In several series of disubstituted benzenes, the IP of the highest occupied orbital has been correlated with the corresponding ionization from the monosubstituted benzene.[4] When benzene is substituted with an electron-donating group and a series of 4-substituents, the slope of the correlation line is less than unity. This slope decreases with an increase in $E_{3,4} = E_3 - E_4$, the displacement energy of the highest occupied orbital, $\pi_4$, from the relatively unperturbed $\pi_3$. The quantity $E_{3,4}$ is not strictly a measure of electron donation to the phenyl group by the substituents. For *N*-phenylaziridines $E_{3,4}$ = 1.0 eV, which falls between the values of 0.83 and 1.16 observed for anisole and aniline, respectively. The slope of 0.678 ($r$ = 0.978, standard deviation = 0.11 eV) for 4-substituted *N*-phenylaziridines is similar to the values of 0.7 and 0.67 found for substituted anisoles and anilines. Thus, the slope of this plot is a rough measure of the interaction between 4-substituents and $\pi_4$ and so may be useful in confirming assignments of PES bands in similar systems.[4]

## Experimental Section

**NMR Spectra.** With the exceptions of solutions of the 4-$NO_2$ and 4-CN compounds, which were 2.2 M, natural-abundance $^{13}C$ and $^{15}N$ spectra of 4 M solutions of the compounds in $CDCl_3$ were determined at 25.03 and 10.09 MHz, respectively, by the pulsed Fourier transform method with a JEOL PS/PFT-100 spectrometer equipped with the JEOL EC-100 data system. For $^{13}C$ spectra, a spectral width of 5 kHz over 4K or 8K data points was used, with pulse angles of ~20° and a repetition time of 2 s. Chemical shifts were measured with respect to internal $(CH_3)_4Si$ (0.0 ppm) or $CDCl_3$ (76.9 ppm). $^{15}N$ spectra were obtained with a 5-kHz spectral width, 4K or 8K data points, and ~20° pulse angles. All compounds were run with 10–20 mg of chromium tris(acetylacetonate), $Cr(acac)_3$, to shorten $T_1$ values. This allowed a repetition time of 3–4 s to be used. Chemical shifts were measured with respect to partially enriched $CH_3{}^{15}NO_2$ is a concentric capillary and are reported on the anhydrous ammonia scale.[21]

$^1H$ NMR spectra were obtained in $CDCl_3$ at 60 MHz on a Varian A-60A spectrometer. Shifts are measured with respect to internal $(CH_3)_4Si$.

**Photoelectron Spectra.** PES ionization potentials of vaporized samples were determined by using a modified[22] Perkin-Elmer PS-16 photoelectron spectrometer. Solid compounds and liquids boiling above 250 °C (760 mm) were placed in the probe and heated to 40–65 °C, while more volatile samples were introduced from a flask connected via a glass stopcock to the probe inlet. The argon (15.75 eV) or nitrogen (15.58 eV) ionization was used for calibration.

**Materials.** ***N*-(2,6-Dimethylphenyl)aziridine** was synthesized by the literature procedure[23] for *N*-(4-methylphenyl)-aziridine. It has the following physical properties: bp 105–106 °C (11 mm); $^1H$ NMR ($CDCl_3$) $\delta$ 6.9 (3 H, s, aromatic CH), 2.35 (6 H, s, $CH_3$), 2.1 (4 H, s, $CH_2$); $^{13}C$ NMR ($CDCl_3$) 150.9, 128.8, 128.7, 121.8, 29.8, 18.6 ppm.

Anal. Calcd for $C_{10}H_{13}N$: C, 81.63; H, 8.84; N, 9.52. Found: C, 81.74; H, 9.03; N, 9.55.

***N*-[4-(Dimethylamino)phenyl]aziridine** was obtained by the literature procedure[24] for *N*-phenylaziridine from the corresponding amino alcohol. This in turn was produced by alcoholic base hydrolysis of the crude hydrochloride salt formed by reaction of *N*,*N*-dimethyl-*p*-phenylenediamine with 2-chloroethyl chloroformate.[25] The product had the following physical properties: bp 63 °C (0.05 mm); $^{13}C$ NMR ($CDCl_3$) 146.5, 145.7, 121.3, 113.6, 41.0, 27.4 ppm.

Anal. Calcd for $C_{10}H_{14}N_2$: C, 74.07; H, 8.64; N, 17.28. Found: C, 73.78; H, 8.48; N, 17.09.

All other compounds are known and were synthesized by literature procedures.[24-26] Structures were confirmed by boiling point or melting point comparisons and $^{13}C$ NMR. Microanalyses were carried out by Schwarzkopf Microanalytical Laboratories.

**Acknowledgment.** This work was supported by NIH Grant No. GM-21148 and by City University of New York PSC-CUNY Research Awards No. 13344, 13118, and 12280 to R.L.L. We are grateful to Dr. Mukund Sibi for helpful discussions.

**Note Added in Proof:** Very recent photoelectron spectroscopic results on *N*-phenyl cyclic amines, including **9** and **10**, support our suggestion that these compounds are not conformationally twisted: Rozeboom, M. D.; Houk, K. N.; Searles, S.; Seyedrezai, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 3448–3453.

**Registry No.** **1**, 696-18-4; **2**, 82027-08-5; **3**, 27347-09-7; **4**, 38201-24-0; **5**, 698-53-3; **6**, 28192-05-4; **7**, 30855-80-2; **8**, 30855-79-9; **9**, 45739-72-8; **10**, 78376-90-6.

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# Micellar Effects upon the Reaction of Hydroxide Ion with *N*-Alkyl-2-bromopyridinium Ion

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The reactivity of *N*-alkyl-2-bromopyridinium ions (alkyl = Me, Et, $n$-$C_{12}H_{25}$, $n$-$C_{14}H_{29}$, $n$-$C_{16}H_{33}$) toward $OH^-$ is affected by cationic micelles of alkyltrimethylammonium chloride or bromide (alkyl = $n$-$C_{14}H_{29}$, $n$-$C_{16}H_{33}$) which inhibit reactions of the methyl and ethyl substrates and catalyze reactions of the more hydrophobic derivatives. These results are understandable, qualitatively, in terms of the distribution of both reactants between the aqueous and micellar pseudophases. The distribution of $OH^-$ between aqueous and micellar pseudophase is governed by an ion-exchange equilibrium. The rate enhancements can be treated quantitatively, and second-order rate constants in the micellar pseudophases are essentially independent of substrate hydrophobicity and are slightly smaller than those in water. The rate differences are understandable in terms of the high electrolyte concentration at the micellar surface.

*Rate* enhancements of many bimolecular reactions by aqueous micelles have been treated quantitatively by estimating the concentrations of both reactants in the aqueous and micellar pseudophases.[2-4] In some cases, e.g.,

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with relatively hydrophobic reactants, the distribution of both reactants between the two pseudophases can be measured directly.[2,5-7] The problem is more difficult for hydrophilic ions, but often the distribution can be determined electrochemically,[8,9] and Sepulveda and his coworkers have developed other methods for measuring the distribution of counterions between aqueous and micellar pseudophases.[10]

Much of the early work on micellar rate effects was on reactions of hydroxide ion,[11,12] and a number of recent treatments have been directed to a study of the binding of this ion to cationic micelles. Most workers have used an ion-exchange model[13]

$$OH^-_M + X^-_W \rightleftarrows OH^-_W + X^-_M$$

where $X^-$ is the micellar counteranion and M and W denote the micellar and aqueous pseudophases, respectively. The ion-exchange constant is given by

$$K_X^{OH} = [OH^-_W][X^-_M]/([OH^-_M][X^-_W]) \quad (1)$$

The ion-exchange constant can be measured directly by using interion competition[10] or estimated by simulating the variations of rate or equilibrium constants with surfactant concentration, in terms of various parameters, including $K_X^{OH}$.[14-17] These treatments depend on the assumption that $K_X^{OH}$ and the rate constant in the micellar pseudophase are independent of the concentrations of surfactant, reactants, and added counteranions, and that $\beta$, the ratio of bound counterions to ionic micellar head groups, is also independent of these concentrations.[13,18] This last assumption may be suspect, especially when only hydrophilic counterions, e.g., $OH^-$ or $F^-$, are present.[19]

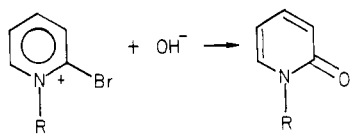
To date this general treatment has been applied to several hydroxide ion reactions. In some systems reaction was in both the aqueous and the micellar pseudophases, so that the substrate distribution has to be taken into account.[14,16,17] In other systems the hydrophobicity of the substrate was such that it was located in only one pseudophase.[15,17b] One such substrate was the 4-methyl-4-cyanopyridinium ion, which does not bind to the micelles.[15] However, in this reaction in the aqueous pseudophase, it was necessary to take into account the kinetic salt effect of the surfactant. This problem also exists for the saponification of hydrophilic betaine esters, but the hydrophobicities of these esters could be changed without affecting the reaction mechanism, so that saponification could be followed by using substrates that were located wholly in the aqueous, or wholly in the micellar, pseudophase.[17b]

We hoped that, in addition to gaining a quantitative understanding of rate-surfactant profiles, we would be able to calculate rate constants in the micellar pseudophase and to compare them with rate constants in water. For many reactions involving nucleophilic anions, second-order rate constants in the micellar pseudophase are not very different from those in water.[2-8,17b,19] But there are differences, which could arise from the high ionic concentrations in the Stern layer at the micellar surface, inhibiting reactions of oppositely charged reagents.

Our approach in this work was to use a series of *N*-alkyl-2-bromopyridinium ions (1), whose hydrophobicities could be varied (Scheme I).

The formation of the pyridone (2) can easily be followed spectrophotometrically,[20] and the surfactants were myristyltrimethylammonium chloride and bromide ($n$-$C_{14}H_{29}N^+Me_3X^-$; X = Cl, Br (MTACl and MTABr, respectively)) and cetyltrimethylammonium chloride and bromide ($n$-$C_{16}H_{33}N^+Me_3X^-$; X = Cl, Br (CTACl and CTABr, respectively)). Reactions of nonmicellized bromopyridinium ions with aqueous hydroxide ion have been studied in detail and the mechanism is well understood.[20]

Scheme I




1 2

a, R = Me
b, R = Et
c, R = $n$-$C_{12}H_{25}$
d, R = $n$-$C_{14}H_{29}$
e, R = $n$-$C_{16}H_{33}$

Table I. Effect of Substrate Concentration on Reactivity[a]

| | R | |
|---|---|---|
| $10^5$[1], M | $n$-$C_{14}H_{29}$ | $n$-$C_{16}H_{33}$ |
| 0.5 | | 1.5 |
| 0.8 | | 1.5 |
| 1.0 | 1.00 | 1.6 |
| 2.0 | 0.94 | 2.0 |
| 4.0 | 2.00 | 4.4 |
| 10.0 | 2.35 | 5.3 |
| 20.0 | 2.60 | 6.6 |
| 40.0 | | 6.4 |
| 60.0 | | 6.9 |

[a] Values of $k_W$ ($M^{-1}$ $s^{-1}$) in 0.01 M NaOH at 25.0 °C.

## Experimental Section

**Materials.** The *N*-alkyl-2-bromopyridinium bromides were prepared by heating equimolar 2-bromopyridine and the alkyl

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Table II. Salt Effects upon Reaction of the Methyl Derivative (1a)[a]

| [salt], M | salt | NaCl | NaBr | $Me_4NBr$ | $Et_4NBr$ |
|---|---|---|---|---|---|
| 0.005 | | 0.63 | 0.57 | | |
| 0.010 | | 0.58 | 0.50 | | |
| 0.015 | | 0.54 | 0.45 | | |
| 0.020 | | 0.52 | 0.44 | 0.50 | 0.50 |
| 0.050 | | 0.45 | 0.41 | | |
| 0.070 | | 0.44 | | 0.43 | 0.44 |
| 0.10 | | 0.40 | 0.38 | 0.41 | 0.43 |
| 0.15 | | 0.39 | | 0.41 | 0.40 |
| 0.20 | | 0.38 | 0.36 | 0.39 | 0.40 |

[a] Values of $k_W$ ($M^{-1}$ $s^{-1}$) at 25.0 °C with $3 \times 10^{-5}$ M substrate.

Table III. Effect of Hydroxide Ion Concentration[a]

| | R | |
|---|---|---|
| [NaOH], M | Me | Et |
| 0.005 | 0.75 | 0.39 |
| 0.01 | 0.71 | 0.37 |
| 0.02 | 0.68 | 0.35 |
| 0.06 | 0.57 | 0.31 |
| 0.10 | 0.51 | 0.29 |
| 0.15 | 0.54 | 0.28 |
| 0.20 | 0.52 | 0.30 |
| 0.50 | 0.53 | 0.25 |

[a] Values of $k_W$ ($M^{-1}$ $s^{-1}$) at 25.0 °C with $3 \times 10^{-5}$ M substrate.

bromide under reflux in MeCN for 4 days.[20] The solvent was removed by evaporation, and the products were recrystallized from $EtOH/Et_2O$.

Preparation or purification of the surfactants has been described.[17] Redistilled, deionized, $CO_2$-free water was the solvent.

**Kinetics.** Formation of the pyridones (2) was followed at 296 nm, and repetitive scanning of the spectrum of the reaction mixture showed that no intermediate built up during reaction.[20]

Except where noted otherwise, $(1–2) \times 10^{-5}$ M substrate was used. Reactions were carried out in water at 25.0 °C, and first-order rate constants, $k_\psi$, are in reciprocal seconds.

**Micellar Binding of Substrate.** The binding constants, $K_s$, were determined by ultrafiltration, using an Aminco 202 cell with a PM 10 membrane.[7] They are given in terms of the concentration of micellized surfactant, eq. 2, where $S_M$ and $S_W$ are substrate in

$$K_s = [S_M]/\{[S_W]([D] - \text{cmc})\} \quad (2)$$

micellar and aqueous pseudophases, D is the surfactant (detergent), and cmc is the critical micelle concentration.

The solute concentrations were determined spectrophotometrically, at 276 nm, after addition of EtOH to break up the micelles.

## Results

**Reactions in Water.** The reactions of the methyl, ethyl, and *n*-dodecyl derivatives, (**1a–c**) are independent of substrate concentration in the range $(2–15) \times 10^{-5}$ M in 0.01 M $OH^-$. The second-order rate constants, $k_W$, are 0.70, 0.40, and 0.50 $M^{-1}$ $s^{-1}$ at 25.0 °C. The slightly decreased reactivities of **1b** and **1c** are probably due to a steric effect.

However, the second-order rate constants for reaction of the tetra- and hexadecyl derivatives (**1d,e**) increase with increasing [substrate] (Table I) almost certainly because of substrate association which attracts $OH^-$ to the cationic aggregate.

Added electrolytes slow reaction, as is general for reactions between oppositely charged ions. The negative salt effect follows the sequence NaBr > NaCl > NaOH (Tables II and III), i.e., it increases with increasing charge density of the anion of the added electrolyte, but change in the cation of the electrolyte has little effect. This specificity

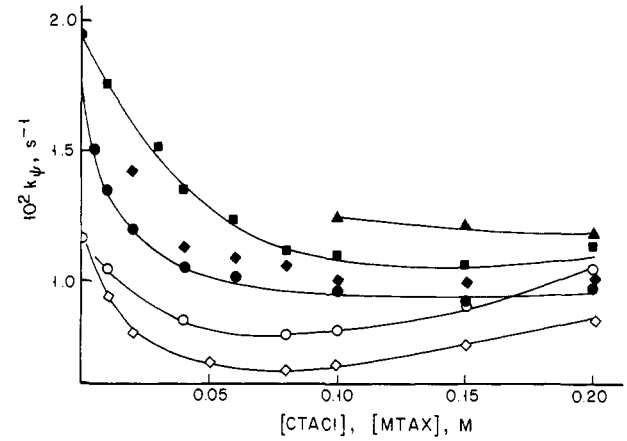


**Figure 1.** Reactions of *N*-methyl- and *N*-ethyl-2-bromopyridinium ion with 0.028 M $OH^-$ in CTACl and MTAX. In CTACl; (●) R = Me; (▲) R = Me with 0.1 M NaCl; (○) R = Et. In MTACl: (■) R = Me; (◊) R = Et. In MTABr: (♦) R = Me.

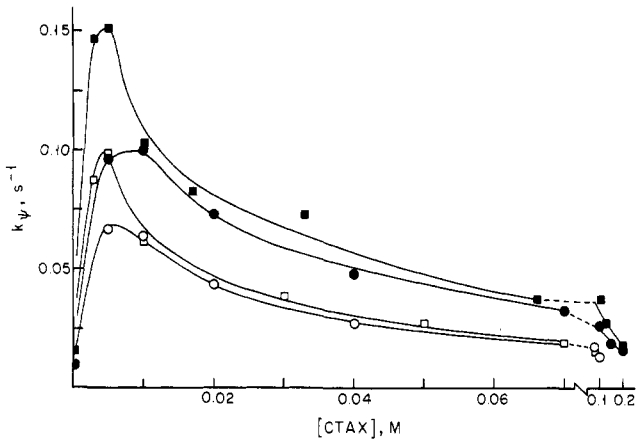


**Figure 2.** Reactions of *N*-tetradecyl- and *N*-hexadecyl-2-bromopyridinium ion with 0.1 M $OH^-$. Solid points in CTACl, open in CTABr: (●, ○) R = $C_{14}H_{29}$; (■, □) R = $C_{16}H_{33}$. Lines are theoretical.

is general and depends upon the nature of the counterion to the substrate.[21]

**Micellar Effects. *N*-Methyl-2-bromopyridinium Bromide (1a).** Reaction is inhibited by micelles of MTACl, MTABr, and CTABr, and added NaCl decreases the inhibition of (Figure 1). The inhibition depends upon the halide anion but not upon the surfactant cation.

***N*-Ethyl-2-bromopyridinium Bromide (1b).** The first-order rate constants go through minima with increasing [MTACl] or [CTACl], but reaction is always faster in CTACl (Figure 1).

**Dodecyl, Tetradecyl, and Hexadecyl Derivatives.** For reactions of these substrates (**1c–e**) with $OH^-$, first-order rate constants go through maxima with increasing [surfactant] (Figures 2 and 3). Reaction is slower when bromide, as compared with chloride, counterions are present, and the rate enhancements increase with substrate hydrophobicity, which decreases the [surfactant] needed for maximum rate enhancement.

**Micellar Binding Constants.** The binding constants, $K_s$, of the *N*-dodecyl-, tetradecyl-, and hexadecyl-2-bromopyridinium ions (**1c–e**) to micelles of CTACl are 80, 250, and 850 $M^{-1}$, respectively, with $3 \times 10^{-5}$ M solute and up to 0.2 M CTACl. However, the binding constants for

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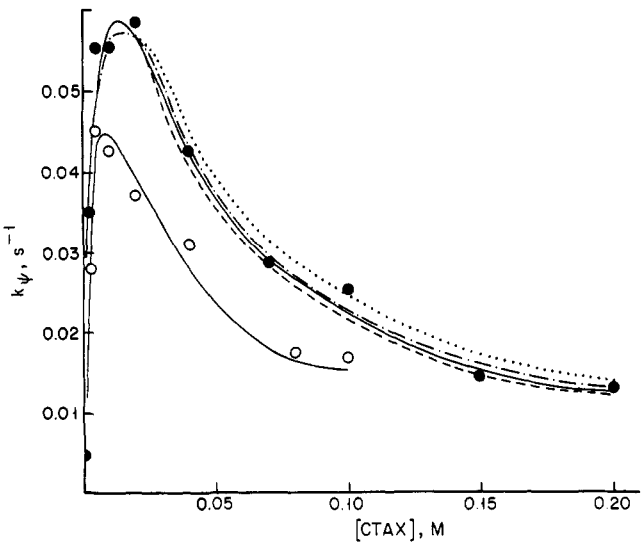



**Figure 3.** Reaction of *N*-dodecyl-2-bromopyridinium ion with 0.01 M $OH^-$. Solid points are in CTACl; open points are in CTABr. The solid lines are calculated by using values of $k_M$ in Table V and by taking $K_{Cl}^{OH} = 4$, $\beta = 0.75$, and $k_M = 0.68\ s^{-1}$. If we take $K_{Cl}^{OH} = 6$, $\beta = 0.75$, and $k_M = 0.84\ s^{-1}$, or respective values of 5, 0.75, and 0.77 $s^{-1}$, we calculate the broken line (- - -); with $K_{Cl}^{OH} = 4$, $\beta = 0.9$, and $k_M = 0.51\ s^{-1}$, we calculate the dotted line (···); with $K_{Cl}^{OH} = 4$, $\beta = 0.8$, and $k_M = 0.62\ s^{-1}$, we calculate the broken line (-·-).

**Table IV. Micellar Binding of Methyl and Ethyl Derivatives**[a]

| [MTACl], M | Me | Et |
|---|---|---|
| 0.1 | 0.13 (0.39)[b] | 0.17 (0.82) |
| 0.15 | 0.22 (0.59) | 0.35 (1.5) |
| 0.2 | 0.24 (1.6) | 0.61 (3.1) |

[a] Values of $K_s$ ($M^{-1}$) at 25.0 °C with $5 \times 10^{-5}$ M pyridinium ion. [b] Values in parentheses are with added 0.1 M NaCl.

the *N*-methyl and *N*-ethyl derivatives increase with increasing [CTACl] and with added NaCl (Table IV). These increases can be ascribed to incorporation of a formally neutral pyridinium chloride ion pair into the micelle or to incorporation of chloride ion into the micelle, so as to maintain the charge on the micelle as it takes up pyridinium ion.[17a,22]

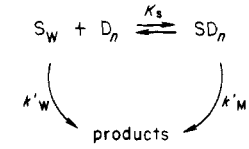
## Discussion

**Reactions of the Methyl and Ethyl Derivatives (1a,b).** Micellar effects upon reactions of the methyl derivative (**1a**) are similar to those observed with the 4-methyl-4-cyanopyridinium ion[15] or hydrophilic betaine esters,[17b] because these substrates bind only weakly to micelles. Therefore, reaction occurs largely, or completely, in the aqueous pseudophase, and this reaction is inhibited, because $OH^-$ is taken up by the micelle by exchange with the halide counterion (eq 1).

However, there is a complication, because the surfactant ions exert a kinetic salt effect upon the reaction in the aqueous pseudophase (Tables II and III). It is sometimes possible to correct for this salt effect,[15,17b] but it introduces uncertainty in the quantitative treatment, and with the methyl derivative (**1a**) added salts and surfactants have similar rate-inhibiting effects (Figure 1).

The situation is more complicated for reaction of the ethyl derivative (**1b**), where $k_\psi$ goes through minima with

Scheme II




increasing [surfactant]. Qualitatively, these observations suggest that in dilute surfactant the substrate is in the aqueous pseudophase, which is depleted in $OH^-$ by the cationic micelles, but that with increasing [surfactant] substrate becomes micellar bound, and there is a contribution from reaction in the micellar pseudophase. This conclusion is consistent with the binding studies (Table IV).

We did not attempt to interpret these micellar rate effects quantitatively, because of the complexity of these opposing effects, which introduce a large number of adjustable parameters into the treatment.

**Reactions of Hydrophobic Substrates.** The micellar rate enhancements of reactions of the do-, and tetra-, and hexadecyl derivatives (**1c–e**) can be treated quantitatively by considering the distribution of both reactants between aqueous and micellar pseudophases and the rate constants in each pseudophase.

The treatment is based upon Scheme II, where $[D_n] = [D] - cmc$ and $k'_W$ and $k'_M$ are first-order rate constants. The observed rate constant is given by[12]

$$k_\psi = \frac{k'_W + k'_M K_s([D] - cmc)}{1 + K_s([D] - cmc)} \quad (3)$$

The first-order rate constants are given by

$$k'_W = k_W[OH^-_W] \quad (4)$$

$$k'_M = k_M m^s_{OH} \quad (5)$$

where $[OH^-_W]$ is a molarity in terms of total solution volume and the second-order rate constant, $k_M$, is written in terms of the mole ratio of micellar-bound $OH^-$ to micellar head groups:[22]

$$m^s_{OH} = [OH^-_M]/([D] - cmc) \quad (6)$$

Equations 3–6 give

$$k_\psi = \frac{k_W[OH^-_W] + k_M K_s m^s_{OH}([D] - cmc)}{1 + K_s([D] - cmc)} \quad (7)$$

Simulation of the rate–surfactant profiles therefore requires analysis of the distribution of $OH^-$ between aqueous and micellar pseudophases.

**Distribution of $OH^-$.** The variation of $m^s_{OH}$ with [surfactant] can be predicted for assumed values of the ion-exchange constant, $K_X^{OH}$, $\beta$, and cmc, provided that these parameters are constant over a range of [surfactant]. With these assumptions eq 7 and mass balance give the quadratic eq 8,[17b] where subscript T denotes total concentration.

$$(m^s_{OH})^2 + m^s_{OH}\left(\frac{[OH^-]_T + K_X^{OH}[X^-]_T}{(K_X^{OH} - 1)[D_n]} - \beta\right) - \frac{\beta[OH^-]_T}{(K_X^{OH} - 1)[D_n]} = 0 \quad (8)$$

Equation 8 has the same general form as that used elsewhere,[2,15,16] except that we write the concentration of micellar-bound $OH^-$ as a mole ratio.

**Simulation of Dependence of $k_\psi$ on Surfactant.** Equations 7 and 8 were combined, and the variation of $k_\psi$

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Table V. Rate Constants in the Micellar Pseudophase[a]

| R | $k_M$, $s^{-1}$ | $k_2^m$, $M^{-1}$ $s^{-1}$ |
|---|---|---|
| $n$-$C_{12}H_{25}$ | 0.68 (0.60) | 0.1 (0.09) |
| $n$-$C_{14}H_{29}$ | 0.66 (0.65) | 0.09 (0.09) |
| $n$-$C_{16}H_{33}$ | 0.68 (0.60) | 0.1 (0.09) |

[a] In CTACl; values in parentheses are in CTABr.

with [D] was simulated by using assumed values of the parameters in these equations. The rate constants of reaction in water, $k_W$, were directly measured (Results). We did not correct for salt effects on $k_W$, because most of the reaction was in the micellar pseudophase. Reported values of $\beta$ are generally in the range 0.6–0.9[13,18] and of $K_{Cl}^{OH}$, ca. 5, and $K_{Br}^{OH}$, 10–20.[10,15-17] We took the cmc as $10^{-3}$ and $8 \times 10^{-4}$ M for CTACl and CTABr, respectively,[23] but our surfactant concentrations were such that the simulated fits were insensitive to the cmc. The values of the substrate binding constant, $K_s$, were measured in CTACl (Results), and we assumed that they would be the same in CTABr. However, $K_s$ has only a small effect on the fitting of the data.

The rate constants that we estimated are given in Table V, and we took $\beta = 0.75$ for both CTACl and CTABr, and $K_{Cl}^{OH} = 4$ and $K_{Br}^{OH} = 9$ (cf. ref 10 and 15–17). As has been found for other systems the fit between experimental and calculated values of $k$ is satisfactory,[14-17] but this agreement does not prove that our values of $K_x^{OH}$ or $k_M$ are correct.[17] The variation of $k_\psi$ with [CTACl] for the dodecyl derivative can be fitted to various combinations of parameters (Figure 3). The insensitivity of the fit to small changes in these parameters suggests that equally good fits would be obtained if the parameters varied over a limited range with variation of [surfactant].[17b]

**Rate Constants in Aqueous and Micellar Pseudophase.** The second-order rate constants, $k_M$ ($s^{-1}$), can be defined without specifying the volume element of the micellar reaction. But they cannot be compared with second-order rate constants, $k_W$ ($M^{-1}$ $s^{-1}$), for reaction in water. Comparison can be made provided that a volume element of reaction is assumed. This element could be the total micellar volume or the assumed volume of the Stern layer at the micelle–water interface. It is difficult to define this volume with any certainty, because the micelle has a very mobile and easily deformed structure and the surface is probably rough.[24,25] We have assumed that reaction occurs in the Stern layer, with a molar volume of ca. 0.14 L, and the second-order rate constant, $k_2^m$, written in terms of moles of reagent/liter of Stern layer, is given by [22]

$$k_2^m = 0.14 k_M \quad (9)$$

If we assumed a molar volume of ca. 0.3 L, approximately that of the whole micelle,[2,15,16] values of $k_2^m$ would be approximately doubled.

The values of $k_M \approx 0.7$ $s^{-1}$ give $k_2^m \approx 0.1$ $M^{-1}$ $s^{-1}$ (Table V), which is smaller than $k_W$ in water, which is 0.5 $M^{-1}$ $s^{-1}$ for the dodecyl derivative and up to 1.5 $M^{-1}$ $s^{-1}$ for the hexadecyl derivative (Results). The more hydrophobic substrates, **1d,e**, may be associated in water, in which case the values of $k_W$ will be too high for reaction of monomeric substrate.

Comparison of second-order rate constants in micellar and aqueous pseudophases depends upon the assumed volume element of reaction, but there is a more serious limitation in the treatment, because it assumes that both reactants are distributed uniformly over the volume element. This assumption is especially suspect when one reactant, e.g., $OH^-$, is very hydrophilic and the other relatively hydrophobic (cf. ref 17c). In reactions of 2-bromopyridinium ions with $OH^-$ the 2-position may be somewhat shielded from $OH^-$ at the micelle–water interface. The situation is different for the somewhat similar reaction of addition of $CN^-$ to the 4-position of $N$-alkylpyridinium ions, where the reaction center is exposed to a hydrophilic reagent and second-order rate constants are similar to aqueous and micellar pseudophases.[26] However, in both these pyridinium ion reactions the second-order rate constants in the micellar pseudophase are not very dependent upon the $N$-alkyl groups, and there is no reason to believe that there are significant reactivity differences due to different depths of insertion of these substrates into the micelles.

The micellar environment could also affect reactivity, because the Stern layer should be akin to a concentrated electrolyte solution.[13] There is a negative salt effect upon the reaction of $OH^-$ with halopyridinium ions in water, and it should also be important for reaction in the micellar pseudophase.

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