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Kinetic Studies of the Nucleophilic Quenching of Photoexcited Nitroaryl Ethers (NArE) by Bromide Ions in Cationic Micellar Solution

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Abstract : *Nucleophilic aromatic photosubstitution reactions of nitroaryl ethers (NArE) with sodium hydroxide were studied in aqueous solution containing N-hexadecyl-N,N,N-trimethylammonium chloride micelles. The increase of quantum yields depended on the length of the n-alkyl chain (maximum for methyl and minimum for decyl). The dependence on the surfactant concentration was in accordance with the mechanistic model of aromatic nucleophilic photosubstitution .*

INTRODUCTION

The first detailed study of micellar effects on bimolecular photoreactivity was the work of Hautala and Letsinger[1] on nucleophilic aromatic photosubstitution reactions. They found that the cationic detergent N-hexadecyl-N,N,N-trimethylammonium chloride (CTACl) markedly increased the quantum yield of photocyanation of 4-methoxy-1-nitronaphthalene, but had little or no effect on the photocyanation reactions of 4-nitrophenyl ethers.

One of the major interests in our study[2] of chemical reactivity in aqueous micellar solutions of simple detergents has been the separation of effects on the probe in high local concentrations in the amphiphilic pseudo-phase relative to those in the bulk concentration. In this work the quantum yield of the alkaline photohydrolysis of 3,5-dinitroanisole was shown to decrease significantly in the presence of micellar N-tetradecyl-N,N,N-trimethylammonium chloride. It was concluded that the decrease in the quantum yield in the presence of micelles is due to kinetic factors, principally a shorter 3,5-dinitroanisole triplet lifetime in the micellar pseudo-phase. In recent work[3] we made a full mechanistic study of nucleophilic aromatic photosusbtitution in water solution for nitroaryl ethers (NArE = 3-nitroanisole **1** , 2-chloro-5-nitroanisole **2** and 2-bromo-5-nitroanisole **3**) probes. Our preliminary experiments confirmed that photohydrolysis of NArE in aqueous solutions is in accord with eq. 1 with a limiting quantum yield at high $[OH^-]$ (ϕ_{aq}^{∞}) of 0.30, 0.41 and 0.29 and a Stern-Volmer constant (K_{SV}) for quenching of aqueous excited NArE by $[OH^-]$ of 510 M^{-1},490 M^{-1} and 360 M^{-1}, respectively, for the probes **1**, **2** and **3**.

$$1/\phi = (1/\phi^{\infty}) \{ 1+ 1/ K_{SV} [OH^-] \} \qquad (1)$$

From the change in the decay constant of the initial laser-induced absorption[3] in aqueous solutions of these probes in the presence of [Br⁻], we obtain values of K'_{SV} for quenching excited $\mathbf{1}^{3*}$, $\mathbf{2}^{3*}$ and $\mathbf{3}^{3*}$ by [Br⁻] of $5000M^{-1}$, $5100M^{-1}$ and $3800M^{-1}$, respectively.

In this paper, we report the micellar (CTACl) effects on the photoreactions of **1**, **2**, **3** and n-decyl 3-nitrophenyl ether **4**. The quantum yields of product formation obtained in N-hexadecyl-N,N,N-trimethylammonium chloride (CTACl) micelles in the absence or in the presence of added NaBr were analyzed according to the mechanistic model proposed for 3,5-dinitroanisole photohydrolysis in TTACl micelles.[2]

The concept of counter ion exchange at the surface of ionic micelles was used in this work for the quantitative analysis of the quantum yield of product in micellar CTACl in the presence of two or three counterions.[4] In particular, several studies have investigated the evolution of the composition of the Stern-layer as a function of the total concentrations of counter ions in the solution or to evaluate selectivity coefficients for ion exchange of inorganic counter ions.[4-12]

EXPERIMENTAL

The preparation and purification of reactants and hexadecyltrimethylammonium chloride (CTACl) have been described.[3,6]

n-Decyl 3-nitrophenyl ether(**4**) was prepared by refluxing the 3-nitrophenoxide ion (**5**) (5.0g) with 1-bromodecane in N,N-dimethylformamide for 19 h, after which the solution was cooled and poured onto ice. Filtration and recrystallization of the precipitate from ethanol-water (80:20, V:V), gave 3,8 g of **4**, mp 30.5-31.5 °C .Compound **4** was identified by elemental analysis. (Found: C, 68.70; H, 8.80; N, 5.00. $C_{18}H_{25}NO_3$ requires C, 68.81; H, 8.96; N, 5.02%).

The critical micelle concentration (cmc) of CTACl in added electrolyte was measured by surface tension at 30°C under an atmosphere of N_2 and no minimum was observed. The value of the cmc is 0.28 mM with 0.01M NaOH.

Absorption spectra and measurements at fixed wavelength were recorded on a Hewlett-Packard 8452A diode array and Carry 2200 spectrophotometer. Measurements of apparent pH were carried out at 30°C with a Micronal B 374 pH meter, equipped with a glass electrode calibrated against standard buffers solutions (Merck).

Photoreaction quantum yields were determined essentially as described previously using a conventional merry-go-round apparatus thermostated at 30°C and equipped with a 450W Hanovia medium pressure mercury lamp.[3]

For the photohydrolysis studies of NArE, the appropriate quantity of standard 0.100 M NaOH containing NArE (2.5 - 3.0 X 10^{-4}M) was added to the filtered aqueous NArE stock (2.5 - 3.0 X 10^{-4} M) with CTACl 0.100M , in the dark, followed by filtration through a Millipore 220 nm membrane filter. For studies of photohydrolysis of NArE in micellar solution, the filtered basic NArE in CTACl 0.1 M stock was used to prepare solutions containing NArE (2.5 - 3.0 X 10^{-4} M), NaOH (0.01 M) and CTACl (0.0 -0.08 M). For studies of quenching by sodium bromide , an appropriate quantity of standard 0.100M NaOH solution of sodium bromide (0.100M) and the filtered basic NArE in CTACl 0.100 M stock were used to prepare solutions containing NArE (2.5 - 3.0 X 10^{-4} M), NaBr (0.0 - 2,0 mM), NaOH (0.01 M) and CTACl (0.0-0.08 M).

Aliquots (3.00 mL) of each final NArE solution contained in 1 cm pathlength Teflon-stoppered quartz absorbance cells, were subjected to sequential irradiations at 313 nm. The absorbance changes were followed at 313 nm and 410 nm . Photoreaction quantum yields (Φ) were calculated from the variation of the optical densities at 313 nm and 410 nm. Apparent extinction coefficients at 410 nm for 3-nitrophenoxide **5**, 2-chloro-5-nitrophenoxide **6** and 2-bromo-5-nitrophenoxide **7** ions were determined independently as a function of added detergent (the phenoxide ions **5**, **6** and **7** are referred in this paper by the general term NArP).

The method based on detergent-induced shifts of spectral absorptions[13] was used to determine the pseudo-phase partitioning coefficients (K_S) for incorporation of **1** (270 nm and 310 nm), **2** (280 nm and 300 nm)and **3** (225 nm and 250 nm), into CTACl micelles. Aliquots of an aqueous solution of NArE, contained in 1-cm path length quartz absorption cells were thermostated at 30.0 °C. After measuring the initial absorbance ($A_{aq}°$) at fixed wavelength (225 - 310 nm) vs. a water reference, successive aliquots of two concentrated aqueous 0.400M CTACl stock solutions, one of them containing NArE (2.5 - 3.0 x 10^{-4}M), were added via a calibrated Hamilton microliter syringe to both the sample and reference cells, the absorbance (A_T) being remeasured after each addition. The absorbance values as a function of total $[\mathrm{CTACl}]_T$ were plotted according to equation 2 to obtain K_S values as previously described.[13]

RESULTS AND DISCUSSION

Binding of NArE to the CTACl Micelle. Aqueous solutions of NArE exhibit a broad, structureless long wavelength absortion band with a λ_{max} of 327 nm, 328 nm and 330 nm, respectively, for **1** (ε = 2290 $M^{-1}s^{-1}$), **2** (ε = 4000 $M^{-1}s^{-1}$), **3** (ε = 4300 $M^{-1}s^{-1}$). Upon addition of CTACl above its critical micelle concentration (cmc = 1.3×10^{-3} M),[6] there is a slight increase in intensity of these absorptions bands with no shift in the λ_{max}. By measurement of the absorption changes for **1** (270 and 310 nm), **2** (280 and 300 nm) and **3** (225 and 250 nm) as a function of CTACl concentrations, equilibria constants (K_S)[2,13] of 80 M^{-1}, 155 M^{-1} and 280 M^{-1} were obtained for **1**, **2**, and **3** , respectively, for incorporation of NArE probes into the micellar pseudo-phase of CTACl (equations. 2, 3 and 4).

In these calculations an appropriate cmc = 2.8×10^{-4} M for CTACl in presence of 0.01 M NaOH was employed. Using the absorption data and these values of K_S, we found the ratio of the extinction coefficients of micellar (ε_{mic}) and aqueous (ε_{aq}) for all probes at the excitation wavelength of 313 nm to be $\varepsilon_{mic}/\varepsilon_{aq} = 1.00 \pm 0.02$.

$$1 / (A_T - A_{aq}^{\circ}) = \{1 / (A_{mic}^{\circ} - A_{aq}^{\circ})\}\{(1 + 1 / (K_S([\mathrm{CTACl}]_T - \mathrm{CMC}))\} \qquad (2)$$

$$NArE_{aq} + CTACl_{mic} \overset{K_S}{\rightleftharpoons} NArE_{mic} \qquad (3)$$

$$K_S = \frac{[NArE]_{mic}}{[NArE]_{aq}([CTACl]_T - cmc)} = \frac{[NArE]_{mic}}{[NArE]_{aq}C_D} \qquad (4)$$

Binding of NArP to the CTACl micelle. In alkaline aqueous solutions, the long wavelength absorptions band for 3-nitrophenoxide **5**, 2-chloro-5-nitrophexoxide **6** and 2-bromo-5-nitrophenoxide **7** ions have a λ_{max} of 390 nm (ε_5 1450 $M^{-1}s^{-1}$), 400 nm (ε_6 1920 $M^{-1}s^{-1}$) and 402 nm (ε_7 2390 $M^{-1}s^{-1}$), respectively. Above the cmc of CTACl, these bands shifts to longer wavelength (λ_{max} = 410 nm) and the extinction coefficients of micellar solutions are 1500±50 $M^{-1}s^{-1}$, 1960±40 $M^{-1}s^{-1}$, and 2350±80 $M^{-1}s^{-1}$ respectively for ions **5**, **6** and **7**. These data of ε_{NArP} were used for calculations of ϕ_T.

Alkaline Photohydrolysis of NArE. In the presence of Micellar CTACl. On the basis of the data of quantum yields for formation of nitro aryloxide ion (ϕ_T) in the photohydrolysis of NArE with hydroxide ion in water reported previously, [3] we suggest an overall kinetic scheme for the reactions in question by addition of NaBr during alkaline photohydrolysis of NArE ethers in CTACl solutions (Scheme 1).

By definition, the overall quantum yield for (ϕ_T) formation of ArNP ions is given by equation 5, where the "aqueous" (ϕ_a) and "micellar" (ϕ_{mic}) contributions were separated for convenience.

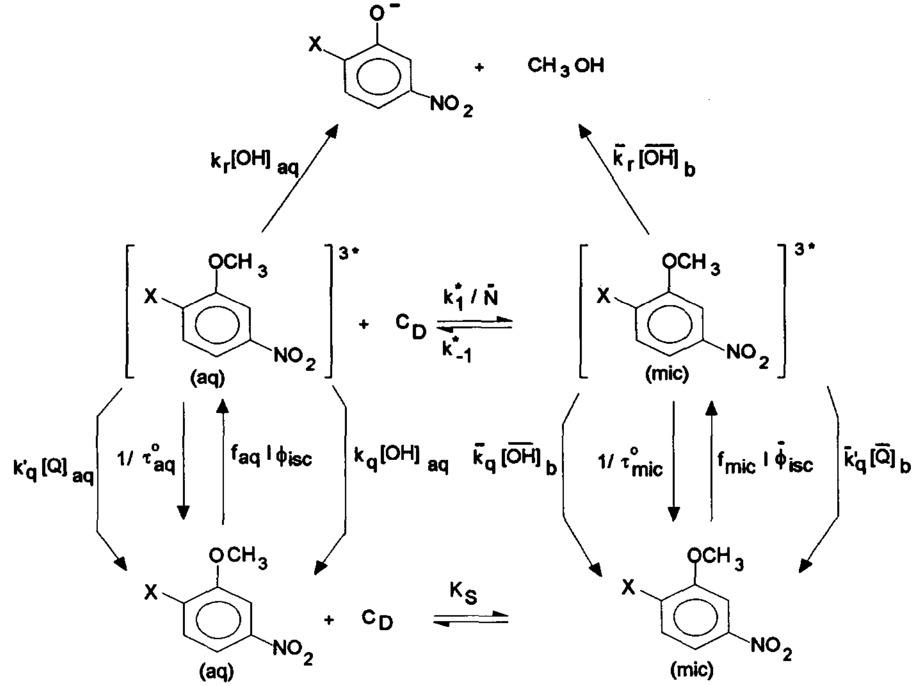
$$\phi_T = (k_r [OH]_{aq} [NArE^{3*}]_{aq} + \bar{k}_r [OH]_b [NArE^{3*}]_{mic}) / I = \phi_a + \phi_{mic} \qquad (5)$$

Using Scheme 1 and a conventional steady-state kinetic treatment of the excited state concentrations one can demonstrate that equations 6 and 7 apply.

$$\phi_a = \frac{f_{aq}\,\phi_{aq\infty}\,K_{sv}[OH]_f\{ (1+(k_{-1}{}^{*}\tau_{mic}{}^{\circ})+\bar{K}_{sv}[\overline{OH}]_b+\bar{K}_{sv}'[\bar{Q}]_b)\} + f_{mic}\,\bar{\phi}_{ISC}\,\beta_{aq}K_{sv}[OH]_f\,(k_{-1}{}^{*}\,\tau_{mic}{}^{\circ})}{\{(1+(k_{-1}{}^{*}\tau_{mic}{}^{\circ})+\bar{K}_{sv}[\overline{OH}]_b+K_{sv}'[Q]_b)\}\{(1+(k_1{}^{*}\tau_{aq}{}^{\circ})C_D/N+K_{sv}[OH]_f+K_{sv}'[Q]_f)\} -(k_1{}^{*}\tau_{aq}{}^{\circ})\,(k_{-1}{}^{*}\tau_{mic}{}^{\circ})C_D/N} \qquad (6)$$

$$\phi_{mic} = \frac{f_{mic}\,\phi_{mic\infty}\,\bar{K}_{sv}[\overline{OH}]_b\{ (1+(k_1{}^{*}\tau_{aq}{}^{\circ})C_D/N+K_{sv}[OH]_f+K_{sv}'[Q]_f)\}+f_{aq}\,\phi_{ISC}\,\beta_{mic}\bar{K}_{sv}[\overline{OH}]_b(k_1{}^{*}\,\tau_{aq}{}^{\circ})\,C_D/N}{\{(1+(k_{-1}{}^{*}\tau_{mic}{}^{\circ})+\bar{K}_{sv}[\overline{OH}]_b+\bar{K}_{sv}'[\bar{Q}]_b)\}\{(1+(k_1{}^{*}\tau_{aq}{}^{\circ})C_D/N+K_{sv}[OH]_f+K_{sv}'[Q]_f)\} -(k_1{}^{*}\tau_{aq}{}^{\circ})\,(k_{-1}{}^{*}\tau_{mic}{}^{\circ})C_D/N} \qquad (7)$$

Scheme 1



X = H, Cl and Br

In the present study we utilized equations 5 - 13 that describe contributions of ϕ_{aq} and ϕ_{mic} to overall quantum yield (ϕ_T) for the formation of ArNP ions, according to the general kinetic model for the photohydrolysis of ArNE ethers under alkaline conditions in micellar cationic solution.[2]

The unknown concentrations of anion [OH] and [Q] = [Br], not shown in Scheme 1, can be determined by employing the ion exchange model.[4] For OH^- reactive ion and Cl^- non-reactive ion as micelle counterion, the ion-exchange equilibrium can be expressed by equation 8, whose selectivity-coefficient is given by equation 9.

$$OH_f + Cl_b \overset{K_{OH/Cl}}{\rightleftharpoons} OH_b + Cl_f \tag{8}$$

$$K_{OH/Cl} = [OH]_b[Cl]_f / [OH]_f[Cl]_b \tag{9}$$

and the following expression for $[OH]_b$ (eq. 10) can be used:

$$[OH]_b = \{-A_1 + [A_1^2 + 4(1 - K_{OH/Cl})[OH]_T K_{OH/Cl}\, \beta C_D\,]^{1/2}\} / [2(1 - K_{OH/Cl})] \tag{10}$$

where $A_1 = (1 - \beta)C_D + \text{cmc} + K_{OH/Cl}\,[OH]_T + \beta C_D\, K_{OH/Cl}$, "b" denotes micellar and "f "denotes bulk. If β is the degree of counter-ion binding to the micelle then

$$[OH]_b + [Cl]_b = \beta([CTACl] - cmc) \quad (11)$$

$$[OH]_f + [OH]_b = [OH]_T \quad (12)$$

$$[Cl]_f + [Cl]_b = [Cl]_T = [CTACl]_T \quad (13)$$

where T denotes the total and cmc the critical micelle concentrations, respectively.

When n-decyl 3-nitrophenyl ether ((**4**), hydrophobic and water insoluble) was irradiated in alkaline micellar CTACl aqueous solutions in the absence of Br^- ion, ion **5** was formed as the only photoproduct. Overall quantum yields for the production of ion **5** were measured at 410 nm at different $[OH^-]$ concentrations. The variation of the quantum yields of decyloxy group substitution of **4** with $[OH^-]$ in the presence of [CTACl] are given in Table 1.

n-Decyl 3-nitrophenyl ether (**4**) was selected because it possesses both the 3-nitrophenoxy chromophore and an apolar chain sufficiently long to ensure incorporation of the probe in the micelles.Thus the photoreaction of 4^{3*} occurs only in the micellar phase ($f_{aq} = 0, \tau^{\circ}_{mic} = 120$ ns)[14] and the appropriate expression for (ϕ_{mic}) is given by equation 14.

$$\phi_{mic} = \phi_{mic}^{\infty} \bar{K}_{SV} [\overline{OH}]_b / (1 + \bar{K}_{SV} [\overline{OH}]_b) \quad (14)$$

where $\phi_{mic}^{\infty} = \phi_{isc} \beta_{mic}$ and $\bar{K}_{SV} [\overline{OH}]_b = \bar{K}_{SV} [OH]_b / \bar{V} C_D$.[2,4]

Table 1: Overall quantum yields for production 3-nitrophenolate ion **5** in the photohydrolysis of **4** with hydroxide ion in aqueous micellar CTACl at different $[OH^-]$.

[CTACl] (x 10^3 M)	Quantum Yield of **5** (ϕ_5)		
	5 mM NaOH	10mM NaOH	15mM NaOH
10	0.22	0.25	0.24
15	0.20	0.25	0.22
20	0.22	0.23	0.23
25	0.21	0.23	0.19
30	0.20	0.23	0.18
35	0.17	0.19	0.20
40	0.16	0.18	0.20
45	0.19	0.18	0.21
50	0.16	0.19	0.20
55	0.15	0.17	0.20
60	0.15	0.18	0.19
65	0.14	0.16	0.20
70	0.15	0.18	0.20
75	0.15	0.18	0.19
80	0.14	0.17	0.18

The analytical concentration $[OH]_b$ of bound ion in this work was related to the local concentration $[OH]_b$ in the micellar pseudophase by the use of the expression $[\overline{OH}]_b = [OH]_b / C_D \bar{V}$, where $\bar{V}$ is the effective volume ($\bar{V} = 0.37\ M^{-1}$)[15] per mole of micellized detergent. Regression analysis of the dependence of ϕ_{mic}^{-1} upon $C_D/[OH]_b$ for the photohydrolysis of **4** case, using the values of the Table 1, gave the linear equation (r = 0.999), $\phi_{mic}^{-1} = (3.85 \pm 0.005) + (0.0166 \pm 0.0001)$, corresponding to a limiting quantum yield at high OH^- $\phi^{\infty}_{mic} = 0.26$ and a Stern-Volmer constant $\bar{K}_{SV}$ ($\bar{K}_{SV} / \bar{V} = 60{,}24 \pm 0.36$, $\bar{V} = 0.37\ M^{-1}$) for quenching of micellar excited **4** by $[OH^-]$ of $22.3 \pm 0.1\ M^{-1}$. Since $\bar{K}_{SV} = \bar{k}_{OHb} \tau^{\circ}_{mic}$, calculation of $\bar{k}_{OHb}$, the second order rate constant for quenching of excited **4** by $[\overline{OH^-}]_b$, using the triplet lifetime of **4** (τ°_{mic} =120ns)[14] in nondeoxygenated aqueous micellar 0.100 M CTACl solution provides a value of 1.8 ± 0.1 x 10^8 $M^{-1}s^{-1}$. Comparison of this value with that for quenching of **1** triplet state in aqueous solution by $[OH^-]$ (k_{OH} =3.2 x 10^8 $M^{-1}s^{-1}$)[3] clearly implies that the reactive state is the triplet state of **4**. This analysis strongly supports the proposed photochemical model, indicating that there is alkaline photohydrolysis in cationic micellar phase.

The experimental data for the quantum yield (ϕ_T) for formation of NArP ions as a function of CTACl concentration at $[OH^-]_T$ = 0.01M are shown in Figure 1.

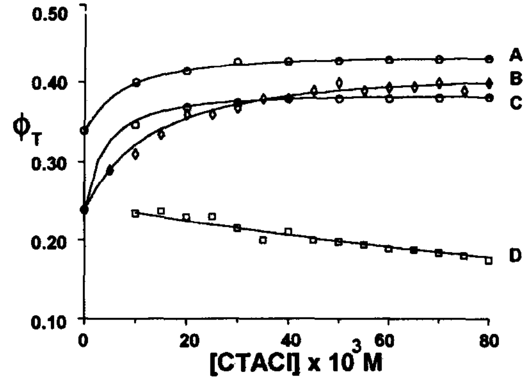


Figure 1. CTACl concentration dependence of the observed quantum yield for alkaline photohydrolysis of NArE in the presence of $[OH]_T$=1.0 x 10^{-2}M. (A) **2**, (B) **1**, (C) **3** and (D) **4**.

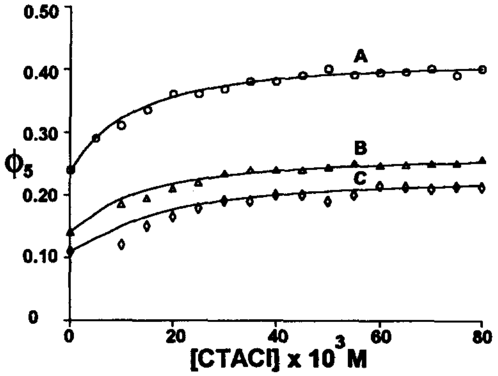


Figure 2 . CTACl concentration dependence of the observed quantum yield for alkaline photohydrolysis of **1** in presence of $[OH]_T$=1.0 x 10^{-2}M. (A) [NaBr]=0.0, [NaBr]=1.0 x 10^{-3}M, and (C) [NaBr]=2.0 x 10^{-3}M.

An increase in the quantum yield (ϕ_T) of ions **5**, **6** and **7** is observed with increase of CTACl concentration. For alkaline photohydrolysis of **4** (Figure 1,curve D) the value of ϕ_T decreases slightly with increasing [CTACl]. The alkaline photohydrolysis of **4** by micelles of CTACl demonstrates that the observed inhibition is due primarily to a small decrease in the lifetime of micellar **4** triplet state (τ^{o}_{mic} = 120 ns), rather than to an intrinsic change in the photoreactivity of the triplet state.

Calculation on computer of the theoretical curves A, B and C from equations 2 - 13 using the experimental data for ϕ_T and the data of Table 2 resulted in good agreement with experimental data (Figure 1). For compound **4** the theoretical curve (Curve D) was calculated by the appropriate equation, equation 14). As can be seen from Figure 1 a very reasonable fit, was obtained being the assumed value[5] for $K_{OH/Cl}$ = 0.13 (see Table 2) is fully consistent with the experimental results. It should be noted that the experimental and calculated values of ϕ_T for compounds **1** and **3** are similar over the range of C_T studied, but in the case of **2**, the ϕ_T values are systematically larger at any given C_T value. Futher, it is noteworthy that for compound **4**, the variation in the experimental and calculated values of ϕ_T with C_T is quite different to that of compounds **1**, **2**, and **3** and ϕ_{ArNP} steadily decreases with increasing C_T value.

Table 2 : Best-fit parameters for alkaline photohydrolysis of NArE in micelar CTACl at 30°C.

Parameters	**1**	**2**	**3**	**4**
CMC (M)	$2.8 . 10^{-4}$	$2.8. 10^{-4}$	$2.8 . 10^{-4}$	$2.8.10^{-4}$
K_S (M^{-1})	80	155	280	
$\phi_{aq}°$	0.25	0.34	0.24	
ϕ_{aq}^{∞}	0.30	0.41	0.29	
K_{SV}(M^{-1})	510	490	360	
k_q' (Br^-) (M^{-1})	5000	5100	3800	
$\tau_{aq}°$ (ns)	1400	1880	625	
$\tau_{mic}°$ (ns)	1200	1275	310	120
N	100	100	100	
ξ_{mic}/ξ_{aq}	1.0	1.0	1.0	
$[OH^-]_T$ (M)	0.01	0.01	0.01	0.01
β	0.8	0.8	0.8	
$K_{OH/Cl}$	0.13	0.13	0.13	
$K_{OH/Br}$	0.08	0.08	0.08	
$\bar{K}_{SV}/\bar{V}$	1000	1300	950	60

It can be see (Figure 1) alkaline photohydrolysis of **1**, **2** and **3** in the presence of micelle CTACl results in a significant increase in ϕ_T in relation to the $\phi_{aq}°$ values (that is the value ϕ_T at $C_T = 0.0$). Since there is good agreement betwen the experimental and theoretical curves calculated according to equations 5 - 13 we may conclude that alkaline photohydrolysis of **1**, **2** and **3** in the presence of micellar CTACl occurs in both the aqueous and micellar phases according to our general mechanistic model.[2]

Alkaline Photohydrolysis of NArE in Micellar Medium. Effect of Salt Addition. As Br^- and OH^- ions tend to replace Cl^- ion at the micellar interface, the competitive binding can be treated on the basis of equation 15 for the corresponding OH^-/Cl^- and Br^-/Cl^- ion exchange equilibrium

$$K_{OH/Br} = [OH]_b[Br]_f/ [OH]_f[Br]_b \tag{15}$$

and the following expressions for $[Br]_b$ and $[OH]_b$ can be used:

$$[Br]_b + [OH]_b + [Cl]_b = \beta ([CTACl] - cmc) \tag{16}$$

$$[OH]_b^3 (1 - K_{OH/Br})(1 - K_{OH/Cl}) + [OH]_b^2 [A_1 (1 - K_{OH/Br})+(1 - K_{OH/Cl})([OH]_T K_{OH/Br} + [Br]_T] + [OH]_b.[OH]_T [K_{OH/Cl} ([Br]_T - \beta C_D (1 - K_{OH/Br})) + K_{OH/Br} A_1] - K_{OH/Cl} \beta C_D K_{OH/Br} [OH]_T^2 = 0 \tag{17}$$

Analysis of the quenching of alkaline photohydrolysis of **1**, **2** and **3** by Br^- ions in micellar CTACl was made in the present study by using the appropriate equations 5 -13 and 15 - 17. We chose quenching reactions of NArE triplet states by Br^- ions in cationic CTACl micelles in order to confirm the photochemical model proposed previously as well as to discover its limitations.[2] The lifetimes of excited **1**, **2** and **3** triplet states in aqueous solutions are 1400, 1880 and 625 ns, respectively.[3] In micellar CTACl medium we have found $\tau°_{mic}$ of 1200, 1275 and 310 ns for $\mathbf{1}^{3*}$, $\mathbf{2}^{3*}$,and $\mathbf{3}^{3*}$, respectively. With the aid of these $\tau°_{aq}$ and $\tau°_{mic}$ of other adjustable parameters, it was possible to calculate the ϕ_T value by equations 5 - 7 in the presence of $[OH]_T = 1.0x\ 10^{-2}$ M and NaBr added to a micellar CTACl solution. In the presence of bromide ions as triplet quencher, the quantum yields for production ot the NArP ions are much lower, as shown in Figures 2 - 4.

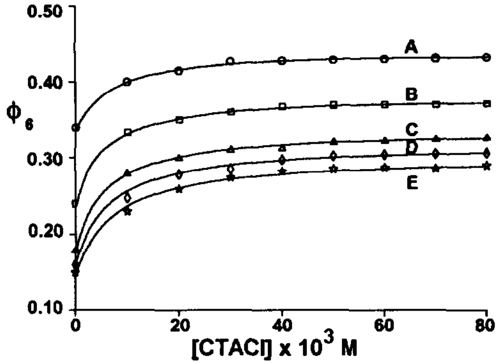


Figure 3 . CTACl concentration dependence of the observed quantum yield for alkaline photohydrolysis of **2** in the presence of $[OH]_T=1.0 \times 10^{-2}$M. (A) [NaBr]=0.0 ,(B) [NaBr] = 0.5 x 10^{-3} M,(C) [NaBr]=1.0 x 10^{-3} M,(D) [NaBr]= 1.25 x 10^{-3} M,and (E) [NaBr]=1.5 x 10^{-3}M.

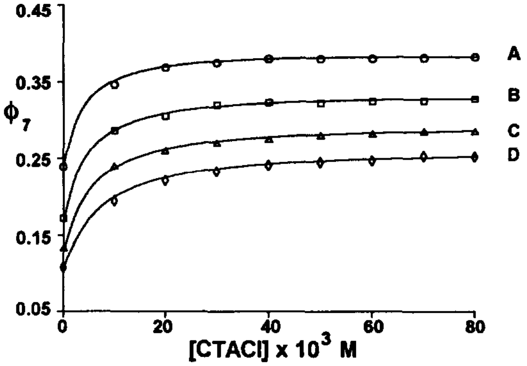


Figure 4 . CTACl concentration dependence of the observed quantum yield for alkaline photohydrolysis of **3** in the presence of $[OH]_T=1.0 \times 10^{-2}$M. (A) [NaBr]=0.0 ,(B) [NaBr] = 0.5 x 10^{-3} M,(C) [NaBr]=1.0 x 10^{-3} M,and (D) [NaBr] = 1.5 x 10^{-3} M.

According to Figures 2 - 4, the adjustment of the theoretical curves to the experimental data for ϕ_5, ϕ_6 and ϕ_7 as a function of [CTACl] shows a reasonably good fit to the calculated curves. The curves were calculated using equations 5 - 13 and 15 - 17 which consider the occurrence of photohydrolysis of the probe and the existence of an equilibrium among the excited molecules of the probes in both the aqueous and micellar phases. During probe photohydrolysis by OH^- in micellar CTACl medium in the absence of a quenching salt (Figure 1, curves A -C) there was competition between OH^- and Cl^- ions according to ion-exchange equilibrium.[4] In the presence of Br ion as probe3^* quencher, the quantum yields for the production of product phenoxide ions were much lower, as shown in Figures 2 - 4. Addition of Br^- ion to the photochemical **1**/CTACl/OH^- system showed a quenching effect similar to that observed for the **2**/CTACl/OH^- and **3**/CTACl/OH^- systems. Figures 2 - 4 show a perfect simulation of the experimental ϕ_T quantum yields in the absence (Curves A) and in the presence (Figures 2 - 4, curves B - E) of bromide ions according to the general mechanistic model (Scheme 1), which indicates that NArE photohydrolysis occurs in both the aqueous and micellar phases of cationic detergents.

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