Influence of Cationic Surfactant on the Photoprocesses of Eosine and Rose Bengal in Aqueous Solution

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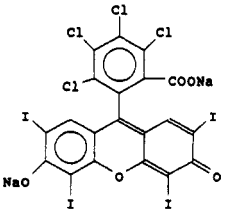
The influence of cetylpyridinium chloride (CPC) on the photoprocesses of rose bengal (RB) and eosine has been investigated in aqueous solutions. When the molar ratio of dye to CPC is 1:2, hydrophobic ion pairs, dye$(CPC)_2$, are formed. In water the ion pairs easily aggregate and can be extracted into benzene. Upon further addition of CPC to an aqueous solution, the ion pairs appear to be hosted individually in the hydrophobic interior of positively charged micelles formed at or above the critical micelle concentration of the surfactant. The aprotic interior of the micelles is responsible for a red shift in the absorption and fluorescence spectra of the dyes and longer singlet lifetimes, which greatly enhances fluorescence. The photochemical properties of the different forms of RB and eosine are affected by bimolecular deactivation processes between the dye molecules in the excited state and those in the ground state. When the dye molecules are separated from each other in the micelles, the dye triplet lifetime becomes longer because the contribution to triplet decay from self-quenching is diminished. As a result, copious singlet oxygen production is observed in micelles, while dye photobleaching is considerably reduced. The quantum yields of singlet oxygen formation for the micellar forms of RB and eosine in D_2O are 0.75 and 0.24, respectively. The dyes in cationic micelles are also less sensitive to acidic pH and to the presence of a fluorescence quencher in the aqueous phase. On the other hand, the fluorescence of the ion-pair aggregates is decreased and their triplet state is effectively self-quenched, resulting in poor singlet oxygen formation and much faster photobleaching. Singlet oxygen does not appear to play a significant role in the photobleaching processes.

Introduction

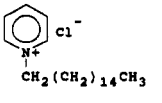
When surfactants associate spontaneously in water to form colloidal agglomerates, their microheterogeneous character can significantly alter the physicochemical properties of many systems.[1,2] Such changes have been widely studied by using fluorescence techniques.[2-4] Agglomerates or micelles can also alter singlet oxygen production and reactivity.[5-13] Among the singlet oxygen photosensitizers, rose bengal (RB) and its derivatives have been studied extensively. Previous investigations have focused on the excited-state properties of these dyes together with singlet oxygen formation,[14-22] aggregation,[23-28] and photobleaching.[29,30]

It has been reported that some neutral and cationic surfactants cause profound changes in the absorption/fluorescence spectra of RB and its derivative eosine.[31-33] During the initial addition of cationic surfactant to RB or eosine solutions, the fluorescence intensity of the dye dropped almost to zero, but then increased greatly when more detergent was added.[31-33] Changes in absorption and triplet lifetime in the presence of cationic surfactant have also been reported for eosine.[34] Again, below the critical micelle concentration (cmc), adding cationic surfactant dramatically decreased eosine's triplet absorbance, which then increased progressively when the cmc was exceeded.[34] One possible explanation for these observations is that premicellar aggregation[34] (to yield so-called dye-rich micelles or dye-rich aggregates) occurs below the cmc, thereby decreasing fluorescence, triplet–triplet absorption, and triplet lifetime. On the other hand, the dramatic enhancement of fluorescence at the micellar stage has been attributed to the binding of the anionic dyes to the neutral or cationic micelles.[30-33] This interaction also affects both triplet absorption[34] and reactivity.[12] However, to our knowledge, neither the structure nor the stoichiometry of the dye-rich aggregates and micelles containing RB or eosine has been elucidated.

In our study we have examined the nature of premicellar aggregation and the type of micelles formed in a system that contained the cationic surfactant cetylpyridinium chloride (CPC) and either RB or eosine. This was achieved by monitoring the sin-



Rose bengal sodium salt, (RB)



Cetylpyridinium cloride, (CPC)

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TABLE I: Visible Absorption (A_{max}) and Fluorescence (F_{max}) Maxima, Fluorescence Lifetime (τ), and Relative Fluorescence Intensity (I_F) for Different Forms of RB and Eosine

dye form	solvent	A_{max}, nm	F_{max}, nm	τ, ns	I_F
		Rose Bengal			
RB^{2-}	water	549	565	0.095[a]	1
RB in CPC micelle	water	564	578	1.2	9
$[RB(CPC)_2]_n$	water	590			
$RB(CPC)_2$	C_6H_6	570	586	1.2	6.8
$RB(CPC)_2$	C_6H_5Cl	570			
$RB(CPC)_2$	CH_2Cl_2	564			
$RB(CPC)_2$	$CHCl_3$	564			
$RB(CPC)_2$	CCl_4	576			
		Eosine			
Eo^{2-}	water	518	540	1.4,[a] 1.6	1
$[Eo(CPC)_2]_n$	water	542			0.02
Eo in CPC micelle	water	532	550	4.6	2.7
$Eo(CPC)_2$	C_6H_6	538			

[a] Reported value.[15]

glet–triplet states of both dyes in the presence of increasing concentrations of the detergent. We also investigated the influence of the micellar system on singlet oxygen formation and photobleaching of the dyes in aqueous solution. Our findings suggest that the formation of hydrophobic ion pairs between the anionic dyes and the cationic surfactant is a step that can not only explain premicellar aggregation but also may determine the structure and properties of the RB/eosine micelles.

Experimental Section

Materials. The following chemicals were used as received: rose bengal, ethanol, sodium azide, deuterium oxide, sodium deuteroxide, deuterated phosphoric acid, methyl chloride, chloroform, chlorobenzene, (Aldrich Chemical Co., Milwaukee, WI); carbon tetrachloride (Brudick & Jackson Lab. Inc., Muskegon, MI); CPC (Sigma Chemical Co., MO); and benzene (Fisher Sci. Co.). Eosine (Merck) was recrystallized from methylene chloride by conversion to its lactone form.[35] For fluorescence lifetime measurements, scintillation grade *p*-bis[2-(5-phenyloxazolyl)]-benzene (POPOP) was used as received (New England Nuclear Corp.). Glycogen (Type II) (Sigma) was used as a scattering solution. The aqueous samples were prepared in deionized water. Where indicated, sodium phosphate buffer (5 mM, pH 8.2) was employed.

$RB(CPC)_2$ solid was prepared by mixing equal volumes of 5×10^{-4} M RB disodium salt and 10^{-3} M CPC in water. After the addition of 2 M NaCl solution (0.1–0.2 M final salt concentration), the precipitate was centrifuged, washed many times with water, and then dried in a desiccator. The precipitate was readily soluble in CH_2Cl_2, $CHCl_3$, and C_6H_5Cl, less soluble in C_6H_6, and only slightly soluble in CCl_4 (Table I). The RB disodium salt itself did not dissolve in any of these solvents.

Instrumentation and Methods. Absorption spectra were recorded on a HP 8451 A diode array spectrophotometer. Fluorescence spectra were obtained in the photon counting mode on an SLM SPC 823/SMC 220 spectrofluorometer interfaced to an Apple II computer. Eosine solutions (5 μM) were excited at 490 nm and RB solutions (5 μM) at 520 nm in a 1 cm path length cell for the excitation beam and 0.1 cm for the emission side. The spectra were corrected for photomultiplier response and compensated for the absorbance at the excitation wavelength. The relative luminescence intensities were calculated from integrated luminescence assuming the same refractive index for all aqueous solutions; for the fluorescence intensity in benzene, the refractive indices of water and benzene were used.

Steady-state fluorescence lifetime measurements were performed on a phase-modulation SLM 4800/SMC 210 polarization subnanosecond lifetime spectrofluorometer operated at 30 MHz.

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TABLE II: Flash Photolysis Results for RB and Eosine in Degassed Buffered (pH 8.2) Aqueous Solution in the Presence and Absence of CPC[a]

dye form	k_{dt}, s^{-1}	$k_{sq} \times 10^{-8}$, M^{-1} s^{-1}	$k_2 \times 10^{-9}$, M^{-1} s^{-1}	τ_T, μs
		6.3[b]	2.0[b]	145[b]
RB^{2-}	6882[b]	7.6[c]	1.5 ± 0.2[f]	150[c]
		3.1 ± 0.3[f]		
RB in micelle	6644[d]	0	0	150[d]
		2.6[b]	1.4[b]	1162[b]
Eo^{2-}	860[b]	3.0 ± 0.3[f]	1.1[e]	1850[e]
			1.1 ± 0.1[f]	
Eo in micelle	550[d]	0	0	1818[d]

[a] We believe that the discrepancy in the measured lifetimes in this work and those reported is probably caused by the presence of residual oxygen in solution. [b] Values of k_{dt} (natural decay) and k_{sq} (self-quenching) were obtained from the intercept and slope of the plot of the observed rate constant, k_1, vs the dye concentration (see Experimental Section). Rate constant of triplet–triplet annihilation, k_2, was calculated by using extinction coefficient for the dye triplet $\epsilon_T = 4.4 \times 10^4$ M^{-1} cm^{-1} for eosine,[44] and $\epsilon_T = 8.4 \times 10^3$ M^{-1} cm^{-1} for RB.[59] [c] Reported by Rodgers and Lee.[43] [d] Decay curves were best fitted to a single-exponential model where $k_1 = k_{dt}$. [e] Reported by Kasche and Lindqvist.[45] [f] Reported by Seret and Van de Vorst.[13]

Fluorescence lifetimes for both dyes in the presence and absence of CPC were determined by a phase modulation method using an air-saturated solution of POPOP in ethanol as the standard (τ = 1.35 ns). Both RB and eosine were excited at 360 and 500 nm giving the same singlet lifetime. The lifetime experiments were carried out according to published procedures.[36]

Transient absorption measurements were performed in a 10 cm long cell on a PRA FP 1000 flash photolysis system (time resolution, 10 μs). The cooling jacket of the cell was filled with an aqueous solution of $CuSO_4 \cdot 5H_2O$ (200 g/dm^3) plus $NH_4Fe(SO_4)_2$ (10 g/dm^3), which provided a window between 400 and 550 nm for excitation. Oxygen was removed from the RB samples by purging with argon for several hours. The eosine samples were vacuum-degassed using five freeze–pump–thaw cycles. Transient absorbance was monitored at 600 nm for both dyes and decay profiles were analyzed according to the method of Catterall and Duddell.[37] Decay curves were analyzed by a mixed (first and second)-order kinetics, where the first-order rate constant $k_1 = k_{dt} + k_{sq}$[dye] and second-order rate constant k_2 = triplet–triplet annihilation rate; k_{dt} is the natural triplet decay and k_{sq} is the self-quenching rate constant; τ_T is triplet lifetime (Table II).

Singlet oxygen phosphorescence was measured in a 0.2-cm^2 cell using previously described equipment.[38] Quantum yields for singlet oxygen formation were calculated for free and micellar forms of RB and eosine in deuterium oxide by using the following expression

$$\varphi_{D_2O} = \varphi_{EtOH} \frac{P_{D_2O}}{P_{EtOH}} \frac{FA_{EtOH}}{FA_{D_2O}} \frac{k^r_{EtOH}}{k^r_{D_2O}} \frac{\tau_{EtOH}}{\tau_{D_2O}} \qquad (I)$$

where P is the intensity of singlet oxygen luminescence signal at 1270 nm, FA is the fraction of photons absorbed by the dye, φ_{EtOH} is the absolute quantum yield of singlet oxygen production in ethanol (0.75),[19] k^r is the radiative rate constant, and τ is $^1O_2$ lifetime. The ratio of radiative rate constants (k^r) in ethanol and D_2O is 2.[39] Singlet oxygen lifetimes (τ) in ethanol and D_2O were taken to be 12 μs[40] and 56 μs,[41] respectively.

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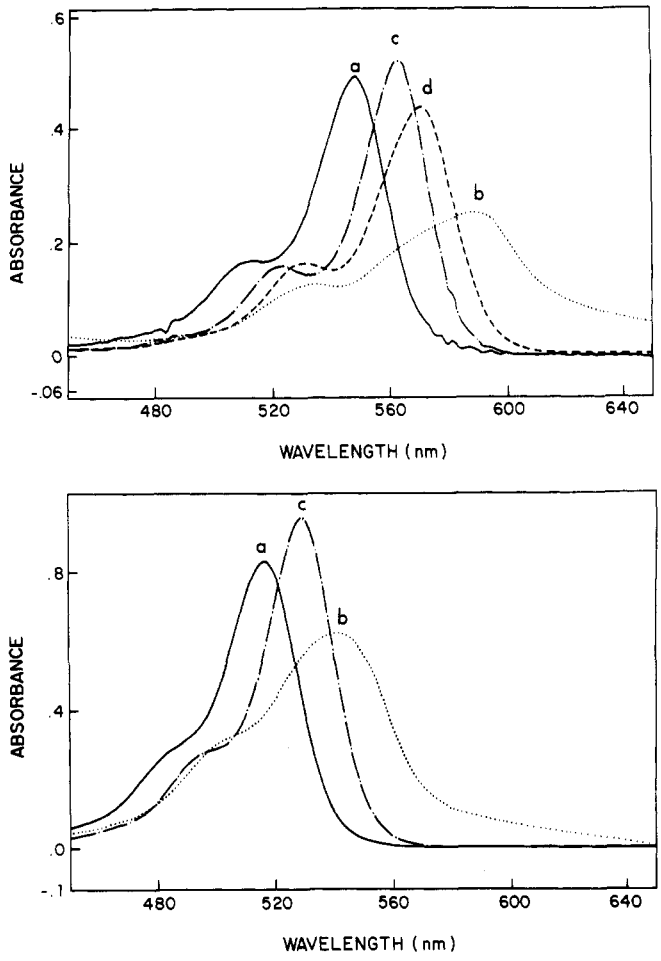

Figure 1. (A, top) Absorption spectra of rose bengal (20 μM) in the presence of cetylpyridinium chloride: (a) RB in aqueous buffer; (b) [CPC]:[RB] = 2:1 in aqueous buffer; (c) [CPC]:[RB] = 100:1 in aqueous buffer; (d) RB ion pair, $RB(CPC)_2$, in benzene. Aqueous solutions contained phosphate buffer (5 mM, pH 8.2); cell path length, 0.2 cm. (B, bottom) Absorption spectra of eosine (50 μM) in the presence of cetylpyridinium chloride: (a) eosine alone, (b) [CPC]:[eosine] = 2:1; (c) [CPC]:[eosine] = 100:1. Aqueous solutions contained phosphate buffer (5 mM, pH 8.2); cell path length, 0.2 cm.

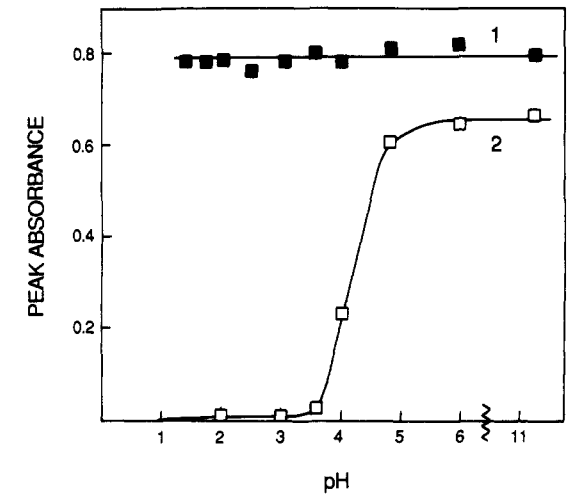

Figure 2. Changes in λ_{max} absorbance of RB (16.6 μM) in free and micellar form as a function of pH; the appropriate buffer concentrations were 0.1 M. RB in micelle (λ_{max} = 564 nm), line 1. Free RB (λ_{max} = 549 nm), line 2.

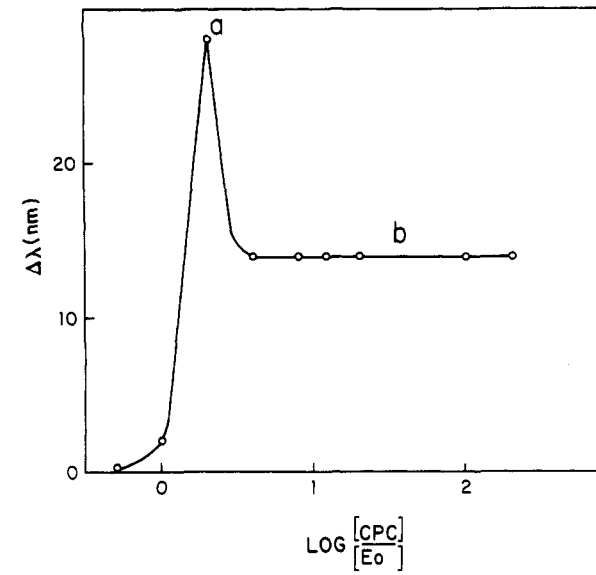

Figure 3. Effect of cetylpyridinium chloride (CPC) on the visible absorption maximum of eosine (Eo). $\Delta\lambda$, wavelength shift (nm) relative to free dye. Solutions contained phosphate buffer (5 mM; pH 8.2).

In photobleaching experiments a 150-W mercury arc lamp was used as a light source. The samples were exposed in a 1 cm path length cell through a combination of 450-nm cutoff filters (Oriel Corp., Stratford, CT) and their absorbance measured (after mixing) as a function of time.

NMR spectra were recorded on a GN-500 spectrometer (General Electric Co., Fremont, CA). The sample was dissolved in deuterated chloroform (99.9%, Sigma) and transferred to a 5-mm o.d. NMR tube. Proton chemical shifts were measured relative to the ^1H chemical shift of tetramethylsilane (TMS) at 0.0 ppm.

All experiments were carried out at room temperature.

Results

Absorbance and Fluorescence. We first reexamined the changes in absorption and luminescence spectra of RB and eosine caused by the addition of CPC. We observed two distinct concentration regions: one where the CPC concentration was twice that of the dye, and a second where the concentration of CPC was considerably higher than that of the dye. The character of these regions was a function of the [CPC]/[dye] ratio rather than the absolute dye concentration (concentrations from 1 μM to 1 mM were checked). When the ratio of [CPC]:[RB] was 2:1, the dye spectrum was broad and its maximum was highly red-shifted compared to free RB (Figure 1A, spectrum b; Table I). The absorbance decreased with time due to dye precipitation. Further addition of CPC resulted in a stable spectrum (Figure 1A, spectrum c), which was also red-shifted by comparison with free RB (Table I). The absorption spectrum of micellar bound RB was unaffected by changes in pH (Figure 2, line 1). This is in contrast to free RB which loses its red color below pH 4 (Figure 2, line 2). RB in CPC micelles also generated singlet oxygen over the pH range 1–12 (data not presented).

Red shifts were also observed in the absorbance of eosine upon addition of CPC (Figure 1B). As may be seen from Figure 3, where the $\Delta\lambda_{max}$ of eosine is plotted vs the logarithm of [CPC]/[dye], the broad spectrum (Figure 1B, spectrum b) was observed over a relatively narrow range of CPC concentrations (region a near 2:1); above this range there was little change in the eosine absorption spectrum (Figure 3, region b). Similar behavior was observed for RB (data not shown).

The fluorescence emission maxima of both dyes were red-shifted, and their relative emission intensities were altered in the presence of CPC (Figure 4, and Table I). When the ratio of [CPC]:[dye] was about 2:1, the fluorescence was unstable and appeared to decrease with time (data not shown). A solution containing eosine and CPC at 1:5 ratio was more stable but showed only very weak fluorescence (Figure 4B, b). As the concentration

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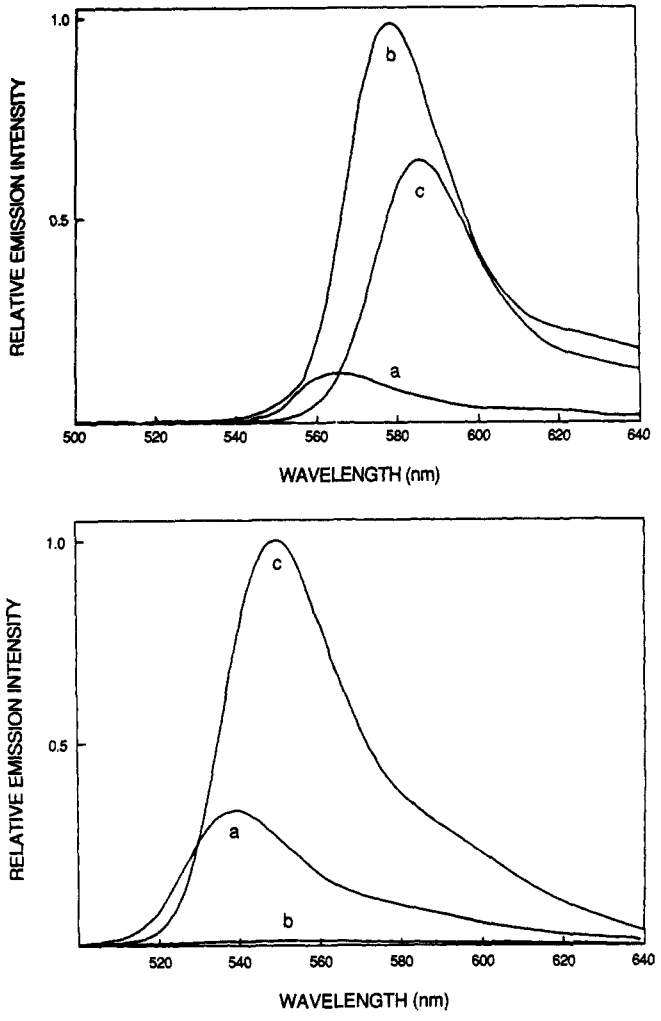

Figure 4. (A, top) Normalized fluorescence spectrum of rose bengal (5 μM): (a) no CPC; (b) [CPC]:[RB], 100:1; (c) $RB(CPC)_2$ in benzene. (B, bottom) Normalized fluorescence spectrum of eosine (5 μM): (a) no CPC; (b) [CPC]:[eosine], 5:1; (c) [CPC]:[eosine], 100:1. All air-saturated aqueous solutions contained phosphate buffer (5 mM; pH 8.2).

of CPC was raised, there was a concomitant increase in the fluorescence intensities of both dyes until a saturating value was reached. The maximal fluorescence of the micellar bound dyes is shown in Figure 4.

The fluorescence of free and micellar bound eosine responded differently to quenching by N_3^- anions. Azide ions quench eosine fluorescence with a rate constant on the order of 10^9 M^{-1} s^{-1}.[42] The Stern–Volmer plot for free eosine has a positive deviation that is probably caused by an increase in ionic strength of the solution (Figure 5, line 1). In contrast, the fluorescence of micellar bound eosine is hardly affected by azide (Figure 5, line 2). A slight initial increase of Stern–Volmer plot for eosine in micelles (Figure 5, line 2) may be caused by a steady-state concentration of HN_3 in the micelle or by an unknown impurity that can saturate the micelles and quench the eosine singlet state.

The fluorescence lifetimes of RB and eosine were also affected by CPC. For eosine dissolved in water or D_2O, the dye fluorescence lifetime initially decreased (Figure 6, region a). Upon further addition of surfactant, the eosine lifetime increased and reached a plateau at [CPC]/[dye] ratios above 40 (Figure 6, region b). The fluorescence lifetime of eosine increased from 1.6 ns in water (1.4 ns previously reported value[15]) to about 4.5 ns in the micellar stage (Figure 6). In the case of RB, we could not measure changes in fluorescence lifetime in *region a* because the lifetime of the dye was shorter than our instrumental limit of detection. The observed value of 1.2 ns for the singlet lifetime

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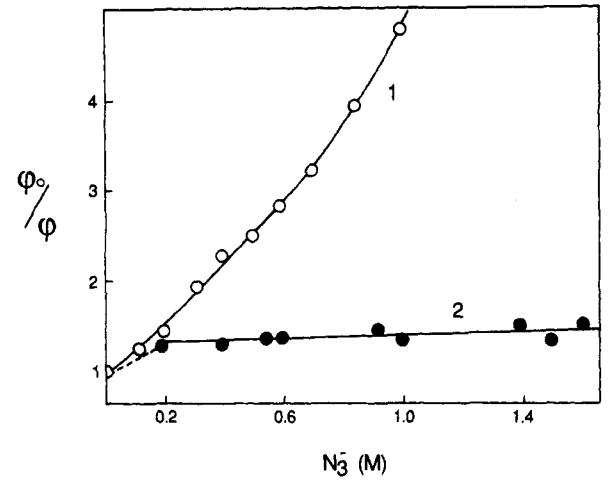


Figure 5. Stern–Volmer plot of fluorescence quenching of eosine (20 μM) by azide anions at pH 9. Free eosine, line 1; eosine in micelle (0.01 M CPC), line 2.

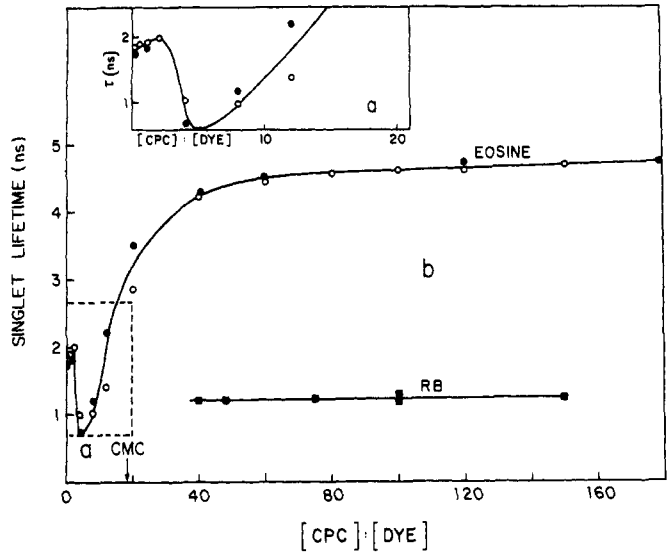


Figure 6. Effect of cetylpyridinium chloride on the fluorescence lifetime of rose bengal (20 μM) and of eosine (50 μM) in phosphate buffer (5 mM): (-O-) eosine in D_2O (pD 8.2); (-●-) eosine in H_2O; (-■-) RB in H_2O (pH = 8.2). The critical micelle concentration (cmc) of CPC in water is marked by an arrow.

of RB in micellar solution (compared to 95 ps[15] in water for free RB) suggests that the behavior of RB in region a (Figure 6) is probably similar to eosine. The nature of the relationship shown in Figure 6 was not affected by dye concentration over the range 1 μM to 1 mM.

The distinctive spectral changes occurring around a [CPC]/[dye] ratio of 2:1 suggest that a $dye(CPC)_2$ ion pair may be formed. Such a species would be electrically neutral and should be soluble in nonpolar solvents. We therefore extracted solutions containing CPC and dye at increasing ratios into benzene and measured the absorbance of the benzene extract. We found that, at [CPC]/[dye] ratios of approximately 2–3, the dyes were readily extracted into the organic phase, with 100% extraction occurring at a [CPC]/[dye] ratio of 2 (Figure 7). In contrast, neither the free dyes nor their micellar bound forms could be extracted into benzene from aqueous solutions nor could the free dyes be dissolved in benzene.

At a [CPC]/[dye] ratio of 2:1 neutral aggregates of the ion pairs could be salted out from aqueous solution. When the precipitate was dissolved in benzene the dye absorption spectrum was markedly shifted compared to the free dye in the aqueous phase (Figure 1, spectrum d). For $RB(CPC)_2$ dissolved in deuterated chloroform, the aromatic region of the proton NMR spectrum showed four resonances with chemical shifts of δ_1 = 7.465 ppm,

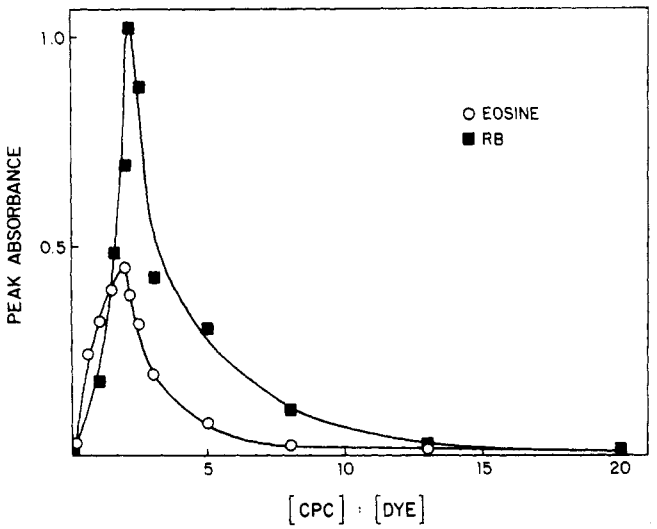


Figure 7. Effect of cetylpyridinium chloride on the extraction of rose bengal and eosine into benzene. Aqueous dye solutions (10 mL) of rose bengal (20 μM) or eosine (50 μM) in phosphate buffer (5 mM; pH 8.2) were extracted with benzene (7.5 mL). The absorbance was measured (1 cm path length) at 568 nm for rose bengal (-■-) or 538 nm for eosine (-O-).

δ_2 = 7.872 ppm, δ_3 = 8.311 ppm, and δ_4 = 8.986 ppm. The value of δ_1 was assigned to the two hydrogens of RB, while those of δ_2, δ_3, and δ_4 were assigned to the $H_{1,5}$ H_3, and $H_{2,4}$ resonances of the pyridinium moiety of CPC. The relative integrated intensities of the pyridinium resonances to that of RB was 10:2 consistent with 2:1 ratio of [CPC]:[RB]. Our preliminary results indicate that RB thus solubilized in organic solvents efficiently sensitizes singlet oxygen formation (data not presented). The photochemical properties of these dyes dissolved in nonpolar solvents as ion pairs with surfactants are under investigation and will be presented later.

Transient Triplet Absorbance. In deoxygenated water, the triplets of RB and eosine decay in microseconds[43] and milliseconds,[44,45] respectively. Both triplet–triplet annihilation and self-quenching of the dye triplet by ground-state dye molecules contribute to triplet decay, which obeys a mixed (first and second)-order kinetic model.[44,45] We examined the influence of CPC on these processes for both dyes. In the absence of CPC, our kinetic analysis (which uses the method of Catterall and Duddell[37]) of triplet decay showed that the best fit was obtained for a mixed-order model (Table II). When CPC was introduced in the solution, the observed triplet lifetime increased as the concentration of CPC was raised above the cmc. Analysis of the decay kinetics revealed that the data were best fitted to a single-exponential model. The rate constant was independent of dye concentration. This kind of behavior suggests that in micellar solution there is no contribution from triplet–triplet annihilation or self-quenching. Thus, the decay of the dye triplet becomes purely monoexponential. Attempts to determine the triplet lifetime of aqueous samples containing the ion pair dye$(CPC)_2$ were unsuccessful. Possibly the triplet-state lifetime of the dye in the ion-pair aggregates was too short to be detected by our instrument.

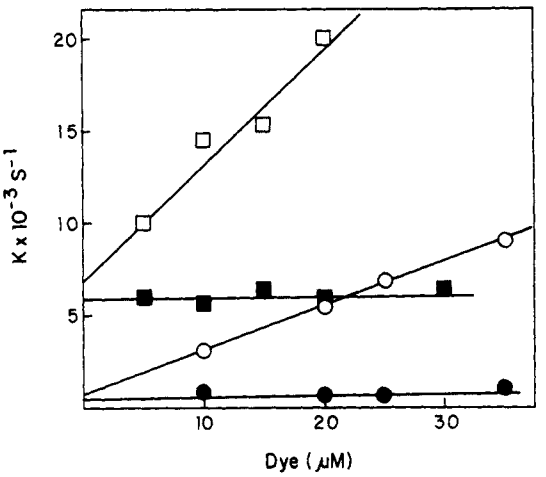


Figure 8. First-order rate constant for the decay of the dye triplet as a function of dye concentration: (-□-) rose bengal; (-■-) rose bengal in micelles; (-O-) eosine; (-●-) eosine in micelles. Solutions with eosine were vacuum-degassed; RB solutions were deoxygenated by bubbling with argon. All solutions contained phosphate buffer (5 mM, pH 8.2). In micellar solutions the [CPC]:[dye] ratio was 100:1.

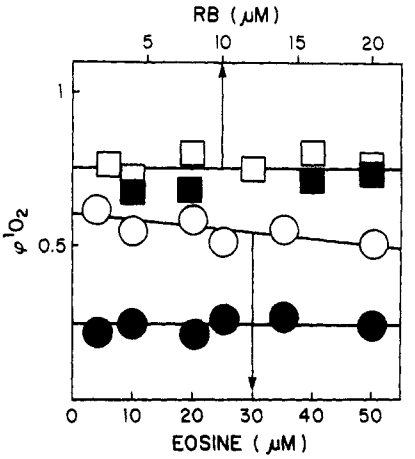


Figure 9. Quantum yield of $^1O_2$ formation by RB and eosine as a function of dye concentration in deuterium oxide containing phosphate buffer (5 mM; pD = 8.2): (-□-) rose bengal; (-■-) rose bengal in micelles; (-O-) eosine; (-●-) eosine in micelles.

A representative plot of the first-order rate constant vs dye concentration, in the absence and presence of surfactant at micellar concentration, is shown in Figure 8. It is evident from the plots that, for RB and eosine in micelles, the triplet decay is independent of the dye concentration. Table II summarizes the rate constants for both dyes in the presence and absence of CPC.

Singlet Oxygen Phosphorescence and Photobleaching. In aerobic solutions, the triplet excited states of eosine and RB are mainly quenched by molecular oxygen, leading to singlet oxygen formation. We examined how CPC influences this process.[45b] The calculated singlet oxygen quantum yield for both free and micellar forms of RB was 0.75 ± 0.05 (Figure 9). For eosine, the absolute singlet oxygen yield (extrapolated to low eosine concentration) was about 0.58, while for the micellar form of eosine this value dropped to 0.24 (Figure 9). For free eosine in air saturated D_2O, only a slight decrease in $^1O_2$ formation was noticed when the concentration of eosine was raised from 5 to 50 μM. This effect disappeared in micelles (Figure 9). RB did not show any concentration dependence over the range 2–20 μM within our experimental error for $^1O_2$ detection (Figure 9). The quantum yields of $^1O_2$ production of eosine and RB ion pairs in water were 0.03 and 0.07, respectively (data not shown).

Eosine and RB are known to undergo photobleaching in aqueous solution.[29,30] Figure 10 shows the effect of CPC on the photobleaching of RB and eosine as measured by changes in their

(43) Lee, P. C. C.; Rodgers, M. A. J. *Photochem. Photobiol.* **1987**, *45*, 79.
(44) Zwicker, E. F.; Grossweiner, L. I. *J. Phys. Chem.* **1963**, *67*, 549.
(45) (a) Kasche, V.; Lindqvist, L. *Photochem. Photobiol.* **1965**, *4*, 923. (b) In micelles, the triplets of eosine and RB live long enough (due to diminished self-quenching) to be entirely deactivated by molecular oxygen. Moreover, oxygen is more soluble in organic solvents than in water so that the oxygen concentration in the non-polar micelles is probably even higher than in the aqueous phase. Therefore, the quantum yield of singlet oxygen production should be determined by the yield of intersystem crossing and not by triplet lifetime. The yields of $^1O_2$ formation were estimated assuming an equal partition of $^1O_2$ between micellar and D_2O phases. Furthermore, it was assumed that $^1O_2$ deactivates mainly in the aqueous phase which is large compared to the micellar volume. The micellar interior consists of surfactant hydrocarbon chains and should be similar to hexane, a solvent in which the lifetime of $^1O_2$ is shorter than in D_2O (30 μs in hexane[46a] vs 56 μs in D_2O[41]). Since singlet oxygen must deactivate also in micelles, the yield of $^1O_2$ phosphorescence may have been slightly underestimated.

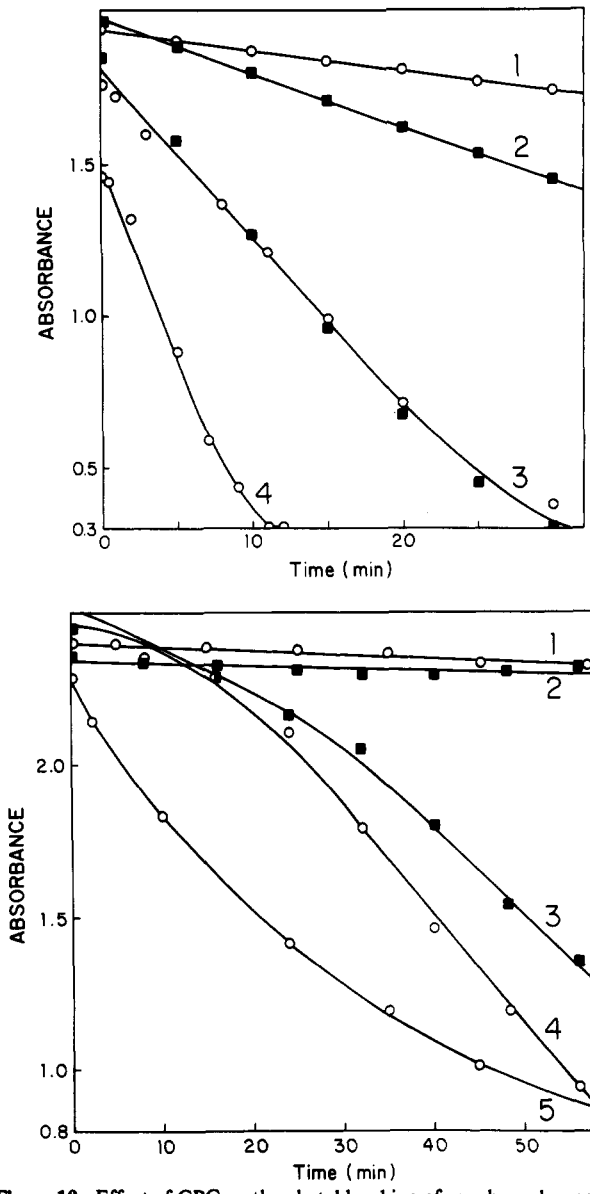
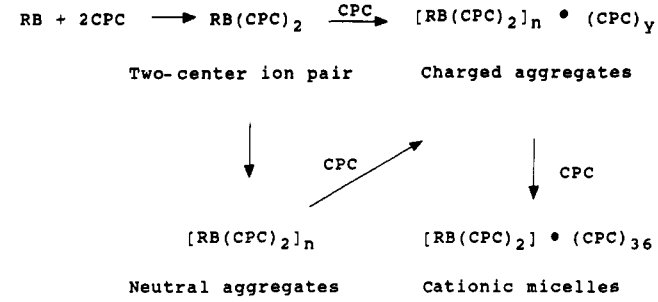


Figure 10. Effect of CPC on the photobleaching of rose bengal or eosine. Dye solutions were irradiated by a Hg arc lamp through 450 nm cutoff glass filter combination. All solutions contained phosphate buffer (5 mM; pH 8.2). (A) Rose bengal. Longwave peak absorbances of RB (20 μM) are plotted as a function of irradiation time: curve 1, [CPC]:[RB] = 100:1; curve 2, [CPC]:[RB] = 100:1, + 10 mM NaN_3; curve 3, RB in the absence (–O) and presence (–■–) of NaN_3; curve 4, [CPC]:[RB] = 2:1. (B) Eosine. Longwave peak absorbance of eosine (50 μM) as a function of irradiation time: curve 1, [CPC]:[eosine] = 100:1; curve 2, [CPC]:[eosine] = 100:1, + 10 mM NaN_3; curve 3, eosine + 10 mM NaN_3; curve 4, eosine, curve 5, [CPC]:[eosine] = 2:1.

absorbance maxima (λ_{max}) as a function of time.[46b] The [RB/eosine$(CPC)_2]_n$ aggregates bleached very rapidly upon irradiation (Figure 10A-4,B-5). On the other hand, the micellar forms of both dyes were highly photostable (Figure 10A-1,B-1). Free dyes (Figure 10A-3,B-4) underwent photobleaching at a slower rate than the aggregated forms. To estimate the extent to which singlet oxygen may contribute to photobleaching, we studied the effect of the azide anion. While azide slightly decreased the rate of photobleaching for eosine in the absence of CPC (Figure 10B-3), it had no effect on uncomplexed RB in solution (Figure 10A-3). For micelles, azide partially increased the photobleaching rate for RB (Figure 10A-2) but did not affect eosine (Figure 10B-2).

(46) (a) Salokhiddinov, K. J.; Byteva, I. M.; Gurinovich, G. P. *Zh. Prikl. Spektrosk.* **1981**, *34*, 892. (b) The absorbance of both dyes is different at the lines of the mercury lamp used for irradiation so that no direct comparison between eosine and RB is possible.

SCHEME I



Discussion

The CPC concentration dependence for the absorption and luminescence of RB and eosine suggests that a new species if formed between the dyes and CPC. We believe that spectral and photochemical observations can best be explained by the formation of a neutral dye$(CPC)_2$ ion pair which undergoes aggregation in water, and by the encapsulation of the dye$(CPC)_2$ ion pair inside micelles (Scheme I).

Ion-Pair Formation. The complete extraction of RB or eosine from aqueous solutions containing CPC at a detergent/dye ratio of 2:1 (Figure 7) suggests that a neutral two-centered ion pair, dye$(CPC)_2$, is formed (Scheme I). In aqueous solutions containing CPC and RB (2:1) the ion pairs aggregate to form a precipitate, $[RB(CPC)_2]_n$, which readily dissolves in nonpolar organic solvents (Table I). NMR spectroscopy confirmed that in $CDCl_3$ the RB chromophore remains associated with two surfactant cations.

The absorption spectrum of the RB$(CPC)_2$ ion pair in organic solvents (Table I, Figure 1) is characteristic of a monomeric xanthene chromophore in nonpolar aprotic surroundings. A very similar spectrum has been observed by Lamberts and co-workers[20] for the RB bis(triethylammonium) salt in CH_2Cl_2, λ_{max} = 556 nm. The absence of new bands in the absorption spectrum of RB$(CPC)_2$ in organic solvents indicates that, due to steric requirements and redox mismatch of the components, electron transfer does not occur. This is in contrast to RB monoesters which exibit new hypsochromic charge transfer bands when forming ion pairs with large onium cations in organic solvents.[47]

Unlike ion pairs derived from RB monoester and small alkali-metal cations,[26,27] which are known to form dimers, the dye$(CPC)_2$ ion pairs are highly hydrophobic and undergo aggregation in water that probably does not stop at the dimer stage. If neutral aggregates, $[RB(CPC)_2]_n$, precipitate out of aqueous solution, the equilibrium between ions and ion pairs should be shifted toward ion pairs. For RB ion pairs, the aggregation proceeds slowly and strongly depends on the substrate and buffer concentrations (data not presented). The progressive aggregation of ion pairs in water made it impossible to obtain the absorption spectrum of either the ion pair or the dimer alone. The freshly prepared sample exhibited a broad absorption spectrum that was red-shifted but did not resemble the known dimer spectrum of the dimeric form of the sodium salt of RB monoester.[26-28] Therefore, the precise structure or size of the neutral aggregates remains unknown. One possibility is that the observed spectra (Figure 1A,B, spectrum b) may be due to a J-type, neutral or slightly charged, large aggregates of ion pairs. It is known that the J-type aggregates usually feature a red shift in their absorption spectra in contrast to H-type aggregates where a blue shift is often observed.[25,27,48]

Aggregation may also account for the observed decrease in singlet lifetime (Figure 6) and fluorescence intensity (Figure 4B, curve b) for the eosine ion pairs. It is noteworthy that the apparent singlet lifetime minimum occurs when the ratio of CPC to eosine is about 5:1. At the stoichiometric 2:1 ratio, the singlet lifetime of eosine is little affected (Figure 6) despite the fact that the absorption spectrum is characteristic of aggregates (Figure 1B,

(47) Linden, S. M.; Neckers, D. C. *Photochem. Photobiol.* **1987**, *47*, 543.
(48) Ishchenko, A. A.; Vasilenko, N. P.; Maidannik, A. G.; Balina, L. V. *Dokl. Akad. Nauk Ukr. SSR, Ser. B: Geol., Khim. Biol. Nauk.* **1988**, *2*, 46.

spectrum b). While it is difficult to explain these observations it should be emphasized that many processes are probably occurring in region a in Figure 6. The neutral aggregates of ion pairs may bind more cetylpyridinium cations forming charged aggregates, $[dye(CPC)_2]_n(CPC)_y$, which remain in solution (Scheme I), while the neutral aggregates precipitate. The fluorescence properties of aggregates should depend on their size and structure which are unknown. The phase-modulation technique employed in this study gives an apparent singlet lifetime[49a] representing the sum of all singlet decay rates weighted by their respective fluorescence intensities. Along the transition path from ion pairs to micelles, neither the actual species nor their fluorescence properties are known, and therefore only the boundary values for the fluorescence lifetimes in micelles and in water can be considered characteristic.

Micelle Formation. Upon further addition of CPC, the hydrophobic ion pairs eventually become surrounded by the hydrocarbon chains of CPC to form micelles after passing the stage of the charged ion pair aggregates (Scheme I). The smooth increase in apparent lifetime as the CPC:dye ratio rises above 5:1 (Figure 6) suggests that aggregates or associates of surfactant molecules begin to provide a micellelike environment even at CPC concentrations well below the cmc of 0.9 mM for CPC in water. The CPC/eosine micellar aggregation number may be estimated from the region where the singlet lifetime of eosine begins to reach a plateau (Figure 6) to be about 45, which is typical for small micelles.[49b]

In micelles, the dyes showed a similar red shift in absorption spectra to the $dye(CPC)_2$ ion pair in organic solvents (Figure 1 and Table 1), suggesting that the micellar environment of the dyes is aprotic. The aprotic nonpolar nature of the dye environment inside the micelles can also explain the observed red shift in the fluorescence emission maxima of the dyes and the enhancement of their fluorescence intensities.[15] The stronger fluorescence must be mainly due to a decrease in the rate of thermal deactivation of the excited singlet state[16] with a concomitant increase in singlet lifetime because the intersystem crossing yield could not be greatly affected (see further discussion). The singlet lifetime for eosine and RB increased about 2-fold and 12-fold, respectively, in the micellar state compared to water (Figure 6). The viscosity of micellar microsurroundings could also influence lifetime of the singlet state. However, no such correlation has been found for RB dissolved in ethanol (τ = 660 ps), 1,4-butanediol (τ = 648 ps), or glycerol (τ = 252 ps).[50]

The observation that the absorption spectrum of micellar bound RB was insensitive to pH (Figure 2) provides evidence that this dye is buried deep inside micelles. Micellar bound eosine was also inaccessible to azide anions since dye fluorescence was little affected by 1.5 M sodium azide. While all the data suggest that the dyes are buried in a nonpolar region of the micelles, their precise location is not known. However, we conclude that in the micelles the dyes must exist in association with neutralizing ions (i.e., as ion pairs; Scheme I) because the dye dianions are insoluble in benzene and other nonpolar solvents.

The spectral changes observed for the RB/eosine–CPC system have been reported for other dye-detergent combinations. Surfactant concentration dependent alterations in absorption and luminescence have been reported for erythrosine, phloxine B, pyronin-B, rhodamine-B, acriflavin, acridine yellow, brilliant blue-R,[33] acridine orange,[51] and some cyanine dyes.[52] In the case of rhodamine B, a variation in fluorescence intensity as a function of ionic surfactant concentration has been observed[53] which resembles the singlet lifetime dependence observed for eosine–CPC in our study (Figure 6). Thus it is possible that hydrophobic ion pairs that aggregate forming nonfluorescent "dye-rich micelles"[33,34,51,54–57a] may play a role in the binding of other charged dyes to micelles.

The Photochemical Properties of Micelles and Aggregates. The nature of dye ion-pair aggregates and dye-containing micelles determines the photochemical behavior initiated by the dye triplet excited states. In anaerobic solution, the eosine and RB triplet lifetimes decrease with increasing dye concentration due to triplet–triplet annihilation and self-quenching.[43–45a] Our observed triplet lifetimes and the self-quenching rate constants are compared with previously reported values in Table II. In the micellar stage, dye molecules are separated from each other and are protected by the micellar envelope (Scheme I).[57b] As a consequence, the triplet decay will be purely monomolecular and independent of the initial dye concentration (Figure 8). Similar behavior for the RB triplet has been reported for a polymer solution of RB in which the dye molecules were separated by poly(4-vinylpyridine) chains.[50] In the ion-pair aggregates the triplet-state lifetime is shortened by self-quenching processes due to the close proximity of dye molecules.

The sensitization yield of $^1O_2$ is more than 10-fold lower for the ion-pair aggregates of both dyes than that for the free dyes. The lower $^1O_2$ yield can be attributed to the proximity of the dye molecules in aggregates, which decreases fluorescence and triplet lifetime and can probably alter the intramolecular energy distribution from excitation.

The quantum yield of $^1O_2$ formation by eosine in micelles is about one-half of that observed in the absence of detergent (Figure 9). The intersystem crossing yield of eosine decreases on going from water to alcohol[15] resulting in $^1O_2$ yields of 0.57 and 0.39 in water and ethanol, respectively.[19,22] Thus the lower $^1O_2$ yield of eosine in micelles may be due to a lower intersystem crossing yield resulting from a decrease in environmental polarity and proton-donating ability. In contrast to eosine, neither the triplet quantum yield[59] nor the $^1O_2$ yield[19,22] of RB changes on going from water to methanol. Thus it is perhaps not surprising that the $^1O_2$ yield of RB is unaffected by micellarization (Figure 9).

The relative insensitivity of $^1O_2$ production to dye concentration suggests that self-quenching cannot effectively compete with the quenching of the triplet state by O_2 in air-saturated solutions. During prolonged irradiation, however, self-quenching together with triplet–triplet annihilation[43] appears to have a decisive influence on the photostability of RB and eosine in aqueous solutions. Encapsulation of RB or eosine in micelles results in much lower photobleaching compared to the free dyes (Figure 10). In contrast, ion-pair aggregates fade much faster (Figure 10A-4,B-5). Singlet oxygen does not appear to play a role in the photobleaching process since addition of azide, a known physical quencher of $^1O_2$,[38] had no effect on photobleaching (Figure 10A,B).

It is claimed that self-quenching can occur via electron transfer from ground-state molecules to the excited triplet, leading to the corresponding radical ions, which in degassed solution recombine to form the parent molecules.[44,45a] Our finding that photobleaching was reduced drastically when self-quenching was eliminated in micelles indicates that radical ions are probably intermediates to photobleaching. Furthermore, photobleaching was not observed when eosine was irradiated in anaerobic solutions.[29] Therefore, it appears that radical ions are able to initiate photobleaching

(49) (a) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, **1983**; pp 55 and 83. (b) The aggregation number of CPC/RB micelles, measured by monitoring RB fluorescence as a function of CPC concentration, is about 38 (unpublished data). This value appears in Scheme I.

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(55) Sato, H.; Kawasaki, M.; Kasatani, K. *J. Photochem.* **1981**, *17*, 243.

(56) Guha, S. N.; Moorthy, P. A.; Rao, K. N. *Proc. Indian Acad. Sci. (Chem. Sci.)* **1982**, *91*, 73.

(57) (a) Hamai, S. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2099. (b) The CPC micelles containing RB are positively charged, so that they will repel each other further separating the dye molecules from close contact. However, repulsion is not a crucial factor for diminished self-quenching, since we observed that $RB(CPC)_2$ in neutral Triton X100 micelles is also well protected and shows spectral features that are characteristic of an aprotic environment.[58]

(58) Bilski, P.; Motten, A.; Chignell, C. F.; Szychlinski, J.; Oleksy, E. *Photochem. Photobiol.* **1990**, *51S*, 58; also a full paper in preparation.

(59) Murasecco-Suardi, P.; Gassmann, E.; Braun, A. M.; Oliveros, E. *Helv. Chim. Acta* **1987**, *70*, 1760.

reactions only in the presence of oxygen. The RB radical cation has been proposed as an active intermediate in promoting photobleaching.[30] Scheme II shows a plausible route to photobleaching of RB and eosine.

SCHEME II

$$^3D + D \rightarrow D^+ + D^- \quad (1)$$

$$^3D + {}^3D \rightarrow D^+ + D^- \quad (2)$$

$$^3D + O_2 \rightarrow D^+ + O_2^- \quad (3)$$

$$D^+ + D^- \rightarrow 2D \quad (4)$$

$$D^- + O_2 \rightarrow D + O_2^{\cdot -} \quad (5)$$

$$D^+ + O_2/O_2^- \rightarrow \text{colorless products} \quad (6)$$

During photolysis, O_2 may accept an electron from the dye (D) radical anion (eq 5) thereby preventing the fast cage recombination of this radical anion with the geminate radical cation (eq 4). An alternative route yielding radical cation is direct electron transfer from the dye triplet to molecular oxygen (eq 3). Such a process, if it accounts for photobleaching, should occur more easily in the aqueous phase than in the nonpolar micelle interior. Thus, the electron-transfer process that is essential for photobleaching (eqs 1-3) is diminished in micelles resulting in a significantly higher photostability of the micellar form of both dyes. In the ion-pair aggregates, electron transfer (eqs 1-3) can contribute to rapid photobleaching.

Conclusions

We have observed the formation of neutral hydrophobic ion pairs between RB or eosine and CPC in water which undergo "premicellar aggregation". These ion pairs make it possible to solubilize RB or eosine in nonpolar polarizable solvents. We postulate that RB/eosine–CPC micelles contain a neutral ion pair hosted deep inside and that the aprotic nonpolar surroundings alter the spectral properties of both dyes. Such a model may also help explain similar spectral changes previously reported for other ionic dyes interacting with oppositely charged surfactants.

We have correlated the photoreactivity of the dyes in aerobic aqueous solutions to the nature of the aggregates and micelles. The proximity of the dye molecules in the aggregates results in the rapid deactivation of excited states, which leads to low $^1O_2$ yield and rapid dye photobleaching. In contrast, the excited states of RB and eosine molecules encapsulated in micelles are protected from bimolecular deactivation observed in the absence of detergent. This also diminishes dye photobleaching that arises from electron-transfer processes. The dye triplet states are deactivated only by molecular oxygen, which promotes efficient $^1O_2$ formation over a wide pH range for RB in the cationic micelles.

Acknowledgment. We thank Dr. A. G. Motten for helpful discussions. We are also grateful to Dr. Don Davis for carrying out the NMR experiments on the $RB(CPC)_2$ ion pair.

Spectrum and Mutual Kinetics of $HOCH_2CH_2O_2$ Radicals

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β-Hydroxyethyl peroxy radicals have been studied by using pulse radiolysis to generate the radicals and kinetic absorption to monitor their formation and decay. The ultraviolet absorption spectrum assigned to $HOCH_2CH_2O_2$ is broadband in nature with a maximum absorption cross section of 3.5 (±0.6) × 10^{-18} cm^2 molecule^{-1} at 230 nm. An overall rate constant for the self-reaction $2HOCH_2CH_2O_2 \rightarrow HOCH_2CH_2OH + HOCH_2CHO + O_2$ (3a), $2HOCH_2CH_2O_2 \rightarrow 2HOCH_2CH_2O + O_2$ (3b) of k_3 = 7.7 (±1.2) × 10^{-12} cm^3 molecule^{-1} s^{-1} was measured at room temperature together with an estimation of the branching ratio, k_{3a}/k_3 = 0.75 (±0.1).

Introduction

Hydroxyethyl radicals play an important role in the gas-phase oxidation of alcohols and alkenes in the atmosphere and in combustion chemistry. The β-hydroxyethyl radical, CH_2CH_2OH, is known to be an important intermediate in the low-temperature photooxidation of ethene, and the α-hydroxyethyl radical, CH_3CHOH, has been identified as a key radical intermediate in the oxidation of ethanol.

In atmospheric chemistry, β-hydroxyethyl radicals are removed by reaction with O_2 to form a peroxy adduct:

$$CH_2CH_2OH + O_2 (+M) \rightarrow HOCH_2CH_2O_2 (+M) \quad (1)$$

Very recently, Miyoshi et al.[1] reported a room-temperature rate constant of k_1 = 3.0 × 10^{-12} cm^3 molecule^{-1} s^{-1} measured using flash photolysis coupled with photoionization mass spectrometry. No pressure dependency was observed over the total pressure range (6.5-22.7) × 10^{16} molecules cm^{-3} suggesting k_1 is at the high-pressure limit. In addition, Niki et al.[2,3] identified the products formed following photolysis of $RONO–NO–C_2H_4–O_2$ (R = C_2H_5 or s-C_4H_{10}) using FTIR and proposed a series of elementary reactions for the oxidation of CH_2CH_2OH radicals in air; formation of the peroxy radical via reaction 1 is followed by conversion of NO to NO_2

$$HOCH_2CH_2O_2 + NO \rightarrow HOCH_2CH_2O + NO_2 \quad (2)$$

and unimolecular dissociation of the substituted alkoxy radical to yield CH_2O and HO_2.

However, no direct kinetic studies have been reported on the β-hydroxyethyl peroxy radical, $HOCH_2CH_2O_2$, and the work

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(2) Niki, H.; Maker, P. D.; Savage, C. M.; Brietenbach, L. P. *J. Phys. Chem.* **1978**, *82*, 135.

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