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Registry No. Benzophenone, 119-61-9; triphenylcarbinol, 76-84-6; benzoic acid, 65-85-0; phenyllithium, 591-51-5.

Micellar Effects upon the E1cB Mechanism of Ester Hydrolysis

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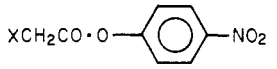
The E1cB mechanism of carboxylic ester hydrolysis is observed with nitrophenyl esters which contain a strongly electron attracting group at the α-carbon atom, as in **1**[1] (Scheme I). The apparent pK_a value of 1 is 8.57, and the reaction rate increases with increase in pH (above 6) to a limiting value at pH >9, which corresponds to rate-limiting decomposition of the preformed carbanion (**2**).[1]

Micellar effects upon E1cB hydrolyses of substituted *p*-nitrophenyl acetates (**3**), have been reported.[2] The rate



3, X = *p*-$O_2NC_6H_4$, *p*-$MeOC_6H_4$, PhS, PhO

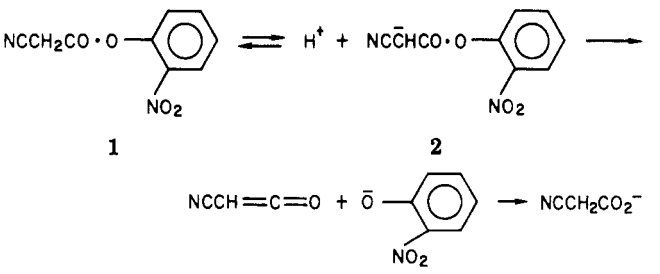
enhancements by cationic micelles of $C_{16}H_{33}NMe_3Br$ (cetyltrimethylammonium bromide, CTABr) were larger than those typical of hydrolyses by the $B_{Ac}2$ mechanism,[3,4] and "saturation kinetics" were observed which were consistent with extensive substrate incorporation in the micelles.[2] The rates in the micellar solutions were stated to be the same at pH values of approximately 8 and 10 for reaction of **3** where X = $O_2NC_6H_4$ and PhS, respectively. The micellar catalysis was measured at pH 8.99 (buffer unspecified), so that some, but not all, of the substrates should have been extensively deprotonated under the reaction conditions (cf. ref 1).

Cationic micelles can affect the rate of an E1cB mechanism of a substrate such as **1** by changing the equilibrium constant for deprotonation of **1** or the rate constant for decomposition of the carbanion (**2**). Cationic micelles markedly increase extents of deprotonation,[5-8] and they catalyze E2 eliminations[6] and related deprotonations,[7] but this effect will not be kinetically significant if the substrate is already deprotonated, as at pH $\gg$ pK_a.

Micelles inhibit S_N1 reactions,[8,9] but cationic micelles catalyze anionic decarboxylations[9,10] and the spontaneous decompositions of aryl sulfate monoanions[11] and aryl and acyl phosphate dianions,[12] so that one can only speculate on their effect on the rate constant for decomposition of **2** (Scheme I).

The aim of our work was to clarify this situation by examining reaction of **1** in CTABr at high pH and at pH < pK_a. At high pH we should follow spontaneous decomposition of the carbanion (**2**), and at low pH both steps could be important.

Scheme I



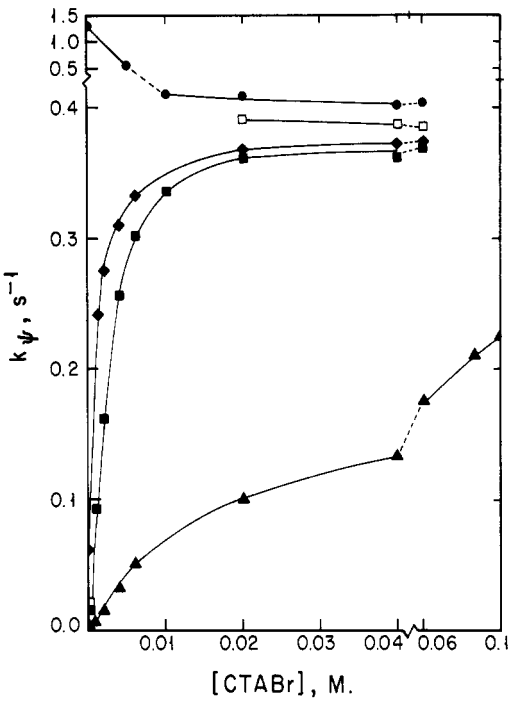


Figure 1. Effect of CTABr on the hydrolysis of *o*-nitrophenyl cyanoacetate: (●) 0.01 M NaOH; (□) pH 7, phosphate buffer; (♦, ■, ▲) maleate buffer, pH 8, 7, and 6, respectively, with 0.01 M buffer.

Experimental Section

Materials. *o*-Nitrophenyl cyanoacetate (**1**) was prepared by heating a mixture of *o*-nitrophenol, cyanoacetic acid, and $POCl_3$ at 60 °C for 3 h.[1] The crushed solid was extracted with Et_2O and was recrystallized from Et_2O, mp 71.5 °C (lit.[1] mp 71.5 °C).

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Purification of the surfactant has been described.[9] Sodium salts were used for the buffers.

Kinetics. The formation of *o*-nitrophenoxide ion at 25.0 °C was followed at 405 nm, using a Gilford spectrometer for the slower reactions and a Durrum stopped flow spectrometer for the faster reactions. The pH of the buffered solutions was measured in the absence of surfactant. The first-order rate constants, k_ψ, are in reciprocal seconds.

Results and Discussion

The variation of k_ψ with CTABr is shown in Figure 1. In 0.01 M NaOH and no CTABr $k_\psi = 1.35\ s^{-1}$,[13] consistent with the value of 1.74 s^{-1} in 1 M KCl at 30 °C.[1] The substrate, 1, is completely deprotonated in 0.01 M NaOH,[1] and CTABr inhibits spontaneous decomposition of the carbanion (2), with a limiting value of $k_\psi = 0.4\ s^{-1}$ at [CTABr] > 0.02 M (Figure 1).

Reaction at pH ≤8 is catalyzed by CTABr (Figure 1), and for reaction at pH 7 and 8 we observe plateau values of k_ψ which are very similar to the limiting rate constant in CTABr and 0.01 M NaOH, showing that the substrate in micelles of CTABr is almost completely deprotonated even at a nominal pH value of 7. The relatively small differences in the limiting values of k_ψ (Figure 1) could be due to the different salt effects of the buffers.[14] In addition, proton equilibria in aqueous micelles are affected by added anions, even at the same nominal pH.[5]

For experiments at pH 6–8 the rate increase with increasing [CTABr] simply means that the equilibrium is shifted in favor of carbanion 2, which should bind very strongly to the cationic micelle (cf. ref 5d, 15, and 16. We did not reach a limiting rate constant even at high [CTABr] at pH 6. This result is understandable because 1 probably does not bind very strongly to cationic micelles. (The α-CN group should make 1 less hydrophobic than *p*-nitrophenyl acetate, which does not bind strongly to CTABr.[4])

We cannot compare our results with 1 directly with those of Tagaki and co-workers[2] because of differences in the pK_a values and hydrophobicities of the substrates, but the direction and magnitude of the micellar effect depends on the extent of deprotonation of the substrate. For example, the rate enhancement by CTABr is by factors of approximately 6- and 25-fold at pH 8 and 7, respectively, but at pH 6, where we do not reach a limiting rate constant in CTABr, the factor is at least 100-fold (Figure 1). Comparison of micellar effects at only one pH value is therefore not very informative.

The small micellar inhibition of the spontaneous decomposition of the carbonion (2) is consistent with the polarity of the micellar surface being similar to, but slightly lower than, that of water. For example, spectral shifts are consistent with the micelle surface having an effective dielectric constant of ca. 40.[17] Menger has suggested that water penetrates the micellar surface,[18] and, consistently, rate and equilibium constants for some water additions are similar to those in water.[19] The spontaneous decomposition of the carbanion (2) involves dispersion of charge from the carbanionic center to the forming *o*-nitrophenoxide ion and is apparently not very sensitive to the medium.

Acknowledgment. Support of this work by the National Science Foundation (Chemical Dynamics) is gratefully acknowledged.

Registry No. 1, 22065-72-1; 2, 78480-13-4; CTABr, 57-09-0.

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Aromatic Amines from Carboxylic Acids and Ammonia. A Homogeneous Catalytic Process

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A homogeneous metal-catalyzed synthesis of aniline from benzoic acid and ammonia (amination reaction) has been described in a short communication[2] and a U.S. patent.[3] In this paper we present details from the amination of a variety of aromatic acids and we discuss the mechanism of the reaction.

A new industrial aniline process may be based on two reaction steps: (1) decarboxylative amination of benzoic acid with concomitant reduction of Cu(II) to Cu(I) and (2) reoxidation of the ammoniacal solutions of Cu(I) with atmospheric oxygen.

$$2Cu(OOCPh)_2{\cdot}NH_3 \rightarrow PhNH_2 + CO_2 + 2CuOOCPh + PhCOONH_4$$

$$2CuOOCPh + 2PhCOONH_4 + {}^1/_2O_2 \rightarrow 2Cu(OOCPh)_2{\cdot}NH_3 + H_2O$$

$$PhCOONH_4 + {}^1/_2O_2 \rightarrow PhNH_2 + CO_2 + H_2O$$

Inclusion of oxygen in the first step for an in situ oxidation of Cu(I) does not result in catalytic yields of aniline. The aniline-yielding reaction is closely related to the Cu(II)-catalyzed oxidation of benzoic acid to phenol.[4] It must be stated at the outset (vide infra) that production of aniline directly from phenol was shown not to occur under the conditions of the amination reaction.

Results

Aniline from Benzoic Acid. Benzoic acid was heated with CuO or copper benzoate at 190–230 °C under ammonia pressure in an autoclave. Aniline was produced in 70% yield, based on the reduction of Cu(II) to Cu(I). Byproducts were phenol, 7%, and diphenylamine, 8%. Benzamide was also produced through dehydration of ammonium benzoate. The amination reaction is very rapid above 200 °C. Temperatures above 230 °C result in the direct decarboxylation of benzoic acid to benzene and

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