fluorometer" and excitation spectra on a "Spex Fluorolog". Temperature was controlled by a stream of nitrogen which was first passed through liquid nitrogen and then heated to the appropiate temperature. The concentration of the fluorescence species in the stationary and nonstationary measurements was 10^{-4} M. All samples were degassed by at least four freeze–thaw cycles. Decay measurements were performed by using the single-photon counting technique on an apparatus composed of Ortec and Canberra modules and an optical part of Applied Photophysics. The observed decays were deconvoluted by using a lamp spectrum and a nonlinear least-squares program. Bis(α-naphthylmethyl) ether and (α-naphthylmethyl) ethyl ether were prepared by a Williamson ether synthesis. Their purity was checked by analytical HPLC. Isooctane and acetonitrile were purchased from Merck (Uvasol) and used without further purification. Methyltetrahydrofuran was twice distilled over sodium hydride. None of the solvents used contained fluorescent contaminant upon excitation in the wavelength region of the experimental interest. Reaction quantum yields and endo/exo ratios were determined according to a method described in a previous paper.[29]

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Photochemical Processes of Benzophenone in Microheterogeneous Systems†

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Abstract: The benzophenone triplet has been observed upon laser flash photolysis of the ketone solubilized in perfluorated micelles; its lifetime is found to be similar (7.87×10^{-6} s) to the value known from experiments in perfluorobenzene and perfluoromethylcyclohexane. Its $\epsilon_{TT}(\lambda_{max}$ 520 nm) of 2660 ± 380 L mol^{-1} cm^{-1} in sodium perfluorooctanoate (SPFO) and of 2460 ± 350 L mol^{-1} cm^{-1} in potassium perfluorooctylsulfonate (PPFOS) have been determined by using the method of Lachish et al. and assuming $\Phi_{isc} = 1$. Its phosphorescence is observed in perfluorated micelles ($\tau_{ph} = (7 \pm 3) \times 10^{-6}$ s), water ($\tau_{ph} = (12 \pm 4) \times 10^{-6}$ s), isooctane ($\tau_{ph} = (1.78 \pm 0.06) \times 10^{-6}$ s), and Freon 112 ($\tau_{ph} = (132 \pm 79) \times 10^{-6}$ s) with a striking resemblance of the weakly structured spectra (λ_{max} 445 nm) in the first two systems. The emission is quenched by nonfluorated surfactants such as sodium laurylsulfate (SLS) or cetyltrimethylammonium chloride (CTAC), presumably due to hydrogen abstraction; phosphorescence, triplet–triplet, and ketyl radical absorption transients are observed at concentrations of SLS above CMC, where the ketone should be nearly completely solubilized in a highly reactive micellar environment. Under micellar conditions, hydrogen abstraction occurs within the duration of our laser pulse (~30 ns). The kinetics of the triplet decay in perfluorated micelles as well as the decay of the ketyl radical, which results from hydrogen abstraction in SLS micelles, is strictly first order. Experiments in mixed micelles of SLS and SPFO indicate a faster decay of benzophenone triplets and a greater optical density of the signal component representing the corresponding ketyl radical when the mean occupancy number of SDS in SPFO is increased. The kinetics show a faster rate constant of hydrogen abstraction in those modelized micelles than in solutions of hydrocarbons. The solubilized ketyl radical may be deprotonated by an alkaline aqueous phase, and a cationic micelle clearly catalyzes this process. The lifetimes of ketyl radical and deprotonated ketyl radical anion are both longer in micellar systems than in homogenous solutions due to their isolation in surfactant aggregates.

During the last 20 years of active research in mechanistic photochemistry benzophenone has always been of particular interest, both as a chromophore, representing carbonyl triplets, and as a probe for the study of environmental reactivity.[4] Passing from homogeneous solutions to organized microheterogeneous systems, such as micelles, microemulsions, or vesicles,[5] the well-known hydrogen abstraction process of a carbonyl triplet[4] may answer as well questions about the structure of the aggregate and the position of the solubilizate[6] within the micellar aggregate.

Micelles have been employed as a means to isolate, and, thus, eventually stabilize reactive intermediates for the purpose of their characterization at ordinary temperatures as well as in order to influence well-known patterns of reactivity by applying experimental conditions which modify the reactivity of those intermediates.[6]

Both water and perfluorated solvents have been shown to be relatively inert with benzophenone triplets, and, thus, those homogeneous solutions served as standards for our measurements in micellar system.[7,8]

Experimental Section

Benzophenone of commercial grade has been recrystallized three times from ethanol, mp 48 °C.

Sodium perfluorooctanoate (SPFO) has been prepared from the corresponding carboxylic acid (perfluorooctanoic acid, PFO, FLUKA). A 0.024-mol sample of PFO in 45 mL of CH_3OH is mixed with an equivalent amount of NaOH in 45 mL of methanol, and the salt is precipitated by adding 170 mL of chloroform to the well-stirred solution. The precipitation is filtered, dried, and reprecipitated from a similar mixture of chloroform and methanol. Anal. Calcd: C, 22.04; Na, 5.27. Found: C, 22.0; Na, 5.11; H, <0.3.

Potassium perfluorooctanesulfonate (PPFOS) has been prepared by hydrolyzing perfluorooctanesulfonyl fluoride[9] with aqueous potassium

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† Dedicated to George S. Hammond on the occasion of his 60th birthday.

(1) To whom correspondence should be addressed.

(2) Part of her thesis, EPFL, Lausanne, 1981.

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Table I. Lifetimes τ_{ph} and τ_t of the Benzophenone Triplet in Perfluorated Media

solvent, aggregate	τ_{ph}	τ_T	ref and notes
C_6F_6	6.25×10^{-7} s	7.14×10^{-7} s	8a
C_6F_{11}-CF_3	7.1×10^{-4} s		8b
$C_{10}F_{18}$	1.0×10^{-3} s		8b
Freon 112	$1.32 \pm 0.79 \times 10^{-4}$ s		2.03×10^{-3} M benzophenone
SPFO, 10^{-1} M	$(5.4 \pm 2.2) \times 10^{-6}$ s		1.94×10^{-3} M benzophenone
3.2×10^{-2} M		$(7.14 \pm 0.54) \times 10^{-6}$ s	4.6×10^{-4} M benzophenone
PPFOS, ~2×10^{-3} M		$(3.57 \pm 0.13) \times 10^{-6}$ s	4.0×10^{-4} M benzophenone
H_2O	$(1.18 \pm 0.37) \times 10^{-5}$ s	$(1.54 \pm 0.3) \times 10^{-5}$ s	benzophenone saturated

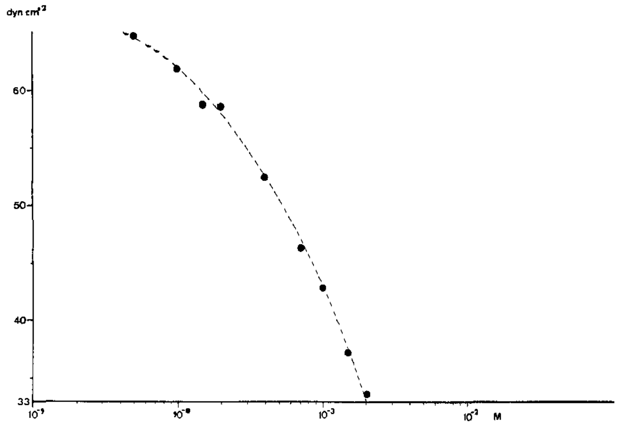

Figure 1. Surface tension measurements of PPFOS at various concentrations in water.

hydroxide.[10] Anal. Calcd: C, 17.85; K, 7.26. Found: C, 17.72; K, 7.05; H, <0.3.

CMC determinations have been made with a KRUESS tensiometer. For SPFO the CMC is $(3.1 \times 0.2) \times 10^{-2}$ M. No cmc has been found for PPFOS within its range of solubility ($<2.5 \times 10^{-3}$ M), although the diminuation of the surface tension indicates some aggregation in saturated solutions (Figure 1).

Mixed micelles have been prepared by dissolving various amounts of SLS in a micellar solution of 0.1 M SPFO containing 3×10^{-3} M benzophenone.

Laser photolyses have been performed by using a frequency doubled ruby laser (J. K. Lasers, series 2000) or an excimer laser (emission = 248 nm (Kr + F_2), Lambda Physik, EMG 101). The intensity of the ruby laser has been measured by a "black-glass" calorimeter (Laser Instrumentations). Technique and fundamentals for the ϵ_{TT} determination have already been published.[11]

Phosphorescence. Phosphorescence quantum yields were measured on a device constructed by Professor C. Cantor of the Department of Chemistry, Columbia University, employing quinine sulfate as a standard, as described elsewhere.[12] Lifetimes were measured by time-correlated single photon counting by using a commercial instrument manufactured by Photochemical Research Associates (London, Ontario), as well as by laser photolysis.

Benzophenone in Micellar Systems. Solubilization of benzophenone in micellar systems has been described earlier.[6] Only argon-saturated solvents have been used for preparing homogeneous and micellar solutions of both pure surfactants and the chromophore. Final solutions have been kept under argon.

Concentrations of benzophenone in the different micellar systems have been calculated so as to limit one chromophore per aggregate.[6]

Results and Discussion

Extrapolating the results in perfluorated solvents,[8] carbonyl triplets should be inert toward perfluorated surfactants and, thus, create a useful environment for their formation and analysis. The triplet–triplet spectra of benzophenone in SPFC and PPFOS are practically identical with the spectra, mostly in benzene, published earlier.[7b,13] Also, isolating the benzophenone molecule within a micelle stabilizes the triplet, as far as the lifetime is concerned (Table I). The large differences of τ_T between solutions of aliphatic fluorocarbons, such as $C_{10}F_{18}$, and perfluorated surfactant aggregates can be explained by a dominant solvent effect of the aqueous phase within the perfluorated micelles.[14] The striking

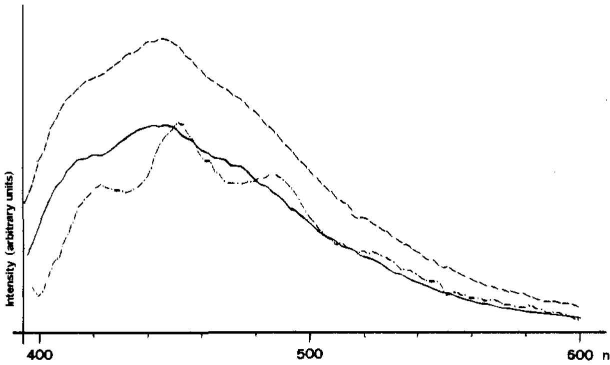

Figure 2. Corrected phosphorescence spectra of benzophenone (λ_{exc} = 345 nm) in different solvents and micellar systems: (—) 0.2 × saturated benzophenone in 10^{-1} M SPFO; (- - -) benzophenone saturateed in H_2O; (-·-) 1.32×10^{-3} M benzophenone in isooctane.

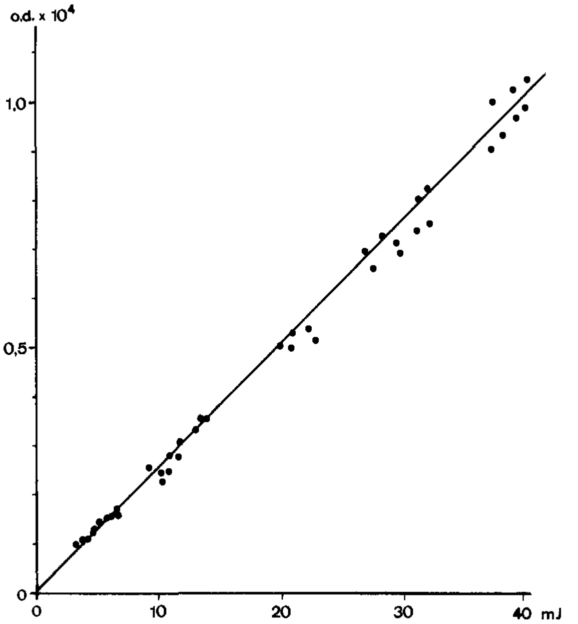

Figure 3. Optical density (530 nm) of the benzophenone (4.6×10^{-4} M in 10^{-1} M SPFO, o.d.$_{347nm}$ = 0.050) triplet as a function of the radiant energy of the laser pulse, sec eq 5, r^2 = 0.99334.

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Table II. Calculation of ϵ_{TT} and Comparison with Values Already Published

solvent, aggregate	$\Phi_{isc}\epsilon_{TT}$[a]	Φ_{ph}[b]	Φ_{isc}	ϵ_{TT}[d]	ref
SPFO	$(2.66 \pm 0.38) \times 10^3$	$(4.5 \pm 2.3) \times 10^{-4}$	0.55 ± 0.37[c]	4800	
H_2O			1.0	5800	7a
C_6H_6				10300	11e
C_6H_{14}			1.0	10300	11a

[a] Experimentally determined, see Figure 3, (M^{-1} cm^{-1}). [b] Experimentally determined. [c] Calculated, see eq 6. [d] In units of M^{-1} cm^{-1}.

Table III. Rate Constants and Activation Energies of the Hydrogen Abstraction Process by Benzophenone Triplets in SLS Micelles and Various Solvents

solvent/aggregate	k_q[a]	E_A[b]	ref
C_6H_6	1.12×10^5	1.3	13d
C_6H_5-CH_3	8.0×10^6	~3	13d
C_6H_{12}	3.3×10^6	~4	13d
C_6H_{11}-CH_3	6.6×10^6	2.9	13d
SLS (H_2O)	2.29×10^7	4.5	
C_nH_{2n+1}-CH_3	3×10^4	4.5	4
$(C_nH_{2n+1})_2\mathit{CH}_2$	7×10^5	2.8	4
$(C_nH_{2n+1})_3\mathit{CH}$	9×10^5	2.2	4

[a] In units of M^{-1} s^{-1}. [b] In units of kcal/mol.

resemblance of both absorption and phosphorescence spectra in perfluorated micellar systems and in water confirms this interpretation (Figure 2). Triplet decay curves from experiments in perfluorated micelles follow strictly first-order kinetics.

Considerable effort has been involved in order to determine the molecular extinction coefficient of the triplet–triplet absorption, ϵ_{TT}, at its $\lambda_{max} = 525$ nm, using the method of Lachish, Shafferman, and Stein.[11a] The resulting plot of the optical density of the triplet–triplet absorption vs. the radiant energy of the laser pulse has, however, not the expected exponential shape (Figure 3), indicating that the maximum radiant energy per laser pulse is too small to saturate the sample volume of solubilized benzophenone. This is due to the very small cross section of absorbance of this chromophore. Consequently, the exponential part of the original equation

$$y = a(1 - e^{bx}) \tag{1}$$

where y = o.d. of the intermediate investigated at a given λ and x = radiant energy per laser pulse is given by the Taylor expansion

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \ldots \tag{2}$$

which can be simplified (error $<10^{-3}$) to

$$e^x = 1 + x \tag{3}$$

This procedure changes eq 1 into a linear function (see Figure 3)

$$y = a(1 - [1 - bx]) \tag{4}$$

or

$$\text{o.d.} = a(1 - [1 - bI]) = abI \tag{5}$$

The two coefficients $a = \epsilon_{TT}c_0l$ and $b = 2.3,\Phi_{isc}\epsilon_G$[13c] cannot be determined separately and constitute the slope of the curve plotted (Figure 3, Table II).

Φ_{isc} has been calculated from phosphorescence data (τ_{ph}, Table I) at room temperature by using eq 6 and adopting the published

$$\Phi_{isc} = \frac{\Phi_{ph}}{k_{ph}^0\tau_t} \tag{6}$$

$k_{ph}^0 = 1.57 \times 10^2\ s^{-1}$.[7b] The resulting ϵ_{TT} in SPFO of 4800 M^{-1} cm^{-1} corresponds to the value determined by Bensasson and Gramain for aqueous solutions.[7a] However, we cannot explain why Φ_{isc} should be as low as 0.55 in perfluorated micelles, and assuming $\Phi = 0.92$ (upper limit of error), we calculate ϵ_{TT} to be ~3000 M^{-1} cm^{-1}. Under similar conditions ϵ_{TT} of benzophenone in PPFOS is 4500 ($\Phi_{isc} = 0.55$) and ~2700 M^{-1} cm^{-1} ($\Phi_{isc} = 0.92$).

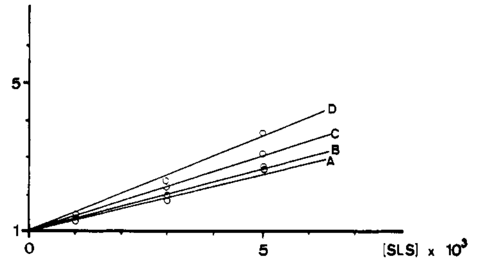

Figure 4. Stern–Volmer plot of the quenching reaction of the benzophenone phosphorescence by SLS in aqueous solution: A, 10 °C; B, 24.8 °C; C, 39.5 °C; *D* 55 °C.

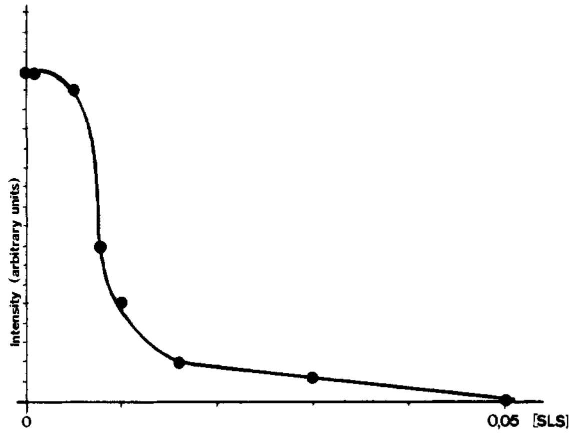

Figure 5. Benzophenone phosphorescence intensity as a function of [SLS], [benzophenone] $\simeq 2.10^{-4}$ M.

Benzophenone triplets are known to react rapidly with compounds (quenchers) possessing abstractable hydrogen (Table III).[4] In fact, this reaction has already been used in order to determine the most probable localization of benzophenone solubilized in micelles.[15]

The phosphorescence of aqueous solutions of benzophenone is quenched by SLS; Figure 4 shows the corresponding Stern–Volmer plots at different temperatures. The slope of the quenching experiments at 24.8 °C, $k_q\tau_T$, is calculated to be 3.52×10^2 M^{-1}. Assuming $\tau_T = 1.54 \times 10^{-5}$ s (see Table I), we obtain a rate constant for this quenching process, k_q, of 2.29×10^7 M^{-1} s^{-1}. This rate constant is about 3–7 times larger as the rate constants of hydrogen abstraction reactions from aliphatic hydrocarbons in homogeneous solution (Table III). Activation energy and A factor for this quenching process in the SLS micellar system are determined to be E_A = 4.5 kcal/mol and $A = 4.5 \times 10^7$ M^{-1} s^{-1}, respectively. These values are of the order of activation energies and A factors determined for hydrogen abstraction in homogeneous solution (Table III).[13d]

A plot of the benzophenone phosphorescence intensity as a function of SLS concentration follows the typical pattern of a

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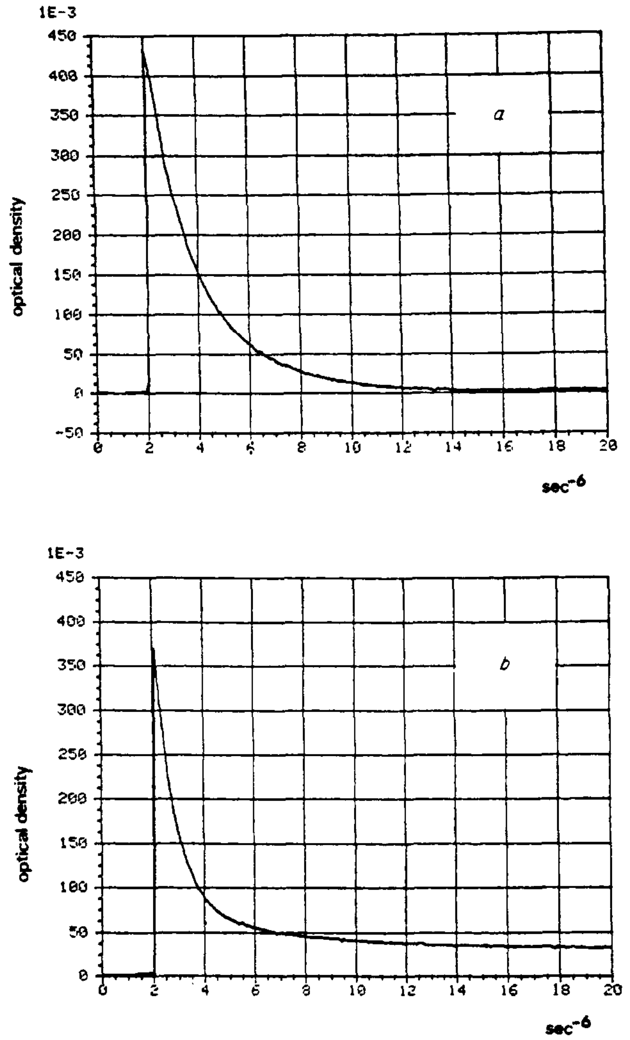

Figure 6. Transient absorption of benzophenone (3×10^{-3} M) at 530 nm: (a) in SPFO, 0.1 M; (b) in SPFO, 0.1 M and SLS, ⟨SLS⟩ = 2.4.

CMC curve showing an almost quantitative quenching for [SLS] > cmc, where practically all benzophenone molecules are solubilized (Figure 5).

The hydrogen abstraction reaction in SLS micelles is so fast, that it cannot be measured with our laser systems (pulse widths 20–30 ns). At 525 nm a mixed absorption due to two transients (benzophenone triplet and ketyl radical) is observed, thereby hindering observation of the buildup of the ketyl radical absorption. At 625 nm a transient absorption is observed whose decay is of the same order as that of benzophenone phosphorescence decay and which is readily quenched by the addition of 10^{-3} NO_2^-. The specific quenching by nitrite leads us to conclude that this absorption is due to benzophenone triplets which are located at a site(s) which effectively inhibits quenching by hydrogen abstraction.

Our results are, however, in sharp contrast to the interpretations of Sakaguchi, Nagakura, and Hayashi[16] on the basis of an indirect rise time determination, where the observed signal of the transient absorption at 330 nm is subtracted from the extrapolated linear decay part, (ln I)f(t) of the same signal. According to their results, there is, however, no rise part in the transient absorption signals obtained at 525 nm. Their argument, that the absorbance at 330 nm is larger for the ketyl radical than for the benzophenone triplet, hence the rise part can be attributed to the ketyl radical formation, while at 525 nm the absorbance of the ketyl radical is smaller than that of the benzophenone triplet, and a rise part therefore cannot be observed, is not very convincing. Bensasson and Gramain[7a] have shown that those ratios of absorbance never exceed a factor of 2; thus, a rise part must also be found at 525 nm, assuming that the rise part of their signal is real. Finally our results are also confirmed by picosecond measurements.[17]

Table IV. Observed Decay Rate Constants of the Benzophenone Triplet and Its Ketyl Radical, k_{obsd}, as a Function of ⟨SLS⟩

$10^{-5}k_{obsd}$[a]	⟨SLS⟩[b]	$10^{-5}k_{obsd}$[a]	⟨SLS⟩[b]
4.4	0	6.7	1.2
5.4	0.59	9.1	2.4

[a] In units of s^{-1}. [b] ⟨SLS⟩ = [SLS]/M_{SPFO}, where M_{SPFO} = concentration of SPFO micelles = [SPFO]/n and n = 10.

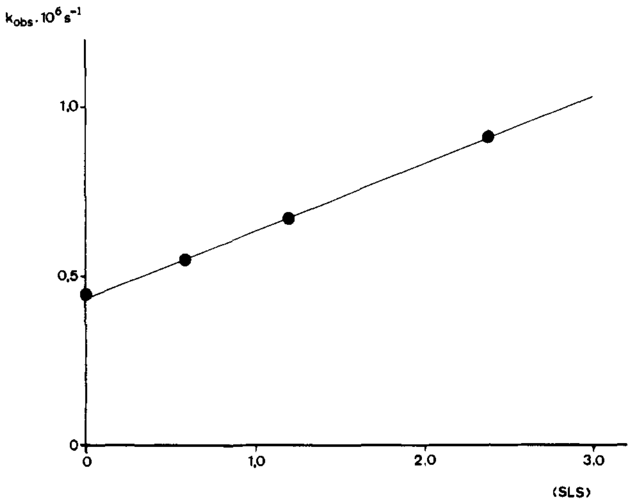

Figure 7. k_{obsd} of the decay of the transient absorption of benzophenone (3×10^{-3} M) in SPFO (0.1 M) as a function of ⟨SLS⟩.

In contrast to emission experiments employing laser excitation with benzophenone in isooctane (Figure 2), where emission of the ketyl radical is observed,[18] no emision is detected from the corresponding experiments in SLS micelles.

The absorption spectrum of the ketyl radical in SLS or lauryltrimethylammonium chloride (LTAC) micelles fits perfectly those already published.[13b,e,19] The rate constant of the decay of the ketyl radical in water is $k_r = 3.3 \times 10^9$ M^{-1} s^{-1}.[18b] The estamated rate constant in cyclohexane, calculated from $2k/\epsilon_r = 2.0 \times 10^6$ cm s^{-1} [13b] and $\epsilon_r = 3.2 \times 10^3$ M^{-1} cm^{-1},[19a] is 3.2×10^9 M^{-1} s^{-1}. This reaction follows in micellar systems first-order kinetics, with rate constants of $(2.4 \pm 0.1) \times 10^6$ and $(2.8 \pm 0.1) \times 10^6$ s^{-1} in SLS and LTAC or cetyltrimethylammonium chloride (CTAC) micelles, respectively. These constants correspond perfectly to those of Sakaguchi, Nagakura, and Hayashi (2.6×10^6 s^{-1}, without magnetic field).[16]

Benzophenone triplets and the corresponding ketyl radicals can also be observed at 530 nm[7,13] in mixed micelles of SPFO and SLS after laser pulse excitation. Parts a and b of Figure 6 show the decay curves of the transient absorption with and without SLS, respectively. In contrast to the phosphorescence of benzophenone, this transient absorption in SPFO deviates from a single exponential decay, indicating the formation of small amounts of the ketyl radical in the aqueous bulk phase.[7b] The slow decay component gets more important with the increase of the SLS concentration, expressed as the mean occupancy number, ⟨SDS⟩, in SPFO, suggesting that this signal component may be assigned to the ketyl radical. At the same time, the decay rate of the fast exponential decay component, assigned to the benzophenone triplet, gets faster. Both observations provide evidence that SLS

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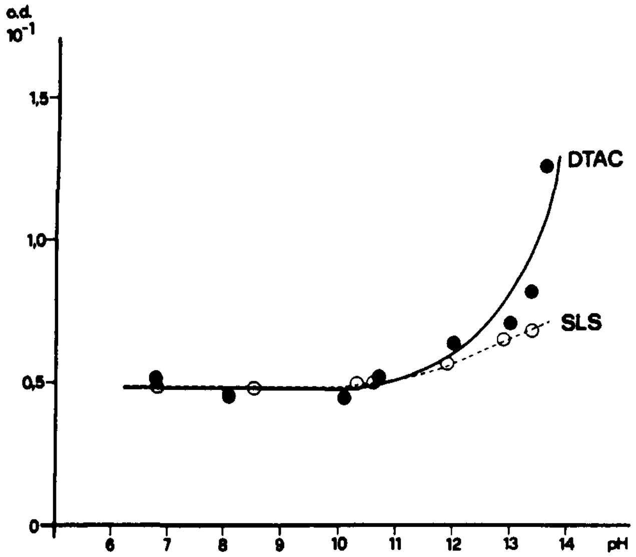

Figure 8. Radical anion formation in SLS and LTAC micelles as a function of pH.

and SPFO form mixed micelles. The decay curves (Figure 6) may be fitted by using eq 7,[20] where $I(0)$ and $I(t)$ represent optical

$$I(t) = I(0)\exp[-(k_d + k_a\langle \mathrm{SLS}\rangle)t] \qquad (7)$$

densities at time 0 and t, respectively, k_d is the decay rate constant in the absence of SLS, and k_a denotes the pseudo-first-order rate constant of hydrogen abstraction from SLS. Thus, the observed rate constant of the initial part of the decay curves in Figure 6 is

$$k_{\mathrm{obsd}} = k_d + k_a\langle \mathrm{SLS}\rangle \qquad (8)$$

Figure 7 and Table IV show k_{obsd} as a function of $\langle \mathrm{SLS}\rangle$. The slope of the linear function in Figure 7 is $k_a = 2.0 \times 10^5$ s^{-1} representing the probability of hydrogen abstraction per unit of time in SPFO micelles containing one benzophenone triplet and SLS molecule. In order to compare efficiencies of hydrogen abstraction of benzophenone triplets from hydrocarbon chains in mixed micelles and homogeneous solutions, we have to convert k_a into a second-order rate constant k_r

$$k_r = k_a N\bar{v} \qquad (9)$$

where N is Avogadro's number and $\bar{v}$ the volume of a SPFO micelle. With the assumption of a diameter of 13 Å for this micelle, $N\bar{v} = 5.5$ M^{-1}. Thus, a calculated $k_r = 1.1 \times 10^6$ M^{-1} s^{-1} is close to the known value of hydrogen abstraction from hydrocarbons in homogeneous solutions of 5×10^5 M^{-1} s^{-1} [4,21]

Having shown at different occasions[4] that negatively charged micelles enhance electron-transfer reactions from solubilized electronically excited chromophores and stabilize the corresponding radical cations, the ketyl radical of benzophenone is a good example in order to demonstrate a similar but opposite effect of a cationic micelle on the deprotonation of the ketyl intermediate. Producing the ketyl radical anion in strong alkaline CTAC micellar systems leads to a transient absorption spectrum with a $\lambda_{\max}$ at 610 nm, as already known from pulse radiolysis experments.[19] A plot of this significant absorption against the macroscopic pH of the system (Figure 8) shows a stronger deprotonation in the cationic than in the anionic micelle. When the macroscopic pH is varied from 6.6 (without NaOH) to 13.6, the lifetime of the ketyl radical, $\tau_r \approx 4 \times 10^{-7}$ s, is shortened by a factor of about 4.[22] But despite the high macroscopic pH value and a known pK of the radical/radical anion equilibrium of 9.2,[19b] only low concentrations of the radical anion are observed. The result indicates that the aqueous channels within the micelles are perfectly shielded against the pH conditions of the bulk solution. Complete conversion to the anion is observed when benzene is added,[17] increasing the volume of the surfactant aggregates. The protecting characteristics of the cationic micelle is finally shown in comparing the lifetime of the radical anion in CTAC ($\tau_{\mathrm{ra}} = (5.1 \pm 0.3) \times 10^{-5}$ s) and the half-lifetimes in water (1.7×10^{-7} s, from $k = 4 \times 10^{-6}$ M^{-1} s^{-1}).[19b]

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