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Effect of hydrocarbon chain length on the hydrolysis of several naphthyl esters in the presence of *o*-iodosobenzoic acid and CTAB micelles

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Summary

The hydrolyses of the naphthyl esters of acetic, propionic, butyric, pentanoic and hexanoic acids proceed at relatively slow rates in solutions near neutral pH. These hydrolysis reactions were found to be accelerated when carried out in surfactant solutions of cetyltrimethylammonium bromide which also contained *o*-iodosobenzoic acid, a strong nucleophile. The reactions followed pseudo-first-order kinetics and the rate constant vs surfactant concentration profiles exhibited the maxima typical of bimolecular reactions conducted in micellar solutions. It was found that there was a systematic increase in the binding constants of the esters to the micelle. However, the ratio of the maximum rate constant observed for each of the compounds to each compound's rate constant in a non-micellar solution remained almost constant.

Introduction

The study of α-naphthyl acetate hydrolysis by *o*-iodosobenzoic acid (IBA) in the presence of cetyltrimethylammonium bromide (CTAB) showed that there was an acceleration of the reaction due to the presence of micelles in the solution (Wurster and Patel, 1992). The attacking nucleophile in this reaction is IBA in its ionized form (Moss et al., 1983, 1984). Since there must be a location on or within the micelle where both the IBA and the ester are approaching each other, it was of interest to determine how dependent this catalysis was on ester structure. The reaction rate would be expected to increase if there was a higher concentration of both reactants at a given site in the micelle; the reaction rate would be expected to decrease if the reactants occupied different locations in the micelle. In the present study, α-naphthyl esters of several saturated straight-chain carboxylic acids were used (Fig. 1). It was desired to use compounds where the polarization of the carbonyl bond would not change appreciably but where the location of the carbonyl in the micelle might change as a function of ester structure. The effect of surfac-

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tant concentration on the rate of ester hydrolysis was also studied for each of the compounds shown in Fig. 1.

Materials and Methods

Test solutions

Solutions of CTAB (Sigma Chemical Co., St. Louis, MO) were prepared in pH 7.5 buffer solutions made up of monobasic sodium phosphate and dibasic potassium phosphate (both from Fisher Scientific, Fair Lawn, NJ). Ionic strength was adjusted to 0.30 M with potassium chloride (Fisher Scientific, Fair Lawn, NJ). Appropriate amounts of IBA (Sigma Chemical Co., St. Louis, MO) were added to these solutions to obtain the required concentrations. The solutions were placed in 100 ml volumetric flasks. These flasks were then kept in a circulating water bath maintained at 30°C.

Kinetic studies

The appropriate ester (Sigma Chemical Co., St. Louis, MO) was dissolved in ethanol and added to volumetric flasks containing CTAB solutions maintained at 30°C. Sufficient ester stock solution was added to make the initial concentration in the micellar solution 2.0×10^{-5} 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 with 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 slow the reaction. These samples were then analyzed for the ester and α-naphthol concentrations using a fluorimetric assay (Shimadzu RF-540 fluorimeter, Kyoto, Japan). The excitation and emission maxima used for each of the esters were 260 and 333 nm, respectively, while the excitation and emission maxima for α-naphthol were 294 and 464 nm, respectively. The dilution process resulted in samples with CTAB concentrations that were lower than the CMC. Therefore, fluorescence quenching was not a problem. Kinetic studies were carried out in duplicate for the acetate, propionate, pentanoate and hexanoate compounds while those for the butyrate compound were carried out in triplicate. The resultant data were analyzed to determine the pseudo-first-order rate constants. The reaction rate constant vs surfactant concentration profile for each compound was then analyzed according

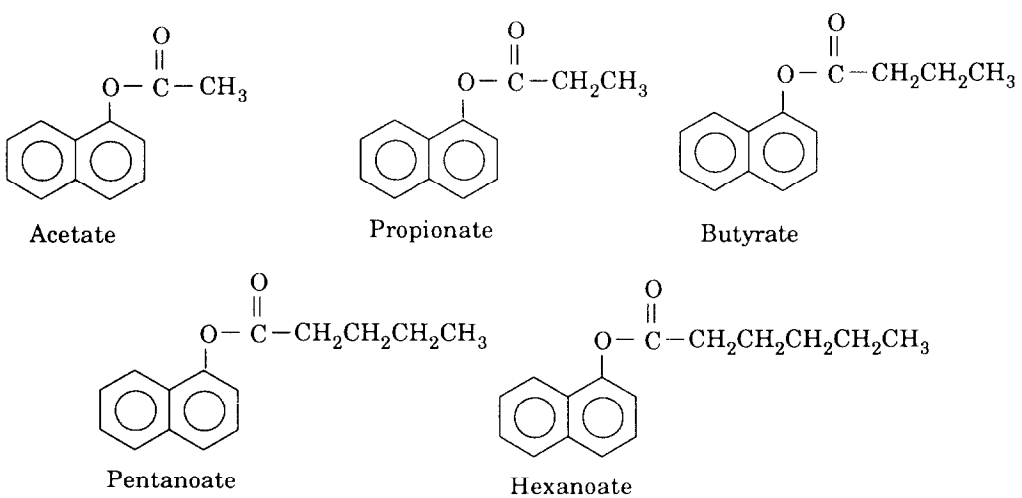

Fig. 1. Structures of the naphthyl esters employed in the kinetic studies.

to the pseudophase model to determine the binding constant for the micelle-substrate interaction.

Results and Discussion

The value of the CMC used in this work was experimentally determined at an ionic strength of 0.30 M and found to be 6.8×10^{-5} M (Mukerjee and Mysels, 1971; Patel and Wurster, 1991). The rate of hydrolysis of α-naphthyl acetate by IBA increased appreciably in micellar solutions which had CTAB concentrations exceeding the experimentally determined CMC (Wurster and Patel, 1992). This enhanced reaction rate in micellar solutions of CTAB was found to be due to the concentrating of both α-naphthyl acetate and IBA in the micellar pseudophase (Wurster and Patel, 1992). Similar enhancement of the rates of hydrolysis of the propionate, butyrate, pentanoate and hexanoate compounds was observed in this work. Rate constant vs CTAB concentration profiles were obtained for each of these compounds. The profile for the propionate was typical and is shown in Fig. 2. Non-linear regression analysis was employed for the rate constant vs surfactant concentration data of each of the compounds and Eqn 1 was used (Berezin et al., 1973, 1974; Wurster and Patel, 1992):

$$k_{obs} = \frac{k_0 + \bar{k}_m K_A K_B C}{(1 + K_A C)(1 + K_B C)} \qquad (1)$$

where k_{obs} is the experimentally observed pseudo-first-order hydrolysis rate constant, k_0 denotes the pseudo-first-order hydrolysis rate constant in the bulk aqueous phase, C is the concentration of the surfactant less the critical micelle concentration, K_A and K_B represent the pseudophase model binding constants for the ester and for IBA, respectively, and $\bar{k}_m$ is equal to the pseudo-first-order micellar rate constant, k_m, divided by the molar volume of the surfactant as it exists in the micellar phase, $\bar{V}$. The coefficient of determination for the propionate data was 0.971; other r^2 values ranged from 0.924 to 0.996. The value of K_B was determined to be the IBA binding constant, since the value of K_B remained essentially constant when both K_A and K_B were allowed to float. K_B was then fixed at 229 l/mol

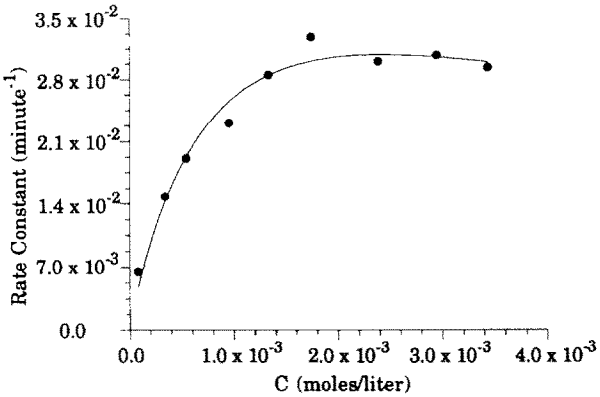

Fig. 2. Influence of CTAB concentration on the rate of α-naphthyl propionate hydrolysis at pH 7.5 ($T = 30$°C) in the presence of 1.0×10^{-4} M IBA. Ionic strength was equal to 0.30 M. Initial α-naphthyl propionate concentration was 2.0×10^{-5} M. The plot is the fitted curve.

TABLE 1

Maximum rate constants (pH 7.5, T = 30°C, ionic strength = 0.30 M) observed in the rate constant vs surfactant concentration profiles for these esters and the CTAB concentrations at which these maxima in rate constant were either observed or calculated to be found

Ester	Binding constant (l/mol)	Calculated CTAB concentration at maximum rate constant (mol/l)	Observed CTAB concentration at maximum rate constant (mol/l)	Maximum rate constant observed (min^{-1})
Acetate	400	3.30×10^{-3}	3.06×10^{-3}	2.89×10^{-2}
Propionate	740	2.43×10^{-3}	1.81×10^{-3}	3.30×10^{-2}
Butyrate	7480	7.64×10^{-4}	3.01×10^{-4}	1.11×10^{-2}
Pentanoate	13000	5.80×10^{-4}	3.74×10^{-4}	1.30×10^{-2}
Hexanoate	42640	3.20×10^{-4}	2.33×10^{-4}	1.20×10^{-2}

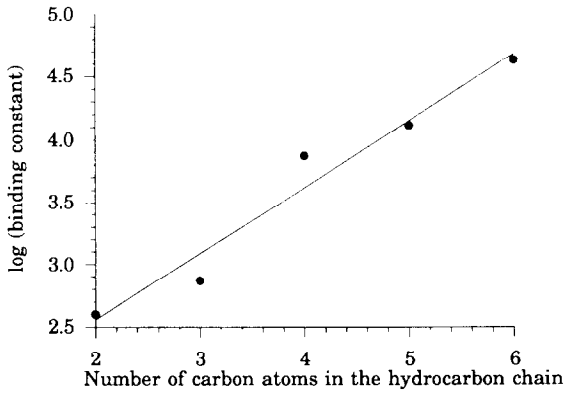

Fig. 3. Effect of increasing the number of carbon atoms in the hydrocarbon chain on the binding constant. The regression parameters determined using non-linear curve fitting with subsequent log transformation were $a = 1.5$, $b = 0.53$ and $r^2 = 0.991$ where b is the slope of the semi-log plot.

for these analyses. This is the same value that was reported previously for the IBA binding constant (Wurster and Patel, 1992). Assuming a fixed value for K_B requires that the IBA partition coefficient be independent of the ester concentration and that the length of the hydrocarbon chain only influence the ester partition coefficient and not, indirectly, the IBA partition coefficient. These assumptions are reasonable. When K_B was made constant, the change in K_A from compound to compound became more regular. There was very little change in any of the coefficients of determination.

The binding constants obtained for the micelle-ester interaction (K_A values) are listed in Table 1. The binding constants for the micelle-ester interaction increased as the number of carbon atoms in the hydrocarbon chain increased. A plot of log(binding constant) vs the number of carbon atoms in the hydrocarbon chain shows good linearity (Fig. 3). Previous studies have revealed such log-linear behavior for the partition coefficients of compounds in a homologous series (Dunn et al., 1986). In general, each methylene group added to a hydrocarbon chain provides roughly the same contribution to the free energy change for the transfer of a solute from one phase to another in the partitioning process. Since the partition coefficient is a function of the exponential of the free energy change involved, a logarithmic relationship should be observed between the partition coefficient and the number of carbon atoms in the compound (Dunn et al., 1986). The pseudophase model binding constant, K_A, is related to the partition coefficient, P_A, according to the expression:

$$K_A = (P_A - 1)\bar{V} \cong P_A\bar{V} \qquad (2)$$

where $\bar{V}$ denotes the molar volume of the surfactant as it exists in the micellar phase and P_A is usually assumed to be much greater than unity (Berezin et al., 1973, 1974; Wurster and Patel, 1992). Therefore, the free energy change associated with the transfer of a methylene group from an aqueous phase to a micellar phase can be calculated using the slope of a plot of log(binding constant) vs the number of carbon atoms in the hydrocarbon chain. Using the slope of 0.53 obtained from Fig. 3, the free energy change per mol of CH_2 groups for this series of compounds was found to be -740 cal. This value agrees reasonably well with that of -640 cal per mol of CH_2 groups for the transfer of solute from the bulk liquid phase to the surface determined using Traube's Rule (Adamson, 1990).

The binding constant values for the ester and IBA can be employed to estimate the CTAB concentration, C_{opt}, for which the maximum rate constant should be observed in a profile of rate constant vs CTAB concentration (Berezin et al., 1973):

$$C_{opt} = (K_A K_B)^{-1/2} \qquad (3)$$

Eqn 3 can be derived from Eqn 1 when it is assumed that the rate constant in the bulk aqueous phase is negligible compared with the overall rate constant in the micellar media. Table 1 shows the results from this calculation and also presents the experimentally observed CTAB concentration at which the maximum rate constant was found. It can be seen that the observed and calculated values for the CTAB concentrations at maximum rate constant agree to varying extents. The extent of agreement is a function of both the success of the curve-fitting procedure and the variability and spacing of the experimental points. Although the

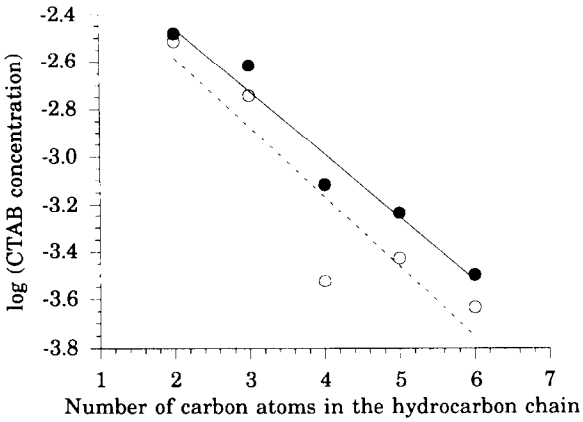

Fig. 4. The CTAB concentration at which the maximum in the rate constant vs surfactant concentration profile was observed (○) and calculated (●) for each of the compounds studied. The regression parameters obtained using non-linear curve fitting with subsequent log transformation were $a = -1.99$, $b = -0.292$ and $r^2 = 0.840$ for the observed points and $a = -1.93$, $b = -0.265$ and $r^2 = 0.959$ for the calculated points (b is the slope of the semi-log plot).

agreement is not as good as one would desire, the fundamental behavior of the system can be properly predicted (see below).

Since there is a log-linear relationship between the binding constant and the number of carbon atoms in the hydrocarbon chain, a similar relationship should exist for the CTAB concentration at which the maximum rate constant is observed. The reason for this correspondence is that the shift in the position of the maximum is a function of the binding constant for the micelle-substrate interaction. When the data in Table 1 were plotted (Fig. 4), log-linear relationships were observed for both the calculated and the observed CTAB concentrations. In Fig. 4, it can also be seen that the line for the calculated optimum CTAB concentrations is displaced from the line for the observed values. Importantly, the two lines are almost parallel (slope = −0.292 for the observed optimum concentrations, slope = −0.265 for the calculated optimum concentrations). This indicates that the effect of each additional methylene group on the binding constant is correctly predicted even if the two methods do not yield exactly equal optimum CTAB concentrations.

TABLE 2

Effect of increasing hydrocarbon chain length on the ratio (k_m / k_o) of the maximum rate constant in micellar solution to the rate constant observed in a non-micellar solution

Ester	k_m / k_o
Acetate	35.5
Propionate	47.4
Butyrate	30.0
Pentanoate	38.9
Hexanoate	31.8

Mean = 36.7; standard deviation = 6.9.

Table 2 shows the ratio of the maximum rate constant in micellar media to the rate constant in non-micellar media (k_m/k_o) obtained for each of the compounds. In micellar solution, the aromatic portion of the α-naphthyl compound is probably solubilized in the Stern layer (Elworthy et al., 1968; Cardinal and Mukerjee, 1978), having penetrated past the point where the charged head groups are situated. In this position, the carbonyl group would probably be close to the surface of the Stern layer where the attacking nucleophile (IBA) is most likely solubilized. Increasing the number of carbon atoms in the hydrophobic chain might be expected to pull the carbonyl carbon farther into the micelle. This change in the position of the carbonyl carbon would decrease its

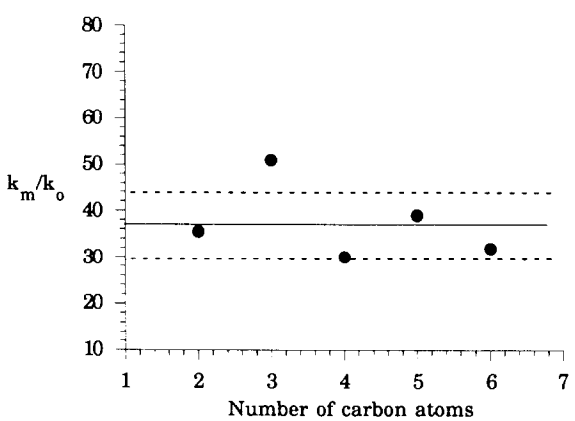

Fig. 5. Ratio (k_m / k_o) of the maximum rate constant observed in the micellar solution to the rate constant in non-micellar solution for α-naphthyl esters with varying numbers of carbon atoms in the hydrocarbon side chain. (———) Mean ratio; (- - - - -) standard deviation about the mean.

accessibility to the nucleophile and the ratio k_m/k_o would systematically decrease.

While the ratio k_m/k_o was rather variable (coefficient of variation equal to 19%), it did not change in a systematic manner (Fig. 5). This indicates that the IBA molecule has approximately equal access to the carbonyl carbon of each of the compounds studied and, therefore, that the position of the carbonyl carbon in the micelle is relatively unaffected by moderate changes in hydrocarbon chain length.

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