Hydrolysis of Imines. 4.[1] Micellar Effects upon the Spontaneous Acid, Base, and Copper(II) Ion Induced Hydrolysis of *N*-Salicylidene-2-aminothiazole and *N*-Salicylidene-2-aminopyridine

Anadi C. Dash,* Bhasker Dash, and Debraj Panda

Department of Chemistry, Utkal University, Bhubaneswar 751 004, India

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The rate of hydrolysis of the title imines in alkaline medium was strongly retarded by the cationic surfactant cetyltrimethylammonium bromide (CTAB) even though both reactants (i.e., the phenoxide forms of the imines and OH^-) might be bound to the micellar pseudophase. Anionic surfactant sodium dodecyl sulfate (SDS) did not affect the hydrolysis rate at pH >12. In mild alkaline medium (pH 9.2) both surfactants retarded the hydrolysis reaction of the imines, the effect being much stronger in the case of CTAB. Inhibition was attributed to selective partitioning of the phenol form of the imines into the micellar pseudophase of SDS, while both the phenol and phenoxide forms of the imines were found to be adsorbed in the micellar pseudophase of CTAB, where these undergo hydrolysis much slower than in the aqueous pseudophase. In the range pH 5.08–7.06, small acceleration in the rate of hydrolysis of the thiazole imine by SDS was observed. There was virtually no kinetic effect of SDS on the copper(II)-induced hydrolysis of the thiazole imine. Strikingly the copper(II)-*N*-salicylidene-2-aminopyridine chelate (CuL^+) was found to undergo faster acid-catalyzed hydrolysis of the aldimine linkage in the micellar pseudophase of SDS than in the aqueous phase.

The surfactant compounds dispersed in aqueous solution are known to form organized assemblies called "micelles". Such entities in aqueous environment are very much like suspended colloid particles. The adsorption phenomenon at the interface of the micellar pseudophase and the bulk aqueous phase plays an important role in controlling the distribution of ions and neutral species between these two phases and hence influencing the dynamics of reactions the adsorbed species are likely to undergo.

It has been generally accepted that the surfactants in aqueous medium affect the rates of many chemical reactions by incorporating the reactants into their micellar pseudophase.[2] The cationic micelles accelerate the rates of bimolecular reactions involving anionic nucleophiles by incorporating both the substrate and the nucleophile into the small volume of the micellar pseudophase.[3-8] Micelles also affect the rates of spontaneous, unimolecular reactions.[3,9]

In preceding papers we have reported on the kinetics and mechanism of aicd-, base-, and copper(II)-induced hydrolysis of the ortho hydroxy imines, namely, *N*-salicylidene-2-aminothiazole[10] and *N*-salicylidene-2-aminopyridine,[11] hereafter referred to, in this paper, as Tzim (I) and Pyim (II), respectively. The basic reaction that concerns us, i.e., the hydrolytic splitting of the aldimine linkage, may be depicted as follows:

$$R_1CH{=}NR_2 \xrightarrow{H_2O} R_1CHO + R_2NH_2$$

This work was undertaken in order to (i) explore the possibilities of interaction of the title imines (neutral, anionic, and protonated forms) and their copper(II) chelates (CuL^+) with the cationic and anionic micelles and (ii) understand the kinetics and mechanism of hydrolysis of the different forms of the imines bound to the micellar pseudophase.

Sodium dodecyl sulfate (SDS) and cetyl trimethyl ammonum bromide were used as the anionic and cationic surfactants, respectively.

Experimental Section

The Schiff bases were prepared and characterized as described earlier.[10,11] SDS was purified by repeated crystallization from ethanol, and purity was checked by cmc determination. The purity of CTAB, checked by estimating bromide content as AgBr, was 99.5%. AnalaR grade reagents were used. pH measurements were made with a ditital pH meter Model 5651 manufactured by Electronic Corporation of India using a glass-calomel combination electrode; saturated NaCl solution was used as the electrolyte for the calomel electrode. The meter was standardized against phthalate (pH 4.01), phosphate (pH 6.86), and carbonate (pH 9.20) buffers. Solutions were prepared in conductivity water. Copper(II) perchlorate solution was prepared and estimated as described earlier.[11] Sodium perchlorate solution was prepared by neutralizing standard $HClO_4$ (2 mol dm^{-3}) with standard NaOH (2 mol dm^{-3}). Sodium hydroxide was standardized against potassium hydrogen phthalate.

Kinetic Measurements. The hydrolysis of the imines was studied spectrophotometrically in methanol–water (5% v/v) medium at 35 °C. A Varian-Cary 634S UV–vis recording spectrophotometer was used, the cell compartment of which was thermostated by circulating water from a constant-temperature thermostat. A fresh solution of the imines in methanol was added to the reaction mixture taken in the Teflon-stoppered thermostated 1-cm quartz cell to initiate the reaction.[10] The decrease of absorbance with time was followed at the preset wave length (420 nm, pH ≥9; 370 or 350 nm, pH ≤9) manually or by using a strip-chart recorder Model 9317. The concentration of the imines [$(0.6\text{–}1.4) \times 10^{-4}$ mol dm^{-3}] was chosen such that there was large absorbance decrease ($A_0 - A_\infty = 0.3\text{–}0.8$) during the course of the reaction. Runs were made under pseudo-first-order conditions and the observed rate constants (k_{obsd}) were calculated from the gradients of the plots of log ($A_t - A_\infty$) against time (t, s). The kinetic plots yielded good straight lines up to four half-lives and replicate runs reproduced k_{obsd} to ±5%.

Results

1. Effect of CTAB on the Basic Hydrolysis of the Imines. (a) Spectral Behavior.

The successive spectral scans for the base hydrolysis of Tzim in the absence of

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Table I. Effect of CTAB on the Hydrolysis of *N*-Salicylidene-2-aminothiazole at 35 °C with Varying $[NaOH]_T$[a] and $[Br^-]_T$[a,b] [in Brackets]

	10^3k_{obsd}, s^{-1}						
$10^3[CTAB]_T$, mol dm^{-3}	0.01 [0.095]	0.02 [0.085]	0.03 [0.075]	0.04 [0.065]	0.05 [0.055]	0.06 [0.045]	0.07 [0.035]
0.00	1.19	1.77		2.77	3.76	4.18	4.62
0.20	1.17	1.67		2.75	3.76	3.93	
0.50	1.19	1.59		2.46	3.46	4.36	
1.00	0.96	1.54		2.28	2.89	3.33	3.61
2.00	0.71	1.02	1.29	1.60	1.88	2.14	2.34
5.00	0.42	0.57	0.62	0.84	0.98	1.09	1.28
10.0	0.30	0.40	0.45	0.50	0.59	0.71	0.83
20.0	0.23	0.30	0.35	0.37	0.47	0.58	0.67

[a] In mol dm^{-3}. [b] $[Br^-]_T = [KBr]_T + [CTAB]_T$.

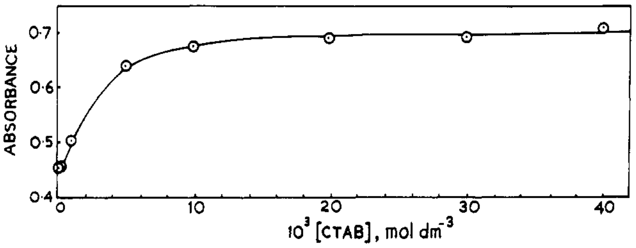


Figure 1. Effect of CTAB on the extrapolated zero-time absorbance data of the phenoxide form of Tzim at 460 nm and 30 °C: $[Tzim]_T = 5.97 \times 10^{-5}$; [NaOH] = 0.0104 mol dm^{-3}.

CTAB and under the conditions at which the imine exists exclusively in the phenoxide form (pK_{OH} 8.96 at 35 °C, 5% MeOH–water, $I = 0.1$ mol dm^{-3})[10] exhibits λ_{max} at 420 and 320 nm with isosbestic points at 375, 362, 280 nm. For the corresponding reaction in the presence of CTAB, the spectral scan for this imine displays λ_{max} at 430 and 300 nm with isosbestic points at 382, 362, and 282 nm. The hydrolysis of the phenoxide form of Pyim is too fast to record precise absorbance–time curves over a wide range of wave lengths. In the presence of CTAB the reaction is, however, considerably slowed down. The successive spectral scans for Pyim at $[OH^-]_T = 0.01$ mol dm^{-3} and $[CTAB]_T = 0.1$ mol dm^{-3} (35 °C, 5% MeOH–water) displayed isosbestic points at 360 and 280 nm. Initially observed λ_{max} at 390 nm and λ_{min} at 340 nm ultimately shifted to 380 and 320 nm, respectively, at the end of base hydrolysis. These spectral evidences (at least for Tzim) suggest that the imine anions are bound to the micellar pseudophase of CTAB.

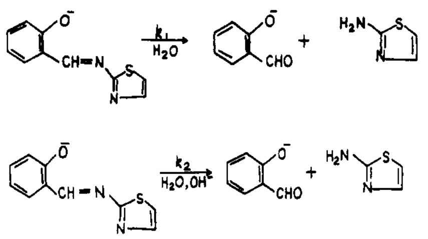
Micellar Binding Constant. Figure 1 presents the zero-time (extrapolated) absorbance data of a fixed total concentration of the anionic form of Tzim at 460 nm as a function of $[CTAB]_T$. The absorbance increases sharply at $[CTAB]_T > 0.0005$ mol dm^{-3}. The micellar binding constant (K_L^M) was calculated by fitting the absorbance data at $0.001 \leq [CTAB]_T \leq 0.06$ mol dm^{-3} to eq 2, which

$$\mathrm{Dn} + \mathrm{L_W}^- \overset{K_L^M}{\rightleftharpoons} \mathrm{L_M}^- \quad (1)$$

$$[L^-]_T/(A - A_0) = 1/(\epsilon_L^M - \epsilon_L^M) + [1/\{(\epsilon_L^M - \epsilon_L^W)K_L^M\}][1/([CTAB]_T - \mathrm{cmc})] \quad (2)$$

applies in the present case,[12] where $[L^-]_T = [Tzim]_T$; A_0 and A denote the absorbance of the imine anion in the absence and presence of CTAB, respectively; ϵ_L^M and ϵ_L^W denote the molar extinction coefficients of the imine anion in aqueous phase and micellar pseudophase, respectively. Dn stands for the micellized surfactant. CMC was used as an adjustable parameter around 0.0005 mol dm^{-3}. The best fit values were cmc = 0.0006 mol dm^{-3}, $(\epsilon_L^M - \epsilon_L^W)^{-1} = (22.59 \pm 0.29) \times 10^{-5}$ mol dm^{-3} cm, and $[(\epsilon_L^M - \epsilon_L^W)K_L^M]^{-1} = (38.58 \pm 0.33) \times 10^{-8}$ mol^2 dm^{-6} cm, which yielded $K_L^M = 585 \pm 10$ dm^3 mol^{-1} and $\epsilon_L^M = 12024 \pm 57$ dm^3 mol^{-1} cm^{-1} ($\epsilon_L^W = 7597$ dm^3 mol^{-1} cm^{-1}). It is worth noting that the value of the binding constant is significantly lower than that for the substituted phenoxide ions ($K_L^M = 10^3$–10^5 dm^3 mol^{-1} for $C_6H_4(X)O^-$, X = H, para-alkyl substituents[12] for CTAB micelle). One possible reason may be that the delocalization of the negative charge of the phenoxide moiety of L^- to the phenyl and thiazole rings annuls the charge effect on micellar binding. The low value of K_L^M further indicates that interpenetration of L^- to the hydrophobic micellar core is unlikely.

Scheme I



(b) Rate Data. The base hydrolysis of Tzim (Scheme I) in absence of CTAB followed the rate law

$$-\mathrm{d} \ln [\mathrm{Tzim}]_T/\mathrm{d}t = k_{obsd} = k_1 + k_2[OH^-] \quad (3)$$

in the range $0.01 \leq [OH^-]_T \leq 0.07$ mol dm^{-3} ($I = 0.1$ mol dm^{-3} adjusted with KBr). At 35 °C the values of $k_1 = (6.0 \pm 1.0) \times 10^{-4}$ s^{-1} and $k_2 = (5.8 \pm 0.3) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} obtained in the present work are in good agreement with those reported earlier.[10] For Pyim, k_{obsd} was also found to be independent of $[KBr]_T$ and $[OH^-]_T$ and averaged to $(2.8 \pm 0.1) \times 10^{-2}$ s^{-1} at $0.01 \leq [OH^-]_T \leq 0.07$ mol dm^{-3} (35 °C), which is in good agreement with our earlier result ($k = (3.5 \pm 0.2) \times 10^{-2}$ s^{-1} at $0.005 < [OH^-]_T < 0.2$ mol dm^{-3}, 35 °C).[11]

The rate data for base hydrolysis of the imines in the presence of CTAB are collected in Table I. It is worth noting that for each set of runs referring to a constant value of $[OH^-]_T$ and $[Br^-]_T$, k_{obsd} decreases to the asymptotic limit with increasing $[CTAB]_T$, reflecting the remarkable rate-retarding influence of this surfactant. On applying the pseudophase ion-exchange model[13] (Scheme II) to the imine anion (L^-) and OH^-, k_{obsd} is given by

$$k_{obsd} = \frac{k_W + (k_1^M + k_2^M m_{OH}^s)K_L^M[\mathrm{Dn}]}{1 + K_L^M[\mathrm{Dn}]} \quad (4)$$

where k_1^M and k_2^M are OH^--independent and OH^--dependent hydrolysis rate constants in the micellar pseu-

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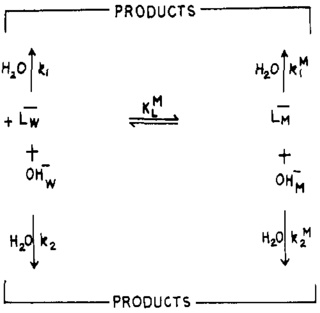
[12] Bunton, C. A.; Sepulveda, L. *J. Phys. Chem.* **1979**, *83*, 680. Hirose, C.; Sepulveda, L. *J. Phys. Chem.* **1981**, *85*, 3689.

Scheme II[a]



[a] Products of hydrolysis are salicylaldehyde anion and the amine, both being distributed in aqueous and micellar phases.

dophase, respectively, k_W ($= k_1 + k_2[OH^-_W]$ for Tzim and $= k_1$ for Pyim since the k_2 path is absent for the latter) is the corresponding rate constant in the aqueous pseudophase, $m_{OH}{}^s = [OH^-_M]/[Dn]$, and OH_M^- denotes the micellar-bound hydroxide ion. Considering the pseudophase ion-exchange equilibrium,[13]

$$OH^-_M + Br^-_W \xrightleftharpoons{K_{Br}{}^{OH}} OH^-_W + Br^-_M \qquad (5)$$

the concentrations of micellar bound OH^- and Br^- ($[OH^-_M]$ and $[Br^-_M]$) at equilibrium could be calculated from eq 6,

$$(m_{OH}{}^s)^2 + m_{OH}{}^s\left(\frac{[OH^-]_T + K_{Br}{}^{OH}[Br^-]_T}{(K_{Br}{}^{OH} - 1)[Dn]} - \beta\right) - \frac{\beta[OH^-]_T}{(K_{Br}{}^{OH} - 1)[Dn]} = 0 \qquad (6)$$

and the relationship $\beta = m_{OH}{}^s + m_{Br}{}^s$, where $m_X{}^s = [X^-_M]/[Dn]$ ($X^- = Br^-$ or OH^-) and $[Dn] = [\text{surfactant}]_T - \text{cmc}$. Cmc, $K_{Br}{}^{OH}$, and β were used as adjustable parameters, their first approximate values being chosen as 0.9×10^{-3} mol dm^{-3},[2] 13.5, and 0.75,[13,14] respectively. This enabled us to compute the ionic composition of the aqueous pseudophase and then calculate the observed rate constant (k_W) for the aqueous pseudophase (see eq 1).[15] Equation 4 can be rearranged to eq 7. With the initial

$$\frac{(k_W - k_{obsd})}{[Dn]m_{OH}{}^s} = -k_2{}^M K_L{}^M + K_L{}^M(k_{obsd} - k_1{}^M)/m_{OH}{}^s \qquad (7)$$

estimates of $m_{OH}{}^s$ and [Dn] and with $k_1{}^M$ as an adjustable parameter, the rate data in Table I were fitted to eq 7 to yield the best linear plot of $(k_W - k_{obsd}/[Dn]m_{OH}{}^s$ vs. $(k_{obsd} - k_1{}^M)/m_{OH}{}^s$, from which the approximate values of $k_1{}^M = 1.0 \times 10^{-4}$ s^{-1}, $k_2{}^M K_L{}^M = 2.0$ dm^3 mol^{-1} s^{-1}, and $K_L{}^M = 611$ dm^3 mol^{-1} were obtained for Tzim. Further refinement of the values of these parameters were made by fitting the rate data to eq 4 by means of a nonlinear least-squres program adopted to IBM 1130 computer of Utkal University. The parameters ($k_1{}^M K_L{}^M$), ($k_2{}^M K_L{}^M$), and $K_L{}^M$ were allowed to vary for each set of values of cmc (=0.0002–0.0008 mol dm^{-3}), $K_{Br}{}^{OH}$ (=12.0–14.0), and β (=0.6–0.8) used to calculate $m_{OH}{}^s$, and CHISQR $= \sum[(k_{calcd} - k_{obsd}/\sigma(k_{obsd})]^2$ ($\sigma(k_{obsd}) = 0.05 \times k_{obsd}$) was minimized. The best fit values of the parameters corresponding to CHISQR = 1.0 (cmc = 0.0006 mol dm^{-3}, $K_{Br}{}^{OH} = 14.0$, and $\beta = 0.8$) are as follows: $k_1{}^M K_L{}^M = 0.134 \pm 0.009$ dm^3 mol^{-1} s^{-1}, $k_2{}^M K_L{}^M = 1.25 \pm 0.18$ dm^3 mol^{-1} s^{-1}, and $K_L{}^M = 787 \pm 26$ dm^3 mol^{-1}. These data yielded $k_1{}^M = (1.7 \pm 0.1) \times 10^{-4}$ s^{-1} and $k_2{}^M = (1.6 \pm 0.2) \times 10^{-3}$ s^{-1} for Tzim. The data for Pyim (see Table II) at varying $[OH^-]$ and [CTAB] are virtually insensitive to $[OH^-]_T$ but decrease with $[CTAB]_T$. This is in keeping with the fact that the micellar-bound imine anion of Pyim, unlike Tzim, is not subject to OH^--catalyzed hydrolysis. Setting $k_2{}^M = 0$, the rate data for Pyim were fitted to eq 4 by the weighted least-squares procedure, which yielded $k^M K_L{}^M = 0.927 \pm 0.006$ dm^3 mol^{-1} s^{-1}, $K_L{}^M = 708 \pm 28$ dm^3 mol^{-1}, and $k_1{}^M = (1.3 \pm 0.1) \times 10^{-3}$ s^{-1}. Both $K_L{}^M$ and $k_1{}^M$ were insensitive to cmc as $[CTAB]_T$/cmc > 8 was maintained (see data in Table II).

Table II. Effect of CTAB on the Hydrolysis of *N*-Salicylidene-2-aminopyridine at 35 °C[a]

$10^3[CTAB]_T$, mol dm^{-3}	$10^2 k_{obsd}$,[b] s^{-1}
0.00	2.8 ± 0.1[c]
5.00	0.77 ± 0.06
10.0	0.48 ± 0.07
20.0	0.33 ± 0.06
30.0	0.26 ± 0.07
40.0	0.23 ± 0.03
50.0	0.23 ± 0.04
60.0	0.19 ± 0.01

[a] $[NaOH]_T + [KBr]_T + [CTAB]_T = 0.105$ mol dm^{-3}. [b] Average of three to four determinations at each $[CTAB]_T$ and different $[OH^-]$ in the range 0.01–0.07 mol dm^{-3}. [c] Average of four determinations at $[OH^-]$ = 0.01, 0.02, 0.05, and 0.07 mol dm^{-3}.

Table III. Effect of CTAB and SDS on the Hydrolysis of *N*-Salicylidene-2-aminothiazole in Mild Alkaline Range of pH at 35 °C

pH[a] = 9.24 ± 0.02, $[Br^-]_T$[b] = 0.05 mol dm^{-3}		pH[a] = 9.25 ± 0.02, $[Na^+]_T$[b] = 0.1 mol dm^{-3}	
$10^3[CTAB]_T$, mol dm^{-3}	$10^3 k_{obsd}$, s^{-1}	$10^3[SDS]_T$, mol dm^{-3}	$10^3 k_{obsd}$, s^{-1}
0.00	2.59		
0.20	2.50		
0.50	2.30		
1.00	2.20		
2.00	1.34		
5.00	0.73		
10.0	0.45	10.0	1.54
20.0	0.31	20.0	1.30
30.0	0.29	30.0	1.07
40.0	0.27	40.0	0.97
50.0	0.24	50.0	0.90

[a] Borate buffer; $[Na_2B_4O_4]_T = 0.025$ mol dm^{-3}. [b] $[Br^-]_T$ and $[Na^+]_T$ were adjusted with KBr and $NaClO_4$, respectively.

2. Effect of SDS on the Base Hydrolysis of the Imines. The effect of SDS on the alkaline hydrolysis of both the imines was examined at constant $[OH^-]_T = 0.02$ mol dm^{-3}, $0 \leq [SDS]_T \leq 0.2$ mol dm^{-3} (35 °C, 5% MeOH). No appreciable influence of SDS was observed ($k_{obsd} = (1.6 \pm 0.1) \times 10^{-3}$ and $(3.2 \pm 0.2) \times 10^{-2}$ s^{-1} for Tzim and Pyim, respectively, under the conditions stated above). Spectral evidence for the interaction of the phenoxide form of the imines with SDS was also negative. Thus it is evident that the imine anions, consistent with electrostatic considerations, tend to avoid the anionic micellar pseudophase region of SDS.

3. Effect of CTAB and SDS on the Hydrolysis of the Imines in Mild Alkaline Medium. The effects of the surfactants on the rates of hydrolysis of slow reacting Tzim were examined at pH 9.2 (borate buffer, 35 °C), and the relevant data are collected in Table III. In the range

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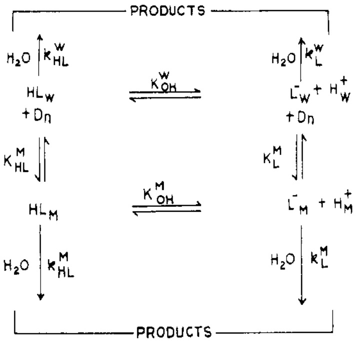
(13) Al-Lohedan, H.; Bunton, C. A.; Romsted, L. S. *J. Phys. Chem.* **1981**, *85*, 2123.

(14) Bunton, C. A.; Mhala, M. M.; Moffatt, J. R.; Monarres, D.; Savelli, G. *J. Org. Chem.* **1984**, *49*, 426.

(15) I_{calcd} for the aqueous pseudophase corresponding to the data in Table I varied from 0.104 to 0.088 mol dm^{-3}. Ionic strength correction of k_2 was made by the relationship log $k_2nI)$ = log $k_2(I = 0.1) + 1.02(I^{1/2} - 0.1^{1/2})$: Eyring H.; Lin, S. H.; Lin, S. M. In "Basic Chemical Kinetics"; Wiley: New York, 1980; p 414.

Scheme III



of [surfactant]$_T$ used the pH of the reaction mixture remained essentially constant. Quina et al.[16] recently demonstrated that although the intermicellar pH of borate-buffered solutions is maintained constant up to [CTAB]$_T$ = 0.1 mol dm^{-3}, the local concentration of OH$^-$ in the micellar phase decreases with increasing concentration of the micellized surfactant (CTAB). Fortunately for us the OH$^-$-catalyzed hydrolysis of the imine anion is negligible at pH 9.2, and the spontaneous hydrolysis (k_1 path) is the only significant path. Hence, variation of pH in the micellar pseudophase is of little kinetic significance. Both CTAB and SDS exert the rate-retarding influence under this conditions, the effect being relatively more pronounced for CTAB. This is attributed to the following facts: (i) both phenol and phenoxide forms of the imine are partitioned into the micellar pseudophase of the cationic CTAB micelle, where they are stabilized to hydrolytic splitting, and (ii) only the phenol form of the imine is selectively adsorbed in the anionic pseudophase of SDS micelle, where it undergoes hydrolysis at a rate presumably different from that in the aqueous pseudophase. The reaction Scheme III is considered to be valid, for which k_{obsd} is given by eq 8.

$$k_{obsd} = \frac{k_{obsd}'(1 + K_{OH}{}^{W}/[H_W{}^+]) + A[Dn]}{1 + K_{OH}{}^{W}/[H_W{}^+] + B[Dn]} \tag{8}$$

where $A = k_{HL}{}^{M}K_{HL}{}^{M} + k_L{}^{M}K_L{}^{M}\,K_{OH}{}^{W}/[H_W{}^+]$, $B = K_{HL}{}^{M} + K_L{}^{M}K_{OH}{}^{W}/[H_W{}^+]$, and $k_{obsd}' = k_{obsd}$ at the same pH and [surfactant]$_T$ = 0; all other terms have their usual meaning. Equation 8 can be rearranged to eq 9:

$$(k_{obsd}' - k_{obsd})(1 + K_{OH}{}^{W}/[H_W{}^+])/[Dn] = Bk_{obsd} - A \tag{9}$$

Disregarding the effect of small variation of ionic strength[17] in the aqueous phase and taking $k_{obsd}' = (2.4 \pm 0.1) \times 10^{-3}$ s^{-1} (i.e., the practically constant value of k_{obsd} at $0 \leq$ [CTAB]$_T \leq 5 \times 10^{-4}$ mol dm^{-3}, pH 9.24), the rate data for CTAB system ($0.002 \leq$ [CTAB]$_T \leq 0.05$ mol dm^{-3}) were fitted to eq 9 by taking cmc = 0.0006 mol dm^{-3}. We obtained $A = 0.38 \pm 0.05$ dm^3 mol^{-1} s^{-1} and $B = (2.0 \pm 0.2) \times 10^3$ dm^3 mol^{-1}. Using $K_{OH}{}^{W} = 1.1 \times 10^{-9}$ mol dm^{-3},[10] $K_L{}^{M} = 787$ dm^3 mol^{-1}, and $k_L{}^{M} = 1.7 \times 10^{-4}$ s^{-1} (i.e., $k_L{}^{M} = k_1{}^{M}$), we obtained $k_{HL}{}^{M} = (2.5 \pm 1.2) \times 10^{-4}$ s^{-1} and $K_{HL}{}^{M} = (4.9 \pm 2.0) \times 10^2$ dm^3 mol^{-1} from the calculated values of A and B.

The rate data (see Table III) in the presence of SDS at pH 9.2 and $0.02 \leq$ [SDS]$_T \leq 0.05$ mol dm^{-3} were also fitted to eq 9. Cmc was varied from 0.001–0.008 mol dm^{-3}. The least-squares best values of the parameters are $A = 0.17 \pm 0.04$ dm^3 mol^{-1} s^{-1} and $B = 283 \pm 35$ dm^3 mol^{-1}, corresponding to cmc = 0.001 mol dm^{-3}. Since the imine anion does not get partitioned into the anionic micellar phase of SDS, A and B are reconciled with $k_{HL}{}^{M}K_{HL}{}^{M}$ and $K_{HL}{}^{M}$, respectively. The value of $k_{HL}{}^{M}$ ($=A/B$) turns out to be $(6.0 \pm 1.6) \times 10^{-4}$ s^{-1}.

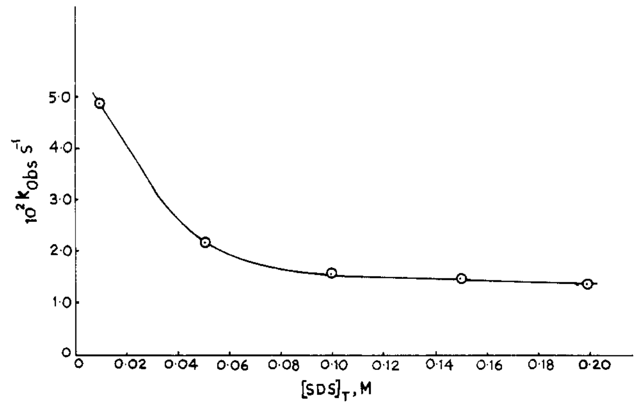


Figure 2. Effect of SDS on the hydrolysis of N-salicylidene-2-aminopyridine at 35 °C: pH 9.20 ± 0.04; [Na$_2$B$_4$O$_7$]$_T$ = 0.025; [NaClO$_4$]$_T$ + [SDS]$_T$ = 0.2 mol dm^{-3}; λ = 320 nm.

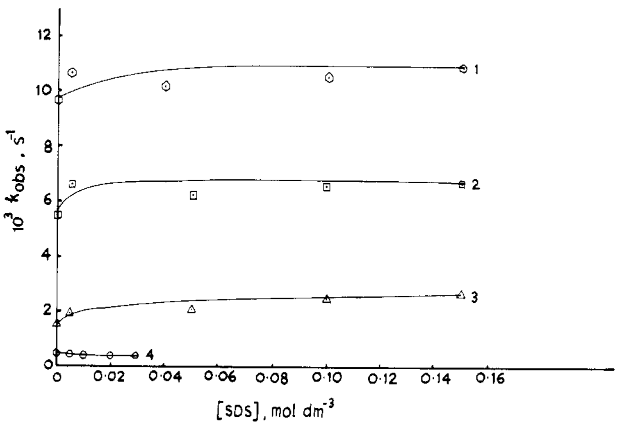


Figure 3. Effect of SDS on the rate of hydrolysis of N-salicylidene-2-aminothiazole at 35 °C. $10^3 k_{obsd}$, s^{-1}, against [SDS]$_T$, mol dm^{-3}, plots at pH values: (1) 5.08 ± 0.03; (2) 5.44 ± 0.04; (3) 6.19 ± 0.04; (4) 7.06 ± 0.04.

The rate data for the hydrolysis of Pyim in the presence of SDS at pH 9.20 also depict the strong retarding influence of the surfactant (see Figure 2). It may be mentioned that the intense band expected for the phenoxide form of the imine around 420 nm virtually disappeared in the presence of SDS (the rate measurements were made at 320 nm). This is attributed to the shift of the quilibrium HL $\rightleftharpoons$ H$^+$ + L$^-$ in the direction of the neutral form of the imine (HL) due to its selective partitioning into the anionic micellar pseudophase. Hence, the asymptotic limit of k_{obsd} at [SDS]$_T$ = 0.2 mol dm^{-3} ($k_{obsd} = (1.35 \pm 0.01) \times 10^{-2}$ s^{-1}, 35 °C) may be tken to be the rate constant of hydrolysis of Pyim (HL form) in the micellar pseudophase of SDS.

4. Effect of SDS on Hydrolysis of Imines in Mild Acidic Medium. The effect of SDS on the rates of hydrolysis of Tzim was examined at pH 5.08 ± 0.03, 5.44 ± 0.04 (acetate buffer, $0 \leq$ [SDS]$_T \leq 0.15$ mol dm^{-3}), 6.19 ± 0.04, and 7.06 ± 0.04 (phosphate buffer, $0 \leq$ [SDS]$_T \leq 0.03$ mol dm^{-3}), [Na$^+$]$_T$ in the reaction mixture being adjusted to 0.2 mol dm^{-3} with NaClO$_4$. The rate data presented in Figure 3 indicate that SDS exerts very little effect on the rate of hydrolysis. Similar observations have been made in the hydrolysis imines,[15] aryl–akyl halides, and benzoyl chloride.[9]

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[16] Quina, F. H.; Pollti, F. H.; Cuccovia, I. M.; Bumgarten, E.; Martins-Franchetti, S. M.; Chaimovich, H. J. Phys. Chem. 1980, 84, 361.

[17] For aqueous phase, 0.10 < I_{calcd} < 0.06 mol dm^{-3} for the runs in the presence of CTAB at pH 9.2 (see Table III).

Table IV. Rate Data for Hydrolysis of *N*-Salicyclidene-2-aminopyridine in the Presence of Cu(II) and SDS (Varying [SDS][a]) in Mild Acidic Medium at 35 °C

		$10^2\ k_{\text{obsd}}$,[b] s^{-1}							
$10^4[Cu^{2+}]$, mol dm^{-3}	pH	0.02	0.05	1.0	3.0	5.0	7.0	10.0	15.0
40.0	5.03 ± 0.04	1.00	1.30			2.2		2.8	
60.0	5.03 ± 0.04	0.70	0.92			1.7		2.6	
80.0	5.03 ± 0.04	0.70	1.0	0.83	2.0	2.1	2.1	2.5	
80.0	5.03 ± 0.04	0.63		1.20	2.4				
60.0	5.22 ± 0.02	0.34	0.61			1.0		1.2	1.4
10.0	5.65 ± 0.02		0.43	0.58	0.64	0.64	0.69		
10.0	5.94 ± 0.02	0.15	0.16		0.18	0.19			

[a] 10^2[SDS], mol dm^{-3}. [b] $[HL]_T = 1.35 \times 10^{-4}$ mol dm^{-3}; λ = 370 nm; *I* adjusted to 0.2 mol dm^{-3} with $NaClO_4$. $10^2(k_1^M)_{CuL^+}$, s^{-1} = 2.4 ± 0.3 (pH 5.03), 1.2 ± 0.2 (pH 5.22), 0.67 ± 0.03 (pH 5.65), and 0.19 (pH 5.96).

5. Effect of SDS on the Copper(II) Ion Induced Hydrolysis of the Imines in the Mild Acidic Medium. The spectral scan for the Tzim in the presence of Cu(II) ($[Cu^{2+}]_T$ = 0.006 mol dm^{-3}, $[Cu^{2+}]/[HL]$ = 50, pH 5.4, 30 °C) exhibited the absorption maximum for CuL^+ species at 420 nm. In the presence of SDS (0.1 mol dm^{-3}), all other conditions remaining the same, λ_{max} for CuL^+ species shifted to 440 nm, indicating thereby that the copper(II)–imine complex is presumably in the micellar pseudophase. Rate measurements, however, yielded $k_{obsd} = (2.2 \pm 0.4) \times 10^{-3}\ s^{-1}$ at pH 4.98 ± 0.05, $[Cu^{2+}]_T$ = 0.006, and $0.2 \times 10^{-3} \leq [SDS]_T \leq 150 \times 10^{-3}$ mol dm^{-3} (*I* = 0.2 mol dm^{-3}, 35 °C, 5% MeOH) as against $k_{obsd} = 2.1 \times 10^{-3}\ s^{-1}$ under similar conditions but in the absence of SDS. At $[Cu^{2+}]_T$ = 0 and $[SDS]_T$ = 0 k_{obsd} is $(12.5 \pm 1.0) \times 10^{-3}\ s^{-1}$ at pH 4.94 ± 0.06 under similar conditions of temperatue, ionic strength, and solvent composition. Thus it is evident that the copper(II)–imine complex of Tzim is virtually equally stable to hydrolysis both in aqueous and micellar pseudophases.

The copper(II)–Pyim complex (CuL^+) exhibited λ_{max} and λ_{min} at 395 and 345 nm, respectively, in the presence of $[SDS]_T$ = 0.1 mol dm^{-3} (at $[Cu^{2+}]/[HL]$ = 50, pH 5.36, 30 °C), while in the absence of the surfactant it had absorption maximum at 388 nm and minimum at 340 nm. This may be taken as an evidence in favor of the micellar binding of the species CuL^+. The rate data presented in Table IV show that k_{obsd} increases with increasing [SDS] and levels off to a constant value at $[SDS]_T > 0.05$ mol dm^{-3} in the range $5.03 \leq pH \leq 5.96$ when $[Cu^{2+}]/[HL]_T$ is maintained at ≃8 (pH 5.96 and 5.65), 45 (pH 5.22), and 30–60 (pH 5.03). Noteworthy is the fact that the limiting rate constants, $(k_1^M)_{CuL^+}$, are very much different from the hydrolysis rate constant of Pyim (calculated k_{obsd} = 0.24–0.034 s^{-1} at pH 5.03–5.96) and of its copper(II) complex (calculated $k_{CuL^+} = 4.1 \times 10^{-3}$ to $0.48 \times 10^{-3}\ s^{-1}$ at pH 5.03–5.96) in the aqueous phase (*I* = 0.1 mol dm^{-3}, 35 °C, 5% MeOH) as calculated from our earlier data.[11] The results at hand, therefore, suggest that the limiting values of the rate constants at $[SDS]_T \geq 0.05$ mol dm^{-3} stand for the hydrolysis rate constant of the copper(II) complex (CuL^+) in the micellar pseudophase. Further the $[H^+]$ dependence of this rate constant (i.e., $(k_1^M)_{CuL^+}$) (eq 10)

$$(k_1^M)_{CuL^+} = (k^M{}_{CuL^+})[H^+]_W \qquad (10)$$

(see Figure 4) reflects that CuL^+ in the micellar phase undergoes hydrolysis exclusively via the acid-catalyzed step. Similar observation has been made by us for hydrolysis of CuL^+ species of Pyim in the aqueous phase,[11] indicating thereby that micellar binding of the complex does not lead to a different mechanism of its hydrolysis. The acid-catalyzed hydrolysis rate constant ($k^M{}_{CuL^+}$) calculated from the slope of the $(k_1^M)_{CuL^+}$ against $[H^+]_W$ plot is $(2.3 \pm 0.6) \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$.

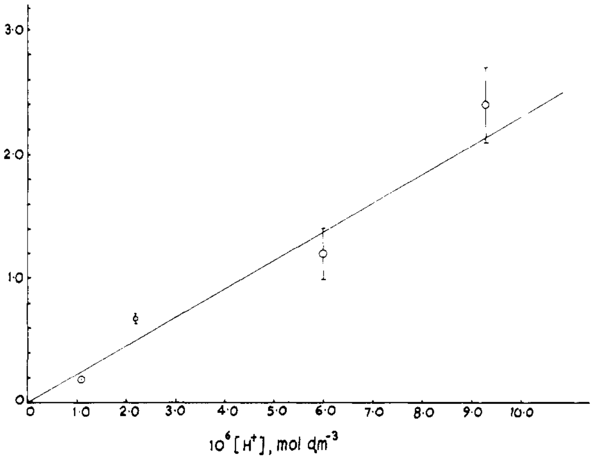


Figure 4. $10^2(k_1^M)_{CuL^+}$, s^{-1}, against $10^6[H^+]$, mol dm^{-3}, plot for the hydrolysis of copper(II)–*N*-salicylidene-2-aminopyridine complex in the SDS micelle.

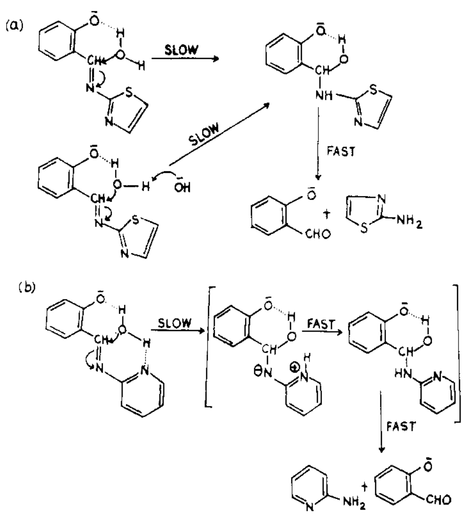
Table V. Comparison of Rate Data in Aqueous and Micellar Phases

	value of rate constant (*k*) at 35 °C, $s^{-1\,a}$	
reaction	aqueous phase	micellar phase
	HL = *N*-Salicyclidene-2-aminothiazole	
$L^- + H_2O$	$(6 \pm 1) \times 10^{-4}$	$(1.7 \pm 0.1) \times 10^{-4}$ (CTAB)
$L^- + OH^- + H_2O$	$(5.8 \pm 0.2) \times 10^{-2}$	$(2.2 \pm 0.3) \times 10^{-4}$* (CTAB)
$HL + H_2O$	$(2.9 \pm 0.2) \times 10^{-4\,b,c}$	$(2.5 \pm 1.2) \times 10^{-4}$ (CTAB) $(6.0 \pm 1.6) \times 10^{-4\,b}$ (SDS)
	HL = *N*-Salicyclidene-2-aminopyridine	
$L^- + H_2O$	$(2.8 \pm 0.1) \times 10^{-2}$	$(1.3 \pm 0.1) \times 10^{-3}$ (CTAB)
$HL + H_2O$	$(0.63 \pm 0.05) \times 10^{-2\,b,d}$	$(1.35 \pm 0.10) \times 10^{-2\,b}$ (SDS)
$CuL^+ + H^+ + H_2O$	$(4.4 \pm 0.3) \times 10^{2\,d}$*	$(2.3 \pm 0.6) \times 10^3$* (SDS)

[a] In $dm^3\ mol^{-1}\ s^{-1}$ when denoted by *. [b] The values are the upper limits for the aqueous phase as the kinetically indistinguishable reaction $H_2L^+ + OH^-$ will also contribute to *k* in the aqueous phase. The values of *k* in the micellar phase are obtained from the rate data at pH 9.2 (see Table III). [c] Reference 10. [d] Reference 11.

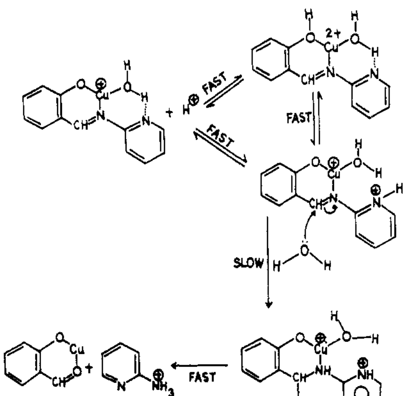
Discussion

Rate data for the hydrolysis reactions of different forms of the imines under investigation are presented in Table V. It is pertinent to note that (i) the imine anions are strongly bound to the micellar pseudophase of the ctionic surfactnat CTAB (K_L^M = 787 $dm^3\ mol^{-1}$ for Tzim and 708 $dm^3\ mol^{-1}$ for Pyim), (ii) micellar binding slows down their OH^--independent hydrolysis rates (k_1/k_1^M = 3.7 for Tzim and 22 for Pyim), and (iii) the anion of Pyim, unlike its Tzim analogue, is not subject to OH^--catalyzed hydrolysis in the micellar pseudophase. Considering the dimensions, Scheme IV[a]



[a] Intramolecular general base catalysis: (a) CH^--independent and OH^--dependent paths of Tzim and (b) OH^--independent path of Pyin.

Scheme V



k_2^M cannot be compared with k_2. If it is assumed that the imine anions are positioned in the Stern layer of the micelle of CTAB, the estimated volume of which is taken to be 0.14 L,[13] then the second-order rate constant ($k_2^{(m)} = 0.14\ k_2^M$) in the micellar pseudophase for Tzim turned out to be $(2.2 \pm 0.3) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}. This is at least 200 times lower than the analogous data for Tzim in the aqueous phase (see Table V). For direct nucleophilic attack of OH^- at the aldimine carbon micellar binding of both OH^- and the imine anion would have resulted in the rate acceleration. This contrasting feature along with complete lack of $[OH^-]$ dependence in the hydrolysis of the anion of Pyim in both the aqueous and micellar pseudophases strongly supports our earlier suggestion[10,11] that the hydrolysis of the phenoxide form of both the imines via both OH^--independent and OH^--dependent paths (the latter path for Tzim) involves intramolecular general base catalysis of the phenoxide group of Tzim and of the phenoxide group and pyridyl nitrogen of Pyim (Scheme IV).

The pseudo-first-order rate constant of hydrolysis of the neutral form of Tzim in the micellar phase (k_{HL}^M) of CTAB is not significantly different from the corresponding rate constant in the aqueous phase (see Table V). This is in contrast with the reported marked inhibitory effect of CTAB on the rate of apparently neutral hydrolysis of benzilidene imines which involves rate-determining attack of OH^- on their protonated form.[18] The observed order of reactivity of the imines is $k_{HL}^M(\mathrm{SDS}) > k_{HL}^M(\mathrm{CTAB})$. The neutral form of the imines undergoes hydrolysis in the micellar pseudophase of SDS twice as fast as in the aqueous phase (see Table V). The observed kinetic effects as well as the low value of the micellar binding constant (K_{HL}^M) point to the fact that the imines, like their anionic forms, are presumably positioned in the Stern layer of the micelles rather than in the hydrophobic interior of the latter.

The second-order acid-catalyzed hydrolysis rate constant of the complex in the micellar pseudophase ($k^M_{CuL^+}$) of SDS is 5 times higher than the corresponding rate constant in the aqueous phase (see Talbe V). The relatively stronger acid catalysis of hydrolysis of CuL^+ in the anionic micelle may be attributed to the micelle-enhanced basicity of the unbound pyridyl nitrogen and the coordinated phenoxide moiety of the imine complex, which may undergo fast protonation preequilibrium preceding the rate determining hydration of the imine linkage (Scheme V). The validity of eq 10, however, suggests that the micelle-bound species CuL^+ is not appreciably protonated in the range of pH studied.

Registry No. N-Salicylidene-2-aminothiazole, 21151-43-9; N-salicylidene-2-aminopyridine, 1823-47-8; cupric perchlorate, 13770-18-8.

Supplementary Material Available: Two figures showing isosbestic points in the base hydrolysis of N-salicylidene-2-aminothiazole in the absence and presence of CTAB (3 pages). Ordering information is given on any current masthead page.

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(18) Behme, M. J. A.; Cordes, E. H. *J. Am. Chem. Soc.* **1965**, *87*, 260.

N-Methylpiperidine *N*-Oxide as a Source of Nonstabilized Ylide: A New and Efficient Route to Octahydroindolizine Derivatives

J. Chastanet and G. Roussi*

Institut de Chimie des Substances Naturelles, C.N.R.S., 91190 Gif-sur-Yvette, France

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N-Methylpiperidine *N*-oxide in the presence of LDA reacts with various nonactivated olefins to give high yields of the corresponding octahydroindolizines. The structure of the nonstabilized ylide intermediate allows the study of the *regiochemistry* and *stereochemistry* of this new cycloaddition reaction.

The 1,3-dipolar cycloaddition is one of the most useful reactions for the synthesis of five-membered heterocyclic compounds.[1] However, the vast majority of syntheses reported involve electron withdrawing group activated

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