Catalysis of Carbaryl Hydrolysis in Micellar Solutions of Cetyltrimethylammonium Bromide

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Carbaryl hydrolysis was studied in micellar solutions of cetyltrimethylammonium bromide (CTAB) at pH 7.5 The hydrolysis followed first-order kinetics with respect to carbaryl concentration. Above the critical micelle concentration (CMC) the rate of hydrolysis increased with increasing CTAB concentration. A plateau was ultimately reached, at which the rate constant was 30 times the rate constant in an equivalent solution without CTAB. Entropies of activation were calculated to prove that the reaction mechanism did not change in the micellar environment. The binding constant of the micelle for carbaryl and the rate constant in the micellar pseudophase were determined from kinetic data using the pseudophase model. To verify this binding constant, a study of the solubility of carbaryl in CTAB solutions was performed. The results were found to be in very good agreement with those from the kinetic studies.

KEY WORDS: micelle; cetyltrimethylammonium bromide; entropy of activation; carbaryl hydrolysis; E1cB mechanism.

INTRODUCTION

Carbaryl is a widely used insecticide belonging to the *N*-methyl carbamate class. Since carbaryl has a labile proton on the atom α to the carbonyl function, it can presumably hydrolyze in an alkaline solution by either the E1cB mechanism or the $B_{Ac}2$ pathway (1), the latter involving the formation of a tetrahedral intermediate as a result of nucleophilic attack on the carbonyl carbon. The presence of a good leaving group and a labile proton suggests that carbaryl should hydrolyze predominantly via an E1cB mechanism (2). This mechanism involves the initial removal of an N-proton by hydroxide ion to produce an unstable intermediate which decomposes to methylisocyanate plus naphthoxide ion (Fig. 1). The methylisocyanate reacts instantaneously with water to give *N*-methyl-carbamic acid, an unstable compound that degrades to methylamine and carbon dioxide (3).

Micelles have been found to influence the rates of many chemical reactions (4). The type and extent of the effect produced depends on the distribution of the reactants between the micellar and bulk phases and the change in reactivity in the micelle. The effect of the micellar concentration of cetyltrimethylammonium bromide (CTAB) on the rate of carbaryl hydrolysis was studied to determine the rate constant in the micellar pseudophase and the binding constant of the micelle for carbaryl. The binding constant was also determined by studying the effect of CTAB concentration on the solubility of carbaryl.

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MATERIALS AND METHODS

Test Solutions

Solutions of CTAB (0–12 m*M*, Sigma Chemical Co., St. Louis, MO) were prepared in pH 7.5 buffer solutions made up of sodium phosphate (monobasic, Fisher Scientific, Fair Lawn, NJ) and potassium phosphate (dibasic, Fisher Scientific, Fair Lawn, NJ). Ionic strength was adjusted to 0.30 *M* with potassium chloride (Fisher Scientific, Fair Lawn, NJ). The solutions were placed in a jacketed beaker controlled at 30°C by means of a circulating water bath. To test the effect of ionic strength on the rate of hydrolysis of carbaryl (Union Carbide Agricultural Products, Research Triangle Park, NC), surfactant solutions (2 m*M*) were prepared with various total ionic strengths. Ionic strength was adjusted using potassium chloride.

Kinetic Studies

Carbaryl was dissolved in ethanol and added to jacketed beakers containing CTAB solutions maintained at 30°C. Sufficient carbaryl stock solution was added that the initial concentration in the micellar solution was 1.5×10^{-4} *M*. The concentration of ethanol in the final solution was never greater than 0.5% (v/v). Samples withdrawn during a kinetic run were diluted using a pH 5.0 acetate buffer solution (sodium acetate, Fisher Scientific, Fair Lawn, NJ, and glacial acetic acid, American Scientific Products, McGaw Park, IL) to stop the reaction. These samples were then analyzed for carbaryl and 1-naphthol using a fluorimetric assay (Shimadzu RF-540 fluorimeter, Kyoto, Japan). The excitation and emission maxima for carbaryl were 280 and 335 nm, respectively, while the excitation and emission maxima for 1-naphthol were 293 and 464 nm, respectively. The resultant data were analyzed to determine the first-order rate constants. The surfactant concentration versus reaction rate profile was then analyzed according to the pseudophase model to determine the binding constant and the micellar rate constant.

Solubility Studies

An excess amount of carbaryl was added to pH 5.0 CTAB solutions of varying concentrations. These solutions were placed in screw-capped test tubes and maintained at 30°C. After equilibration, the samples were filtered using 0.45-μm Millipore filters and then analyzed for carbaryl content using the fluorimetric assay described above.

Critical Micelle Concentration Determination

CTAB solutions in pH 7.5 phosphate buffer, ionic strength equal to 0.30 *M*, were prepared with a wide range of CTAB concentrations. The surface tension of each solution was then determined using the du Nouy ring method. The break in the plot of surface tension versus log (CTAB concentration) gave the critical micelle concentration (5).

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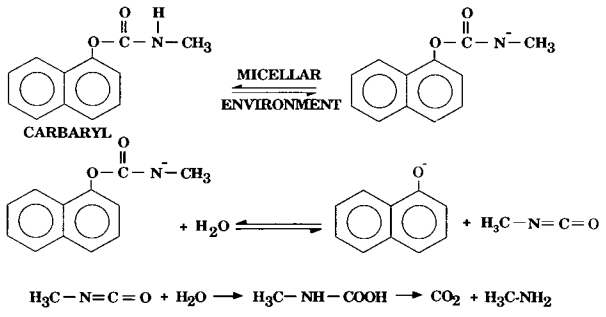


Fig. 1. Carbaryl hydrolysis by the E1cB mechanism.

RESULTS AND DISCUSSION

Reaction Mechanism

Comparison of the fluorescence spectra of the reaction mixtures with that of pure 1-naphthol confirmed that hydrolysis of carbaryl yielded 1-naphthol quantitatively. Since both the E1cB and the $B_{Ac}2$ mechanisms of hydrolysis would lead to the formation of 1-naphthol, it was necessary to determine which mechanism was operational. The E1cB mechanism requires the abstraction of a proton to yield the nitranion (Fig. 1). Attempts to determine titrimetrically the pK_a of carbaryl were not successful except to indicate that the pK_a must be greater than 13. This is consistent with the report (2) that the pK_a values of carbamates are usually greater than 12. Extremely small amounts of the nitranion would be consistent with the molecule's reasonable aqueous stability (pH 7.5) when not in the micellar environment. Activation parameters have been found to be useful in distinguishing between the two mechanisms (1,6,7). Since the E1cB mechanism is a unimolecular elimination-addition process, it should yield an entropy of activation that is positive, while that of the bimolecular $B_{Ac}2$ mechanism should be negative (1). Figure 2 shows the results of the temperature dependence studies of carbaryl hydrolysis in pH 7.5 aqueous solutions (ionic strength of 0.30 *M*) with and without CTAB. The CTAB concentration used in this study (10 m*M*) was higher than the CTAB concentration at which essentially all of the carbaryl is solubilized in the micelles. This means that the rate constants obtained represent the micellar reaction. The entropy of activation at 30°C, calculated from the temperature effects using Eq. (1) (8),

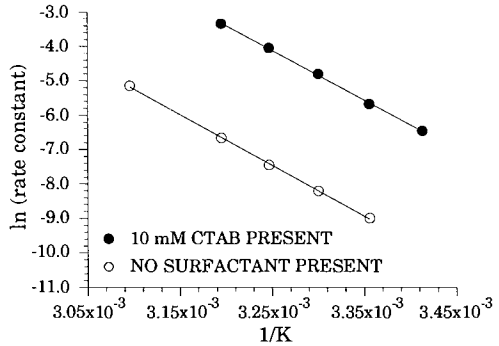


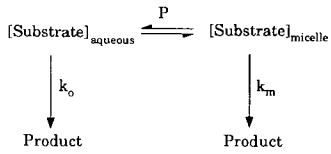
Fig. 2. Arrhenius plots for carbaryl hydrolysis carried out in 10 m*M* CTAB (●; $r^2 > 0.999$) and in an equivalent solution without any CTAB (○; $r^2 > 0.999$).

$$k = e\frac{k_B T}{h} exp\frac{\Delta S\dagger}{R} \exp^{-\frac{E_a}{RT}} \quad (1)$$

was found to be 12.2 cal/mol * K in solutions without surfactant and 16.4 cal/mol * K in CTAB solutions. In this equation, k_B is the Boltzmann constant, k is the rate constant, h is Planck's constant, and T is the temperature. $\Delta S\dagger$, E_a, and R have their usual meanings. Since the values of $\Delta S\dagger$ are substantially positive, the hypothesis that carbaryl should follow the E1cB hydrolysis mechanism is confirmed. Further, the values of $\Delta S\dagger$ in the presence and absence of surfactant are essentially the same, thus proving that the operative mechanism is not dependent upon whether the reaction occurs in the bulk solution or in the micellar pseudophase. In similar fashion, the activation energies in the aqueous solution without surfactant (29.5 kcal/mol) and the micellar solution (28.7 kcal/mol) are essentially equal. This provides additional proof that the hydrolysis mechanism does not change in the two different environments.

Pseudophase Model

In this model the substrate is distributed between two distinct phases, the bulk aqueous phase and the micellar phase. This is shown in Scheme I;



Scheme I

where k_o is the rate constant for product formation in the aqueous solution, k_m is the rate constant for product formation in the micellar phase, and P is the partition coefficient of the substrate. The overall reaction rate for product formation is given by (9)

$$k_{obs}[S]_t = k_o[S]_o(1 - CV) + k_m[S]_m CV \quad (2)$$

where $[S]_t$ is the total substrate concentration, $[S]_o$ and $[S]_m$ are the substrate concentrations in the aqueous and micellar phases, respectively, k_{obs} is the observed rate constant, C is the total surfactant concentration less the CMC, and V is the molar volume of the surfactant. The product CV gives the volume fraction of the micellar phase and $(1 - CV)$ gives the volume fraction of the aqueous phase. The total substrate concentration and the partition coefficient can be expressed as

$$[S]_t = [S]_o(1 - CV) + [S]_m CV \quad (3)$$

$$P = \frac{[S]_m}{[S]_o} \quad (4)$$

Since the molar volume of the surfactant as it exists in the micelle is difficult to obtain (9), a binding constant K is defined according to Eq. (5):

$$K = V(P - 1) \quad (5)$$

Using Eqs. (2)–(5), the following equation can be derived:

$$\frac{1}{k_o - k_{obs}} = \frac{1}{k_o - k_m} + \left[\frac{1}{k_o - k_m}\right]\left[\frac{1}{KC}\right] \quad (6)$$

This expression was used to determine K, the binding constant, and k_m, the micellar rate constant from the kinetic data. Using Eqs. (3)–(5), Eq. (7) can be derived. This equation can be used to analyze solubility data since the increase in solubility of carbaryl is due to its incorporation into the micellar phase (10).

$$\frac{S_t - S_o}{S_o} = KC \quad (7)$$

Micellar Effects

The CMC determined from the break in the surface tension versus log (surfactant concentration) plot was found to be 6.8×10^{-5} M. This is substantially less than the value of 9.2×10^{-4} M obtained in the absence of added buffer or salt (11). The electrolytes present in this study (ionic strength equal to 0.30 M) act to reduce the repulsion between the ionic head groups of the surfactant molecules and facilitate micellization. The value of the CMC obtained compares well with the CMC values compiled by Mukerjee and Mysels at various ionic strengths (12).

The rate of hydrolysis of carbaryl increased appreciably in micellar solutions which had CTAB concentrations exceeding the experimentally determined CMC (Fig. 3). The enhanced reaction rate in the micellar pseudophase is most likely due to increased ionization of carbaryl in the micelles. Such an increase in the ionization of carbamates has been reported previously (6,13). One possible reason for this increased ionization is that the hydroxide ion concentration at the micellar surface is higher than in the bulk solution, thus making the pH at the micelle surface higher. Since hydroxide ion binds to CTAB micelles less strongly than chloride, bromide, or dibasic phosphate ions (14) ($Br^- > Cl^- > HPO_4^{2-} > OH^-$) and since these three ions are present at higher concentrations than hydroxide ion, the aforementioned hypothesis is not thought to be correct. The two pH profiles presented in Fig. 4 offer supporting evidence for this hypothesis. It can be seen that the nonmicellar solution would need to have a pH of 9.0 in order for carbaryl to have the same hydrolysis rate constant as that exhibited in a pH 7.5 solution that is 10 mM in surfactant. A pH at the micelle surface that is 1.5 pH units higher than in the bulk solution is not thought to be reasonable for this system. Rather, the increased carbaryl hydrolysis rate is thought to be a result of the stabilization of the nitranion by the positively charged micelle. Such stabilization would decrease the pK_a of carbaryl and result in an increased concentration of the reactive nitranion. Cationic micelles have been shown to cause a similar decrease in the pK_a of o-nitrophenyl cyanoacetate (15), a compound which also hydrolyzed according to an E1cB mechanism.

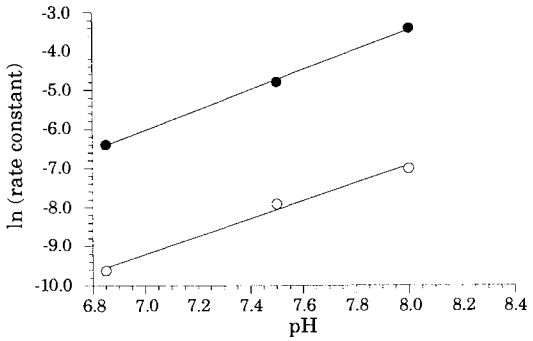


Fig. 4. Effect of pH on carbaryl hydrolysis in a 10 mM CTAB solution (●; $r^2 > 0.999$) and in an equivalent solution without any surfactant (○; $r^2 > 0.999$).

The maximum increase in the overall rate constant, obtained at a surfactant concentration of 8.0×10^{-3} M, was 30 times that in an equivalent solution without surfactant. The plateau value in the rate constant versus surfactant concentration profile is reached at the point where essentially all of the carbaryl molecules are bound to micelles. If the micelle is to have an accelerating effect on the reaction rate, two criteria must be met. First, the micellar rate constant, k_m, must be greater than the rate constant in a solution without the surfactant, k_o. Second, a significant fraction of the reactant must be bound to the micelle. When the pseudophase model was employed [Eq. 6, Fig. 5], a value of 1.23×10^{-2} min^{-1} was found for k_m. This is large in comparison to the k_o value of 2.75×10^{-4} min^{-1} obtained for hydrolysis in the absence of micelles. The value of the binding constant obtained from analysis of the rate constant versus surfactant

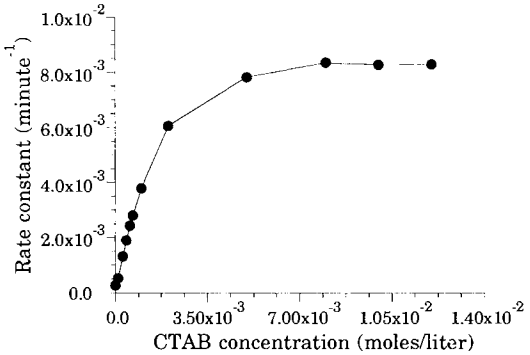


Fig. 3. Effect of CTAB concentration on carbaryl hydrolysis rate constant.

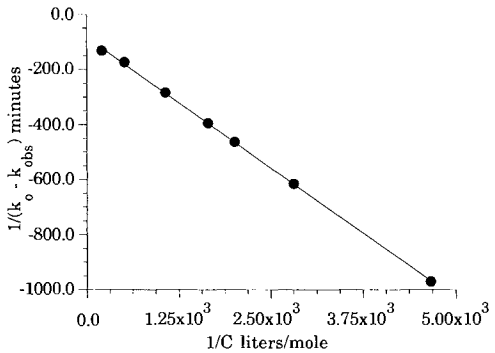


Fig. 5. Pseudophase analysis of carbaryl hydrolysis in micellar solutions of CTAB. The binding constant and micellar rate constant were determined from the slope (−0.190) and intercept (−83.1). The coefficient of determination (r^2) was 0.999.

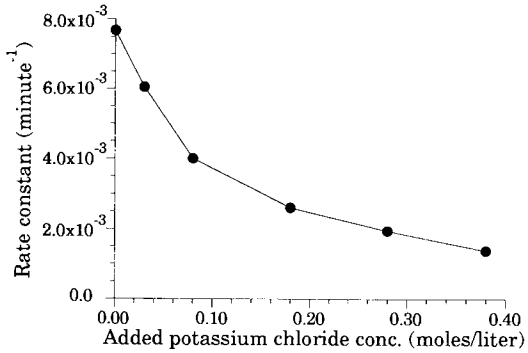


Fig. 6. Effect of potassium chloride addition on the rate of hydrolysis of carbaryl in micelles of CTAB. A concentration of 0.0 *M* represents the 0.27 *M* ionic strength contributed by the buffer components.

concentration data using Eq. (6) was found to be 438 liters/mol. This high value for the binding constant obtained indicates that carbaryl partitions strongly into the micellar phase.

It can be seen that k_m is larger than the maximum experimentally observed rate constant. This is not unexpected. As the surfactant concentration is increased, the concentration of free bromide ion is increased. This higher bromide ion concentration results in increased binding of bromide ion to the micelle. The resulting decrease in the extent of ionization of the quaternary ammonium functions decreases the stabilization of the nitranion, thus raising the pK_a of carbaryl, and the catalytic effect of the micelle is reduced. Such changes in micellar charge occur continuously with increasing surfactant concentration and cause a lowering of all points along the rate constant versus surfactant concentration profile. This lowering is greatest, of course, at the highest surfactant concentrations. Since k_m is usually calculated using rate constant values below the plateau region, which are reflective of solutions having lower surfactant concentrations, k_m usually overpredicts the observed plateau rate constant. This effect is demonstrated by the decrease in the rate constant for carbaryl hydrolysis as the chloride ion concentration is increased (Fig. 6).

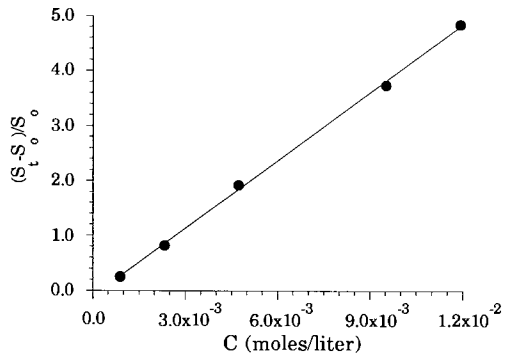


Fig. 7 Pseudophase analysis of carbaryl solubility in micellar solutions of CTAB. The slope (410 liters/mol) gives the binding constant of the micelle for carbaryl. The coefficient of determination (r^2) was 0.999.

The value for the binding constant obtained using the pseudophase model and kinetic data was verified using the pseudophase model and solubility data [Eq. (7), Fig. 7]. The latter study was performed at a lower pH (5.0) where the carbaryl was quite stable. As stated previously, the pK_a of carbaryl, when not in the micellar environment, is greater than 13. Therefore, the amount of nitranion is quite small at either pH and the binding behavior of carbaryl should not be appreciably changed by conducting the solubility study at pH 5.0. The binding constant so obtained was 410 liters/mol. This is in very good agreement with the previous value when it is considered that a different buffer (acetate) was required.

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