cyclopropylbenzene has a greater stabilization energy than cyanocyclopropane should also receive closer scrutiny.

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Registry No. **2**, 5500-21-0; **2**-^{13}CN, 16637-46-0; **2**-C^{15}N, 85267-42-1; **3**, 6746-94-7; **3**-1-^{13}C, 85267-43-2; **3**-2-^{13}C, 85267-44-3; **3**-4-^{13}C, 85267-45-4; **3**-5-^{13}C, 85267-46-5.

Supplementary Material Available: Tables SI-SVII present complete listings of the observed isotopic spectra of the subject molecules (7 pages). Ordering information is given on any current masthead page.

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Photoreactivity of Surfactant Ketones as a Probe of the Microenvironment of Organized Media[1]

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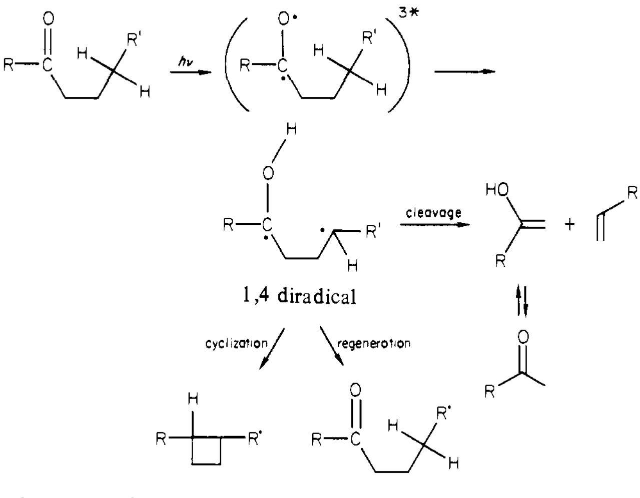
Abstract: The Norrish type II photoprocess of surfactant keto acids has been used to examine the relative environment of the ketones in certain organized media. Values for ϕ of 0.81 in SDS micelles and 0.72 in CTAC micelles were obtained for **1**, which are intermediate between the value of 0.29 in benzene and 1.0 in *tert*-butyl alcohol. The ketone thus experiences a fairly hydrophilic environment in micelles. Addition of heptanol to SDS micelles containing **2** causes a decrease in ϕ_{II} values, suggesting that a more hydrophobic region is seen by the ketone, possibly owing to water expulsion from the micelle. Incorporation of **1** into dioctadecylmethylammonium chloride (DODAC) vesicles on irradiation gives values similar to those of a benzene-like medium below the phase-transition temperature, and the ϕ_{II} values slowly increase as the temperature increases. Multilayer assemblies of **1** exhibit very little type II reactivity when irradiated, having values $\phi < 0.01$. The close packing of the molecules which prevents the proper six-membered transition-state geometry to be reached can explain the very low ϕ_{II}.

The ability of carbonyl compounds possessing γ C–H bonds to undergo photochemical intramolecular hydrogen atom abstraction has been well documented.[2-5] It has been found that in the case of aromatic ketones the type II reaction occurs exclusively from the n,π^* triplet state. As shown in Scheme I, upon excitation of the ketone, formation of a 1,4-diradical occurs by hydrogen atom abstraction via a six-membered transition state. The 1,4-diradical may then undergo one of three possible reactions. It can cleave to form the enol of a methyl ketone and an olefin, cyclize to a cyclobutanol derivative, or merely revert back to starting material.

The type II process has been well studied from a photophysical as well as a chemical standpoint. Scaiano and Wagner[6] have studied the kinetics and lifetimes of the triplet state and the intermediate biradical for a variety of aromatic ketones. In general, the triplet lifetimes are somewhat shorter than the biradical lifetimes, with triplet lifetimes being between 5 and 30 ns for valerophenone and substituted valerophenones in methanol, whereas the biradical values are all about 100 ns in the same solvent. Biradical and triplet lifetimes for butyrophenone, however, are somewhat higher, on the order of 150 ns in methanol.

Scheme I



Inductive effects, steric factors, and substituent effects have all been examined for the reaction, and it has also been found that a solvent dependency on the quantum yield (ϕ_{II}) occurs for most aromatic ketones.[7] *n*-Butyrophenone, for example, has a ϕ_{II} in *tert*-butyl alcohol of 1.0 but only 0.3 in benzene. It has been

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[1] Photochemical Reactivity in Organized Assemblies 32. A preliminary account of a portion of this work has appeared (ref 10).

[2] Wagner, P. J.; Kelso, P. A.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7480.

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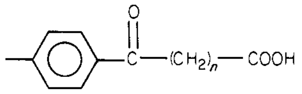
[6] (a) Small, R. D.; Scaiano, J. C. *J. Phys. Chem.* **1977**, *81*, 2126. (b) Small, R. D.; Scaiano, J. C. *Ibid.* **1977**, *81*, 828. (c) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7495.

[7] Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898. Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *Ibid.* **1972**, *94*, 7506.

postulated that in alcohol hydrogen bonding by solvent molecules stabilizes the 1,4-diradical to the extent that regeneration of starting material via reverse hydrogen atom abstraction is not favorable, thereby allowing for the high ϕ_{II} values.

Turro and co-workers used the solvent sensitivity of the type II process as a probe to examine certain properties of micellar solutions.[8] Using valerophenone and octanophenone as nonsurfactant probe ketones in cationic cetyltrimethylammonium chloride micelles, they found that the ketone chromophore resided in a relatively polar environment based on quantum yield results. For both ketones, ϕ_{II} values in *tert*-butyl alcohol were 1.0 and values in benzene were ~0.3. When incorporated into cationic micelles, ϕ_{II} for valerophenone remained at unity, but the value for octanophenone dropped to 0.71, the difference being attributed to the increased hydrophobicity of octanophenone resulting in the ketone's residing in a more hydrophobic region of the micelle. The relatively high ϕ_{II} values, taken in conjunction with some quenching studies, suggests that the ketone experiences a relatively hydrophilic environment but spends little time in the hydrocarbon core and no time in the bulk aqueous phase.

We report here our findings on the type II process with the surfactant keto acids shown below in a variety of organized media.[9]



1, $n = 14$
2, $n = 10$

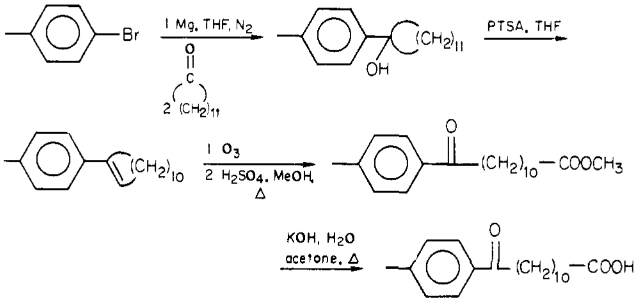
In a previous communication[10] we examined the behavior of **1** in multilayer assemblies and calculated the quantum yield for the type II process, reporting that $\phi_{II} < 0.01$ in all types of assemblies. The low values were attributed to geometrical constraints on the process due to the close packing of the molecules, similar to the conclusion which was reached in studies by Guillet and co-workers on the type II process in polymer matrices.[11-13] This paper expands on the prior work in our group to include the ketone reactivity in cationic and anionic micelles, in alcohol swollen micelles, and in vesicles. Differences observed in the efficiencies, ϕ_{II}, can be interpreted in terms of the relative polarities and solubilization sites experienced by the probe ketone in the various media.

Experimental Section

Materials. Butyrophenone (Aldrich), *p*-methylbutyrophenone (Pfaltz & Bauer), and octanophenone (Eastman Kodak) were all vacuum distilled before use. Hexadecane (Aldrich, 99+%) and *p*-methylbutyrophenone were used as internal standards and were added during the work-up procedures after the photoreaction had occurred. Heptanol (Aldrich, 99%), for use in the swollen micelle experiment, and pentane (Aldrich, spectrophotometric grade), for extraction purposes of the photoproducts, were used as received. *tert*-Butyl alcohol (Fisher) was recrystallized several times prior to use. Europium chloride (Aldrich) was also used as received.

Sodium dodecyl sulfate (SDS; Biorad, electrophoresis grade) was recrystallized once from ethanol. Cetyltrimethylammonium chloride (CTAC) was a gift from Dr. João Bonilha.[14] Dioctadecyldimethylammonium chloride (DODAC), was made by passing the bromide salt (Eastman) through a column containing an ion-exchange resin (Biorad, chloride form) in methanol several times followed by recrystallizations from ethyl acetate. Dipalmitoyllecithin (Sigma) was used as received. Water was triply distilled.

Scheme II



Synthesis of Keto Acids. The synthesis of ketone **1** (mp 96.5–97.5 °C) has been previously reported.[10,15] Ketone **2** was prepared in the following manner, as shown schematically in Scheme II. Magnesium turnings (Mallinkrodt; 1.70 g, 0.074 mol) were added to 40 mL of freshly distilled tetrahydrofuran under N_2 with stirring. A solution of 4-bromotoluene (Eastman; 12.0 g, 0.07 mol), distilled prior to use, in tetrahydrofuran was slowly added to the round-bottomed flask and stirred for 10 min, after which time a small amount of iodine was added to the vessel. An ordinary sunlamp was used to irradiate the round-bottomed flask to help initiate formation of the Grignard precursor magnesium bromide. After 2 h of stirring under inert atmosphere, cyclododecanone (Aldrich: 12.7 g, 0.07 mol) was slowly added to the mixture, and the contents were refluxed for 1 h. The reaction was monitored by TLC using silica plates. The reaction was quenched by addition of dilute acid and cold water, and the crude alcohol (12.8 g) was extracted with ether. The alcohol was dissolved in THF, and a few milligrams of *p*-toluenesulfonic acid was added to the flask; the reaction mixture was allowed to reflux for 1 h. The formation of styrene was also followed by TLC. Upon completion, water was added to quench the reaction, and the styrene was extracted with ether. Purification of the product by column chromatography on silica gel using chloroform afforded 10 g of relatively pure styrene. The styrene was then ozonolyzed by use of a Welsbach Model T-816 ozonator. The voltage was set at 90 V and the pressures at 1 psi and 8 lb. The reaction vessel containing the styrene dissolved in methanol was cooled in an ice bath, and when TLC showed the reaction to be complete, the voltage was shut off and the solution was refluxed after addition of 10 mL of concentrated H_2SO_4 for 2 h. Addition of more water and removal of methanol afforded precipitation of white crystals in the flask. Filtration and recrystallization of the white solid from hexanes afforded 8.0 g of pure ester: IR 1733, 1680 cm^{-1}; mp −48.5 °C. Anal. Calcd for $C_{20}H_{30}O_3$: C, 75.43; H, 9.49. Found: C, 74.87; H, 9.64. The ester (200 mg) was then saponified by dissolving it in 30 mL of a 50:50 mixture by volume of acetone and water containing a small amount of potassium hydroxide (KOH) and then refluxing gently for 1 h. After reflux, more water was added to the vessel, and the solution was acidified to pH 4–5. White crystals formed upon cooling after loss of acetone. Recrystallization from hexane yielded 140 mg of pure ketone **2** (mp 55.5–56.5 °C). Anal. Calcd for $C_{19}H_{28}O_3$: C, 74.96; H, 9.27. Found: C, 74.49; H, 9.43.

Procedures. Micellar solutions were prepared with the aid of Bronson ultrasonic cleaner. Vesicles were prepared by gently warming a solution of the desired amount of ketone and surfactant in triply distilled water for about 15 to 30 min to help promote solubilization. Upon dilution to the desired volume, the solution was then sonicated at 40 °C for 15 min or until the solution cleared using a Heat Systems-Ultrasonics cell disruptor, Model W-220F.

Irradiations were performed using a Schoeffel Model LPS-255 1000-W Hg–Xe arc lamp. The emission of the lamp was passed through a Bausch and Lomb high-intensity monochromator. Solutions were either bubble deaerated with purified argon for 30 min or else degassed by repeated freeze–pump–thaw cycles to a pressure of at least 10^{-5} torr. Photolyses were carried out at either 254 or 313 nm. Fluorimetry measurements were carried out on a Hitachi Perkin-Elmer MPF-2A recording spectrofluorimeter. Ultraviolet absorption spectra were recorded on a Perkin-elmer 576 ST recording spectrophotometer. Gas chromatography was performed with a Varian Aerograph series 1400 instrument equipped with a flame ionization detector. Columns used for the detection of photoproducts were either 5 or 20% SE-30 on Chromosorb G; all columns were 8 ft × $^1/_8$ in.

Laser Flash Photolysis. Transient lifetimes have been measured utilizing a laser flash photolysis system. For excitation the fourth har-

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[9] For a general review of organized media, see: (a) Tanford, C. "The Hydrophobic Effect", 2nd ed.; Wiley: New York, 1980. (b) Tanford, C. In "micellization, Solubilization and Microemulsions"; Mittal, K. L., Ed.; Plenum Press: New York, 1977; Vol. 1.

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[14] Dr. João Bonilha, Visiting Scholar, Department of Chemistry, Faculdade de Filosofia Ciencies e Letras de Ribeirao Preto da Universidade de Sao Paolo, Brasil.

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Table I. Quantum Yield Efficiencies for the Type II Process of Ketone **1** in Various Media[a,b]

medium	ϕ_{II}	medium	ϕ_{II}
t-BuOH[c]	1.02 ± 0.03	benzene[c,f]	0.27 ± 0.03
SDS[d]	0.81 ± 0.02	assemblies[f]	<0.001
CTAC[e]	0.72 ± 0.02		

[a] Results from studies at ambient temperatures. [b] Quantum yields are relative to $\phi_{II} = 1.0$ for butyrophenone in *t*-BuOH solvent. [c] 1.25×10^{-4} M **1** in appropriate solvent. [d] 3.22×10^{-4} M **1** in 0.02 M SDS. [e] 1.25×10^{-4} M in 0.006 CTAC. [f] See ref 10.

Table II. Temperature Study on ϕ_{II} of Ketone **1** in Micelles[a]

T, °C	SDS micelles[b] ϕ_{II}[d]	CTAC micelles[c] ϕ_{II}
30	0.81 ± 0.01	0.72 ± 0.01
40	0.81 ± 0.01	0.72 ± 0.01
50	0.79 ± 0.01	0.73 ± 0.01
60	0.79 ± 0.01	0.74 ± 0.02

[a] Relative to $\phi_{II} = 1.0$ for *n*-butyrophenone in *t*-BuOH. [b] 3.22×10^{-4} M **1** in 0.02 M SDS. [c] 1.25×10^{-4} M **1** in 6×10^{-3} M CTAC. [d] ϕ_{II} for production of *p*-methylacetophenone.

monic from a Quanta Ray DCR 2A Nd:YAG laser is utilized (266 nm, pulse width 5 ns, av pulse power 10–20 mJ). For monitoring a 1000-W Hg/Xe lamp is focused onto a 1 cm × 1 cm square cell at a right angle to the laser beam, subsequently collimated, then focused onto the entrance slit of a 0.25-m Bausch and Lomb monochromator (Ebert mount). A shutter between the lamp and the cell is gated to open for 10 ms, with the laser pulse occurring after the shutter has been open for 5 ms. A RCA 1P28A photomultiplier (wired specifically for high light intensities) and a Tektronix transient digitizer (R7912) are utilized to monitor transient absorbances. Signal averaging and data processing are accomplished by a Digital PDP 11/34 computer which is interfaced with the digitizer. The monitoring lamp is filtered (CS 0-52) and a flow cell utilized in order to minimize effects due to photoreaction of **1**.

Results

The behavior of **1** in assemblies has been previously reported[10,15] but will be summarized here so that comparisons of the type II process among the various media are easily discerned. Surface pressure-area isotherms[16] of pure **1** showed poor behavior, with only gradual increases in the surface pressure upon compression; the films formed in this manner collapsed readily at low pressures. Upon addition of an equimolar amount of arachidic acid, an enhanced stability of the films resulted with a calculated molecular area of ~20 Å^2, similar to the behavior of a condensed fatty acid monolayer.[10] Multilayer assemblies were prepared consisting of varying numbers of layers with the films deposited onto quartz slides for UV spectroscpic studies. Upon irradiation of the slides at 254 nm, a rapid bleaching of the ketone absorption was detected when UV spectra before and after irradiation were compared. IR spectroscopy confirmed that the ketone chromophore had reacted.

In order to determine the photoreaction occurring in the assemblies, an irradiation was performed in which slides containing several layers of the probe molecule and cosurfactant were irradiated in a closed quartz cell with a small amount of hexane present to dissolve any volatile materials produced in the photoreaction. After the slides were washed off with hot hexane, the solution was analyzed for products by gas chromatography. The quantum yield for production of *p*-methylacetophenone via a type II process was found to be ~10^{-3}–10^{-4}; the quantum yield for loss of **1** is ≤0.06 and no products from a type I photoprocess were detectable.

Table III. Effect of Added Heptanol on ϕ_{II} for **2** in SDS Micelles

[heptanol], M	ϕ_{II}[a,b]	[heptanol], M	ϕ_{II}[a,b]
0	0.84	0.04	0.68
0.01	0.73	0.06	0.66
0.02	0.68		

[a] Irradiations performed at 254 nm. [b] Values reported are within ~7% error.

Table IV. Quenching of *p*-Methylacetophenone Production from Ketone **1** in SDS by EuCl$_3$[a]

[Eu^{3+}], M	ϕ_{II}	% quenching
0.0	0.81 ± 0.01	0
1×10^{-5}	0.81 ± 0.01	0
5×10^{-5}	0.80 ± 0.01	0
1×10^{-4}	0.76 ± 0.02	~5
2×10^{-4}	0.66 ± 0.04	~15
5×10^{-4} [b]	0.64 ± 0.05	20

[a] 3.22×10^{-4} **1** in 0.02 M SDS. [b] A slight turbidity in the solution occurred upon addition of EuCl$_3$ to a micellar solution of **1** at this concentration but cleared up after sonication. Attempts were made to try samples of Eu^{3+} at 1×10^{-3} M, but the cloudiness remained.

Table V. Quenching Study of Octanophenone and Ketones **1** and **2** in SDS Micelles by Eu^{3+}[a]

ketone	ϕ_{II}, [Eu^{3+}] = 0	ϕ_{II}, [Eu^{3+}] = 2×10^{-4} M	% quenched
octanophenone	0.76 ± 0.03	0.75 ± 0.02	0
1	0.81 ± 0.01	0.66 ± 0.04	~15–20
2	0.84 ± 0.02	0.76 ± 0.03	~10

[a] ϕ_{II} values were measured for quenching of acetophenone or *p*-methylacetonone. [b] All ketones were 3.22×10^{-4} in 0.02 M SDS.

Table VI. Temperature Study of **1** in DODAC Vesicles[a]

T, °C	ϕ_{II}	*T*, °C	ϕ_{II}
20	0.22 ± 0.02	34	0.30 ± 0.03
24	0.21 ± 0.02	36	0.33 ± 0.03
28	0.21 ± 0.02	38	0.36 ± 0.03
30	0.27 ± 0.02	40	0.34 ± 0.03
32	0.31 ± 0.03	44	0.40 ± 0.03

[a] 1.25×10^{-4} M **1** in 2.5×10^{-3} M DODAC solution.

Incorporation of **1** into anionic SDS micelles and cationic CTAC micelles and subsequent irradiation of degassed solutions[17] gave the results for type II products shown in Table I. For all of the aqueous micellar and vesicle systems examined it was found that neither the intensity nor the shape of the band at 250–260 nm changed upon even prolonged irradiation. The product ketone was found to show absorption spectra in these media nearly identical with those starting material. The absence of bleaching in these media thus indicates there is negligible formation of cyclobutanol products or other reactions such as photoreduction. Quantum yields in both cases are similar to those obtained for **1** in *tert*-butyl alcohol, suggesting a relatively hydrophilic environment for the ketone. The temperature independence of the type II process for the probes in micelles is demonstrated in Table II.

The effect of adding heptanol to SDS micelles containing **1** is shown in Table III. A decrease in ϕ_{II} values was observed, though the limiting value of 0.68 at 0.06 M heptanol still implies fairly hydrophilic surroundings.

The quenching of formation of type II product *p*-methylacetophenone from ketone **1** in SDS by Eu^{3+} is summarized in Table IV. It is known that Eu^{3+} quenches the n,π^* triplet states of aromatic ketones at or near-diffusion-controlled rates.[18-20] At relatively low Eu^{3+} concentrations in the micelles, little or no quenching of product formation occurs; at the limiting value of

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(17) It was not certain if bubble degassing of solutions would remove oxygen to the extent that no quenching of the triplet would occur. A 1.25×10^{-4} M **1** solution in 6×10^{-3} M CTAC was degassed by both the freeze–pump–thaw method and argon bubbling. Analysis of products after irradiation and calculation of ϕ_{II} gave the same values within experimental error. Bubble degassing was for 30 min.

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Table VII. Laser Flash Photolysis of **1**. Initial Transient Absorbance at 410 nm and Decay Lifetimes[a]

solution	quencher	initial ΔOD	lifetime, ns
methanol		0.035	220
SDS, 0.02 M		0.027	440
SDS, 0.02 M	DMH,[b] 5.4×10^{-5} M	0.012	410
SDS, 0.02 M	Eu^{3+}, 1.4×10^{-4} M	0.011	500
DODAC, 2.5×10^{-3} M		0.003	400-500[c]

[a] Argon degassed solutions. Pulse energy constant, ~ 15 mJ/pulse. [b] 2,5-Dimethyl-2,4-hexadiene. [c] Lifetime approximate because of weak signal.

5×10^{-4} M $EuCl_3$, however, a 20% reduction in *p*-methylacetophenone production is observed.

A comparison of Eu^{3+} quenching of both surfactant and nonsurfactant ketones is given in Table V. Studies with octanophenone and ketones **1** and **2** show that, at the same concentration of ketone and of quencher, only the surfactant compounds **1** and **2** are quenched with **1** being quenched almost twice as much as **2**.

The effect of temperature on the ϕ_{II} for **1** incorporated into DODAC vesicles is shown in Table VI. The ϕ_{II} values in general indicate that the ketone experiences an environment similar to that in hydrocarbon solvents such as benzene, especially below 30 °C. The quantum efficiencies gradually increase with temperature, reaching a value of 0.40 at 44 °C; the parallel between ϕ_{II} and temperature is probably a direct consequence of configurational adaptions by the vesicles as discussed below.

Laser Flash Photolysis. Pulsed laser photolysis at 266 nm of solutions of **1** in methanol, SDS micelles, and DODAC vesicles initiated a weakly absorbing transient with λ_{max} 400–410 nm and a lifetime of 200–500 ns (see summary, Table VII). With the pulse energy held constant, a strong variation in signal intensity is noted, following the order methanol > SDS micelles > DODAC vesicles. 2,5-Dimethyl-2,4-hexadiene at a concentration of 5.4×10^{-5} M in 0.02 M SDS (effective micellar concentration 0.017 M) is observed to quench the transient intensity 55%, without quenching the lifetime substantially. Eu^{3+} at a concentration of 1.4×10^{-4} M in 0.02 M SDS (effective micellar concentration 0.045 M) quenches the transient intensity 60%, also without changing the lifetime significantly.

Discussion

Monolayer Studies. The results obtained for ketone **1** in the multilayer assemblies reflect the close packing of the molecules to the extent that the proper geometry for reaction to occur—a six-membered transition state—is not attained very often. The fact that an appreciable decrease in the C=O absorption in the UV spectrum ($\phi_{-1} \gg \phi_{II}$) was obtained when the quartz slides were irradiated may suggest that the ketone abstracts a hydrogen atom from the neighboring cosurfactant arachidic acid or else from another ketone molecule; the radical pairs thus formed may then either combine or disproportionate to yield final products. It is evident that the major excited-state decay pathway in the assemblies does not involve a type II process, primarily because of geometrical constraints. These findings are very similar to those of Guillet regarding the type II photoprocess in polymers and in crystals.[11-13] The rigidity of the medium at temperatures below the glass transition point is reflected by the lack of any type II elimination; evidently the decrease in mobility of the chains fixes the system in a geometry which also does not allow for a cyclic transition state to be reached. Yet in melted crystals as well as in polymer systems at temperatures above the glass point, results similar to solution studies were obtained for quantum yield efficiencies. This implies that the type II process has the ability to serve as a useful indicator of the rigidity of various media.

Micellar Systems. The high ϕ_{II} values found for **1** and the other ketones studied in SDS and in CTAC micelles suggest a very different environment from that occurring in multilayer assemblies. The high efficiencies obtained clearly indicate that there is no restriction to forming the diradical precursor for the type II process; the fact that the values are much closer to those obtained for polar protic solvents such as *tert*-butyl alcohol than for hydrocarbon solvents further suggests that the carbonyl or diradical or both residue in a relatively hydrophilic site during the reaction. The absorption spectrum of the carbonyl chromphore is relatively sensitive to solvent polarity; as seen in Table VIII the major absorption band of **1** is red shifted relative to acetonitrile. Since this is a π,π^* transition which generally shows a red shift with an increase in polarity, the values in Table VIII suggest a polar site for **1** in the micellar media. Several recent studies have suggested that micelles may not be as highly organized as once thought and that there is either water penetration into the interior of the micelle or much hydrocarbon–water contact such that most solubilization occurs at what are essentially interface sites.[22-24] While ketone **1** would be expected to serve as an intrinsic probe of the micelle interior, possibilities for its distorting the micelle upon incorporation, or its residing at an interface site, must also be considered. For example, it is certainly possible that the ketone could "pull" water along with it into the micelle. While **1** is clearly associated with the micelle, the ketone chromophore could either be located in the interior of the micelle, or the molecule would assume a bent configuration such that both carboxylate and carbonyl portions are located at interface sites. Moreover, while the ϕ_{II} results show that **1** is in a hydrophilic area, this must represent an average of where it resides in the micelle since the total process is dynamic as is the micelle itself.[25,26]

Table VIII. UV Absorption Data for **1** in Various Media[a,b]

medium	λ_{max} (nm)	ϵ^c
methylcyclohexane	250	
acetonitrile	254	8400
tert-butyl alcohol	255	
SDS (2×10^{-2} M)	257	9400
CTAC (6×10^{-3} M)	256	9700
DODAC (2.5×10^{-3} M)	252	

[a] All studies done at room temperature. [b] [**1**] = 1.25×10^{-4} M in cases except SDS, where [**1**] = 3.22×10^{-4} M. [c] Units in L mol^{-1} cm^{-1}.

Some indications of the time scale for the photochemical and thermal events occurring in the micelles can be obtained by laser flash photolysis studies of **1** in SDS. Thus we find transient absorption at 410 nm with a lifetime of 420 ns where previous investigations have established that the triplet and biradical absorb.[43,44] The triplet lifetime is not easily determined in these solutions owing to its overlap with the biradical; however, the observation that addition of 2,5-dimethyl-2,4-hexadiene to an effective intramicellar concentration of 0.017 M reduces the intensity by 55% without reducing the transient lifetime suggests that the long-lived transient is the biradical. The extent of the quenching would suggest a triplet lifetime for **1** on the order of 15 ns if it assumed the intramolecular quenching constant is 5×10^9 M^{-1} s^{-1}.[44] The biradical lifetime for **1** in the micelles is thus considerably longer than that for **1** in methanol (220 ns) or for structurally similar ketones in other homogeneous solutions. With lifetimes for the triplet state and biradical of the time scale indicated above, it is certainly plausible that as **1** changes from the ground state to the excited state to the diradical the "solubilization" site can change reflecting the varying polarities of the different species. The diradical is probably the most polar species, with the ground state a likely intermediate between the diradical and triplet excited state in polarity. From these investigations, however, it is impossible to prove or disprove that the site changes as these photophysical processes occur; however, the results imply that the ketones are solvated in a region having

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some hydrogen-bonding capacity.

The fact that there is a significant difference between the values for SDS (0.81) and CTAC (0.72) suggests that the ketone resides in a somewhat less polar region in the cationic micelles. This could imply that CTAC micelles may be somewhat "tighter" because of less head-group repulsion. Similar results have been found between these two types of micelles using derivatized stilbene probes to measure their fluorescence in the organized media.[23] In the case of stilbenes in CTAC micelles, the ϕ_F increased relative to values in SDS, suggesting that the stilbene experiences a somewhat more hydrophobic environment. Zachariasse and coworkers[27] have found similar differences between SDS and CTAC micelles using *N*-phenolbetaine (E_T (30)) as a polarity probe. They found that a large difference of the effective dielectric constant (ϵ_F) of the micellar surface existed between SDS (ϵ_F of 51) and CTAC (ϵ_F of 31) with E_T (30) incorporated into each, implying a greater surface area and consequently more water near the surface in SDS micelles. The ketone results suggest that the chromophore "experiences" water in both micelles, with differences between the two due to differences in either the microviscosity or more likely in the exposure to water.

Table II shows that the ϕ_{II} values remain essentially unchanged as the temperature increases; this is interesting since it has been shown that a temperature dependence exists for several ketones in fluid solution.[28] However, it is noteworthy that *n*-valerophenone shows an essentially constant $\phi_{II} = 0.79$ in acetonitrile over roughly the same temperature range as used in this study.[29] The similarity of the present results with those for valerophenone in acetonitrile suggests that the results in both micellar solutions reflect a solvent effect with little, if any, role of "microviscosity".

It has been suggested that addition of intermediate chain alcohols such as 1-heptanol results in a "swelling" of the micelle structure; the polar neutral hydroxy group increases the head-group separation while the hydrocarbon portion interacts with the hydrophobic counterparts in the micelle.[30,31] The net result of these effects is thought to be formation of a more stable, "tighter" micelle. Results with ketone **2** as seen in Table III seem to support this concept. Addition of heptanol causes a decrease in ϕ_{II} values but produces no new products, though the limiting value of 0.66 in 0.06 M heptanol still implies fairly hydrophilic surroundings. The alcohol may have the function of replacing water molecules in the micellar interior, resulting in a more organized and more hydrophobic micelle.

Europium Quenching with Various Ketones. Since Eu^{3+} is a water-soluble quencher of aromatic ketone excited states, Turro used it in his study with valerophenone and octanophenone in CTAC micelles.[8] He found that there was no effect on ϕ_{II} with valerophenone in CTAC micelles with Eu^{3+} present, yet, in an aqueous solution containing Eu^{3+}, ϕ_{II} for valerophenone decreased about 40% to a value of 0.61. The lack of any quenching with CTAC is not too surprising since charge repulsion would prevent Eu^{3+} from being near the micellar surface, yet the result clearly shows that no valerophenone is in the bulk aqueous phase. Incorporation of **1** in CTAC micelles resulted in no change in ϕ_{II} as Eu^{3+} was added to a limiting value corresponding to roughly 30 Eu^{3+} per micelle, in keeping with Turro's results. When **1** was incorporated into SDS micelles, however, quenching was observed with added Eu^{3+} as shown in Table IV.

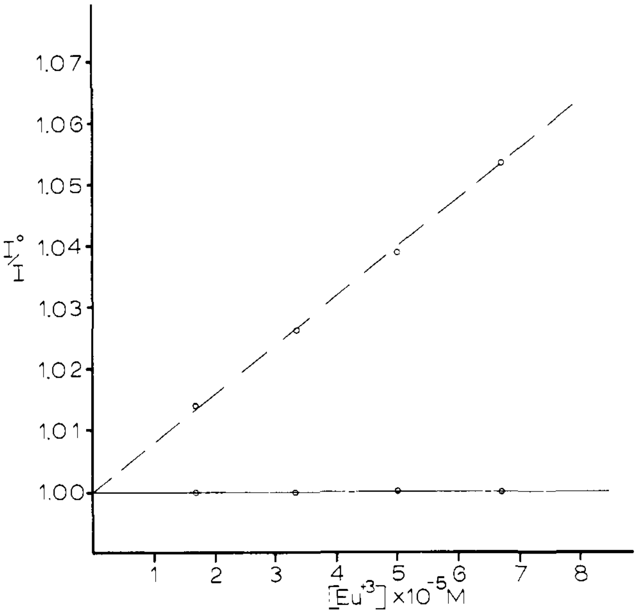
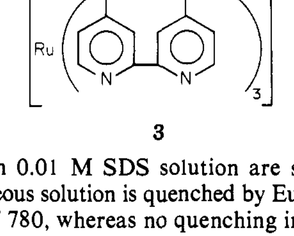


Figure 1. Stern–Volmer plot of europium quenching of Ru^{2+} complex **3** in water (---) and in 0.01 M SDS (—).

A study of the effect of added Eu^{3+} on the trnsient at 410 nm observed by laser flash photolysis shows that at $[Eu^{3+}] = 1.4 \times 10^{-4}$ M (effective intramicellar concentration = 0.04 M) the transient intensity is reduced by 60% with no attendant reduction in lifetime. The reduction in intensity observed using Eu^{3+} as quencher is similar to that observed at a comparable concentration of 2,5-dimethyl-2,4-hexadiene (vide supra). Since it has been shown that Eu^{3+} quenches triplet ketones by a factor of ~100 less efficiently than conjugated dienes,[2,6,7] the observed quenching can be ascribed to Eu^{3+} scavenging both the ketone triplet and the biradical. As conversion of the long-lived triplet biradical from **1** to either product or starting material should involve an intersystem crossing, it is likely that a proximal Eu^{3+} can induce an accelerated intersystem crossing with quite possibly an altered product/starting material partitioning. The residual transient observed with an unaltered lifetime can probably be attributed to biradicals of **1** in micelles not containing a Eu^{3+} ion; at these concentrations Poission statistics indicate that an appreciable fraction of the micelles will not contain Eu^{3+}. At a Eu^{3+} concentration of 2×10^{-4} M in SDS, the ϕ_{II} is quenched almost 20%; the effective micellar concentration at this value is 0.07 M.[32]

Somewhat striking results are observed when octanophenone and ketones **1** and **2** in SDS micelles are compared with regard to Eu^{3+} quenching as shown in Table V. No quenching is observed with octanophenone whereas ketone **2** is quenched by 10% and **1** by almost 20%. The ϕ_{II} values with no quencher suggest that the ketone experiences a fairly hydrophilic environment for all three cases, but results with Eu^{3+} present suggest that the average location of each within the micelle may be different. Strong complexation between metal ions and charged surfactants has been shown to occur with Cu^{2+} and other metal ions in anionic detergent solution.[33] The fact that Eu^{3+} complexes with SDS is shown in Figure 1 where Stern–Volmer plots of the Eu^{3+} quenching of in water and in 0.01 M SDS solution are shown. The Ru^{2+} complex in aqueous solution is quenched by Eu^{3+} up to 6.6×10^{-5} M with a K_{sv} of 780, whereas no quenching in the SDS solution is observed at these concentrations. The fact that **1** is quenched more than **2** by Eu^{3+} may be due more to a mismatch in the size



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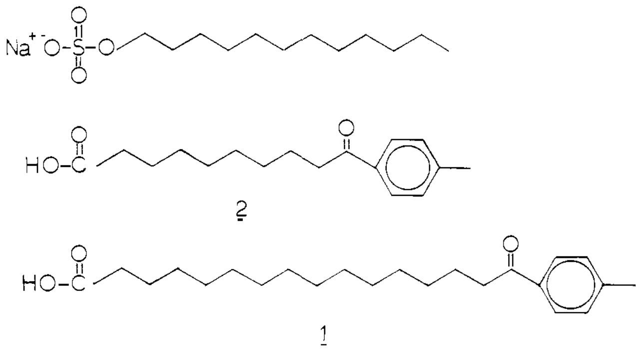

Figure 2. Relative sizes of an SDS molecule, ketone **1**, and ketone **2**.

of ketone **1** relative to an SDS molecule than for any other reason. The ketone may be on the average stretched to such an extent that in an elongated form the ketone is more exposed to micellar surface, and thus is more readily quenched (see Figure 2). The differences between quenching of **1** and **2** compared to octanophenone are less easily explained. However, the lower ϕ_{II} for the latter compound (0.76 as compared to 0.81 for **1** and 0.84 for **2**) may reflect its average occupancy of a more hydrophobic site which may be generally less accessible to the sulfate-bound Eu^{3+}.

Type II Process in Vesicles. Dioctadecyldimethylammonium chloride (DODAC), is reported to form single compartment bilayer vesicles when sonicated for the appropriate time.[34-36] Vesicles resemble most closely the physical and chemical properties of biological membranes[21,37] and have the ability to entrap fairly large molecules within the hydrocarbon interior. DODAC is known to undergo phase transitions at 30 and 36 °C.[35] Below 30 °C, the hydrocarbon chains are believed to be fully extended and somewhat tilted,[38] such that the vesicles are relatively rigid and highly structured. Between 30 °C, the pretransition temperatue, and 36 °C, changes in the structure and dimensionality of the vesicles occur. At 36 °C, the phase transition temperature, a "melting" of the hydrocarbon chains occurs resulting in more mobile, liquid-like arrangements within the vesicular interior.

The low ϕ_{II} values for **1** in DODAC vesicles (see Table VI) suggest that reverse hydrogen atom abstraction occurs with efficiencies similar to those for hydrocarbon solvents or that geometrical constraints imposed by the hydrocarbon chains at these temperatures limit the frequency at which the six-membered cyclic transition state can be reached.[39] As the temperature increases during the pretransition and transition phases, a gradual increase in ϕ_{II} values is observed, reaching a maximum of 0.40 at 44 °C. This implies that as the vesicle changes configuration and the hydrocarbon chains begin to melt, increased mobility may allow for the proper geometry to be reached more easily or perhaps for more possibilities of water to penetrate the interior (it has been shown previously that synthetic vesicles exhibit osmotic activity). Similar results were found when **1** was incorporated into dipalmitoyllecithin (DPL) vesicles;[40-42] ϕ_{II} is 0.28 at 30 °C and increases to 0.38 at 45 °C. The phase transition temperature for DPL is 36.4 °C.[42] In order to ensure that the low values were not due to predominant formation of a cyclization or reduction product, the electronic absorption spectrum of the ketone in the vesicles was monitored to see if the intensity or shape of the C=O band changed or bleached upon irradiation. No changes were observed, implying that the cleavage is the only photoreaction.

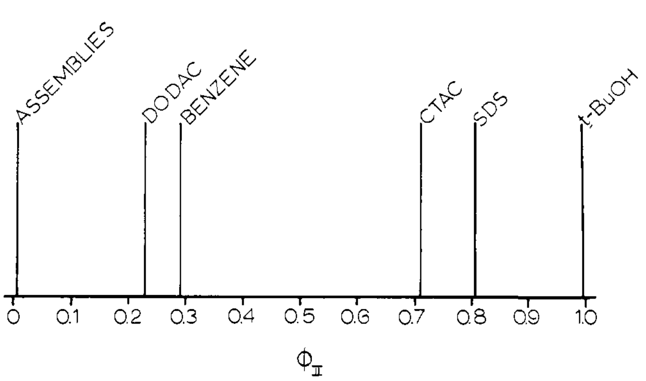

Figure 3. Summary of room-temperature ϕ_{II} values for **1** in various media.

The results with the vesicles clearly show that the ketone is in a much more hydrophobic environment than when it is incorporated into micelles, probably owing primarily to the higher ordering of surfactant molecules in vesicles and to less hydrocarbon–water contact in the latter. The increase in ϕ_{II} as the vesicles undergo pretransition and phase transitions could be accounted for by several factors. First, it is certainly possible that increased fluidity makes possible easier attainment of the requisite geometry for intramolecular hydrogen-atom abstraction. However, it is also possible that biradical reversal to the starting ketone becomes less favorable in the higher temperature phases either because of its enhanced conformational freedom or interactions with the higher concentration of water entering the bilayer at elevated temperature.

As was observed for **1** in SDS micelles, laser flash photolysis in vesicles at 20 °C resulted in a transient absorbing at 410 nm with a lifetime of ≈400 ns. The intensity of this transient was substantially lower than that observed for the micelles. This suggests that in the low-temperature phases in vesicles at least part of the reduction in quantum efficiency must be due to steric constraints inhibiting the initial intramolecular hydrogen atom step.

Summary

Results form these studies with the surfactant ketones **1** and **2** show that the Norrish type II process occurring with these two compounds is highly sensitive to the relative environment of the ketones in different media as shown schematically in Figure 3. We can readily discern differences in the accessibility of the carbonyl chromophore to hydrogen-bonding solvents, yet a clear statement as to exactly where the probe ketone resides in the media cannot be made.

While it is perhaps valid to critize the use of either intrinsic probes such as **1** and **2** or extrinsic probes since they may create their own microenvironment or even modify the structure of more dynamic surfactant assemblies, their behavior can provide a good picture of the type of solubilization sites occupied by other molecules of similar "hydrophobicity". The wide differences observed for ketone **1** in the various media studied point out rather clearly pronounced differences in solubilization environments that can be anticipated for different surfactant assemblies.

Acknowledgment. We are grateful the National Science Foundation (Grant No. CHE-8121140) for support of this research.

Registry No. 1, 68869-17-0; **2**, 23334-73-8; **2** methyl ester, 85554-56-9; $EuCl_3$, 10025-76-0; octanophenone, 1674-37-9; 4-bromotoluene, 106-38-7; cyclododecanone, 830-13-7; 1-(4-methylphenyl)cyclodecanol, 85554-57-0; styrene, 100-42-5.

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