Micellar Effects upon the Hydrolysis of N-(Trifluoroacetyl)indole

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The rate constants of acid hydrolysis of N-(trifluoroacetyl)indole (1) in 0.03 or 0.1 M HCl are slightly increased by anionic micelles of sodium lauryl sulfate (NaLS). From these data, and the distribution of hydrogen ions and substrate between water and the micelles, we estimate the second-order rate constant for the hydrogen ion reaction in the micellar pseudophase to be smaller than that in water by a factor of ca. 30. Cationic micelles of cetyltrimethylammonium bromide (CTABr) retard the acid hydrolysis, but they speed hydrolysis at pH 3–4, and their effect is reduced by NaCl or NaBr. Hydrolysis at pH 4.85 is inhibited by NaLS. These micellar effects can be interpreted in terms of mechanisms in which the hydrate of 1 is a key intermediate.

The rates of acid hydrolysis of N-(trifluoroacetyl)pyrrole, -indole, and -carbazole go through maxima with increasing acid concentration.[2,3] This kinetic form is ascribed to prior addition of water, followed by acid-catalyzed breakdown of the hydrate which is shown for the hydrolysis of N-(trifluoroacetyl)indole (1) in Scheme I.

This mechanism appears to be general for the acid hydrolysis of weakly basic esters and related compounds which contain strongly electron-withdrawing substituents.[3,4] Rate maxima are often observed in acid hydrolysis of relatively strongly basic substrates such as aliphatic amides, but these rate maxima are due to extensive protonation of the substrate followed by rate-limiting attack of water upon the protonated substrate.[5] Thus these apparently similar kinetic forms have completely different mechanistic origins.

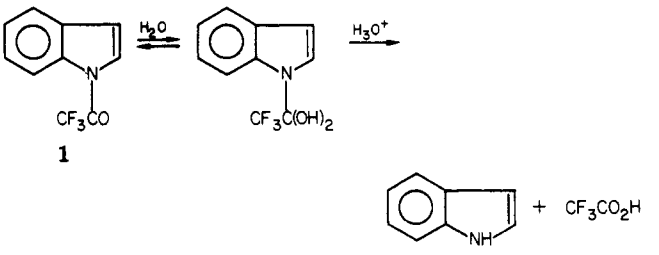
The hydrolysis of N-(trifluoroacetyl)indole is also unusual in that there is a rate minimum at pH 2–3, and then the first-order rate constant increases linearly with the reciprocal of the hydrogen ion concentration, until it levels off at pH ca. 6.5. (At pH >8.5 the rate constant again increases with increasing pH).

The dependence of rate constant on pH in the region pH 3–7 can be explained in terms of the reactions shown in Scheme II.

In Scheme II the anion 2 is treated as a steady-state intermediate.

Acid hydrolyses are typically catalyzed by anionic and inhibited by cationic micelles.[6] For a given hydrogen ion concentration the rate constants generally go through maxima with increasing concentration of the anionic surfactant, and the rate surfactant profiles can be interpreted quantitatively by estimating the concentrations of each reactant in the micellar pseudophase.[10,11] The second-order rate constants in the micellar psuedophase are typically smaller than those in water by approximately one order of magnitude.

Scheme I



Scheme II

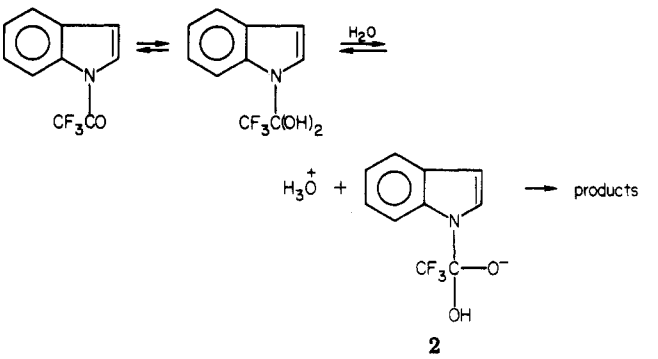


Table I. Inhibition of Hydrolysis by NaLS[a]

10^3[NaLS], M	10^3k_Ψ, s^{-1}	10^3[NaLS], M	10^3k_Ψ, s^{-1}
	3.40	5.0	1.35
0.5	3.46	7.5	0.92
1.0	3.52	10.0	0.72
2.5	2.31	15.0	0.49

[a] At 25.0 °C, pH 4.85, 0.1 M acetate buffer.

Micellar effects upon the base hydrolyses of amides have been studied[12,14] and show the expected behavior, but

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(13) (a) Broxton, T. J.; Deady, L. W.; Duddy, N. W. *Aust. J. Chem.* **1978**, *31*, 1525. Broxton, T. J.; Duddy, N. W. *Ibid.* **1979**, *32*, 1717. (b) O'Connor, C. J.; Ah-Lek Tan *Ibid.* **1980**, *33*, 747.
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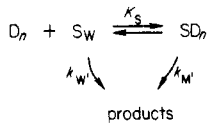
Scheme III



because of the unusual mechanisms of hydrolysis of *N*-(trifluoroacetyl)indole[2,3] we have examined micellar effects upon the acid hydrolysis (Scheme I) and the hydrolysis at pH 3–4 (Scheme II).

Experimental Section

Materials. *N*-(Trifluoroacetyl)indole,[2] CTABr, and NaLS were prepared or purified by methods already described.[10] There were no minima in plots of surface tension against surfactant concentration.

Kinetics. Hydrolyses were followed at 246 nm in a Beckman spectrophotometer in aqueous solution at 25.0 °C. The first-order rate constants, k_ψ, are in reciprocal seconds.

Results

Binding of Substrate of Micelles. Trifluoroacetyl derivatives such as 1 are readily hydrolyzed in aqueous solutions, so that it is difficult to demonstrate micellar binding of the substrate (1) by the usual methods. However, we observe inhibition by NaLS of hydrolysis at pH 4.85 (Scheme II) and by CTABr of hydrolysis in 0.1 M HCl (Scheme I), which allows us to estimate binding constants of 1 to micellized surfactant.

The rate constants for reaction in NaLS are in Table I, and we use this inhibition to estimate the binding constant, K_S, of the substrate to the micellized surfactant, following Scheme III, where D_n denotes micellized surfactant (detergent) and k_W' and k_M' are, respectively, the first-order rate constants in the aqueous and micellar pseudophases respectively. The binding constant is given by eq 1,[7-9] where the subscript W denotes the substrate,

$$K_S = [SD_n]/[S_W]([D] - cmc) \quad (1)$$

S, in the aqueous psuedophase and the amount of monomer is assumed to be given by the critical mcelle concentration, cmc.

Scheme III leads to eq 2 for the relation between k_ψ and

$$k_\psi = (k_W' + k_M'K_S([D] - cmc))/(1 + K_S([D] - cmc)) \quad (2)$$

[D]. Equation 2 can be written as eq 3,[15] so that, given

$$1/(k_W' - k_\psi) = 1/(k_W' - k_M') + 1/(k_W' - k_M')K_S([D] - cmc) \quad (3)$$

k_W' k_M', and K_S can be estimated from a plot of $1/(k_W' - k_\psi)$ against $1/([D] - cmc)$. This type of plot is sensitive to the value of the cmc, which is assumed to give the concentration of monomeric surfactant.[15] But we see considerable inhibition at concentrations of NaLS below the cmc in water, which is ca. 8×10^{-3} M.[16] This behavior is very common and is ascribed to interactions between surfactant and solutes which induce micellization or formation of submicellar aggregates.[10,17] The problem can be treated in various ways: (i) the cmc is treated as an adjustable parameter chosen to fit eq 3,[18] and we obtained a linear fit taking cmc = 1.4×10^{-3} M, and then K_S = 420 M^{-1} and $k_W' - k_M' \approx 3.5 \times 10^{-3}$ s^{-1}, and as expected $k_M' \approx 0$; (ii) one can assume that $k_M' = 0$, and then eq 2 reduces to eq 4[19] and a plot of $(k_W' - k_\psi)/k_\psi$ against [D] should

$$(k_w' - k_\psi)/k_\psi = K_S([D] - cmc) \quad (4)$$

be linear with slope = K_S. This method gives K_S = 500 M^{-1}. In the following discussion we take K_S = 420 M^{-1}.

Table II. Inhibition of Acid Hydrolysis by CTABr[a]

10^3[CTABr], M	10^4k_ψ, s^{-1}	10^3[CTABr], M	10^4k_ψ, s^{-1}
	3.68	3.0	0.60
0.45	1.75	5.0	0.46
0.60	1.52	7.5	0.39
1.0	1.16	15.0	0.25

[a] At 25.0 °C, 0.1 M HCl, μ = 0.3 (NaCl).

Table III. Rate Enhancements of the Acid Hydrolysis by NaLS[a]

	[HCl], M	
10^3[NaLS], M	0.03	0.1
0.50	1.10	3.7
0.63	1.10	
1.00	1.07	
1.26	1.11	
2.50	1.08	
3.15	1.65 (2.54)	
5.00	3.13 (3.40)	3.50 (2.84)
6.30	3.67 (3.62)	
7.50	3.79 (3.73)	3.92 (4.30)
9.45	3.82 (3.77)	
10.0	3.99 (3.77)	4.10 (4.11)
12.6	3.86 (3.70)	
20.0		4.01 (3.89)
35.0		3.60 (3.46)
50.0		3.20 (3.12)

[a] Values of 10^4k_ψ, s^{-1}, at 25.0 °C. The values in parentheses are calculated by using eq 8 and values of k_M.

Inhibition of Acid Hydrolysis by CTABr. As expected cationic micelles of CTABr inhibit the acid hydrolysis of *N*-(trifluoroacetyl)indole (Table II). The reaction was carried out in 0.3 M NaCl, so that the cmc should be very small, and we assume it to be zero. The data then fit eq 3 and give K_S = 2700 M^{-1}. The intercept gives $k_W' - k_M' = 3.5 \times 10^{-4}$ s^{-1}. Under these conditions $k_W' = 3.7 \times 10^{-4}$ s^{-1}, so that k_M' is zero or very small relative to k_W'.

The value of K_S is an approximate one, because the concentrations of the mixed counteranions are changing with [CTABr] and this change will alter the properties of the micelle, including the cmc. However, the results show that the substrate binds strongly to cationic micelles.

Hydrolysis in Dilute HCl. There is a small rate enhancement by NaLS of hydrolysis in 0.03 M HCl but almost none in 0.1 M HCl (Table III) and there is even a slight inhibition in the presence of 0.3 M NaCl relative to reaction in water, due to competition between hydrogen and sodium ions for the anionic micelle. In 7.5×10^{-3} M NaLS and 0.3 M NaCl and 0.1 M HCl $k_\psi = 2.7 \times 10^{-4}$ s^{-1}, whereas in 0.1 M HCl in water it is 3.7×10^{-4} s^{-1}, even though added salt lowers the cmc and increases the concentration of micellized surfactant, which should of itself promote reaction. These observations do not mean that there is no hydrogen ion catalyzed reaction of the substrate in micelles of NaLS, because if this were so the overall

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Table IV. Rate Enhancements by CTABr[a]

10^3[CTABr], M	pH ca.3.5[b]	pH 4.8[c]	pH 4.8[d]
	0.11	3.4	3.3
0.125	0.12		
0.25	0.14		33.0
0.50	0.20	80.6	51.5
0.75	0.44		
1.00	11.4	94.4	67.5
2.00		95.6	
2.50	20.6		77.8
3.00		92.2	
4.00		81.5	
5.00	16.0		77.7
6.00		73.8	
7.50			74.4
10.0			76.4

[a] Values of $10^3 k_\psi$, s^{-1}, at 25.0 °C. [b] 3.15×10^{-4} M HCl. [c] 0.02 M acetate buffer. [d] 0.1 M acetate buffer.

reaction would be slowed as the substrate is transferred from water into the anionic micelles.

Rate Enhancements by CTABr. The maximum rate enhancement at pH 3.5 is by a factor of ca. 200, whereas it is only by a factor of ca. 30 at pH 4.8 (Table IV). The variation of k_ψ with [CTABr] is affected by the concentration of acetate buffer, probably bcause of an electrolyte effect which lowers the cmc[20] and the maximum values of k_ψ are slightly larger in the more dilute buffer (Table IV) because of salt effects on the micellar reaction.

These rate enhancements depend upon the concentrations of both reactants in the micellar pseudophase,[9,21-23] and although they can often be treated quantitatively, the problem becomes more complex when buffers are present, because the distribution of the buffer components between aqueous and micellar pseudophases must also be considered.[24,25]

The lower overall rate enhancement at the higher pH (Table IV) can be understood qualitatively in terms of Scheme II and the pH–rate profile in the absence of surfactant.[2] The rate constant becomes independent of pH when formation of the anionic intermediate, **2**, becomes rate limiting. This step, deprotonation by water, should be little affected by cationic micelles, which will, however, inhibit the reverse reaction. Thus the pH-independent region will be reached at a lower pH in the presence, as compared with the absence, of cationic micelles, and in CTABr formation of **2** will probably be partially rate limiting at pH 4.8, though not at pH 3.5. The mechanism of the reactions in the absence of surfactant will be discussed elsewhere.

Salt Effects upon Hydrolysis in CTABr. Added salts typically reduce micellar rate enhancements, and the extent of inhibition increases with increasing hydrophobicity of the added counterion to the micelle.[7-9] We see this effect here for reaction at pH 3.5, in the region where k_ψ increases with increasing pH (Tables IV and V). Table V also shows that there is only a small salt effect on reaction in the absence of surfactant.

Table V. Salt Effects in Hydrolysis of *N*-(Trifluoroacetyl)indole[a]

[salt], M	NaCl	NaBr
	160 (1.55)	
0.01	96	57
0.025		37
0.05	51 (1.99)	24
0.075		18
0.10	(2.05)	14
0.15	(2.25)	13
0.20	25 (2.21)	
0.30	22 (2.17)	
0.40	18	
0.50	17 (2.14)	
1.00	(2.22)	

[a] Values of $10^4 k_\psi$, s^{-1}, at 25.0 °C, in 3.15×10^{-4} M HCl and 0.005 M CTABr. The values in parentheses are rate constants in the absence of CTABr.

Discussion

Anionic Micellar Effects upon Acid Hydrolysis. Although anionic micelles increase k_ψ for hydrolysis of *N*-(trifluoroacetyl)indole the effects are small (Table III). There is almost no rate enhancement of reaction in 0.1 M HCl, over that in water, but this does not mean that reaction is not occurring in the micellar pseudophase. The substrate is micellar bound, with $K_S = 420\ M^{-1}$, and we would therefore see extensive overall inhibition if there was no reaction of micellar-bound substrate.

The micellar effects for both 0.03 and 0.1 M HCl can be interpreted provided that we separate the contributions of the reactions in the aqueous and micellar pseudophases. The first-order rate constants, k_W' and k_M' (eq 2), can be expressed in terms of the corresponding second-order rate constants, k_W and k_M, as in eq 5, where $m_{H^+}{}^s = [H_M^+]/$

$$k_W' = k_W[H_W^+] \text{ and } k_M' = k_M m_{H^+}{}^s \quad (5)$$

([NaLS] – cmc); i.e., it is the mole ratio of micellar bound hydrogen ions to micellized surfactant.[9-11]

Equations 2 and 5 give eq 6.

$$k_\psi = \frac{k_W[H_W^+] + k_M K_S m_{H^+}{}^s([NaLS] - cmc)}{1 + K_s([NaLS] - cmc)} \quad (6)$$

The mole ratio of hydrogen ions to head groups of micellized NaLS is given by eq 7,[26] where the subscript T

$$m_{H^+}{}^s = 0.82[H_T^+]/([H_T^+] + [Na_T^+]) \quad (7)$$

denotes the total molar concentration of the specified ion in terms of the total solution volume.

Equations 5 and 6 give eq 8 and 9.

$$k_\psi = \frac{k_W[H_W^+] + k_M K_s[H_M^+]}{1 + K_s([NaLS] - cmc)} \quad (8)$$

$$k_M = \frac{k_\psi(1 + K_s([NaLS] - cmc) - k_W[H_W^+]}{K_s[H_M^+]} \quad (9)$$

Values of k_M can be estimated by using eq 9 with $K_s = 420\ M^{-1}$ and $[H_M^+]$ and $[H_W^+]$ calculated from eq 7. We take the value of the cmc in 0.1 M HCl as 1.4×10^{-3} M, based on the inhibition by NaLS in 0.1 M NaOAc (Results and Table I) and we assume a cmc of 3×10^{-3} M in 0.03 M HCl (cf. ref 10). These assignments of the cmc seem to be satisfactory because we obtain values of k_M which are similar for the two acid concentrations, and $10^4 k_M =$ 8 and 5.8 s^{-1} in 0.03 and 0.1 M HCl, respectively.[27] We

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used these parameters to predict values of k_ψ which are in reasonable agreement with the experimental values (Table III).

The values of k_M cannot be compared directly with those of k_W, because they have different dimensions,[18] but they can be compared by using the volume element of reaction in the micellar pseudophase. The volume of Stern layer of 1 mol of micellized NaLS has been estimated as ca. 0.14 L,[9] and the second-order rate constant, k_2^m, written in terms of the molarity of hydrogen ions in the Stern layer, in the micellar pseudophase is given by eq 10.

$$k_2^m = 0.14k_M \quad (10)$$

Therefore $10^4k_2^m = 1.1$ and 0.8 M^{-1} s^{-1} in 0.03 and 0.1 M HCl, respectively, and the values of k_2^m are considerably smaller than that of k_W, which is 3.7×10^{-3} M^{-1} s^{-1}.[2] This low catalytic efficiency of hydrogen ions in an anionic micelle, relative to that in water, is observed in other micellar-catalyzed acid reactions[10] and can be ascribed either to deactivation by strong hydrogen bonding to the anionic head groups or to the sulfuric acid not being strong when micellized (cf. ref 11).

Significance of Negative Salt Effects. Decreases of micellar rate enhancement of ionic reactions by added salts can be explained in terms of an exclusion of a reactive counterion from the micelle because of competition with an inert counterion; e.g., a halide ion could exclude a nucleophilic anion from a cationic micelle.[7-9,22,23] But it is difficult to apply this explanation in its simplest form to the salt effects upon hydrolysis of 1 in CTABr (Table V) in terms of Scheme II.

The effect of pH is interpreted in terms of a decrease of protonating power of the solution (Scheme II); thus halide ions must inhibit the reaction in CTABr by increasing protonating power in the micellar pseudophase. Cationic micelles do not effectively bind hydrogen ions, as shown by their effects on acid rates and equilibria,[7-9] but if equilibrium between hydrogen and hydroxide ions is maintained in the micellar pseudophase (cf. ref 28) expulsion of hydroxide ions from the micelle by halide ions (Table V) will increase acidity in the micellar pseudophase and therefore slow hydrolysis (Scheme II). In other words we could interpret the salt effect in terms of a halide ion induced binding of hydrogen ions to the cationic micelle.

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Registry No. 1, 62615-78-5; NaLS, 151-21-3; CTABr, 57-09-0.

(27) These values of k_M are not very sensitive to small changes in the cmc.

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Conformational Analysis and Stability of Substituted 4-Hydrindanones. A Thermodynamic and Magnetic Resonance (^1H and ^{13}C) Study

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The relative stereochemical configurations of the 4-hydrindanones 1–6 have been determined by ^{13}C and ^1H NMR. The cis isomers **1a–6a** show ^{13}C chemical shifts of the carbonyl carbon around 214 ppm, whereas the shifts of the trans isomers **1b–4b** are around 211 ppm. These configurations are confirmed by differences in the ^1H chemical shifts of the hydrogen or methyl at C7a. The conformations of the cis isomers **1a–6a** have also been determined. The ^{13}C chemical shifts of C5 and the values of J(H3a,H3α) (when C3 is not α-substituted) show that these isomers exist at room temperature in only one or the other of the two possible conformations. The configuration of a methyl group at C3 affects the relative stabilities of the cis and trans isomers of these hydrindanones. If the methyl is in the α configuration, the trans isomer is the more stable; if it is in the β configuration, the cis isomer is favored. The entropy of the cis–trans isomerization between **3a** and **3b** has been determined.

The relative configurations and stabilities of the 4-hydrindanones 1–6 have been determined in order to analyze the stereochemistry of the hydrogenation of $\Delta^{3,3a}$-4-hydrindanones.[1] The configurations of **3b**, **5a**, and **6a** have been established by X-ray diffraction analysis using single crystals of the semicarbazones or thiosemicarbazones.[2,3] We have been able to deduce the structures of the other isomers from their ^{13}C and ^1H NMR spectra and from study of equilibrations in the presence of base. These equilibrations show that the cis isomers of **1**, **2**, **5**, and **6** (R_α = H) are more stable than their trans epimers, whereas

Table I. Results of Equilibrations in a Basic Medium

epimeric pair	composition of the equilibrated mixture: % cis	% trans
1a ⇌ **1b**	76	24
2a ⇌ **2b**	92	8
3a ⇌ **3b**	6	94
4a ⇌ **4b**	31	69
5a ⇌ **5b**	100[a]	0
6a ⇌ **6b**	100[a]	0

[a] Enolization and equilibrium are shown by incorporation of deuterium at the 3a-position in D_2O (cf. Experimental Section).

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