Ethyl Cyclohexanone-2-carboxylate in Aqueous Micellar Solutions. 2. Enol Nitrosation in Anionic and Cationic Micelles

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Micellar-mediated rates of both the ester hydrolysis and enol nitrosation reactions of ethyl cyclohexanone-2-carboxylate, ECHC, were measured in aqueous acid media. In equal acid concentration, the enol nitrosation reaction rate is more than 10 times faster than the ester hydrolysis reaction rate; this fact makes possible the separate (independent) study of both reactions undergone by ECHC. Anionic micelles of sodium dodecyl sulfate, SDS, inhibit the ester hydrolysis; by contrast, the nitrosation reaction goes through maxima as the [SDS] increases above the critical micelle concentration. A similar pattern of behavior is observed in the study of the effect of anionic micelles of hydrogen dodecyl sulfate, HDS, on the rates of the two reactions: the first-order rate constant (k_0) of the ester hydrolysis goes through minima as [HDS] increases, even though the rates are actually affected very little by HDS addition; in sharp contrast, the overall rate constant of the nitrosation reaction is enhanced by HDS addition and levels off at high surfactant concentration. The values of the rate constant at high surfactant concentration is more than 6 times that determined in the absence of HDS. Despite the different micellar effects observed in the two reactions occurring in the same substrate, experimental data fit the pseudophase ion exchange (PPIE) model and predict similar values for the secondorder rate constant of each reaction in the different types of micelles of a given counterion. The implications of these findings for the reactivity in micelles are discussed. Cationic micelles inhibit the nitrosation reaction throughout the surfactant concentration range; although the reaction at the micellar phase is not negligible, the physicochemical properties of this reaction region account for the lower reactivity in this medium. Experimental data are quantitatively explained by means of the pseudophase model, and kinetic rate constants or equilibrium constants appearing in the proposed reaction scheme are reported.

Introduction

Oxime formation from the nitrosation of enols derived from ketones, keto esters, and related compounds is a well-known synthetic procedure.¹ Recently, Williams demonstrated that the nitrosation of ketones proceeds via the enol tautomers.² Either the enolization or the nitrosation of the enol can be made rate-limiting, depending on the experimental conditions and on the nature of the ketone. For ketones with high enol content, the rate-controlling step is, in general, the reaction between the enol and the nitrosating agent.³

The most convenient and useful reagent for affecting nitrosation is nitrous acid, generated in situ in an aqueous solution of sodium nitrite and mineral acid. In aqueous perchloric acid solutions of sodium nitrite, the only nitrosating agent is NO^+ (or $H_2NO_2^+$, i.e., $ON^+\cdots OH_2$, where a discrete water molecule is covalently bound to the nitrosonium ion) which is formed from protonation of nitrous acid:

$$HNO_2 + H^+ \rightleftharpoons NO^+ + H_2O$$

with $K_{\rm NO} = 3 \times 10^{-7} \text{ mol}^{-1} \text{ dm}^3$ being the corresponding equilibrium constant.⁴ In the presence of nonbasic nucleophiles (X⁻), such as Cl⁻, Br⁻, or SCN⁻, equilibrium formation of nitrosyl compounds, namely XNO, also occurs:

$$X^- + HNO_2 + H^+ \rightleftharpoons XNO + H_2O$$

with $K_{\rm XNO}$ being the corresponding equilibrium constant. At 25 °C $K_{\rm XNO}$ takes on values of 1.14 × 10⁻³ when X⁻ = Cl⁻; 5.1 × 10⁻² when X⁻ = Br⁻; or 30 mol⁻² dm⁶ when X⁻ = SCN^{-.5}

Nitrosyl compounds act as nitrosating species, and despite their lower reactivity with regard to that of NO⁺, catalysis by X⁻ is generally observed, due to the greater concentration of the nitrosyl compounds resulting from the high value of $K_{\rm XNO}$ in comparison to $K_{\rm NO}$. When one uses high nitrite concentration (e.g., higher than 0.1 M), nitrosation by N₂O₃ might also be observed, in which case a second-order dependence of the rate equation on [nitrite] appears:

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O$$

with $K = 3 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^{3.6}$

The nitrosation reaction of the enol of ethyl cyclohexanone-2-carboxylate (ECHC) has been previously studied in water.⁷ This β -keto ester is nearly 100% enolized in water. Consequently, enolization cannot be rate-limiting. In fact, we have shown that the reaction is first-order in both [ECHC] and [H⁺] and is also first-order in the total nitrite concentration. (We worked with low nitrite concentration, 1.7×10^{-3} M). When X⁻ is also present in the reaction medium, the nitrosation pathway via XNO is also detected. Thereupon, eq 1 can be written to account for the experimental facts.

$$rate = (k_1 + k_2[X^-])[ECHC][nitrite][H^+]$$
(1)

In this equation, k_1 corresponds to the rate constant when the nitrosation is promoted by NO⁺, i.e., $k_1 = k_{\text{NO}}K_{\text{NO}}$, while k_2 is the rate constant when the nitrosation is promoted by XNO, i.e., $k_2 = k_{\text{XNO}}K_{\text{XNO}}$, with k_{NO} and k_{XNO} being the bimolecular rate constants for NO⁺ or XNO attack, respectively, on the enol.

The present work analyzes the influence of the anionic surfactants sodium dodecyl sulfate (SDS) and hydrogen docecyl sulfate (HDS) on two reactions that may occur with ECHC in

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aqueous acid solutions: the ester hydrolysis and also the nitrosation of the enol when sodium nitrite is added to the reaction mixture. Addition of either SDS or HDS to the reaction mixture affects the rate of the two reactions occurring with the same molecule in quite different ways. Thus, while the ester hydrolysis reaction is inhibited throughout the SDS concentration range, the nitrosation reaction goes through maxima; i.e., low [SDS] raises k_0 values ($k_0 = \text{rate}/[\text{ECHC}]$) to reach a maximum level, after which a further increase in [SDS] decreases k_0 . Similarly, the pseudo-first-order rate constant, k_0 , of the ester hydrolysis reaction goes through minima with increasing [HDS] (though k_0 is modified only slightly by HDS addition), whereas the observed rate constant for the nitrosation reaction increases gradually with [HDS] and levels off at high [HDS]. This study closes with the analysis of the influence of the cationic surfactants dodecyltrimethylammonium bromide (DTABr), tetradecyltrimethylammonium bromide (TTABr), and tetradecyltrimethylammonium chloride (TTACl) on the nitrosation reaction. In each case, addition of cationic surfactants diminishes the reaction rate.

Experimental Section

Ethyl cyclohexanone-2-carboxylate, a Merck product of maximum purity, was used as supplied. Surfactants SDS, DTABr, and TTABr of the highest purity available were purchased from Sigma and were used without further purification. Both TTACl and HDS were prepared through ion exchange. An Amberlite IRA-400 (Cl) anionic-exchange resin was used to prepare TTACl from TTABr solutions, and a Dowex 50W cationic-exchange resin was used to prepare HDS from SDS solutions. The complete exchange of Na⁺ by H⁺ can be obtained from Na flame photometer analysis. Due to hydrolysis of HDS surfactant, its solutions were used on the same day of preparation. All other reagents were supplied by Merck and were used as received. Solutions were prepared with doubly distilled water (first distilled over potassium permanganate solution and then redistilled).

Pure ECHC was dissolved in dry dioxane (spectrophotometric grade). Either the hydrolysis or the nitrosation reaction of ECHC was initiated with the addition of 10 or 15 μ L of a solution of ECHC in dioxane to the reaction mixture to reach a final reaction volume of 3.0 mL.

Kinetic measurements were recorded with a Kontron-Uvikon (Model 942) double-beam spectrophotometer, provided with multiple cell carriers thermostated by circulating water. All experiments were performed at 25 °C. Kinetic experiments were carried out under pseudo-first-order conditions, with the acid and nitrite concentrations greatly exceeding the ethyl cyclohexanone-2-carboxylate concentration ($\sim 6 \times 10^{-5}$ M). In each kinetic experiment the integrated method was applied. The decreasing absorbance at 256 nm⁷ was noted during the course of the reaction, fitting the experimental data (absorbance-time, A-t) to the first-order integrated equation.

Results and Discussion

The Ester Hydrolysis Reaction in Anionic Micelles. Ethyl cyclohexanone-2-carboxylate has both ester and enol functionalities within the molecule. The ester hydrolysis reaction occurs spontaneously in water at moderate rates, but is also subject to acid and base catalysis. When electrophiles are present, such as NO⁺ or the nitrosyl halides XNO ($X = Cl^-$, Br⁻, SCN⁻, ...), the nitrosation reaction of the enol also takes place (Scheme 1).

At the same acid concentration, for example, 0.03 M HCl, and at low [nitrite], such as 2×10^{-3} M, the enol nitrosation



Figure 1. Influence of [SDS] on the observed rate constant of the hydrolysis of ECHC studied in aqueous buffered solutions of 0.067 M acetic acid–acetate at pH 4.40. Solid line fits eq 3. The inset shows the linearization of the data according to eq 4.





SCHEME 2: Mechanism of the Base-Catalyzed Hydrolysis of ECHC in SDS Micelles



reaction in water is more than 10 times faster than the ester hydrolysis reaction. The difference becomes even greater if HBr is used instead of hydrochloric acid, or if there are SCN^- ions in the reaction medium. In sharp contrast, in aqueous acetic acid—acetate buffers, the ester hydrolysis reaction is much faster than the nitrosation reaction; in fact, no nitrosation reaction can be found to have occurred.

In this study we have analyzed the effect of anionic and cationic micelles on the enol nitrosation reaction. However, to conduct a complete interpretation of the experimental facts, it was first deemed necessary to investigate the effect of anionic surfactants on the ester hydrolysis reaction in acid media.

Reaction in Acetic Acid–*Acetate Buffers.* For the sake of simplicity, the influence of SDS micelles on the ester hydrolysis of ECHC was first studied in an aqueous buffered solution of 0.067 M acetic acid–acetate at pH 4.57. Figure 1 shows the variation of the observed rate constant, k_o , as a function of [SDS]. The pseudo-first-order rate constant decreases as the SDS

concentration increases above the critical micelle concentration, cmc = 3.5×10^{-3} M.

Under these experimental conditions, the observed rate constant measured in water is given by eq 2 with $k_0^w = 0.987 \times 10^{-3} \text{ s}^{-1}$, $k_H = 8.98 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, and $k_B = 0.260 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, and where AcO⁻ represents the acetate anions.⁷

$$k_{\rm o} = k_{\rm o}^{\rm w} + k_{\rm H} [{\rm H}^+] + k_{\rm B} [{\rm AcO}^-]$$
 (2)

Therefore, at pH 4.57 the second term in the right-hand of eq 2 can be omitted. In the presence of SDS micelles, acetate ions are excluded from the anionic micellar interface due to electrostatic repulsions. Furthermore, the [H⁺] is much lower $(2.7 \times 10^{-5} \text{ M})$ than the [Na⁺] (equal to the cmc at the onset of micellization). Therefore, the [H⁺] is too low to observe ion-exchange effects since the ionic-exchange equilibrium constant between both ions at the micellar surface, i.e., H⁺_m + Na⁺_w \rightleftharpoons H⁺_w + Na⁺_m, with an average value of $K_{\rm I} \sim 0.8$,⁸ favors the binding of Na⁺, i.e., the much more concentrated ion. Consequently, if the reaction at the micellar interface occurs, it is due only to spontaneous hydrolysis. Hence, the application of the pseudophase model enables the proposal of Scheme 2 to quantitatively explain the results.

The overall rate constant is given by eq 3, where k_w ($k_w = k_o^w + k_B[AcO^-]_w$) and k_o^m are the first-order rate constants in the aqueous and micellar pseudophases, respectively, referred to the total solution volume, and K_s is the binding constant of ECHC enol written in terms of the concentration of micellized surfactant, [Dn] ([Dn] = [SDS]_t - cmc).

$$k_{\rm o} = \frac{k_{\rm w} + k_{\rm o}^{\rm m} K_{\rm s}[{\rm Dn}]}{1 + K_{\rm s}[{\rm Dn}]} \tag{3}$$

The solid line in Figure 1 was drawn by applying eq 3 for the case of $k_w = (7.64 \pm 0.05) \times 10^{-3} \text{ s}^{-1}$, $k_o^{\text{m}} = (1.0 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$, and $K_s = 340 \pm 10 \text{ mol}^{-1} \text{ dm}^3$ ($r = 0.999_7$). The last two terms were treated as adjustable values. Alternatively, eq 3 can be rewritten in the form of eq 4, a Lineweaver–Burk type of representation.

$$\frac{1}{k_{\rm w} - k_{\rm o}} = \frac{1}{k_{\rm w} - k_{\rm o}^{\rm m}} \left(1 + \frac{1}{K_{\rm s}} \frac{1}{[{\rm SDS}]_{\rm m}} \right)$$
(4)

The Figure 1 inset shows the graph thus obtained. As expected, it results in a straight line whose intercept at the origin and the slope values turned out to be (133.5 ± 1.0) s and (0.3985 ± 0.0050) mol·dm⁻³ s ($r = 0.9999_8$), respectively. The appropriate combination of these data leads to K_s and k_o^m values, which are in fine agreement with those obtained by nonlinear regression analysis and thus corroborate the previous assumptions made in proposing Scheme 2.

Reaction in Hydrochloric Acid. At fixed acid concentration, [HCl] = 0.050 M, we studied the effect of the concentration of both SDS and HDS surfactants on the ester hydrolysis reaction of ECHC. The variations of the observed rate constant as a function of [SDS] (or [HDS]) are shown in Figures 2A and 3A, respectively. While k_0 decreases on increasing [SDS] above the cmc (the value obtained in water is nearly 7 times that obtained at 0.3 M [SDS]), by contrast, the increase in [HDS] has very little effect on the overall rate constant, which goes through a minimum.

The ester hydrolysis of ECHC is an acid-catalyzed reaction. On the other hand, from the previous section we demonstrated that ECHC binds strongly to SDS micelles; in fact, at 0.10 M SCHEME 3: Mechanism of the Acid-Catalyzed Hydrolysis of ECHC in Anionic Micelles



SDS, for example, the substrate concentration in the micellar phase is more than 35 times the concentration in the bulk water phase (concentrations refer to the total solution volume). Furthermore, as $[H^+] = 0.050$ M, the ion-exchange process between H⁺ and the surfactant counterion, Na⁺, concentrates the H⁺ ions at the micellar interface when the surfactant concentration is not high. Consequently, the usually observed shape of k_0 -[SDS] profiles in acid-catalyzed reactions are curves with well-defined maxima at low [SDS].9-12 At low [surfactant], the effect of concentrating both reactants in the small volume of the micelle enhances k_0 , but a further increase in the [surfactant] dilutes the reactants in the micellar phase (even though the reactivity at the micellar interface is lower than that of the bulk water phase), and decreases the $\left[H^{+}\right]$ at the interface owing to the increase in [Na⁺] that is being introduced with the surfactant. Both effects reduce k_0 values.

By arguing in a similar manner, increasing [HDS] enhances the [H⁺] in the micellar interface and in water. Thus k_0 versus [HDS] profiles were expected to increase gradually with the surfactant concentration and to level off at high surfactant concentration, i.e., when all the substrate was micellar bound.^{9,13} However, the behavior observed here is definitively different.

For our starting hypothesis, we assumed that the pseudophase ion exchange (PPIE) model, which had been successfully applied to many other examples of acid-catalyzed reactions,¹⁴ would also work in the present case. We attributed the "apparently" different behavior to the similarity in reactivities between the spontaneous and the acid-catalyzed hydrolysis of the ester of ECHC. Then, on the basis of the PPIE model, Scheme 3 was proposed, which in turn leads to eq 5, taking into account that the overall rate is the sum of the reaction rates in both aqueous and micellar pseudophases, i.e., rate = $(k_o^w + k_H[H^+]_w)[ECHC]_w$ + $(k_o^m + k_H^m[H^+]_m)[ECHC]_m$.

$$k_{\rm o} = \frac{k_{\rm w} + k_{\rm o}^{\rm m} K_{\rm s}[{\rm Dn}] + [(k_{\rm H}^{\rm m}/V)K_{\rm s} - k_{\rm H}]m_{\rm H}[{\rm Dn}]}{1 + K_{\rm s}[{\rm Dn}]} \quad (5)$$

In this equation k_w ($k_w = k_o^w + k_H[H^+]_t$) is the pseudo-firstorder rate constant measured in the absence of SDS; k_o^m is the first-order rate constant for the spontaneous hydrolysis in the micellar phase; k_H^m is the second-order rate constant for the acid-catalyzed hydrolysis in the micellar phase referred to the volume of the micelle, *V*; and $m_H = [H^+]_m/[SDS]_m$.

The molar ratio, $m_{\rm H}$, can be determined by solving eq 6 at each surfactant concentration if the values of both $K_{\rm I}$ and β ,



Figure 2. (A) Variation of k_0 as a function of [SDS] measured in the kinetic study of the acid-catalyzed hydrolysis of the ester of ECHC at [HCI] = 0.050 M; the insert shows the plot of $k_0(1 + K_s[SDS]_m)$ versus [SDS] by taking $K_s = 340 \text{ mol}^{-1} \text{ dm}^3$. (B) Plot of k_0^{mod} , eq 7, against m_{H} , whose values were calculated by using eq 6.

the degree of micelle neutralization, are assumed. Thus, $m_{\rm H}$ and $k_{\rm o}$ can be estimated by simultaneously fitting eqs 5 and 6 to experimental data (vide infra, the case of sodium dodecyl sulfate in nitrosation).

$$m_{\rm H}^{2} + m_{\rm H} \left(\frac{[{\rm H}^{+}]_{\rm t} + K_{\rm I} [{\rm Na}^{+}]_{\rm t}}{(1 - K_{\rm I}) [{\rm Dn}]} - \beta \right) + \frac{[{\rm H}^{+}]_{\rm t} \beta}{(1 - K_{\rm I}) [{\rm Dn}]} = 0 \quad (6)$$

Nevertheless, it is difficult to attain a convergence in the program. Hence, we treated the results as follows. We took up the K_s value determined in the previous section, that is, in the study of the influence of SDS in aqueous buffered solutions of acetic acid—acetate, where no appreciable ionic-exchange effects were detected. ECHC binds to micelles by hydrophobicity, i.e., the ECHC enol solubility is higher in nonpolar solvents. Yet, the nature of SDS micelles formed in aqueous buffered solutions of 0.067 M acetic acid—acetate should not be different from those in 0.050 M HCl. The only noticeable difference should be the cmc. Equation 5 can be rewritten in the form of eq 7. Then, since k_w is known, the constant k_o^{mod} can be calculated at each [SDS]. If eq 5 works here, then the graph of k_o^{mod} against $m_{\rm H}$ should be a straight line. To determine $m_{\rm H}$ from eq 6, we used $K_{\rm I} = 0.75^8$ and $\beta = 0.64.^9$

$$k_{\rm o}^{\rm mod} = \frac{k_{\rm o}(1 + K_{\rm s}[{\rm Dn}]) - k_{\rm w}}{[{\rm Dn}]} = k_{\rm o}^{\rm m}K_{\rm s} + \left(\frac{k_{\rm H}^{\rm m}}{V}K_{\rm s} - k_{\rm H}\right)m_{\rm H}$$
(7)

Figure 2B shows the plot obtained. One can see the reasonable agreement between experiments and theoretical treatment. The



Figure 3. (A) Values of k_o obtained in the acid-catalyzed hydrolysis of the ester of ECHC at [HCl] = 0.050 M as a function of [HDS]. (B) Linearization of the data according to eq 8 with $K_s = 340 \text{ mol}^{-1} \text{ dm}^3$.

intercept and slope values of the corresponding straight line are $(5.25 \pm 0.4) \times 10^{-2}$ and $(0.35 \pm 0.01) \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$, respectively, which yields $k_0^{\text{m}} = 1.5 \times 10^{-4} \text{ s}^{-1}$ and $k_{\text{H}}^{\text{m}}/V = 1.06 \times 10^{-3} \text{ s}^{-1}$, or $k_{\text{H}}^{\text{m}} = 1.6 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ if $V = 0.15 \text{ dm}^3 \text{ mol}^{-1}$, meaning that the acid-catalyzed reaction in the micellar phase is about 60 times lower than that in water and takes on a value quite similar to that of spontaneous decomposition.

Increasing the amount of HDS in the reaction mixture does not incorporate any counterion different from H⁺, the reactive ion. Hence no ion exchange takes place. By defining the overall rate of the reaction as the sum of the reaction rates occurring in both aqueous and micellar phases and taking into account the following mass balance equations, $[H^+]_t = [H^+]_{ad} + [HDS]_t =$ $[H^+]_w + [H^+]_m$ ("ad" signifies added as HCl and "t" denotes stoichiometric), which in turn gives $[H^+]_w = [H^+]_t - \beta [HDS]_m$ and $[H^+]_m = \beta [HDS]_m$ (or $m_H = \beta$), we obtain eq 8.

$$k_{o} = \frac{k_{w} + k_{H}\text{cmc} + [k_{H}\alpha + k_{o}^{m}K_{s} + (k_{H}^{m}/V)\beta K_{s}][\text{HDS}]_{m}}{1 + K_{s}[\text{HDS}]_{m}}$$
(8)

In eq 8 $k_w = k_o^w + k_H[H^+]_{ad}$ is the observed rate constant obtained in water in the absence of HDS; k_o^m represents the rate constant of the spontaneous decomposition in the micellar phase; k_H^m is the bimolecular rate constant of the acid-catalyzed reaction in the micellar phase; and α and β are the ionized and neutralized micellar degrees, respectively, measured by conductivity measuments as $\alpha = 0.36$ and $\beta = 0.64.9$

A qualitative explanation of the shape k_0 versus [HDS] data displayed in Figure 3 is possible if one considers the strong binding of ECHC to micelles and supposes a very low reactivity

TABLE 1: Experimental Conditions and Parameters Obtained in the Kinetic Study of the Influence of Anionic Micelles in the Acid-Catalyzed Hydrolysis of ECHC at [HCl] = 0.050 M

surfactant	cmc/M	$k_{ m w}^{a/ m s^{-1}}$	β^{b}	$k_{\rm H}/{ m mol^{-1}}~{ m dm^3}~{ m s^{-1}}$	$K_{\rm s}/{ m mol}^{-1}~{ m dm}^3$	$k_{\rm o}^{\rm m}/{\rm s}^{-1}$	$k_{\rm H}{}^{\rm m}/{\rm mol^{-1}}~{\rm dm^3}~{\rm s^{-1}}$
SDS	$\begin{array}{c} 2.5 \times 10^{-3} \\ 3 \times 10^{-3} \end{array}$	1.42×10^{-3}	0.64	9.0×10^{-3}	340^{c}	1.5×10^{-4}	1.6×10^{-4}
HDS		1.4×10^{-3}	0.67	9.0×10^{-3}	340^{c}	$1.5 \times 10^{-4} c$	2.1×10^{-4}

^a Experimental value. ^b From ref 9. ^c Assumed value.

TABLE 2: Experimental Conditions and Parameters Obtained in the Kinetic Study of the Influence of Anionic Surfactants on the Nitrosation of ECHC at $[H^+] = 0.025$ M (HCl) and [Nitrite] = 1.67×10^{-3} M

surfactant	cmc/M	β	K_{I}	$k^{\rm w}/{ m mol}^{-2}~{ m dm}^6~{ m s}^{-1}$	$K_{\rm s}/{ m mol}^{-1}~{ m dm}^3$	$k_1^{\rm m}/{\rm mol}^{-2}~{\rm dm}^6~{\rm s}^{-1}$	GF
HDS	2.5×10^{-3}	0.64		268	328 ± 13	6.82 ± 0.03	0.999_7^a
HDS	b	b	b	$1.12 \times 10^{-2 c}$	328	7.06	0.999_8^a
SDS	3.0×10^{-3}	0.67	0.75	270	313 ± 17	6.68 ± 0.06	2.79^{d}
SDS	b	b	b	$1.12 \times 10^{-2 c}$	313	6.75	0.999_8^{a}

^{*a*} Correlation coefficient as the goodness of fit (GF). ^{*b*} From linear correlation. ^{*c*} Value of $k^{w}[H^+]$ [nitrite] in s⁻¹ measured experimentally. ^{*d*} rmsd (%).



Figure 4. Variation of the pseudo-first-order rate constant, k_0 , obtained in the nitrosation of the enol of ECHC at [HCl] = 0.025 M and [nitrite] = 1.67 × 10⁻³ M as a function of [HDS]. Solid line fits eq 9; for parameters, see Table 2. The inset shows the linearization of the data according to eq 9 by using $K_s = 328 \text{ mol}^{-1} \text{ dm}^3$.

in the micellar phase in comparison with that in the bulk water phase. These characteristics cause the denominator of eq 8 to increase faster than the numerator, with the net effect being an inhibition. Experimental data of ko versus [HDS] was quantitatively treated by plotting $k_0(1 + K_s[Dn])$ against [HDS]_m (assuming $K_s = 340 \text{ mol}^{-1} \text{ dm}^3$). As expected, on the basis of the validity of eq 8, a good straight line is obtained (see Figure 3B), whose intercept and slope values resulted to be (1.40 \pm 0.03) $\times 10^{-3}$ s⁻¹ and (0.364 ± 0.004) mol⁻¹ dm³ s⁻¹, respectively. The intercept value is in good agreement with the value of the observed rate constant in the absence of HDS, just as predicted in eq 8; from the slope value, one determines $k_{\rm H}^{\rm m}$ $= 2.1 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ by assuming the k_0^{m} determined in the previous section. As one can see from the data in Table 1, there is reasonable agreement between the values determined here or even with the k_0^{m} values determined in SDS micelles in aqueous buffered solutions of acetic acid-acetate.

The Enol Nitrosation Reaction in Micellar Media. Further arguments in favor of our statements made in the previous section are presented below. The enol nitrosation of ECHC is a reaction which requires an acid medium to proceed. To better elucidate the results, they will be discussed by sections.

Hydrogen Dodecyl Sulfate, HDS. Figure 4 shows the variation of the pseudo-first-order rate constant, k_0 , as a function of [HDS] obtained in the nitrosation of ECHC studied at fixed [ECHC]

= 6×10^{-5} M, [nitrite] = 1.67×10^{-3} M, and [H⁺] = 0.025 M (HCl). In sharp contrast to the k_o -[HDS] profile depicted in Figure 3, k_o in the nitrosation reaction increases gradually with increasing [HDS] to reach a limiting value at high [HDS]; k_o^{max} is more than 6-fold k_o in water in the absence of HDS. The HDS effect is negligible at concentrations below 3×10^{-3} M, which is taken as the cmc value. For example, $k_o = 1.12 \times 10^{-2} \text{ s}^{-1}$ at [HDS] = 1.07×10^{-3} M increases to $k_o = 1.3 \times 10^{-2} \text{ s}^{-1}$ at [HDS] = 2.7×10^{-3} M, but at [HDS] = 4.3×10^{-3} M, just above the cmc, $k_o = 2.93 \times 10^{-2} \text{ s}^{-1}$. The slight catalysis observed below the cmc is probably due to the increase in [H⁺] added with the surfactant.

Since ECHC is distributed between both water and micellar pseudophases, the quantitative treatment of the experimental data must, a priori, contain terms for reaction in the two phases: rate = k^{w} [ECHC]_w[H⁺]_w[HNO₂]_w + k^{m} [ECHC]_m[H⁺]_m[HNO₂]_m. One may notice that we neglect the hydrolysis reaction, since the rate of nitrosation is more than 10 times the rate of hydrolysis. For example, at [HDS] = 4.3×10^{-3} M, $k_0^{\text{nitrosation}}$ $= 2.93 \times 10^{-2} \text{ s}^{-1}$, whereas $k_0^{\text{hydrolysis}} = 0.11 \times 10^{-2} \text{ s}^{-1}$; the difference becomes greater on increasing [HDS]. However, as values of k_0 versus [HDS] are also known for the hydrolysis reaction, they can be subtracted from the corresponding values obtained for the nitrosation reaction. Taking into account the mass balance equations of $[H^+]_t = [H^+]_{ad} + [HDS]_t$, [ECHC]_t = $[ECHC]_w + [ECHC]_m$, and $[nitrite]_t = [HNO_2]_w + [HNO_2]_m$ (since the p K_a of nitrous acid is 3.1,¹⁵ we understand that [nitrite] means [HNO₂] under the acidity conditions of this study), one may easily arrive at eq 9 by considering that $m_{\rm H} = [{\rm H}^+]_{\rm m}$ $[HDS]_m = \beta$ and that $[H^+]_w = [H^+]_{ad} + cmc + \alpha [HDS]_m$. (In these expressions t = total, ad = added, w = water, m =micellar phase, and α and β refer to ionization and neutralization degrees of the micelle, respectively.)

$$k_{\rm o} = \frac{k^{\rm w}(\rm cmc + [H^+]_{ad}) + (k^{\rm w}\alpha + k^{\rm m}K_{\rm s}K_{\rm s}^{\rm n}\beta)[\rm HDS]_{\rm m}}{(1 + K_{\rm s}[\rm HDS]_{\rm m})(1 + K_{\rm s}^{\rm n}[\rm HDS]_{\rm m})}$$
(9)

In eq 9, $K_{\rm s}^{\rm n}$ represents the equilibrium constant for the association of H–ONO to HDS micelles; its value was estimated as 0.20 mol⁻¹ dm³ from the variation of the free energy of alkyl nitrites (R–ONO) transfer, $\Delta G_{\rm mc}$, through water–micelle interface.^{10a} Nitrous acid is regarded as the model compound for alkyl nitrites; the value of ΔG determined when the number of C-atoms in the R-substituent is zero then equals $\Delta G_{\rm mc}$. A value of $K_{\rm s}^{\rm n} = 0.20 \text{ mol}^{-1} \text{ dm}^3$ means that $1 + K_{\rm s}^{\rm n}$ [HDS]_m \approx 1. The inset of Figure 4 confirms this assumption since the plot



Figure 5. (A) Experimental (•) and simulated (\bigcirc) k_0 values obtained in the nitrosation of the enol of ECHC at [HCl] = 0.025 M and [nitrite] = 1.67 × 10⁻³ M as a function of [SDS]. Solid line fits eq 10; for parameters, see Table 2. (B) Linearization of the data according to eq 10 by using $K_s = 313 \text{ mol}^{-1} \text{ dm}^3$; the m_{H} values were determined by solving eq 6 for each [SDS].

of $k_o(1 + K_s[HDS]_m)$ against [HDS]_m draws a perfectly straight line. In addition, the solid line in Figure 4 consists of points calculated by using eq 9 with the assumption $1 + K_s^n[HDS]_m = 1$ and the values reported in Table 2 of the corresponding kinetic and equilibrium constants.

Sodium Dodecyl Sulfate. The influence of [SDS] on the enol nitrosation reaction of ECHC was studied under the same experimental conditions of [acid], [nitrite], and [ECHC] that were used in the preceding section. The experimental results are displayed in Figure 5. (Note again the different k_0 -[SDS] profile shown in Figure 2 for the hydrolysis reaction.) The maximum in rate profile is consistent with the PPIE model. At [SDS] just above the cmc, increasing [SDS] increases k_0 because anionic micelles bind and concentrate both organic substrate and the ionic reagent H⁺ within the small volume of the micellar pseudophase. However, increasing the [SDS] also increases the totality of the micellar pseudophase, which dilutes both reactants within that pseudophase. The competition between Na⁺ and H⁺ at the micellar interface accelerates even more the dilution process. Thus, k_0 passes through a maximum with increasing [SDS] as the effect of the dilution of the reactants on the overall rate begins to dominate the effect of reactant binding.

Following the same treatment as that for the effect of SDS on the hydrolysis reaction, we obtain eq 10, in which $k^w = k_1$ + k_2 [Cl⁻], with $k_1 = 220 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$ is equal to $k_{\text{NO}}K_{\text{NO}}$, the product of the bimolecular rate constant between the ECHC enol and NO⁺ and the equilibrium constant of NO⁺ formation in water; $k_2 = 1990 \text{ mol}^{-3} \text{ dm}^9 \text{ s}^{-1}$ is equal to $k_{\text{XNO}}K_{\text{XNO}}$, that is, the product of the bimolecular rate constant between the ECHC enol and ClNO and the equilibrium constant of ClNO



Figure 6. (A) Influence of [DTABr] on the pseudo-first-order rate constant, k_0 , obtained in the nitrosation of the enol of ECHC at [HBr] = 0.0165 M and [nitrite] = 1.67×10^{-3} M. (B) Influence of [TTACl] on k_0 measured at [HCl] = 0.025 M and [nitrite] = 1.67×10^{-3} M. Solid lines fit eq 11; for parameters, see Table 3.

formation in water.9

$$k_{\rm o} = \frac{k^{\rm w}[{\rm H}^+]_{\rm t} + [(k_1^{\rm w}/V)K_{\rm s}K_{\rm s}^{\rm n} - k^{\rm w}]m_{\rm H}[{\rm SDS}]_{\rm m}}{1 + K_{\rm s}[{\rm HDS}]_{\rm m}} [{\rm nitrite}] (10)$$

In eq 10, $m_{\rm H}$ can be determined at each [SDS] by solving the quadratic equation in $m_{\rm H}$ given in eq 6, with $[{\rm Na}^+]_{\rm t}$ being the sum of $[{\rm NaNO}_2] + [{\rm SDS}]_{\rm t}$. The open points in Figure 5A correspond to the calculated points from eq 10 when a simulation procedure is applied in the following way. The $m_{\rm H}$ values were calculated from eq 6 by means of a BASIC program which creates a data file for three entries corresponding to k_0 , [SDS]_m, and $m_{\rm H}$ values, respectively. This file data is then read by a FORTRAN program which fits the three variables to eq 10 to obtain the parameters of $k_{\rm m}$ and $K_{\rm s}$ that yield the lowest rmsd (root-mean-square deviation) of the calculated points from the experimental data. Here, we used $K_{\rm I} = 0.75$, $\beta = 0.67$, and cmc = 3.0×10^{-3} M as the best values for obtaining the optimized parameters reported in Table 2 that correspond to lower rmsd = 2.79%.

Values in Table 2 show that the association of ECHC is insensitive to both the counterion of the micelle and the electrolyte type in the water phase. In fact, similar K_s values are obtained from studying the hydrolysis or the nitrosation reaction, either in strong mineral acid or in buffer solutions. This was an expected result because ECHC is a neutral substrate that binds to micelles by hydrophobicity, as has been observed with benzoylacetone, also a β -diketone.¹⁶ On the other hand, the rate of nitrosation by NO⁺ in the micellar phase, k_1^{m} , attains similar values in either HDS or SDS micelles. Again, this is an expected result because the micellar interface should not be

TABLE 3: Experimental Conditions and Parameters Obtained in the Kinetic Study of the Nitrosation of the Enol of ECHC in Aqueous Micellar Solutions of Cationic Surfactants at [Nitrite] = 1.67×10^{-3} M, [HBr] = 0.0165 M (DTABr and TTABr), and [HCl] = 0.025 M (TTACl)

-							
surfactant	acid	cmc/M	α	$K_{\rm s}/{\rm mol^{-1}}~{\rm dm^3}$	$A/10^{-3} \mathrm{s}^{-1}$	$B/mol^{-1} dm^3 s^{-1}$	r ^a
DTABr	HBr	0.0114	0.24^{b}	220 ± 10	12.3 ± 0.3	0.180 ± 0.020	0.9998
DTABr	с	с	с	220	14.4 ± 0.5	0.160 ± 0.002	0.9999
					14.7^{d}	$2.0 \times 10^{4 e}$	
TTABr	HBr	1.7×10^{-3}	0.24^{t}	338 ± 5	10.3 ± 0.1	0.224 ± 0.010	0.999_3
TTABr	с	с	с	338	10.7 ± 0.2	0.220 ± 0.003	0.999
					11.15^{d}	$1.9 \times 10^{4 e}$	
TTACl	HCl	2.0×10^{-3}	0.34^{t}	360 ± 7	10.8 ± 0.3	0.1615 ± 0.014	0.999 ₃
TTACl	с	с	с	360	10.6 ± 0.2	0.162 ± 0.002	0.999_1
					11.26^{a}	$3.2 \times 10^{5 g}$	

^{*a*} Correlation coefficients of the fit. ^{*b*} From ref 19. ^{*c*} From linear regression analysis. ^{*d*} Expected. ^{*e*} $k^{\rm m}_{\rm BrNO}K_{\rm s}^{\rm X}/V$; determined from *B* values in mol⁻¹ dm³ s⁻¹. ^{*f*} From ref 9. ^{*s*} $k^{\rm m}_{\rm CINO}K_{\rm s}^{\rm X}/V$; determined from *B* values in mol⁻¹ dm³ s⁻¹.

sensitive to the nature of the counterion; however, this value is 60 times lower than that found in water, which undoubtably is due to the lower polarity of the micellar interface.

Cationic Surfactants. The influence of the cationic surfactants DTABr, TTABr, and TTACl were investigated at fixed [ECHC] $(6.0 \times 10^{-5} \text{ M})$, NaNO₂ $(1.67 \times 10^{-3} \text{ M})$, and [H⁺]. To avoid further complications due to ion exchange, HBr $(1.65 \times 10^{-2} \text{ M})$ was used with surfactants having Br⁻ counterions and HCl (0.025 M) with TTACl.

Figure 6 shows the experimental results of the variation of k_0 as a function of [surfactant] for the representative cases of DTABr and TTACl. A comparison with the results reported in Figure 2 of part 1²⁰ shows that k_0 for nitrosation is greater than 10 times k_0 for hydrolysis. In each case, an inhibition of the reaction is observed on the addition of increasing amounts of the cationic surfactants above the cmc, but the nitrosation reaction is not suppressed even at high surfactant concentration. This fact indicates that the reaction in the micellar phase is not negligible; hence, the reactivity in this region is significantly lower than that in the water phase.

When working with DTABr, a small catalysis of the reaction at [DTABr] below the cmc is observed; e.g., $k_0 = 1.12 \times 10^{-2}$ s⁻¹ measured in the absence of DTABr increases to $k_0 = 1.26 \times 10^{-2}$ s⁻¹ at [DTABr] = 0.0102 M. This effect is due to the increase of [Br⁻] added with the surfactant, and Br⁻ catalyzes the reaction in water.⁷ Since the cmc of DTABr was measured as 0.012 M,¹⁷ working with [HBr] = 0.0165 M, the amount of Br⁻ added with the surfactant is not negligible. In fact, leastsquares fitting of k_0 versus [Br⁻]_t (=[HBr] + [DTABr]) gives k_1 and k_2 values (eq 1) in good agreement with those determined from the influence of [Br⁻] in water (i.e., $k_1 = 220 \text{ mol}^{-2} \text{ dm}^6$ s⁻¹ and $k_2 = 1.12 \times 10^4 \text{ mol}^{-3} \text{ dm}^9 \text{ s}^{-1}$.9

With cationic micelles, the only nitrosating agent capable of promoting the reaction in the micellar phase is XNO. Both NO^+ and H^+ are excluded from the micellar interface, so XNO must be generated in water, followed by its partitioning between the two pseudophases. These considerations lead to Scheme 4 to a quantitative treatment of the experimental data by means of the pseudophase model.

Departing from this scheme, eq 11

$$k_{o} = \frac{[\mathrm{H}^{+}][\mathrm{nitrite}]}{1 + K_{s}[\mathrm{Dn}]} \left[(k_{1} + k_{2}[\mathrm{X}^{-}]_{\mathrm{ad}}) + \left(k_{2}\alpha + \frac{k_{\mathrm{XNO}}}{V} K_{s}^{\mathrm{X}} K_{\mathrm{XNO}} K_{s}[\mathrm{X}^{-}]_{\mathrm{ad}} \right) [\mathrm{Dn}] \right] (11)$$

was derived based on the following assumptions. The association constant of nitrous acid to TTABr micelles is estimated at $K_s^n = 0.48 \text{ mol}^{-1} \text{ dm}^3$ by following the same procedure as in the

SCHEME 4: Reaction Mechanism for the Nitrosation of ECHC in Aqueous Acid Micellar Solutions



case previously discussed for SDS micelles.^{10a} Therefore, as before, the approximation $(1 + K_s^n[TTABr]_m) \approx 1$ is correct (the same for TTACl or DTABr). On the other hand, the small values of the equilibrium constants K_{CINO} or K_{BrNO} lead to [nitrite] = [HNO₂]_w + [HNO₂]_m. Furthermore, it is known that $[X^-]_w = [X^-]_{ad} + \text{cmc} + \alpha[Dn]$, with $[X^-]_{ad}$ being the halide ion concentration added to the reaction medium as the mineral acid. In the case of DTABr, since the cmc is comparable to $[Br^-]_{ad}$, we considered both quantities; however, with TTABr or TTACl the cmc is much smaller than $[X^-]_{ad}$ and the approximation $[X^-]_w = [X^-]_{ad} + \alpha[Dn]$ is correct.

The experimental data were fitted to the equation $k_0 = (A + A)$ $B[Dn])/(1 + K_s[Dn])$, which by comparison with eq 11 produces $A = (k_1 + k_2[X^-]_{ad})[H^+]$ [nitrite] and $B = \{k_2\alpha + (k_{XNO}^m/V) - k_2\alpha + (k_{XNO}^m/V) - (k$ $K_s^X K_{XNO} K_s [X^-]_{ad} \} [H^+] [nitrite].$ In these expressions, $k_1 (=k_{NO})$ $K_{\rm NO}$), k_2 (= $k_{\rm XNO}K_{\rm XNO}$), and $k^{\rm m}_{\rm XNO}$ refer to nitrosation by NO⁺ and XNO in water and by XNO in the micellar phase, respectively. The three parameters A, B, and K_s were treated as adjustable values. The results arrived at in the fitting processes are reported in Table 3 along with the expected values of A, which can be calculated by taking into account the previously determined values of k_1 and k_2 from the study of the reaction in water $(k_1 = k_{NO}K_{NO} = 220 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}; k_2 = k_{CINO}K_{CINO}$ = 1990 mol⁻³ dm⁹ s⁻¹, and $k_2 = k_{\text{BrNO}} K_{\text{BrNO}} = 1.12 \times 10^4$ mol⁻³ dm⁹ s⁻¹)⁹ and the experimental conditions used in the present experiments. As shown in Table 3, there is good agreement between the optimized A values and those expected. The curves in Figure 6 are the points calculated by using eq 11 and the values of A, B, and K_s listed in Table 3. The agreement between experiments and theoretical treatment is satisfactory.

Values of *B* yield those of $k^{\rm m}_{\rm XNO}K_{\rm s}^{\rm X}$ if the known values of the included parameters are used. The volume fraction of the micellar pseudophase where the reaction takes place should not be different in considering DTABr, TTABr, or TTACl, which could be taken as $V = 0.15 \text{ dm}^3 \text{ mol}^{-1}$, i.e., half of the molar micellar volume, assuming that the density value of the aqueous surfactant solutions equals 1 g/cm^{3.18} This implies $k^{\rm m}_{\rm XNO}K_{\rm s}^{\rm X}$

CHART 1: Structures of Nitrosyl Salts and Nitrous Acid



= 3.0×10^3 , 2.9×10^3 , and $4.8 \times 10^4 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$ for the cases of DTABr, TTABr, and TTACl, respectively. The equal values found with DTABr and TTABr are understandable because the nitrosating agent is BrNO in both cases, the polarity of the micellar interface is probably similar for both surfactants, and the binding constant of BrNO, K_s^X , to DTABr or TTABr is probably quite similar. The latter equilibrium constant is an unkown parameter; however, taking into account the similarity of the XNO and HNO₂ structures (see Chart 1) one could assume $K_{\rm s}^{\rm X}$ will approximate $K_{\rm s}^{\rm n}$ (=0.48 mol⁻¹ dm³). This assumption allows us, first, to estimate the reactivity of ClNO and BrNO toward the enol of ECHC in the micellar pseudophase at more than 10 times less than that in water. Second, in the micellar phase CINO is more reactive than BrNO, just as we have seen in water: $k_{\text{CINO}} = 1.75 \times 10^6$, whereas $k_{\text{BrNO}} = 2.20 \times 10^5$ mol⁻¹ dm³ s⁻¹. These findings indicate that the ECHC enol must reside in a very hydrated region, which is consistent with the generally held assumption that reactions in micelles occur at the water-rich surface and not in the hydrocarbon core.

Conclusions

Frequently, one reads in the literature regarding kinetic micellar effects that for reactions between an organic neutral substrate and an ion, as in the situation here, simple electrostatic considerations lead to the conclusion that anionic micelles will catalyze reactions between hydrophobic neutral substrates and cationic species and will inhibit reactions with anions, while the opposite will hold for cationic micelles. The present results show us the necessity for caution when interpreting the previous statements; in fact, the influence of anionic micelles, of either SDS or HDS on two reactions occurring with the same substrate, both being acid-catalyzed reactions, shows opposite effects. The result is a consequence of the extension of the catalysis.

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