CTAC (0.02)	DMB	8.6 ± 1.3			
	CTAC (0.03)	DMB	12 ± 4			
acetone	Brij-35 (0.06)	biphenyl	3.0 ± 0.6			1.6 ± 0.3
	Brij-35 (0.12)	biphenyl	3.2 ± 0.7			1.6 ± 0.2
	Brij-35 (0.02)	DMB	4.8 ± 0.5	3.6 ± 1.2		2.0 ± 0.1
acetaldehyde	SDS (0.2)	biphenyl	4.2 ± 0.4	5.1 ± 0.5		3.4 ± 0.8
butanone	SDS (0.2)	biphenyl	3.2 ± 0.4	4.1 ± 0.7		8.6 ± 0.6

[a] Typical concentrations ~0.3 M. [b] In units of 10^9 M^{-1} s^{-1}. [c] In units of 10^{10} M^{-1} s^{-1}, included only when a meaningful value could be determined (see text). [d] In units of 10^6 s^{-1}. [e] DMB = 4,4'-dimethylbiphenyl.

Volmer plots (I_0/I_Q vs. [Q]) for the quenching of biphenyl fluorescence by acetone in solutions of varying concentrations of SDS (0.05–0.4 M) were linear with slopes ($=k_Q^F\tau_F$) ranging from 97.4 to 76.9 M^{-1}. Analysis of these data according to the method reported[23] yields a value of K_{eq} = 52 ± 5 M^{-1} for the acetone/SDS system.[24]

Quenching of acetone triplets by biphenyl and DMB was also examined in cationic CTAC and neutral Brij-35 micelles, and the results are summarized in Table II. Representative plots are shown in Figure 4 for the acetone/DMB/0.01 M CTAC system, in which the quencher/micelle occupancy level has been varied to a maximum of ca. 2.

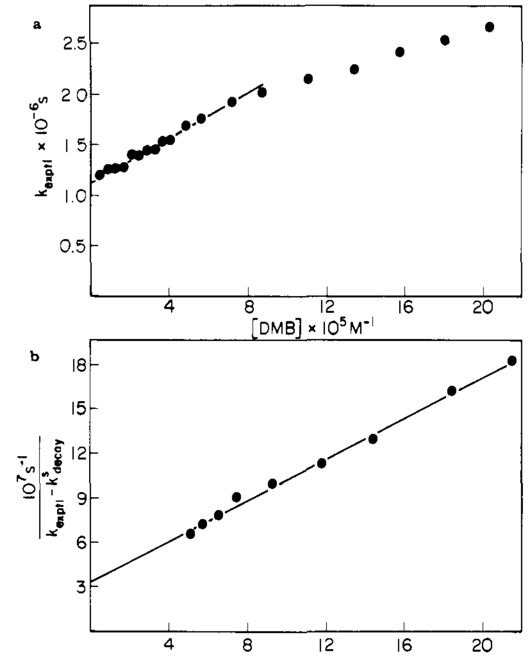

Figure 4. Quenching of acetone triplets by DMB in 0.01 M CTAC solution, plotted (a) according to eq 5 and (b) according to eq 7.

Discussion

A number of studies of carbonyl compounds in surfactant solutions have already been reported, and these lead to a reasonable understanding of the behavior of predominantly micelle-solubilized substrates. Thus, for example, benzophenone probes have been used to examine the conformation of hydrocarbon chains in micelles[25] (benzophenone itself has been the controversial subject of several recent flash studies),[2,26-28] and the Norrish Type I[29] and Type II reactions[30,31] as well as several aspects of carbonyl photocycloadditions[32] have been studied in detail in various laboratories. In addition, we have recently examined the dynamics of carbonyl exit and entry processes,[31,33] triplet self-quenching,[33] and energy migration[31] in micellar media.

Apparently, the most water-soluble ketone examined has been acetophenone,[31,33] for which k_- = 7.8 × 10^6 s^{-1} for the triplet state in SDS micelles. The entry–exit equilibrium constant (k_+/k_-) is 2040 M^{-1} at 299 K. From the known dependence of exit rates on molecular structure, it is clear that acetone should be expected to reside almost exclusively in the aqueous phase. This is borne out by our determination of K_{eq} = 52 M^{-1} for the acetone/SDS system; for 0.1 M SDS solution, 94% of the acetone should be resident in the aqueous phase. Micellar entry rates are only slightly sensitive to structural details for a neutral solute,[7,33,34] and for a

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[23] Encinas, M. V.; Lissi, E. A. *Chem. Phys. Lett.* **1982**, *91*, 55–57.

[24] This method is based upon the premise that I_0/I_Q for the micellized probe fluorescence is determined primarily by the occupancy number $\bar{n}_Q$ of the quencher in the pseudophase, and furthermore that this relationship is independent of the mechanism and efficiency of quenching. In cases where both the quenching efficiency and $\bar{n}_Q$ are low, we find the method to be insensitive. For example, quenching of 1-methylnaphthalene fluorescence by acetone is essentially independent of the SDS concentration; the measured value of K_{SV} of (17 ± 1) M^{-1} is essentially the same as that obtained in homogeneous solution (1:1 water:acetonitrile). The method seems reasonably sensitive when $k_q^F K_{eq} \geq 2 \times 10^4$.

[25] Breslow, R.; Kitabatake, S.; Rothbard, J. *J. Am. Chem. Soc.* **1978**, *100*, 8156–8160.

[26] Sakaguchi, Y.; Hayashi, H.; Nagakura, S. *J. Phys. Chem.* **1982**, *86*, 3177–3184.

[27] Braun, A. M.; Krieg, M.; Turro, N. J.; Aikawa, M.; Graff, G. A.; Lee, P. C.-C. *J. Am. Chem. Soc.* **1981**, *103*, 7312–7316.

[28] Lougnot, D. J.; Jacques, P.; Fouassier, J. P. *J. Photochem.* **1982**, *19*, 59–71. Jacques, P.; Lougnot, D. J.; Fouassier, P. P. In "International Symposium on Surfactants"; Mittal, K. L., Ed.; Plenum Press, Lund, Sweden, in press.

[29] (a) Turro, N. J.; Kraeutler, B.; Anderson, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 7435–7437. (b) Kraeutler, B.; Turro, N. J., *Chem. Phys. Lett.* **1980**, *70*, 266–269, 270–275. (c) Turro, N. J.; Cherry, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 7431–7432.

[30] (a) Worsham, P. R.; Eaker, D. W.; Whitten, D. G. *J. Am. Chem. Soc.* **1978**, *100*, 7091–7093. (b) Whitten, D. G. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 440–450. (c) Turro, N. J.; Liu, K.-C.; Chow, M. F. *Photochem. Photobiol.* **1977**, *26*, 413–415.

[31] Scaiano, J. C.; Selwyn, J. C. *Photochem. Photobiol.* **1981**, *34*, 29–32.

[32] (a) Lee, K. H.; de Mayo, P. *Photochem. Photobiol.* **1980**, *31*, 311–314. (b) de Mayo, P.; Sydnes, L. K. *J. Chem. Soc., Chem. Commun.* **1980**, 994–995.

[33] Scaiano, J. C.; Selwyn, J. C. *Can. J. Chem.* **1981**, *59*, 2368–2372.

[34] Selwyn, J. C.; Scaiano, J. C. *Can. J. Chem.* **1981**, *59*, 663–668.

polar molecule such as acetone can be expected[33,35] to be around $2 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$, in agreement with the values obtained. Thus, k_- for acetone is expected to be large, such that the exit of acetone triplets from the micelle will be competitive with fast intramicellar processes. Combination of the data above yields a predictive estimate of $\sim 5 \times 10^{8}\ \mathrm{s^{-1}}$ for the rate constant for exit of acetone from SDS micelles.

At low light intensities and concentration, the lifetime of acetone triplets in micellar solutions is determined primarily by the rate at which they undergo photoreduction by the surfactant, in agreement with the residual absorptions observed following triplet decay. Unfortunately, extensive overlap of the triplet and ketyl radical signals frustrated our attempts to monitor the growth kinetics of the acetone ketyl radical by direct detection or by deconvolution of decay traces recorded at two different wavelengths (315 and 340 nm).[2]

The overall rate of quenching of acetone triplets by SDS (above the cmc) of $4 \times 10^{6}\ \mathrm{M^{-1}\ s^{-1}}$ is substantially faster than the value of ca. $1.4 \times 10^{5}\ \mathrm{M^{-1}\ s^{-1}}$ for *n*-hexane in acetonitrile,[19] even allowing for the larger number of secondary hydrogens in SDS. It is clear that despite the fact that acetone is largely resident in the aqueous phase, there is still some association with the nonpolar media, a fact that is also reflected in the value of K_{eq} ($52\ \mathrm{M^{-1}}$). The increased reactivity may also be the result of a preference by acetone for attack at the methylene group α to the sulfate moiety, reflecting the weaker C–H bond at this position and the hydrophilic nature of acetone.[36]

The lifetime of acetone triplets in cationic cetyltrimethylammonium chloride (CTAC) micelles is only slightly shorter than that in SDS (see Table I), a fact that may reflect the usual increased solubility in the former.[35] The lifetime is reduced in Brij-35, presumably as a result of the greater ease of hydrogen abstraction from the hydrophilic polyether chains in the neutral micelles.

The equilibrium constant[10] describing the association of biphenyl with SDS micelles has been estimated as $2.2\text{–}5.4 \times 10^{4}\ \mathrm{M^{-1}}$. Thus, in 0.1 M SDS solution, ~98% of added biphenyl will reside in the micellar phase. Furthermore, since the exit rate of biphenyl from SDS micelles (ca. $10^{5}\ \mathrm{s^{-1}}$) is at least a factor of 10 slower than the decay rate of acetone triplets in SDS solution even in the absence of the added quencher, it can be safely assumed that >97% of the triplet quenching events will occur in the micellar phase.

From the reported effects of methyl substitution on the micellar solubility of naphthalene derivatives,[10] we estimate that K_{eq} and k_- must be at least a factor of 5 larger and smaller, respectively, for 4,4′-dimethylbiphenyl (DMB) in SDS solution compared to the corresponding quantities for biphenyl. The similarity in the quenching behavior of these two molecules (see Table II and Figure 2) demonstrates that the (slow) mobility of biphenyl does not play a role in our kinetic measurements.

As Figure 2 exemplifies, plots of k_{exptl} vs. [Q] in all cases show very little hint of curvature; at the quencher and surfactant concentrations employed in this study, we are clearly well below the point at which quenching of acetone triplets is determined primarily by their rate of entry into the quenching environment (i.e., the micelles). Thus for quencher concentrations such that $\bar{n} \leq 0.5$, the limiting behavior of eq 5 holds, and the slopes of these plots yield $K_{\mathrm{eq}}k_{\mathrm{Q}}$ for the quenching of acetone triplets in SDS micelles. As the model predicts, there is no variation in the value of $K_{\mathrm{eq}}k_{\mathrm{Q}}$ obtained for different surfactant concentrations. With the assumption that the solubilization of acetone triplets in the micelles is more or less the same as that found for the ground-state molecules, we obtain a value of ca. $1 \times 10^{8}\ \mathrm{s^{-1}}$ for k_{Q},[37] the (first order) rate constant for acetone triplet decay via quenching in an SDS micelle containing a single quencher molecule. In order to compare this with the rate of quenching in homogeneous solution, we convert k_{Q} to a second-order rate constant, k_{q}', according to eq 8, where N_{A} is Avogadro's number and $\bar{v}$ the micellar volume.

$$k_{\mathrm{q}}' = k_{\mathrm{Q}} N_{\mathrm{A}} \bar{v} \qquad (8)$$

A micellar diameter of 20 Å for SDS[38] yields $k_{\mathrm{q}}' = 4.8 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$, while 30 Å gives $1.6 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$. For comparison, the value in homogeneous (aqueous acetonitrile) solution is $\sim 4 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$. The difference probably reflects a combination of higher microviscosity in the micellar system and some preference for different regions of the micelle by acetone (Stern-layer) and the very hydrophobic quenchers (near the center). In this sense, the decreased efficiency with which acetone triplets are quenched in SDS micelles is reminiscent of the very low efficiencies of quenching of enzymatically generated triplet acetone by external quenchers.[39] Here it has been proposed that the triplet is shielded in some way from deactivating collisions.[15]

The reciprocal plots ($(k_{\mathrm{exptl}} - k^{\mathrm{S}}_{\mathrm{decay}})^{-1}$ vs. $[\mathrm{Q}]^{-1}$) provide a means of determining the rate of entry of acetone triplets into the micelles. Unfortunately, the solubilities of biphenyl and 4,4′-dimethylbiphenyl in SDS micelles are too low ($\bar{n} < 2$) to provide meaningful data close to the origin in these plots. Hence, the error in the intercepts is usually large, often 50–60%, so that reliable determinations of k_+ are very difficult for SDS micelles. The value of $k_+ \approx 1 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$ in these cases does, however, coincide with that expected from the reported rates of entry for other carbonyl compounds into SDS micelles (ca. $2 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$)[33] and the observation that entry rates are generally independent of solute structure.[10,33-35] As Table II reveals, the values of $K_{\mathrm{eq}}k_{\mathrm{Q}}$ obtained from the slopes of these plots agree rather well with those obtained from the limiting slopes of the k_{exptl} vs. [Q] plots.

Cationic CTAC micelles allow for a somewhat higher solubilization of the quenchers, and thus lead to more reliable values of k_+ ($\sim 4 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$) in this case (see Figure 4). In this surfactant we also observe an unexpected increase of the product $K_{\mathrm{eq}}k_{\mathrm{Q}}$ with increasing surfactant concentration. This cannot be readily explained with the model proposed. The differences are unlikely to be the result of changes in K_{eq}, since other techniques have not revealed such a sensitivity. A possible explanation would be a cooperative effect in the intramicellar quenching, i.e., the exponent of $\bar{n}$ in eq 3 being higher than 1.0. The final answer to this problem remains at this point a matter for speculation, and certainly deserves further study. It should be noted that these problems were not encountered in SDS, where the model presented seems to fully explain the data.

The behavior of acetaldehyde and butanone (Table II) with respect to triplet quenching by biphenyl is very similar to that of acetone, although the measurements in these systems are considerably more difficult, because self-quenching in the case of acetaldehyde[40] and the Type I reaction for butanone[41] tend to shorten considerably the triplet lifetime. Further, acetaldehyde may exist largely as its acetal.

Conclusion

Acetone triplets are highly mobile species in micellar solutions. Residing largely in the aqueous phase ($K_{\mathrm{eq}} \approx 52\ \mathrm{M^{-1}}$), their entry into and exit from the micellar environment are extremely fast processes; an entry rate in excess of $1 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$ and an exit rate of $1\text{–}4 \times 10^{8}\ \mathrm{s^{-1}}$ have been estimated for this species in the case of SDS micelles. Micellar quenching of the triplet, e.g., by biphenyl, is competitive with triplet exit from the micelle. In the absence of added quenchers, hydrogen abstraction from the surfactant is an important triplet deactivation pathway.

While studies with acetone were relatively uncomplicated, the situation changes drastically if the size of the carbonyl compound

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(35) Infelta, P. R.; Grätzel, M.; Thomas, J. K. *J. Phys. Chem.* **1974**, *78*, 190–195.

(36) By contrast, benzophenone abstracts more or less statistically along the hydrocarbon chain.[25]

(37) Which is in line with the kinetics for other intramicellar processes which in homogeneous media occur at close to the diffusion-controlled limit.[35]

(38) Kenney-Wallace, G. A.; Flint, J. H.; Wallace, S. C. *Chem. Phys. Lett.* **1975**, *32*, 71–75.

(39) Wilson, T. *Int. Rev. Sci.: Phys. Chem., Ser. Two* **1975/1976**, 265–322.

(40) Encinas, M. V.; Lissi, E. A.; Olea, F. A. *J. Photochem.* **1980**, *14*, 233–244.

(41) Lissi, E .A.; Abuin, E.; Encinas, M. V. *J. Photochem.* **1974**, *2*, 377–392.

is changed. Thus, aldehydes lead to shorter lifetimes and complications owing to acetal formation and self-quenching, while larger ketones lead to lifetime shortening owing to Norrish Type I and Type II processes. In view of these complications, it is not surprising that triplet acetone appears to be the only simple aliphatic carbonyl compound of importance in biological systems.

Experimental Section

Acetone (Fisher Spectrograde), acetaldehyde (BDH reagent), and 2-butanone (Aldrich Gold Label) were used as received. Biphenyl and 4,4′-dimethylbiphenyl were obtained from Aldrich Chemical Co. and sublimed under vacuum. Sodium dodecyl sulfate (BDH, specially pure) and Brij-35 (Aldrich) were used as received. Cetyltrimethylammonium chloride (K&K) was precipitated from the 50% methanol solution with acetone, washed several times with anhydrous ether, and dried under vacuum. Distilled water (Fisher HPLC grade) and acetonitrile (Eastman Kodak Spectro) were used as obtained.

Ultraviolet absorption spectra were recorded on a Cary 219 UV spectrometer, and fluorescence emission spectra were recorded on a Perkin-Elmer Model LS-5 spectrofluorometer with a PE Model 3600 data station.

Samples for laser flash photolysis were contained in Suprasil cells made of 7 × 7-mm^2 rectangular tubing (Vitro Dynamics). All experiments were carried out under oxygen-free conditions. Quenchers were added as aliquots of standard alcoholic solutions. Other details are similar to those reported previously.[2,16]

The samples were excited with the pulses from a Lumonics TE-861S Excimer laser, with mixtures of Xe/HCl/He as the lasing medium. Details of experimental technique and a full description of the instrument have been given elsewhere.[16]

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Registry No. SDS, 151-21-3; CTAC, 112-02-7; Brij-35, 9002-92-0; acetone, 67-64-1; acetaldehyde, 75-07-0; 2-butanone, 78-93-3; biphenyl, 92-52-4; 4,4′-dimethylbiphenyl, 613-33-2.

Onium Ions. 26.[1] Aminodiazonium Ions: Preparation, ^{1}H, ^{13}C, and ^{15}N NMR Structural Studies, and Electrophilic Amination of Aromatics

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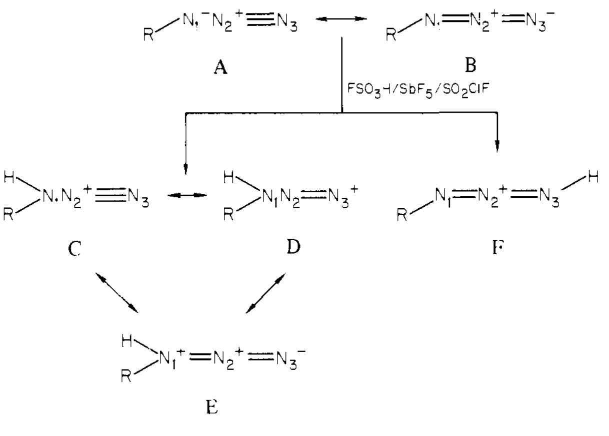
Abstract: Protonation of hydrazoic acid and alkyl azides with FSO_3H/SbF_5, HF/SbF_5, or HF/BF_3 results in the formation of stable aminodiazonium ions as shown by ^{1}H, ^{13}C, and ^{15}N NMR spectroscopic studies. Molecular orbital calculations of the thermodynamics of the protonation of hydrazoic acid also support preferential formation of the aminodiazonium ion. The aminodiazonium ion was also prepared in situ from $NaN_3/AlCl_3/HCl$ or $(CH_3)_3SiN_3/AlCl_3/HCl$ [$(CH_3)_3SiN_3/HF/BF_3$]. Aminodiazonium salts were found to affect electrophilic amination of aromatics in high yields, with generally high regioselectivity and low substrate selectivity.

Aromatic diazonium ions are quite stable, isolable as salts in some cases, and important compounds in organic synthesis, such as dyestuffs.[3] However, their aliphatic counterparts[4,5] can only be obtained in strong acid solutions without elimination of nitrogen. In spite of the preparation of X-ray study of the fluorodiazonium ion (FN_2^+) as the stable hexafluroantimonate salt,[6] little is known about heteroatom-substituted diazonium ions. Schmidt[7] described the preparation and IR spectra of the hydrohexachloroantimonates of methyl azide and hydrozoic acid, and suggested them to be the aminodiazonium salts (although several IR-active absorptions were missing in the obtained IR spectra). No other study of aminodiazonium ions is known.

Scheme I



Results and Discussion

Protonation of Hydrazoic Acid and Alkyl Azides. We now achieved clear unequivocal protonation of methyl and ethyl azides, as well as hydrazoic acid under superacidic stable ion conditions. Considering the mesomeric structures of azides (A ⇄ B), protonation could take place on N-1 or N-3 leading either to ami-

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(1) For part 25 see: Olah, G. A.; Gupta, B. G. B.; Garcia-Luna, A.; Narang, S. C. *J. Org. Chem.* **1983**, *48*, 1760.

(2) Postdoctoral research Fellow 1981-1982.

(3) Patai, S. "The Chemistry of Diazonium and Diazo Groups"; Interscience: New York, 1978; Vol. 1 and 2.

(4) (a) Friedman, L. In "Carbonium Ions"; Olah, G. A., Schleyer, P.v.R. Eds.; Interscience: New York, 1970; Vol. II, Chapter 16. (b) Mohrig, J. R.; Keegstra, K. *J. Am. Chem. Soc.* **1967**, *89*, 5492. (c) Mohrig, J. R.; Keegstra, K.; Maverick, A.; Roberts, R.; Wells, S. *J. Chem. Soc., Chem. Commun.* **1974**, 780. (d) Bott, K. *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 954. (e) Bott, K. *Ibid.* **1971**, *10*, 821; (f) *Chem. Ber.* **1975**, *108*, 402.

(5) Berner, D.; McGarrity, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 3135.

(6) Moy, D.; Young, A. R., II *J. Am. Chem. Soc.* **1965**, *87*, 1889.

(7) Schmidt, A. *Chem. Ber.* **1966**, *99*, 2976.

0002-7863/83/1505-5657$01.50/0