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Micellar effect upon the rate of alkaline hydrolysis of carboxylic and carbonate esters

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Abstract The alkaline hydrolysis of carboxylate (1-naphthylbutyrate) and carbonate esters (2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate) in the presence of different surfactants has been studied. The rate of hydrolysis of these esters was determined under pseudo first order condition in which the concentration of NaOH was kept in large excess over the [ester]. The cationic micelles of cetyltrimethylammonium bromide (CTABr) and cetyltrimethylammonium sulfate ((CTA)$_2$SO$_4$) enhanced the rate of hydrolysis of esters to a maximum value and thereafter, the increasing concentration of surfactant decreased the reaction rate. The anionic micelles of sodium dodecyl sulfate (SDS) inhibited the rate of the hydrolysis. The reaction proceeds through the attack of OH$^-$ ions on the carbonyl carbon forming tetrahedral intermediate. The tetrahedral intermediate is unstable and collapses immediately to yield respective acid and alcohol. The micelles influence the stability of tetrahedral intermediate, in turn, altering the rate of hydrolysis. The variation in the rate of hydrolysis by micelles was treated by considering the pseudophase ion-exchange model and Menger–Portnoy model. The added salts *viz*. NaBr, NaCl, and LiCl inhibited the rate of the reaction in the presence of cationic and anionic micelles. The kinetic parameters i.e. k_m and K_s were determined from the rate–[surfactant] profile.

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1. Introduction

Hydrolysis is among the most important reactions of organic molecules with water in aqueous environments that plays a significant environmental fate process for many organic compounds. Many classes of organic compounds like alkyl halides, carboxylic acid esters, phosphate esters, carbamates, epoxides, nitriles, amides, amines, etc. undergo hydrolysis in the medium of acidic, alkaline or neutral [17,18]. The determination of rate

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constants for the hydrolysis reaction can be significant for the identification of the chemical formed or species present in the ecosystem and to determine the possibility of the parent compounds. The hydrolysis of carboxylic acid esters involves bimolecular nucleophilic attack analogous to the SN_2 mechanism on the saturated carbon [2,14,21]. Ester functional groups are among the most common acid derivatives present in natural and man-made chemicals. Carboxylic acid esters are used industrially to make flavors, soaps, herbicides etc. The base-catalyzed or alkaline hydrolysis of esters generally takes place via SN_2 reaction [3]. The presence of water as solvent changes the rate and mechanism of hydrolysis reactions in many ways such as nucleophilic reagent, as a high dielectric-constant; and as a specific solvating agent for organic reactants and products [16,25]. The modifications in the reaction medium i.e. by adding organic solvents or by adding surfactant molecules also affect the solvating power and thus alter the hydrolytic rate [4,23]. The variation in the values of rate constant with the alteration in the medium may involve the interaction of the solvent medium with the reactants, transition states and/or products. The rate of hydrolysis of ester increases when the transition state is better solvated or stabilized by the H-bonding than the initial state [15]. The negatively charged transition states of base and general base-catalyzed ester hydrolysis are strongly stabilized by solvent alpha sites, while the solvent beta sites play a minor role [19].

Surfactants are the amphiphilic molecules consisting of the polar or charged headgroup and non-polar hydrocarbon chain [11]. The surfactant molecules aggregate at concentrations above critical micellar concentrations (cmc) to form micelles [24]. The micelles have a tendency to influence the reaction rates by enhancing it or by retarding the rates of reaction [5]. The influence of cationic cetyltrimethylammonium bromide (CTABr), cetyltrimethylammonium sulfate ((CTA)$_2$SO$_4$), and anionic sodium dodecyl sulfonate (SDS) was investigated on the rate of alkaline hydrolysis of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitro-phenylcarbonate to elaborate the medium role on the rate of hydrolysis. The effects of salts e.g. NaCl, LiCl, NaBr, trimethyl ammonium bromide (TMABr), tetraethyl ammonium bromide (TEABr) etc. on the reactivity of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitro-phenyl carbonate in the presence of surfactant molecules were also studied and are described in this paper.

2. Experimental

2.1. Materials

1-Naphthylbutyrate (98%, Merck, Germany), 2-(methylsulfonyl)-ethyl-4-nitro-phenylcarbonate (98%, Merck, Germany), sodium dodecyl sulfate (SDS, 99%, BDH, England), and cetyltrimethylammonium bromide (CTABr, 99%, BDH, England) were used during the experiment. Sodium bromide (NaBr, 99%, BDH, England), lithium chloride (LiCl, 99%, BDH, England), sodium chloride (NaCl, 99%, BDH, England), tetramethylammonium bromide (TMABr, 99%, Sigma, USA), and tetraethylammonium bromide (TEABr, 99%, Sigma, USA) were used as supplied. Anal R grade sodium hydroxide was used during the experimental work. Deionized double-distilled water with specific conductance; $1-2 \times 10^{-6} \, \Omega^{-1} \, cm^{-1}$ was used as a solvent throughout the experiment. Cetyltri-

methylammonium sulfate, (CTA)$_2$SO$_4$ was synthesized in the laboratory by mixing 50% excess of Ag$_2$SO$_4$ with CTABr in absolute alcohol. The reaction mixture was sonicated for 1.5 h and then AgBr was removed by filtration. The product was then recrystallized three times from the mixture of absolute methanol-diethyl ether. The purity of the synthesized surfactant was checked by determining the melting point. The melting point of the final product was 215 °C.

2.2. Kinetic measurements

The repetitive scans for the alkaline hydrolysis of 2.0×10^{-5} mol dm^{-3} 1-naphthylbutyrate in 1.0×10^{-4} mol dm^{-3} NaOH were recorded at 25.0 ± 0.1 °C at the intervals of 2 min. Similarly, the scans for the hydrolysis of 2-(methylsulfonyl)-ethyl-4-nitro-phenylcarbonate (1.0×10^{-5} mol dm^{-3}) in 1.0×10^{-4} mol dm^{-3} NaOH were recorded at 25.0 ± 0.1 °C. The spectra are given in Figs. 1 and 2, respectively. It is observed that the values of absorbance increase with the progress in reaction in both the cases. The values of λ_{max} for 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate were observed at 248 nm and 400 nm, respectively. Therefore, all the kinetics studies were followed by monitoring the absorbance at 248 nm (for 1-naphthylbutyrate) and 400 nm (for 2-(methylsulfonyl)-ethyl-4-nitro-phenylcarbonate). The absorbance was recorded on Perkin-Elmer 330 UV–visible spectrophotometer. The constant temperature was maintained at 25.0 ± 0.1 °C using the L.K.B. 2209 multi-temperature water bath. The values of first-order rate constants (k_{obs}, s^{-1}) were obtained from slopes of plots of ln ($A_\infty - A_t$) versus time with an average linear regression coefficient, $r^2 \geqslant 0.98$. The rate of reaction was studied until the reaction completed to 3–4 half-lives. Each kinetic run was repeated at least 3 times and the results were found to be reproducible within $\pm 5\%$. The concentration of sodium hydroxide was kept large excess over the carboxylic and carbonate esters.

3. Results

3.1. Hydrolysis of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate in the aqueous medium

The rate of hydrolysis of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate was determined at different concentrations of sodium hydroxide. The concentration of NaOH was taken in the range from 1.0×10^{-3} mol dm^{-3} to 1.0×10^{-1} mol dm^{-3} for 1-naphthylbutyrate. The concentration of NaOH varied from 1.0×10^{-4} mol dm^{-3} to 1.0×10^{-3} mol dm^{-3} for the hydrolysis of 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate. The concentrations of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitro-phenylcarbonate were kept constant at 2.0×10^{-5} mol dm^{-3} and 1.0×10^{-5} mol dm^{-3}, respectively. The observed values of rate constant (k_{obs}) increased linearly with the increase in [NaOH] (Fig. 3 and inset: 3a). The slope of the plot of log (k_{obs}) versus log [NaOH] was found to be 0.948 (with $r^2 \geqslant 0.999$) and 0.825 (with $r^2 \geqslant 0.995$), for hydrolyzes of 1-naphthylbutyrate and 2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate, respectively, indicating that the order of the reaction is close to unity. Little influence of [salt] on the values of first order rate constant was observed indicating that the reaction occurs between the