

EFFECT OF CYCLIC ACETAL-TYPE CATIONIC SURFACTANTS ON THE BASIC DEHYDROBROMINATION REACTION

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The reaction of 2-(*p*-nitrophenyl)ethyl bromide with hydroxide ion was studied at 50 and 25 °C in the presence of cationic chemodegradable surfactants, i.e. [2-alkyl(1,3-dioxolan-4-yl)methyl]trimethylammonium bromides **Ia-c** (alkyl: a = *n*-C₉H₁₉, b = *n*-C₁₁H₂₃, c = *n*-C₁₃H₂₇). The kinetic data were interpreted with the pseudo-phase ion-exchange (PIE) formalism at both temperatures. The results indicate that the major source of rate enhancement is the increased reactant concentration in the small micellar reaction volume. The surfactant stability in micellar conditions was probed by means of a hydrolysis reaction of the surfactant 1,3-dioxolane ring. The kinetics of acid hydrolysis of **Ia-c** micelles, as a result of specific hydronium ion concentration, is one order of magnitude smaller than that of unaggregated systems.

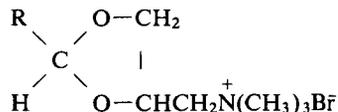
INTRODUCTION

In recent years, reactions that take place at charged surfaces of self-assembling colloids in solution (e.g. micelles, microemulsions, vesicles) have been investigated with increasing interest.¹ One major feature of all micellar systems is that they can alter the reaction rates of many chemical reactions. Various kinetic theories have been developed to analyse the catalytic and inhibitory effects of micelles on chemical reactions.² In most of these approaches, reactivities are assumed to arise from reactions taking place in the bulk aqueous and micellar pseudo-phases. One of the most extensively explored pseudo-phase models for bimolecular reactions is the pseudo-phase ion exchange (PIE) model, which satisfactorily explains a wide range of experimental conditions (pH, surfactant and added electrolyte concentrations) from a single set of parameters.³ Part of our work on micelle-catalysed elimination reactions has also been addressed to the problem of the PIE model predictions for the dehydrobromination reaction of 2-phenylethyl derivatives⁴.

Most of studies of micellar effects on rates or products of organic reactions, especially in aqueous micelles, have been made with very low concentrations of reactants,^{2b} and this scale of work is not very encouraging for the synthetic chemist. However, much more disadvantageous is that the presence of surfac-

tants may complicate product separation by forming foams and emulsions during extraction and distillation. To solve this problem, the micellar systems applied as reaction media should be stabilized by surfactants which are stable during the micellar catalysis but susceptible to chemical decomposition afterwards.

Aqueous micelles based on chemodegradable cationic surfactants (for an explanation of the term, see Ref. 5a) containing a 1,3-dioxolane moiety as a linkage between the hydrophobic and hydrophilic units:



a: R = C₉H₁₉; b: R = C₁₁H₂₃; c: R = C₁₃H₂₇

(**Ia-c**) provide one of the best examples of such a chemodegradable reaction medium. Burczyk and co-workers^{5b,c} first used 2-alkyl-4-hydroxymethyl-1,3-dioxolanes as hydrophobic intermediates in the synthesis of non-ionic chemodegradable surfactants. This cyclic acetal moiety was later used in synthetic applications by Jaeger and co-workers,⁶ Piasecki⁷ and Yamamura *et al.*⁸ and also recently by us.⁹ Adsorption and micellization properties of ionic cyclic acetal-type surfactants bearing a 1,3-dioxolane ring show that the presence of this moiety in the surfactant molecule induces hydrophobic character comparable to the effect of more than two oxyethylene groups or approximately two methylene groups of the alkyl hydrophobic

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chain.^{5a} This labile 1,3-dioxolane group is susceptible to acid hydrolysis in which the surfactants lose their surface-active properties.

In this work, we quantitatively analysed the alkaline dehydrobromination reaction of 2-(*p*-nitrophenyl)ethyl bromide in aqueous micelles of the studied cyclic acetal-type cationic surfactants **Ia–c**. The organic reagent was selected as a model compound since its dehydrobromination under non-micellar conditions¹⁰ and in normal aqueous cationic micelles¹¹ has been studied in detail. We expressed the chemodegradable reaction media stability in terms of the 1,3-dioxolane ring hydrolysis under the micellar conditions, which may be important from a practical point of view.

EXPERIMENTAL

2-(*p*-Nitrophenyl)ethyl bromide was synthesized by nitration of commercial 2-phenylethyl bromide (Aldrich) by the procedure described previously;¹² yield 30%; m.p. 70 °C. The preparation and purification of surfactants **Ia–c** has recently been described.⁹ All other reagents were of analytical-reagent grade or better.

The kinetic measurements were performed at 25 and 50 ± 0.1 °C using an HP 8452 A diode-array UV–visible spectrophotometer. The rate constants were determined by following the appearance of *p*-nitrostyrene (*p*-NO₂, 318 nm). Individual pseudo-first-order rate constants were obtained from linear plots of ln(absorbance) vs time. All these plots showed good linearity up to 80% of the reaction (60% for the slower ones), the correlation coefficients being greater than 0.99. The second-order rate constants, *k_w*, for dehydrobromination reactions of *p*-NO₂C₆H₄CH₂CH₂Br promoted by hydroxide ion in the absence of micelles are 3.61 × 10⁻² l mol⁻¹ s⁻¹ at 50 °C and 2.61 × 10⁻³ l mol⁻¹ s⁻¹ at 25 °C.

The hydrolysis rate constants of micellar systems stabilized by surfactants **Ia–c** were determined by observing carbonyl group formation at 280 nm. All reactions followed first-order kinetics up to approximately 40% of reaction. We studied the micelles hydrolysis towards hydrobromic, hydrochloric and sulphuric acid at 50 °C by a UV technique.

The binding constants for the organic reagent in the absence of hydroxide ion (*K_S*) were calculated from spectrophotometric data by a method developed by Bunton *et al.*¹³ The *K_S* values for 2-(*p*-nitrophenyl)ethyl bromide to micelles of **Ia–c** are, respectively, 208, 215, 218 l mol⁻¹ at 50 °C and 217, 219, 225 l mol⁻¹ at 25 °C. Absorbances were measured at 278 nm for the studied reagent.

The critical micelle concentration (cmc) and the micellar degree of dissociation (α) of surfactants **Ia–c** were determined by electric conductivity measurements, performed on a Tesla bridge voltmeter connected to a thermostated cell capable of regulating the sample

temperature. Deionized, doubly glass-distilled water was used throughout. The cmc values for **Ia–c** were, respectively, 16 × 10⁻³, 3.6 × 10⁻³ and 1.2 × 10⁻³ l mol⁻¹ at 50 °C and 15 × 10⁻³, 3.4 × 10⁻³ and 1 × 10⁻³ l mol⁻¹ at 25 °C. The values of 1 – α were extracted from the conductivity data by means of the Evans estimate¹⁴ as 0.72 (50), 0.79 (60) and 0.83 (80) for surfactants **Ia–c**, respectively, at 50 °C and 0.72 (55), 0.75 (65) and 0.79 (85) at 25 °C, where the values in parentheses are the micelle aggregation numbers assumed according to directions given in Refs 5a and 15.

RESULTS AND DISCUSSION

Dehydrobromination reaction in the presence of chemodegradable micelles

Aqueous micelles of the chemodegradable surfactants **Ia–c** speed up the basic dehydrobromination reaction of 2-(*p*-nitrophenyl)ethyl bromide. The dependence of the reaction rate on concentrations of **Ia–c** at 50 °C was similar to the behavior observed at 25 °C (Figures 1–3). The maxima of the experimental pseudo-first-order rate constants, *k_ψ*, with increasing surfactant concentration and at different NaOH concentrations are typical of micellar rate enhancements for bimolecular reactions. Rate enhancements (at the apparent rate maxima) are factors of 13.2, 34.3 and 49.5 for micelles of **Ia–c**, respectively, in relation to reaction in water. The rate–surfactant profiles can be analysed quantitatively by using the PIE formalism.^{2b,3}

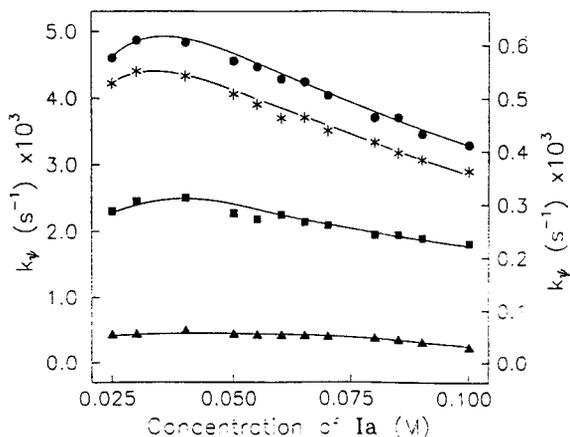


Figure 1. Reaction of 2-(*p*-nitrophenyl)ethyl bromide with OH⁻ in **Ia** at 50 °C (left-hand ordinate): (▲) [NaOH] = 0.001; (■) [NaOH] = 0.005; (●) [NaOH] = 0.01 M. For comparison (*) [NaOH] = 0.01 M at 25 °C (right-hand ordinate). Lines are predicted values

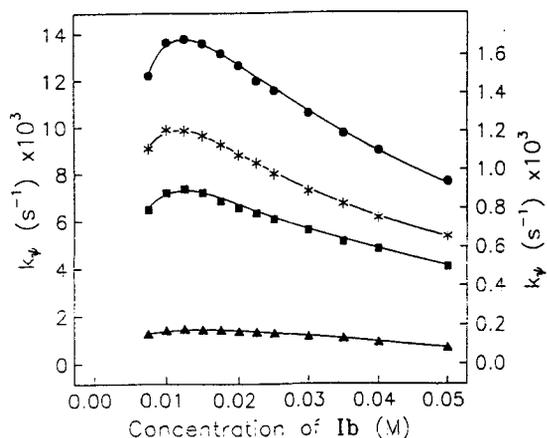


Figure 2. Reaction of 2-(*p*-nitrophenyl)ethyl bromide with OH^- in **Ib** at 50 °C (left-hand ordinate): (\blacktriangle) $[\text{NaOH}] = 0.001$; (\blacksquare) $[\text{NaOH}] = 0.005$; (\bullet) $[\text{NaOH}] = 0.01$ M. For comparison (*) $[\text{NaOH}] = 0.01$ M at 25 °C (right-hand ordinate). Lines are predicted values

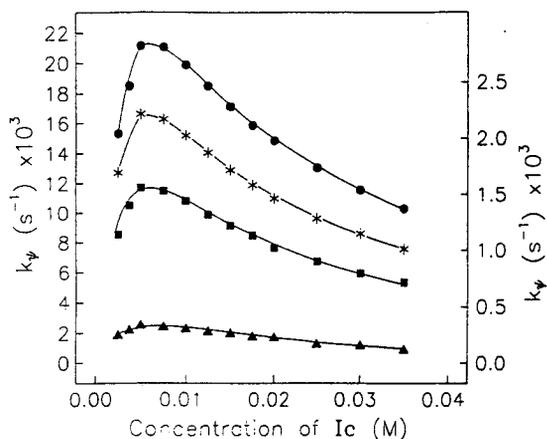
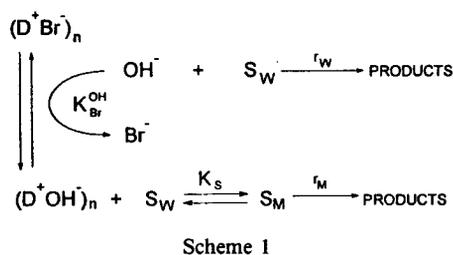


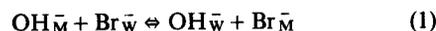
Figure 3. Reaction of 2-(*p*-nitrophenyl)ethyl bromide with OH^- in **Ic** at 50 °C (left-hand ordinate): (\blacktriangle) $[\text{NaOH}] = 0.001$; (\blacksquare) $[\text{NaOH}] = 0.005$; (\bullet) $[\text{NaOH}] = 0.01$ M. For comparison (*) $[\text{NaOH}] = 0.04$ M at 25 °C (right-hand ordinate). Lines are predicted values

Quantitative predictions follow from Scheme 1, where subscripts M and W refer to the micellar and aqueous pseudo-phases, respectively, D_n represents the surfactant in micellar form (so that $[D_n] = [D] - \text{cmc}$, where $[D]$ is the bulk concentration and cmc is the critical micelle concentration), K_S is the substrate-micelle association constant, and r_w is the reaction rate in water described in terms of the hydroxide ion concentration in water ($[\text{OH}_w^-]$) and the



rate r_M corresponds to dehydrobromination promoted by hydroxide ion that is bound to the Stern layer (OH_M^-).

The affinities of hydroxide and bromide ions for the cationic micelle are expressed in terms of the ion-exchange parameter $K_{\text{Br}}^{\text{OH}}$ based on a model similar to that developed for counterion binding for polyelectrolytes.^{3a} Thus, the concentration of OH^- in the micellar phase depends critically on the quantity of counter ion, Br^- , in the solution, and the relative affinities of these two ions for the micelle surface result from the ion-exchange equilibrium:



The PIE formalism considers the fraction of neutralised micellar head groups ($\beta = 1 - \alpha$) to be a constant that is independent of surfactant and ion concentrations.

The distribution of substrates between aqueous and micellar pseudo-phases can be measured (see Experimental), but that of OH_M^- has to be calculated by means of ion-exchange phenomena [equation (1)] according to the following equation:^{2b,3a,16}

$$\begin{aligned}
 (m_{\text{OH}})^2 + m_{\text{OH}} \left[\frac{[\text{OH}_T^-] + K_{\text{Br}}^{\text{OH}} [\text{Br}_T^-]}{(K_{\text{Br}}^{\text{OH}} - 1)([D] - \text{cmc})} - \beta \right] \\
 - \frac{\beta [\text{OH}_T^-]}{(K_{\text{Br}}^{\text{OH}} - 1)([D] - \text{cmc})} = 0 \quad (2)
 \end{aligned}$$

where $\beta = m_{\text{OH}} + m_{\text{Br}}$ and m are the mole ratios $m_{\text{OH}} = [\text{OH}_M^-]/([D] - \text{cmc})$ for $[\text{OH}_T^-] = [\text{OH}_W^-] + [\text{OH}_M^-]$ and $m_{\text{Br}} = [\text{Br}_M^-]/([D] - \text{cmc})$ for $[\text{Br}_T^-] = [\text{Br}_W^-] + [\text{Br}_M^-]$. The quantities in brackets are molarities calculated in terms of the total solution volume and subscript T denotes total concentration.

The studied reactions are promoted by hydroxide ion uniformly distributed between aqueous and micellar pseudo-phases. The overall observed first-order rate constant, k_ψ , with respect to S (Scheme 1) can be easily derived as^{1,2b,3}

$$k_\psi = \frac{k_w [\text{OH}_T^-] + (k_M K_S - k_w) m_{\text{OH}} ([D] - \text{cmc})}{1 + K_S ([D] - \text{cmc})} \quad (3)$$

where k_w is the second-order rate constant for the reaction in aqueous phase and k_M is the rate constant

in the micellar pseudo-phase written in terms of OH_M^- to the micellized surfactant.

The value of k_M , with units s^{-1} , which indicates the reactivity in the micellar phase, cannot be directly compared with k_w because of the way in which it was defined. The true bimolecular constant for the micellar pseudo-phase, k_2^m , can be expressed as

$$k_2^m = \bar{V}k_M \quad (4)$$

where \bar{V} , the volume element of the reaction in micelles, has been assumed to be that of a Stern layer, with an approximate molar volume of $ca\ 0.14\ \text{l}$.¹⁷

Equations (2) and (3) can be applied to predict variations of the observed first-order rate constant, k_ψ , with concentrations of surfactant and reactive or inert ions, by means of simulation techniques. The parameters cmc, k_w and β were fixed and k_M , K_S and $K_{\text{Br}}^{\text{OH}}$ were adjustable. The K_S values of numerical analysis for the best fit were in good agreement with the experimental spectrophotometric data. The value of $K_{\text{Br}}^{\text{OH}}$ was selected so as to obtain the best fit to the kinetic results. In fitting the data we allowed it to vary between 10 and 40 basing on the literature data.^{1,3a,4} The $K_{\text{Br}}^{\text{OH}}$ constant thus obtained is nearly the same at both temperatures and for the studied micelles of **Ia–c**, indicating that the factors that control the affinity of Br^- and OH^- ions for the Stern layer should be essentially the same, independent of the alkyl chain length. The optimized values of k_M and $K_{\text{Br}}^{\text{OH}}$ are given in Table 1 together with the values of k_2^m calculated from equation (4). The values of k_M for all the surfactants **Ia–c** were similar, suggesting that the Stern layer of **Ia–c** has analogous properties as a reaction medium. Comparing k_M of the surfactant **Ic** with its hydrophobic analogue hexadecyl-

trimethylammonium bromide⁴ led to conclusion that the 1,3-dioxolane ring as a portion of the surfactant does not introduce significant changes in the catalytic ability of its micelles. The similarities of the values of k_2^m and k_w for the studied systems are consistent with micellar effects on other reactions where second-order rate constants are similar at micellar surfaces and in water.^{1,2b,12} The magnitude of k_2^m indicates that the major source of rate enhancement is the increased reactant concentration in the small micellar reaction volume.

The fitting of rate data by the PIE model has been extensively discussed in the literature.^{2b,4,16,18} The parameters that describe these distributions depend on arbitrary assumptions, and there is no general agreement on the best values, indicated by the global maxima of the fitting criteria. Additionally, the PIE model makes no assumptions about the shape or size of micelles and the fits of kinetic data for reactions of strongly hydrophilic ions depend on assumed values of counter-ion binding and aggregation parameter, since the Coulombic attraction for these ions is a result of the charge density at the micellar surface.

The observation of similar cmc values at 50 and 25 °C and dilute hydroxide ion concentration applied in the present study lends support to the belief that the shape, size and number of micelles seem to remain unchanged under the experimental conditions.

The k_2^m values at 50 and 25 °C given in Table 1 were applied to calculate thermodynamic parameters for the dehydrobromination reaction in **Ia–c** micelles in the form of all present micelles in the reaction medium. The results are summarized in Table 2. The activation parameters for the studied systems are similar, proving that

Table 1. Parameters that best fit the kinetic results for $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Br}$ at 25 and 50 °C in the presence of **Ia–c** micelles^a

Surfactant	T (°C)	[NaOH] (M)	$k_M \times 10^2$ (s^{-1})	K_S (l mol^{-1})	$K_{\text{Br}}^{\text{OH}}$	$k_2^m \times 10^3$ ($\text{l mol}^{-1} \text{s}^{-1}$) ^b
Ia	50	0.001	50.5	208	32	70.7
	50	0.005	50.6	208	32	70.8
	50	0.01	50.6	208	32	70.8
	25	0.01	5.1	217	30	7.1
Ib	50	0.001	50.0	215	30	70.0
	50	0.005	50.2	215	30	70.3
	50	0.01	50.0	215	30	70.0
	25	0.01	5.1	219	29	7.1
Ic	50	0.001	49.0	218	30	68.6
	50	0.005	49.5	218	30	69.3
	50	0.01	49.0	218	30	68.6
	25	0.01	5.1	225	30	7.1

^a The values of β were taken as 0.72, 0.79, 0.83, respectively, for **Ia–c** at 50 °C and 0.72, 0.75, 0.79 at 25 °C.

^b For comparison $k_w = 3.61 \times 10^{-2} \text{ l mol}^{-1} \text{ s}^{-1}$ at 50 °C and $2.61 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$ at 25 °C.

Table 2. Activation parameters for dehydrobromination of $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Br}$ in water and in the micellar pseudo-phase of **Ia-c**

Medium ^a	$E_a(\text{kcal mol}^{-1})^b$	$\Delta H_{\ddagger 23}(\text{kcal mol}^{-1})^b$	$\Delta S_{\ddagger 23}(\text{cal mol}^{-1} \text{K}^{-1})^b$
Water	20.1	19.5	-5.0
Ia	17.5	16.9	-11.6
Ib	17.4	16.8	-11.9
Ic	17.3	16.6	-12.5

^a The values of k_w and k_2^m are given in Table 1.

^b 1 cal = 4.184 J.

the reaction mechanism is the same and the surfactant molecules interact to the same extent with initial and transition states of the dehydrobromination reaction. The similar values of activation energies in micelles **Ia-c** and in water lend further support to the notion that the rate acceleration afforded by the micellar solutions is due to a concentration effect. Similar conclusions have been drawn for other micellar systems.¹⁹ The rate of dehydrobromination increases in the less polar micellar pseudo-phase solvent, which is in accord with the predictions of Ingold²⁰ that reactions which involve a dispersal of charge in the transition state will be faster in solvents of lesser solvating power.

Stability of the reaction medium

The stability of the chemodegradable reaction media can be determined in the acid-catalysed hydrolysis of the 1,3-dioxolane moiety present in the surfactant molecule which splits the surfactant molecules into non-surface-active aldehydes and diols.

Recently, we have described the hydrolytic reactivity of the surfactants **Ia-c** under acidic conditions in unaggregated systems.⁹ According to the literature findings,^{6a} the hydrolytic reactivities of aggregated ketal-based chemodegradable surfactants in acidic solutions are much smaller than those of unaggregated forms, which suggests that the microenvironmental effects of surfactant-organized structures cause electrostatic depletion of hydronium ion and a lower polarity of the reaction medium.

The rate constants of acid hydrolysis of a series of dioxolane ring-containing acetal type surfactants **Ia-c** in micelles, determined at 50 °C in solutions of hydrochloric acid for 0.09 M surfactant solutions, are shown in Figure 4. Additionally, for the surfactant **Ia** the reaction was followed in solutions of hydrobromic and sulphuric acid. As in unaggregated form, the observed pseudo-first-order rate constant, k_ψ , introduces a weighted average of rate constants for *trans/cis* diastereoisomers in the case of acetal-type derivatives.

The hydrolysis rates of surfactants **Ia-c** in micelles

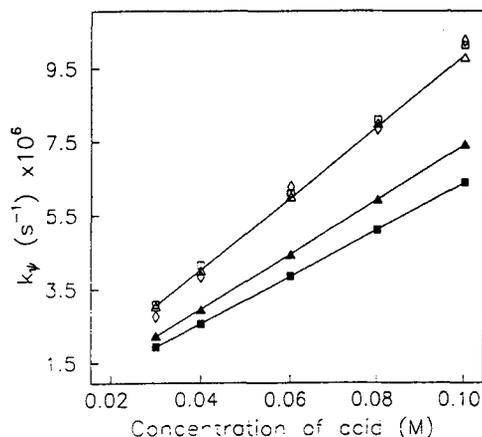


Figure 4. Acid hydrolysis of 1,3-dioxolane moiety in micelles of **Ia-c** at 50 °C at a fixed surfactant concentration of 0.09 M and different acid concentrations: (■) **Ia**, HCl; (▲) **Ia**, HBr; (◇) **Ia**, H₂SO₄; (▲) **Ib**, HCl; (■) **Ic**, HCl

do not vary much with the length of the 2-alkyl group. The stabilities of surfactants **Ia-c** in homogeneous solution are much lower than those in micelles. Generally, the surfactants hydrolyse one order of magnitude faster in 1 : 1 (v/v) 1,4-dioxane-water mixtures⁹ than in aggregated systems. The kinetics of acid hydrolysis of **Ia** in the presence of hydrochloric, hydrobromic and sulphuric acid indicate that a specific hydronium ion concentration, similar for all the acids, determines the hydrolytic reagent reactivity under micellar conditions.

The studied micellar systems can be applied as chemodegradable reaction media. The studied surfactants are liable to chemical degradation in both homogeneous and micellar systems, which makes them the most promising components not only of micelles but especially of microemulsions. Owing to acidic decomposition of the surfactant, which leads to non-surface-active compounds, we can avoid unfavourable processes such as foaming and emulsification.

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