# Micellar Effect on the Photosensitized Debromination of 2,3-Dibromo-3-phenylpropionic Acid

Control of Forward and Back Electron Transfers

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The zinc tetraphenylporphyrin (ZnTPP)- and zinc tetrasodiumtetra(*p*-sulphonatophenyl)porphyrin (ZnTPPS)-sensitized photodebromination of 2,3-dibromo-3-phenylpropionic acid (1) in the presence of a sacrificial reductant yielding cinnamic acid has been studied in cationic cetyl-trimethylammonium bromide (CTAB) micellar solution. The photosensitized electron transfer and the resultant debromination are significantly affected by the solubilizing sites of sensitizer and dibromide (1) in the micelle. The debromination proceeds most efficiently when the anionic sensitizer and (1) are adsorbed on the cationic micellar surface. The overall efficiency is controlled mostly by the back electron transfer rather than the forward one, which is competitive with the subsequent debromination steps. The cationic micellar surface is effective for the electron-transfer debromination when both or either of the sensitizers is anionically charged.

Electron transfer across biological membrane is an essential process for cellular energy storage. In order to understand and mimic the chemical details in these biological systems, considerable efforts have been paid to delineate the role of organized assemblies such as micelles, microemulsions and vesicles.<sup>1</sup> The partitioning or binding of solutes to micelles is an important methodology in membrane mimetic chemistry.<sup>2</sup> Micellar systems are sometimes effective in facilitating electron transfers between excited donor D\* and acceptor A and also in controlling subsequent chemical reactions.<sup>3,4</sup> For example, cationic micelles tend to adsorb anionic compounds by means of electrostatic interaction, and to accelerate an electron transfer between anionic D\* and A on their surface. On the other hand, the electron transfer occurs

$$\mathbf{D}^* + \mathbf{A} \to \mathbf{D}^+ + \mathbf{A}^- \tag{1}$$

across the micellar surface when A is hydrophobic and solubilized in hydrophobic interior of the micelle. To the best of our knowledge, there have been very few examples in which electron-transfer reactions along and across the micellar surfaces are compared or evaluated. We have reported on an electron-relay chain mechanism for the *cis-trans* isomerization of *N*-methylstyrylpyridinium ion on anionic micelles.<sup>5</sup> In our preceding paper dealing with a homogeneous reaction in the absence of surfactant,<sup>6</sup> the anionic zinc porphyrin-sensitized photodebromination is shown to involve a one-electron transfer and subsequent chain debromination. The present paper demonstrates that the photodebromination is facilitated significantly by the addition of cationic micelles, and

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that the net electron transfer along the micellar surface is more efficient than that across the surface or inside the micelle.

## Experimental

# Materials

Erythro-2,3-dibromo-3-phenylpropionic acid (1) was prepared by the bromination of *trans*-cinnamic acid.<sup>6</sup> Cetyltrimethylammonium bromide (CTAB) (extra-pure grade, Wako Pure Chemicals) was used without further purification. Tatrasodium tetra(p-sulphonatophenyl)porphyrin (ZnTPPS) was prepared according to a literature method<sup>7</sup> and purified with column chromatography. Water was distilled three times and stored.

## **A Typical Photolysis**

An aqueous solution  $(3 \text{ cm}^3)$  of 6.7 mmol dm<sup>-3</sup> sodium *erythro*-2,3-dibromo-3phenylpropionate (1a), 0.12 mmol dm<sup>-3</sup> ZnTPPS, and 12 mmol dm<sup>-3</sup> triethanolamine (TEOA) or bissodium salt of ethylenediaminetetraacetic acid (EDTA) in the presence of 6.7 mmol dm<sup>-3</sup> CTAB was placed in a 1 cm cuvette and degassed by three freeze-thaw cycles (pressure < 10<sup>-4</sup> mmHg).<sup>†</sup> The solution was photolysed at room temperature with a 150 W tungsten halogen lamp (Sylvania) using a Corning filter 0–51 to cut out light below 355 nm. The progress of the photochemical debromination was monitored by the growth of the absorbance at *ca*. 267 nm due to cinnamate produced. No formation of cinnamate was observed on standing for over 5 h in the dark under the reaction conditions. Products were analysed by a h.p.l.c. instrument using a ODS reversed phase column (Fine Sil C<sub>18</sub>-10, Japan Spectroscopic Co. Ltd) with a mixture of aqueous NaH<sub>2</sub>PO<sub>4</sub> and methanol (2/1 in vol) as the eluent.

Quantum yields were determined by a potassium ferrioxalate actinometry. The degassed reaction mixture was irradiated at  $426 \pm 10$  nm using a 150 W xenon lamp in combination with a monochrometer.

### Quenching of Excited Triplet ZnTPPS with Dibromide (1)

Aqueous solutions containing 0.2 mmol dm<sup>-3</sup> ZnTPPS, 6.7 mmol dm<sup>-3</sup> CTAB, and various amounts of dibromide (1) in 1 cm cuvettes were degassed by the three free-thaw cycles, sealed and irradiated at 590 nm. The lifetime<sup>8</sup> of the excited triplet ZnTPPS in the presence of a quencher Q is expressed by

$$1/\tau = 1/\tau_0 + k_q[Q]$$
 (2)

where  $\tau_0$  denotes the lifetime in the absence of quencher, and  $k_q$  and [Q] represent the quenching constant and the quencher concentration, respectively. The lifetimes of ZnTPPS<sup>\*3</sup> was measured on an Applied Photophysics laser kinetic spectrometer employing a laser beam (532 nm) emitting from a Nd: YAG laser (Quanta-Ray PHS-1 prism harmonic separator). Degassed aqueous solutions containing 0.2 mmol dm<sup>-3</sup> ZnTPPS and various amounts of the dibromide (1) were irradiated by the light source, and the decay of ZnTPPS<sup>\*3</sup> was monitored at 840 nm. The detailed procedures were described previously.<sup>6</sup>

#### Estimation of Adsorption of ZnTPPS on CTAB

The Soret band spectrum of ZnTPPS at 421 nm was utilized to estimate the adsorption efficiency of ZnTPPS on CTAB. A double reciprocal relationship was derived from eqn (12) in the text: 1/4 (r = 1/4 (r = 1/4) (r =

$$1/\Delta A = K_{\rm d}/\Delta A_{\infty}[{\rm CTAB}] + 1/\Delta A_{\infty}.$$
(3)

 $\dagger 1 \text{ mmHg} = 101 325/760 \text{ Pa}.$ 

From eqn (3) the binding stoichiometry may be derived, when  $\Delta A/\Delta A_{\infty}$  is substituted with Y,<sup>9</sup> to give  $\log[Y/(1-Y)] = \log[\text{CTAB}] - \log K_{d}$ . (4)

The plot of  $\log[Y/(1-Y)]$  against  $\log[CTAB]$  afforded the  $K_d$  value with a slope of 0.94. The slope is nearly unity, which means the formation of a 1:1 complex between ZnTPPS and CTAB.

# **Results and Discussion**

In the preceding paper<sup>6</sup> we reported that the photosensitized debromination of 2,3-dibromo-3-phenylpropionic acid (1) to cinnamic acid (2) takes place smoothly in the presence of zinc tetrasodium tetra (*p*-sulphonatophenyl)porphyrin (ZnTPPS) by way of one-electron transfer from the excited ZnTPPS<sup>\*3</sup> to the dibromide (1):

PhCHBrCHBrCO<sub>2</sub>R 
$$\xrightarrow{\text{ZnTPPS/hv}}$$
 PhCH=CHCO<sub>2</sub>R  
(1) (2)  
(a) R = Na; (b) R = H; (c) R = CH<sub>3</sub>. (5)

The photodebromination is shown to proceed in the presence of a sacrificial reductant, e.g. triethanolamine, via a radical chain sequence as shown in scheme 1.

$$ZnTPPS^{*3} + PhCHBrCHBrCO_2R \xrightarrow{\sim_q} ZnTPPS^{++} + (1^{-})$$
(6)
(1)

PhCHBrCHBrCO<sub>2</sub>R<sup>--</sup>  $\xrightarrow{k_7}$  PhĊHCHBrCO<sub>2</sub>R + Br<sup>-</sup> (7) (1<sup>--</sup>) (5)

$$Ph\dot{C}HCHBrCO_{2}R \longrightarrow PhCH = CHCO_{2}R + Br'$$
(8)
(5)

$$Br' + N(CH_2CH_2OH)_3 \longrightarrow HBr + (HOCH_2CH_2)_2N\dot{C}HCH_2OH$$
(6)
(9)

$$(1) + (6) \longrightarrow (5) + Br^{-} + (HOCH_2CH_2)_2N = CHCH_2OH$$
(7)
(7)

(10)

$$\mathbf{Br'} + (\mathbf{6}) \xrightarrow{\text{termination}} (\mathbf{7}) + \mathbf{Br}^{-}.$$
(11)

Scheme 1.

Since the bromo acid (1) is readily debrominated by one-electron transfer and is soluble in either a hydrophilic or hydrophobic environment depending on the pH, it may be a good model for the examination or evaluation of electron-transfer efficiencies along and across the micellar surface.

#### Photochemical Debromination sensitized by ZnTPP or ZnTPPS in the Presence of Micelles

The photosensitized debromination of sodium 2,3-dibromo-3-phenylpropionate (1a) or its acid (1b) took place with a large variety of efficiencies depending on the formal charges of both the sensitizers and (1) in the presence of micelles (table 1). The photosensitized electron transfers from sensitizer to 1 in micellar solutions may be

donor	acceptor/reductant	surfactant	system <sup>b</sup>	Φ
ZnTPP	(1a) (H)/EDTA	СТАВ	I → I	0.04
ZnTPP	(1a) (H)/TEOA	SDSme <sup>c</sup>	$I \rightarrow I$	0.01
ZnTPP	(1b) (Na)/EDTA	CTAB	$I \rightarrow S$	0.28
ZnTPPS	(1a) (H)/EDTA	СТАВ	$S \rightarrow I$	0.36
ZnTPPS	(1b) (Na)/TEOA	CTAB	$S \rightarrow S$	1.39

Table 1. Debromination of PhCHBrCHBrCO<sub>2</sub>R (1)<sup>a</sup>

<sup>a</sup> 0.12 mmol dm<sup>-3</sup> donor; 6.7 mmol dm<sup>-3</sup> (1); 6.7 mmol dm<sup>-3</sup> surfactant; 12 mmol dm<sup>-3</sup> reductant. <sup>b</sup> Symbols for the systems are defined in the text. <sup>c</sup> SDS microemulsion, a mixture of sodium dodecyl sulphate (10 mmol dm<sup>-3</sup>), amyl alcohol (61 mmol dm<sup>-3</sup>) and dodecane (16 mmol dm<sup>-3</sup>) in water.

Table 2. Effect of CTAB and pH on the photochemical debromination of  $(1)^a$ 

donor	acceptor	reductant	CTAB /mol dm <sup>-3</sup>	рН	relative yield of <i>trans-</i> ( <b>2</b> ) <sup>d</sup> /% min <sup>-1</sup>	
		effect of [CT	AB] <sup>b</sup>			
ZnTPPS	<b>(1 a)</b>	TEOA	0	9.4	1.4	
ZnTPPS	<b>(1 a)</b>	TEOA	$1.0  imes 10^{-6}$	9.4	1.9	
ZnTPPS	( <b>1 a</b> )	TEOA	$9.2  imes 10^{-5}$	9.4	2.2	
ZnTPPS	( <b>1 a</b> )	TEOA	$2.8  imes 10^{-4}$	9.4	4.4	
ZnTPPS	( <b>1 a</b> )	TEOA	$4.6  imes 10^{-4}$	9.4	6.1	
ZnTPPS	( <b>1</b> a)	TEOA	$9.2 \times 10^{-4}$	9.4	6.4	
ZnTPPS	( <b>1</b> a)	TEOA	$3.5  imes 10^{-3}$	9.4	7.1	
		effect of pl	H°			
ZnTPPS	( <b>1 b</b> )	EDTA	$6.7  imes 10^{-3}$	3.5	1.3	
ZnTPPS	(1 b)	EDTA	$6.7 \times 10^{-3}$	5.6	3.3	
ZnTPPS	( <b>1 b</b> )	EDTA	$6.7  imes 10^{-3}$	7.2	10.9	
ZnTPPS	( <b>1 a</b> )	EDTA	$6.7 \times 10^{-3}$	9.6	12.4	

<sup>a</sup> An aqueous solution of (1), a sensitizer and a reductant was irradiated at  $\lambda > 355$  nm and room temperature. <sup>b</sup> [ZnTPPS], 0.12 mmol dm<sup>-3</sup>; [(1a)], 6.7 mmol dm<sup>-3</sup>; [TEOA], 12 mmol dm<sup>-3</sup> in aqueous solution. <sup>c</sup> The pH was adjusted by adding 1 mmol dm<sup>-3</sup> NaOH into the reaction mixture of 0.12 mmol dm<sup>-3</sup> ZnTPPS, 5 mmol dm<sup>-3</sup> (1), 12 mmol dm<sup>-3</sup> EDTA and 6.7 mmol dm<sup>-3</sup>. <sup>d</sup> Obtained from the plot of yields of *trans-*(2) vs. time at the initial stage.

classified into four types of systems, *i.e.*  $I \rightarrow I$ ,  $I \rightarrow S$ ,  $S \rightarrow I$  and  $S \rightarrow S$ . Here  $I \rightarrow I$  means that both the sensitizer and (1) are solubilized in the micellar interior (I).  $S \rightarrow I$  shows that the sensitizer is adsorbed on the micellar surface (S) and the dibromide (1) is in the interior, and hence electron transfer should occur across the micellar surface.  $S \rightarrow S$  means that both are adsorbed on the micellar surface and the electron transfer is to occur along the surface. We have studied a number of reaction systems where ZnTPP(S) and (1) are residing in either interior (I) or surface (S) of micellar particles owing to their hydrophobic or electrostatic interaction.<sup>†</sup>

 $<sup>\</sup>dagger$  A more comprehensive review of micellar structure is reported [ref. (10)]; the present results may be interpreted in terms of the depth with which reactants are embedded in the interface region of the micelles. For a classification, however, we adopt here a naive picture of the interior, *i.e.* surface vs. outer region, as a working hypothesis, rather than the final interpretation.





Fig. 1. Spectral changes upon the addition of CTAB to an aqueous ZnTPPS solution of 2.0  $\mu$ mol dm<sup>-3</sup> ZnTPPS at *ca*. pH 7 and room temperature. The concentrations of CTAB are as follows: (1) 0, (2) 2.0, (3) 4.0, (4) 6.0, (5) 8.0, (6) 10.0 and (7) 12.0  $\mu$ mol dm<sup>-3</sup>.

Table 1 clearly indicates that the debromination efficiency as measured by the quantum yield  $\Phi$  is greatly influenced by the type of system, *i.e.* a combination of sensitizer and (1). Note that the participation of the surface (S) is necessary for efficient debromination. The best results were obtained for the S  $\rightarrow$  S case, *i.e.* the adsorption of both the sensitizer (ZnTPPS) and the dibromide (1a) on the cationic micellar surface of cetyltrimethylammonium bromide (CTAB). To clarify the micellar effect more explicitly, ZnTPPS-sensitized debromination of (1a) to give sodium cinnamate (*trans-2a*) was studied in presence of cationic CTAB and reductant TEOA.

The chemical yield of *trans*-2a was almost quantitative, *i.e.* 98%, and the debromination rate was *ca*. 5 times faster than that in a homogeneous solution without CTAB (table 2). The effect of added CTAB on the quantum efficiency became discontinuously greater at  $[CTAB] \approx 1 \times 10^{-4}$  mol dm<sup>-3</sup>, which is close to the c.m.c. of CTAB (*ca*. 0.5 × 10<sup>-4</sup> mol dm<sup>-3</sup>) under the reaction conditions. Above the c.m.c of CTAB, the efficiencies of the debromination were sensitively dependent on the initial pH of the reaction solutions. As shown in table 2, the efficiency at pH.> 7 was *ca*. ten times higher than that in the lower pH region. This clearly reflects the importance of adsorption of the carboxylate ion on the cationic CTAB micelle.



Fig. 2. Quenching of 9-methylanthracene fluorescence by the dibromide anion (1a) in CTAB (○) and SDS (●) micelles. 9-Methylanthracene (0.1 mmol dm<sup>-3</sup>) was dissolved in an aqueous solution containing 4 mmol dm<sup>-3</sup> (*i.e.* above the c.m.c.) of surfactant, irradiated at 290±2 nm and its fluorescence was monitored at 390 nm.

# Adsorption of Anionic ZnTPPS and Dibromides on CTAB Micelles

The Soret band spectrum of ZnTPPS at 421 nm changed significantly, when CTAB was added (fig. 1). The addition of CTAB caused a shift of absorption peak from 421 to 423 nm with an isosbestic point at 426 nm, indicating the formation of an association complex between anionic ZnTPPS and cationic CTAB. The complex formation may be expressed by the following equilibrium

$$ZnTPPS \cdot CTAB \stackrel{\kappa_{d}}{\Longrightarrow} ZnTPPS + CTAB$$
(12)

where  $K_d = [ZnTPPS][CTAB]/[ZnTPPS CTAB]$ . According to the reported procedure<sup>9</sup> the resulting  $K_d$  values were as low as  $3.6 \times 10^{-6}$  and  $6.3 \times 10^{-6}$  mol dm<sup>-3</sup> in the absence and the presence of (1a), respectively, suggesting a facile formation of 1:1 complex between ZnTPPS and CTAB (see Experimental section). The absorption or fluorescence spectra of ZnTPPS was not shifted or changed by the addition of (1a), suggesting no complex formation with (1a).

Since the hydrophobic dibromocarboxylic acid (1b) is difficult to dissolve in water, but easily dissolvable in CTAB micelle solution, the acid is apparently dissolved inside the hydrophobic micelle. The dissociated anion (1a), in turn, is sparingly soluble in water

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Fig 3. Absorption spectra of ZnTPPS<sup>\*3</sup> in the presence of the dibromide (1a) irradiated by a Nd:YAG laser (532.1 nm), (1) 10, (2) 500 and (3) 1000 μs after the irradiation. Initial concentrations: 5 mmol dm<sup>-3</sup> (1a), 0.2 mmol dm<sup>-3</sup> ZnTPPS and 6.7 mmol dm<sup>-3</sup> CTAB in water.

and may possibly interact with the oppositely charged surface of the CTAB micelle. The extent of electrostatic adsorption of (1a) on the CTAB micellar surface was estimated by means of fluorescence quenching of 9-methylanthracene.<sup>†</sup> Fig. 2 shows that the fluorescence of 9-methylanthracene dissolved inside CTAB micelle is quenched efficiently by (1a). At a molar ratio of (1a) to CTAB > 1.2, the fluorescence quenching by (1a) almost levels off. This observation indicates that the 9-methylanthracene fluorescence is effectively quenched by (1a) electrostatically adsorbed on CTAB micelles. We can deduce the aggregation percentage of (1a) on the CTAB micelle to be *ca*. 90% from the saturation point at [1a] = 3.6 mmol dm<sup>-3</sup> for fluorescence quenching in the presence of 4.0 mmol dm<sup>-3</sup> CTAB. In contrast, the addition of an anionic surfactant such as sodium dodecylsulphate (SDS) had no effect, the quenching by (1a) being inefficient. Negatively charged (1a) is repelled by the anionic micelle surface, so that (1a) may not be in close contact with 9-methylanthracene inside the micelle.

† The oxidative quenching of 9-methylanthracene ( $E_{ox} = 1.45$  V vs. SCE in aqueous 0.1 mol dm<sup>-3</sup> CTAB solution) with (1a) should be an efficient process as judged from the free-energy change for the one-electron transfer ( $\Delta G = 0$ ).

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run	donor	acceptor	reductant	system <sup>b</sup>	quantum yield Φ for the debromination <sup>c</sup>	
1 2 3 4 5	ZnTPPS ZnTPPS ZnTPPS ZnTPPS ZnTPPS	(1 a) (1 a) (1 a) (1 a) (1 b)	TEOA TEOA TEOA TEOA EDTA	$O \to O^{d}$ $O \to O^{e}$ $S \to S$ $S \to S$ $S \to I$	$\begin{array}{c} 0.28 \pm 0.04 \\ 0.10 \pm 0.02 \\ 1.39 \pm 0.01'(11 \pm 2)^{h} \\ 1.47 \pm 0.01^{g} \\ 0.36 \pm 0.01 \end{array}$	

Table 3. Efficiency for the photosensitized debromination of (1) in various systems<sup>a</sup>

<sup>a</sup> Aqueous solution of 0.12 mmol dm<sup>-3</sup> donor, 6.7 mmol dm<sup>-3</sup> acceptor, 12 mmol dm<sup>-3</sup> TEOA, a reductant and 6.7 mmol dm<sup>-3</sup> CTAB was degassed by three freeze-thaw cycles and photolysed at  $426 \pm 10$  nm with a 150 W xenon lamp. <sup>b</sup> The symbols I, S and O represent the interior, the micelle surface and the bulk solution out of micelles, respectively. The arrow indicates the direction of electron transfer. <sup>c</sup> The yields were determined from the formation of *trans*-(2). <sup>d</sup> Debromination in the absence of CTAB. <sup>e</sup> Determination in the absence of CTAB under air. <sup>f,g</sup> Incident light quanta absorbed by ZnTPPS are  $1.03 \times 10^{-8}$  and  $3.4 \times 10^{-9}$  mol min<sup>-1</sup>, respectively. <sup>h</sup> The figure in parenthesis is the quantum yield in the presence of 200 mmol dm<sup>-3</sup> TEOA.

In summary, the CTAB micelles efficiently adsorb both ZnTPPS and dibromide anion (1a) on their surface, and thereby place the two reagent molecules closer.

## Comparison of Three Electron-transfer Systems, $S \rightarrow S$ , $S \rightarrow I$ and $O \rightarrow O$

As described in the preceding paper,<sup>6</sup> the present photodebromination is initiated by a one-electron transfer from the excited triplet ZnTPPS<sup>\*3</sup> to the dibromide (1). Irradiation of a 0.2 mmol dm<sup>-3</sup> ZnTPPS aqueous solution in the presence of 5 mmol dm<sup>-3</sup> (1a) and 6.7 mmol dm<sup>-3</sup> CTAB with a laser beam (532.1 nm) from the Nd:YAG laser resulted in the formation of ZnTPPS<sup>\*3</sup> within 0.01 ms, as shown in fig. 3. The following electron transfer is apparent, since the spectrum changed within 1 ms to the ZnTPPS radical cation, with an absorption maximum at *ca*. 660–700 nm, which is in agreement with the reported spectra<sup>11</sup> (fig. 3).

The solubilization sites of (1) in the CTAB micelle may be controlled by the charge of (1) whereas negatively charged ZnTPPS is adsorbed on the cationic surface of the micelle. Thus the present debromination system may be classified into the following three types, *i.e.* systems  $S \rightarrow S$ ,  $S \rightarrow I$  and  $O \rightarrow O$ , depending on the charge on the substrate (1). The system  $O \rightarrow O$  indicates electron transfer in the bulk solution. The quantum efficiencies in these systems are summarized in table 3. The cationic CTAB micelle accelerated the sensitized photodebromination of anionic (1a), *i.e.* system  $S \rightarrow S$ . The efficiency of the debromination by  $S \rightarrow I$  was much lower than that by  $S \rightarrow S$  and was comparable with that in the bulk solution ( $O \rightarrow O$ ).

The efficiency is surely controlled not only by electron transfer [eqn (6)] but also by the radical chain length of the subsequent chemical sequences [eqn (7)–(10)]. For example, the quantum yields for debromination in the CTAB micellar solutions increased with increasing concentration of dibromide anion (1a) and was > 1 at concentrations > 6 mmol dm<sup>-3</sup> (fig. 4). The enhancement indicates that radical-chain debromination becomes important at higher concentrations of (1a). Furthermore, the photodebromination was enhanced significantly at the higher concentrations of TEOA (fig. 5). The limiting quantum yields at [TEOA] =  $\infty$  are estimated to be > 20 in the presence of CTAB micelle. The quantum efficiencies decreased steadily with decreasing TEOA concentration; the limiting quantum yields,  $\Phi_0$ , extrapolated to [TEOA] = 0, where the chain reaction is of no importance, were 0.25 and 0.05 in the presence and absence of

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Fig. 4. Dependence of the quantum yields on the concentration of dibromide (1) under various conditions: reaction in water with 2.4  $\mu$ mol dm<sup>-3</sup> ZnTPPS and 12 mmol dm<sup>-3</sup> TEOA; (a) (1a) and 6.7 mmol dm<sup>-3</sup> CTAB ( $\odot$ ); (b) (1a) and the homogeneous solution without CTAB ( $\bigcirc$ ).

CTAB, respectively (fig. 5). The concentration dependence clearly suggests that the photochemical debromination proceeds *via* a chain reaction and the reductant TEOA plays a crucial role.

The net electron transfer yields  $(\Phi_{\rm ET})$  [eqn (6)] may be represented as the limiting quantum yields  $(\Phi_0)$  by minimizing the effect of the subsequent processes. Thus the limiting quantum yields  $(\Phi_0)$  can be estimated according to

$$\Phi_{0} = \Phi_{\rm ST} \frac{\tau_{0} - \tau}{\tau_{0}} \frac{k_{7}}{k_{\rm p} + k_{7}}$$
(13)

as a product of efficiencies for the related elementary steps. Here,  $\Phi_{\rm ST}$  is the efficiency for the formation of ZnTPPS<sup>\*3</sup> (reported to be 0.85),<sup>12</sup>  $\tau_0$  and  $\tau$  denote the lifetimes of ZnTPPS<sup>\*3</sup> in the absence and the presence of (1), respectively. The second term,  $(\tau_0 - \tau)/\tau$ , represents a fraction for the quenching of ZnTPPS<sup>\*3</sup> with (1), and may be measured by a laser flash study. The third term,  $k_7/(k_b + k_7)$ , denotes the fraction of the debromination process  $[k_7$  in eqn (7)] in the decay processes of (1<sup>-</sup>), which are the debromination [eqn (7)] and back electron transfer  $[k_b$  in eqn (14)]. The resulting lifetimes, quenching constants  $(k_q)$ , and quantum yields  $(\Phi_0)$  are summarized in table 4. It is easily expected that the back electron transfer

$$ZnTPPS^{+} + (1^{-}) \xrightarrow{k_{b}} ZnTPPS + (1)$$
(14)

is an important retarding factor for the debromination. A direct measurement of the  $k_{\rm b}$  value was unsuccessful with the available laser flash apparatus, but the value may be deduced according to eqn (13) from the  $\Phi_0$  value and the fraction of ZnTPPS<sup>\*3</sup> quenching by (1).

Inspection of the values of  $(\tau_0 - \tau)/\tau_0$  in table 4 reveals that most of ZnTPPS<sup>\*3</sup> is quenched effectively by dibromides under the reaction conditions. The most interesting point in table 4 is that the limiting quantum yields ( $\Phi_0$ ) are affected most by the de-



Fig. 5. Dependence of the quantum yields of the debromination on [TEOA] with 2.4 μmol dm<sup>-3</sup> ZnTPPS in water: (a) 6.7 mmol dm<sup>-3</sup> 1a and 6.7 mmol dm<sup>-3</sup> CTAB (●); (b) 6.7 mmol dm<sup>-3</sup> (1a), homogeneous without CTAB (○); (c) 6.7 mmol dm<sup>-3</sup> (1b) and 6.7 mmol dm<sup>-3</sup> CTAB (●). EDTA was used in place of TEOA in case (c).

Table 4.	Quantum	yields,	lifetimes,	rate	constants	for	the	quenching	and	debromination
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-11	quer	nching study	det	promination	
system <sup>a</sup>	$(\tau_0 - \tau) / \tau_0^{\ b}$	$k_{\rm q}/{\rm dm^3\ mol^{-1}\ s^{-1}}$	$\Phi_0{}^d$	$k_{7}/(k_{7}+k_{b})^{e}$	
$S \rightarrow S$ $S \rightarrow I$ $O \rightarrow O$	0.96 0.68 0.87	$\begin{array}{c} (2.5\pm0.3)\times10^6\\ (2.1\pm0.3)\times10^5\\ (6.5\pm0.2)\times10^5\end{array}$	0.25 0.06 0.05	0.33 0.10 0.068	

<sup>a</sup> Definition of the systems  $S \rightarrow S$ ,  $S \rightarrow I$  and  $O \rightarrow O$  are described in the text. <sup>b</sup> Fraction for the electron-transfer quenching of ZnTPPS<sup>\*3</sup> by (1) for the case of 6.7 mmol dm<sup>-3</sup> (1) without TEOA. <sup>c</sup> The quenching rate constant of ZnTPPS<sup>\*3</sup> with (1) obtained by a laser flash spectroscopy (see Experimental section for details). <sup>d</sup> The limiting quantum yields ( $\Phi_0$ ) for debromination extrapolated to zero concentration of TEOA from fig. 5. <sup>e</sup> The fraction of debromination plotted against the consumption of (1<sup>-</sup>) involving back electron transfer at zero concentration of TEOA.

bromination efficiency,  $k_7/(k_7+k_b)$ , which varies in the order:  $S \rightarrow S \rightarrow I > O \rightarrow O$ . The order is governed by the retarding effect of the micelle surface for the back electron transfer. It is recognized that efficiencies for back electron transfer are affected by electrostatic forces between D<sup>+</sup> and A<sup>-</sup> [eqn (14)].<sup>13,14</sup> However, this is not the case for  $S \rightarrow S$ , since ZnTPPS<sup>+</sup> and (1<sup>-</sup>) formed by the one-electron transfer are neutralized and kept close together on the cationic micellar surface. Hence the electrostatic repulsion between the two ions is expected to be much less effective than that in  $O \rightarrow O$ . The apparent five-fold efficient retardation for the back electron transfer in  $S \rightarrow S[k_7/(k_7+k_b)$  values in table 4] may also be explicable on the basis of the enhanced reactivity of (1) adsorbed during bromide-ion release [eqn (7)]. Elimination of the bromide ion from (1<sup>-</sup>) is expected to be accelerated by the charged electrostatic field

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forming an electron double layer, *i.e.* the Stern region. Such a highly polar region would promote the release of bromide ion from the doubly charged radical anion of (1a) [eqn (7)]. Mizuno and Otsuji<sup>15</sup> recently found a related salt effect on the photosensitized one-electron oxidation of arylcyclopropanes.

Note also that the quenching rate constant is the highest for the system  $S \rightarrow S$  and decreases in the order  $S \rightarrow S > O \rightarrow O > S \rightarrow I$  (table 4). This is readily understood by assuming that the CTAB micelle helps the two ions with the same charge [*i.e.* ZnTPPS and (1a)] to come closer to each other, resulting in an efficient electron transfer on the micellar surface. In the absence of CTAB surfactant (*i.e.* the system  $O \rightarrow O$ ), the similarly charged species repel each other to lower the electron transfer efficiency. In the case of  $S \rightarrow I$ , electron transfer from ZnTPPS<sup>\*3</sup> to (1b) is less efficient than that for  $S \rightarrow S$ . This is readily understood, since the hydrophobic acid (1b) is dissolved in the non-polar micelle interior.

#### **Oxygen Inhibition of the Debromination**

The present photodebromination of (1a) with ZnTPPS and TEOA was affected by oxygen. A short induction period (*ca*. 4 min) was observed for the debromination of (1a) in an aerated CTAB micellar solution. However, the reaction rate after the induction period was comparable to that under deaerated conditions. In contrast, the reaction without CTAB under aerated conditions was slowed to 60% without an induction period.

Molecular oxygen readily penetrates the micelles and quenches excited sensitizers in micelles as well as in homogeneous solutions.<sup>16</sup> In fact, no excited triplet absorption  $(\lambda_{max} = 840 \text{ nm})$  of ZnTPPS was observed for both systems under aerated conditions. The rate of debromination, however, in the aerated micellar solution was practically the same as that under deaerated conditions. This micellar effect is of interest in relation to electron transfer in biological systems, where such processes should be facile under aerated conditions.<sup>17</sup>

In summary, we have found an interesting micellar effect in the photosensitized debromination of the dibromide (1) in the presence of ZnTPP(S) and TEOA, where the efficiency can be controlled by changing the charges of the sensitizer and substrate. Electron transfer on the surface  $(S \rightarrow S)$  takes place most efficiently in comparison with that across the surface  $(S \rightarrow I)$  or in the bulk  $(O \rightarrow O)$ . A radical chain reaction plays an important role in the debromination at higher concentrations of TEOA, resulting in quantum yields  $\ge 10$ . The S  $\rightarrow$  S system is shown to be most effective for net electron transfer and also for chain debromination owing to the micellar effect in concentrating the substrate.

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