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Synthesis of 2-(2-Nitrophenoxy)quinoxaline and its Basic Hydrolysis in Aqueous Solutions of Non-Reactive Counter-Ion Surfactants with Bulky Head Groups.

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Abstract: The synthesis of the novel compound 2-(2-nitrophenoxy)quinoxaline (2) is described and its basic hydrolysis was studied in the presence of non-reactive counter-ion surfactants with different head group size. Micellar effects upon the reaction of OH⁻ with (2) were analyzed by using a massaction-like equation Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Micellar effects upon bimolecular reactions in aqueous systems have been extensively studied.^{1,2} Many kinetics results have been explained by the pseudophase kinetic model³ which treats micelles as a separate phase and by considering the distribution of reactants between water and the micelles. Reactant concentration at the micellar surface can be determined experimentally,⁴ or estimated.^{1,2,5} A variety of quantitative treatments have been developed to measure reactant distribution between micelles and water.^{1,3,a,5,8} The pseudophase ion exchange model (PIE)^{6,8} describes counter-ion distribution using an ion exchange equilibrium. The model fits many experimental data, although its validity has been questioned^{1,a,9} and it fails for concentrated electrolyte solutions. Alternatively coulombic contributions to counter-ion binding to ionic micelles can be estimated by solving the Poisson-Boltzmann equation.^{1,10} Another treatment involves the assumption that micellar binding of each counter-ion is governed by a mass-action-like equation.^{1,11} The various pseudophase treatments are reasonably satisfactory for reactions with dilute ionic reagents. Micellar effects on rate constants and ion and molecular binding are usually interpreted by a combination of separating non-specific, coulombic effects, and specific effects which depend on dispersive and hydration forces.^{1,10}

The effect of substrate hydrophobicity, micellar charge, nature of counter-ions and chain length of surfactant tail upon reactions carried out in the presence of micellar systems has been studied¹ but the effect of the surfactant head group hydrophobicity has not been systematically investigated and recently there has been considerable interest in reactions carried out in the presence of micelles containing bulky head groups. ¹²⁻¹⁵ The rate of spontaneous hydrolysis of the 2,4-dinitrophenyl phosphate dianion is strongly increased by aqueous cationic micelles of cetyltrialkylammonium bromides (alkyl = Me, Et, *n*-Pr, *n*-Bu) and tetradecylquinuclidinium bromide; rate enhancements increase with increasing bulk of the head group and are associated with decreases in activation enthalpies. ¹² An increase in head group hydrophobicity of cetyltrialkylammonium halides also effects the rate of spontaneous decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion which depends strongly on the polarity of the medium. ¹³ The rate of bimolecular reactions is affected by the bulk of the head group. ^{14,15}

There is little information in the literature concerning micellar effects upon nucleophilic heteroaromatic substitution on quinoxaline derivatives. ¹⁶⁻¹⁸ Quinoxaline and its derivatives are commercially important as antibiotics, agrochemicals, fungicides, herbicides. ¹⁹ 2-Substituted quinoxaline derivatives undergo facile nucleophilic substitution and in many reactions this property has been widely use with synthetic purposes. ²⁰

We had synthesized the novel quinoxaline derivative, 2-(2-nitrophenoxy)quinoxaline (2). The aim of the present work was to examine micellar effects upon the reaction of hydroxide ion with compound (2) and to investigate the effect of the micellar head group size upon the reaction. We used as surfactants cetyltrialkyammonium salts C_{16} $H_{33}NR_3^+Cl^-$, where R = Me (CTACl), Et (CTEACl), n-Pr (CTPACl) and n-Bu (CTBACl).

RESULTS AND DISCUSSION

Synthesis of 2-(2-nitrophenoxy)quinoxaline (2). 2-(2-Nitrophenoxy)quinoxaline (2) was synthesized from 2-chloroquinoxaline (1), Scheme 1, under reflux for several days (Experimental). Mager and Berends²¹ reported

$$\begin{array}{c|c}
 & O K^{+} \\
\hline
 & NO_{2} \\
\hline
 & PO \\
\hline
 & NO_{2}
\end{array}$$

$$\begin{array}{c|c}
 & PO \\
\hline
 & PO \\
 & PO \\
\hline
 & PO \\
\hline
 & PO \\
 & PO \\
\hline
 & PO \\
 & PO \\
\hline
 & PO \\
 & PO \\$$

Scheme 1.

that no 2,3-di-o-nitrophenoxyquinoxaline was obtained from 2,3-di-chloroquinoxaline by fusion with sodium o-nitrophenoxide on account of a reaction with pyrotechnic effects. The synthesis described herein proceeds in a controlled fashion, with no side effects.

Anderson and Cheeseman²² reported that when 2-chloroquinoxaline was treated with a sodium aryloxide in an excess of the corresponding phenol, a mixture of the expected quinoxalinyl ether and the corresponding benzofuro[2,3-b]quinoxaline was obtained. In the synthesis of compound (2) no cyclised products were obtained as by-products as evidenced by the presence of a proton at the C-3 position in the ¹NMR spectrum (Experimental).

Reactions in water. In water, 2-(2-nitrophenoxy)quinoxaline (2) reacts with hydroxide ion to produce 2-quinoxalone (3) (Scheme 2). The reaction was followed at 25 °C over a range of hydroxide ion concentration from 0.001 M to 0.20 M. Repetitive scanning of the reaction mixture showed that no intermediate built up during the reaction. Formation of 2-quinoxalone (3) is overall second-order in water. The second-order rate constant (k_w) value is 7.4 x 10⁻² M⁻¹ s⁻¹. In some cases, the reaction was also followed by monitoring the appearance of 2-nitrophenoxide ion at 402 nm. The kinetics followed at 362 nm and 402 nm were in agreement within 1% error.

Reactions in micelles. The basic hydrolysis of compound (2) was investigated in C₁₆ H₃₃NR₃⁺Cl⁻, where R= Me (CTACl), Et (CTEACl), n-Pr (CTPACl) and n-Bu (CTBACl), at different OH⁻ concentrations, 0.001 M,

0.01 M, and 0.2 M. The rate constants versus surfactant concentration profiles are shown in Figures 1-4. First-order rate constants of reaction of (2) with hydroxide ion, k_{ψ} , go through maxima with increasing concentrations of quaternary ammonium chloride surfactants as previously found for numerous micellar catalyzed reactions. 1,2,6-8,17,18,23

Scheme 2

Quantitative Treatment.

The relation between rate and surfactant concentration can be written in terms of Scheme 3, where S denotes organic substrate, X^* the anionic reagent, D_n is the micellized surfactant given by ([D] - cmc) and K_S the binding constant of S to D_n . Scheme 3 leads to equation 1, where the subscripts M and W denote the micellar and aqueous phases, respectively, the bracketed quantities represent concentrations in moles per liter of solution, m_X^S is the mole ratio of bound X^* to micellized surfactant D_n , k'_M and k'_W are first-order rate constants.

Scheme 3.

The overall first-order rate constant with respect to S is given by^{3a}

$$k_{\Psi} = \frac{k_{W}[X_{W}^{-}] + k_{M}K_{S}([D_{n}] - cmc)}{1 + K_{S}([D_{n}] - cmc)}$$
(1)

The first-order rate constants, k'_W and k'_M can be converted to second-order rate constants, k_W and k_M by

$$\mathbf{k}_{W}^{'} = \mathbf{k}_{W}[OH_{W}^{-}] \tag{2}$$

$$\vec{k}_M = k_M m_M^{OH} \tag{3}$$

The classical PIE model⁶⁻⁸ has been widely used and we try to apply it to our kinetic data; the fit was unsatisfactory under the moderately concentrated hydroxide ion solutions used here. A major weakness of the original PIE model is the assumption of constant fractional charge neutralization, $\beta_1^{1,9,10}$

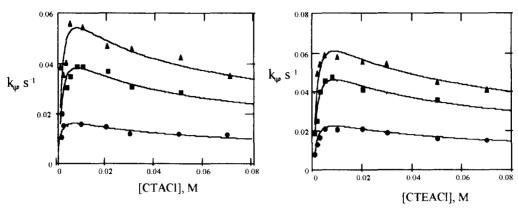


Figure 1. First-order rate constants for the basic hydrolysis of compound (2) in CTACl. Symbols: (a) with 0.001 M OH; (a) with 0.01 M OH and (b) with 0.2 M OH; Curves are predicted.

Figure 2. First-order rate constants for the basic hydrolysis of compound (2) in CTEACl. Symbols as in Figure 1. Curves are predicted.

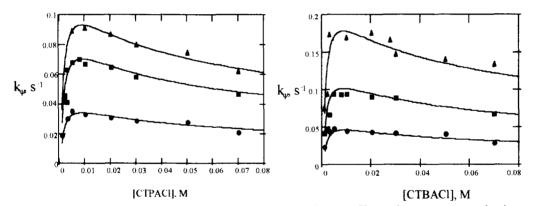


Figure 3. First-order rate constants for the basic hydrolysis of compound (2) in CTPACl. Symbols as in Figure 1. Curves are predicted.

Figure 4. First-order rate constants for the basic hydrolysis of compound (2) in CTBACl. Symbols as in Figure 1. Curves are predicted.

This implies that the concentration of ionic reactant at the surface of micelles of a "reactive counter-ion" surfactant should be constant because k_{ij} will reach a plateau when substrate is fully micellar bound. This behavior is observed for reactions of hydrogen ions in micellized alkanesulfonic acid²⁴ and addition of CN⁻ to N-alkylpyridinium ions in micellized CTACN.²⁵ Nucleophilic reactions in CTAOH and CTAF do not fit this pattern and it appears that with hydrophilic anions the concentration of micellar bound OH⁻ and F⁻ increases with increasing total concentration.^{11,24} The PIE model depends critically upon the value of β and its equations contain several parameters, viz. β , K_X^{OH} , the rate constant in the micelle, and the concentration of the monomeric surfactant, which is assumed to be given by the cmc. However, this approach does not give unique values for any of the parameters, because equally good fits can be obtained by using different combinations of assumed

values of the various parameters. Values of β appears to depend upon the method of measurements. However, at low electrolyte concentration, the fit of the PIE model with the experiments is often good. 1a,9,17,18

An alternative theoretical treatment involves the assumption that micellar binding of each counter-ion is governed by a mass-action-like equation and that β increases with ionic strength. He we will when two ions compete for the micellar head groups, it is possible to define independent equilibria for each of them. The rate-surfactant profiles for the alkaline hydrolysis of compound (2) in the quaternary ammonium chloride surfactants can be fitted on the assumption that the distribution of hydroxide and chloride ion between water and micelles follows equations 4 and 5^{11}

$$K'_{OH} = [OH_M^-]/([OH_W^-]([Dn] + [OH_M^-] - [X_M^-]))$$
(4)

$$K_{X} = [X_{M}^{-}]/([X_{W}]([Dn] - [OH_{M}] - [X_{M}]))$$
(5)

These mass-action-like equations have the form of Langmuir isotherms with binding constants used to describe counter-ion distributions. Rate-surfactant profiles for mixed ion systems can be fitted by using 4 and 5 without the assumption of constant β . These two equations are solved simultaneously with an iterative calculation method to give the values of $[OH_M]$ and $[X_M]$ as a function of K'_{OH} and K'_X for each surfactant concentration. The model was originally proposed by Bunton^{11a,b} and similar treatment has been developed by Rodenas. ^{14c}

The experimental pseudo-first-order rate constants, k_{ψ} , for reactions in micellar solutions of CTACl, CTEACl, CTPACl and CTBACl shown in Figures 1-4 were calculated by using this treatment. The computer simulations give reasonable fits to the rate-surfactant profiles. The second-order rate constant, $k_{\rm w}$, was measured directly, and $k_{\rm M}$ and $K'_{\rm Cl}$ were treated as adjustable parameters. Values of $K'_{\rm OH}$ are from the literature ($K'_{\rm OH}$ = 55, 45, 25, and 12 for CTA+, CTEA+, CTPA+, and CTBA+, respectively). 11a,14e The fitting parameters are in Table 1. The values of $k_{\rm M}$ and $K'_{\rm Cl}$ are insensitive to changes in surfactant or OH⁻ concentration (Table 1). The ion binding parameter for chloride ion is larger than that of hydroxide ion, but both follow the sequence Me > Et > n-Pr > n-Bu (Table 1). This behavior is similar to that observed in other ionic micelles. 14a Table 1 shows, for all surfactants, the interfacial counterion concentrations calculated at a selected surfactant concentration (0.01 M), near the rate maximum. The kinetic cmc were measured by a method proposed by Broxton 26 and, as was expected, the cmc decreases as the size of the head group increases (Table 1).

The second-order rate constant, k_M , for reactions in the micellar pseudophase increases slightly with head group size; this increase in k_M value may be explained by the increased nucleophilicity of hydroxide ions as water is squeezed out from the micelle surface. For the reaction of methyl naphthalene-2-sulfonate with bromide ion in micelles with bulky head groups, micellar incorporation of the halide ion markedly increases the NMR spectral line width of ⁷⁹Br, due to a disruption of hydration that is largest for the bulkiest surfactant head groups. ^{14f} The Hammett equation has been applied to the reaction of hydroxide ion with phenyl *p*-substituted benzoates in the presence of cetyltrialkylammonium bromide (alkyl = Me, Et, Pr and Bu) and tetradecylquinuclidinium bromide. ²⁷ Values of ρ increase with increasing bulk of the surfactant head group and are considerably larger that in water, corresponding to decreases in micellar surface polarity.

Second-order rate constants are typically expressed as M^{-1} s⁻¹ in homogeneous solvents, and cannot be compared directly with k_M , where concentration is written as a mole ratio. Second-order rate constants in the micellar phase with the same dimensions, k_2^m , M^{-1} s⁻¹, are given by

$$k_2^{m} = k_M V_M \tag{6}$$

Surfactant	10 [OH ⁻ _T] ^b M	10 ³ [OH _M] ^c M	10 ⁴ [Cl _M] ^c M	K _{Cl} '	10 ³ cmc M	10 ² k _M s ⁻¹
CTAC1	0.10	-	-	125	1.1	17.0
CTACl	2.00	-	-	125	1.1	16.0
CTACI	4.00	9.08	5.01	125	1.1	13.0
CTEACI	0.01	-	-	110	0.9	18.0
CTEACI	0.10	-	-	110	0.9	18.0
CTEACI	2.00	-	-	110	0.9	18.0
CTEACI	4.00	8.96	5.30	110	0.9	18.0
CTPACI	0.01	-	-	60	0.8	21.0
CTPACI	0.10	-	-	60	0.8	20.0
CTPACI	2.00	-	-	60	0.8	21.0
CTPACI	4.00	8.62	5.90	60	0.8	21.0
CTBACI	0.01	-	-	50	0.6	23.0
CTBACI	0.10	-	-	50	0.6	23.0
CTBACI	2.00	-	*	50	0.6	23.0
CTBACI	4.00	7.63	7.50	50	0.6	23.0

Table 1. Parameters that Best Fit the Kinetic Results for 2-(2-Nitrophenoxy)quinoxaline (2) in Micelles.^a

^aAt 25.0 °C and with $K_s = 8.200 \text{ M}^{-1}$, $k_w = 7.40 \text{ x } 10^{-2} \text{ M}^{-1}$ s⁻¹, $K'_{OH} = 55.45$, 25 and 12 M⁻¹ for CTA⁺, CTEA⁺, CTPA⁺ and CTBA⁺, respectively. ^{11a,14e} ^bTotal OH⁻ concentration. ^cCalculated interfacial counterion concentration at [surfactant] = 0.01 M.

where V_M is the molar volume of the reactive region at the micellar surface. We take $V_M = 0.14 \text{ L mol}^{-1}$, on the basis of earlier estimates.^{6,11}

The mass-model fits the data reasonably well within an ample range of OH⁻ concentration with no restriction on the extent of charge neutralization of the micellar head groups by counter-ions as it is required by the PIE model. The exchange constant, defined by the PIE model, may vary with extensive changes in [counter-ion] because non-specific coulombic and specific dispersive interactions will have different dependencies upon [counter-ion] and their relative importance depends upon the counter-ion

All the experimental results for the basic hydrolysis of compound (2) can be explained by assuming independent equilibrium distribution for ions in solution between aqueous and micellar pseudophases. The increase of the second-order rate constants with the size of the micellar head group is consistent with a decrease in hydration of the hydroxide ions at the micellar surface; *i.e.* as the size of the micellar head group is increased, water is squeezed away from the micelle surface creating a less polar reaction environment.

EXPERIMENTAL

General Methods. Melting points are uncorrected. Unless otherwise indicated, all reagents and solvents were purchased from Aldrich or Merck and used without further purification. Silica gel TLC plates (MN Sil G/UV₂₅₄) were used to monitor reactions. IR spectra were recorded on a Nicolet FT-IR 7500 spectrophotometer. ¹H-NMR spectra were recorded in a Bruker AM-300 apparatus with TMS as an internal reference in CDCl₃

solutions. Chemical shifts are given in ppm (δ). Mass spectra were obtained on a Hewlett-Packard 5971A spectrometer at 70 eV. Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN.

Materials.

Synthesis of 2-chloroquinoxaline (1). 2-Chloroquinoxaline was synthesized from 2-hydroxiquinoxaline by the method of Castle and Onda²⁸ All spectral data are consistent with reported values.²⁹

Synthesis of 2-(2-nitrophenoxy)quinoxaline (2). 2-Chloroquinoxaline (2.01 g, 12,2 mmol) was added to a solution of 2-nitrophenol (8.03 g, 57.7 mmol), potassium hydroxide (2.04 g, 36.4 mmol) in 15.6 ml of N,N-dimethylformamide. The mixture was stirred and refluxed at 98 \pm 2 °C. After 114 h when TLC revealed that no starting material remained, the solution was cooled (ice-water), and the products were filtered and the residue was extracted with dichloromethane. After eliminating the solvent, the dried residue was identified as 2-(2-nitrophenoxy)quinoxaline (2.52 g, 77.4%, M.P. 140 \pm 1 °C). IR (KBr) 3091-3041 (C-H, Ph), 1578 (C=C, conj.), 1347, (-NO₂), 866 (C-N) cm⁻¹. ¹H-NMR (300 MHz, CDCl₃): δ = 8.85 (s, 1H, H-3), 8.47-8.10 (m, 3H, Ph-H), 7.97-7.42 (m, 5H, Ph-H). MS: m/e (%) 267 (10, M⁺), 221 (100, M⁺-NO₂), 129 (21, M⁺-C₆H₆O), 102 (31, M⁺-HCN). Anal. Calcd. for C₁₄H₉N₃O₃: C, 62.9; H, 3.39; N, 15.7. Found: C, 62.4; H, 3.66; N, 15.8.

Synthesis of Surfactants. The cetyltrialkylammonium chloride surfactants were prepared from the 1-hexadecane chloride (0.1 M) and the appropriate trialkylamine (0.12 mol, alkyl = Et, n-Pr, n-Bu) by heating them under reflux in absolute EtOH for 5-30 days depending upon the reactivities of amines; these decrease considerably with the increase of the bulk of the alkyl groups. The surfactants were recrystalized from EtOAc-Pentane. The purity of surfactants was tested by means of surface tension measurements and there were no minima in plots of surface tension of the purified surfactants against -log [surfactant]. The critical micelle concentrations values for $C_{16}H_{33}NR_3^+Br^-$ were: Me, 0.88 mM, Et, 0.80 mM, n-Pr, 0.60 mM, n-Bu, 0.27 mM.

Kinetics. The basic hydrolysis of compound (2) was followed spectrophometrically using a Perkin-Elmer, Lambda II UV-Visible instrument at 362 nm. All kinetics were measured at 25.0 °C. Solutions were made up under N_2 , in deionised and distilled, CO_2 -free water. The substrate was added as solutions in MeCN (4-10 μ L); the final amount of acetonitrile in the reaction mixture was 0.1%. All reactions followed first-order kinetics for at least four half-lives. The first-order rate constants, k_{ij} , are in reciprocal seconds and are the averages of at least three separate runs with a maximum deviation of 5%.

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