Asian Journal of Chemistry Vol. 20, No. 1 (2008), 505-508

Role of Polymer in the Catalysis of Acyl Transfer Reactions

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Preliminary study of kinetics of the hydrolysis of esters in the presence of polymer polyethyleneglycol (PEG) 6000 by hydroxide ion in varying solvent media has been carried out conductometrically. The results obtained throw light on the role of the catalysts in the mechanism of hydrolysis of esters. Further, the presence of polymer is found to modify the role of solvent during the course of the reaction. These preliminary results will pave way for predicting the nature of attack by enzymes on various substrates in biochemical reactions.

Key Words: Polymer, Catalysis, Acyl transfer.

INTRODUCTION

Acids, bases and enzymes catalyze the hydrolysis of esters. A nucleophilic attack takes place on the carbonyl carbon and an electrophilic attack takes place on the alcoholic oxygen atom in the hydrolysis of ester in aqueous medium. The study of these reactions are important for predicting the mechanism of several biological reactions[1,2]. The interactions between a nucleophile and ester is as depicted in the following scheme:

$$X^- + R\text{-}COY \rightarrow R\text{-}COX + Y^-$$
$$R\text{-}COX + H_2O \rightarrow RCOOH + XH$$

where X^- is a nucleophile, which replaces Y^- from the ester forming an acyl intermediate which will be attacked upon latter by water to give final products.

Solvent plays an important role in these reactions. The solvent water apart from acting as a reactant, it solvates the nucleophile or provides proton for attacking the carbonyl oxygen or polarize the carbonyl group of the ester or stabilizes the acyl intermediate or solvates the leaving group. A polar aprotic solvent such as acetonitrile is added and the effect of polarity change on the reaction rates has been studied. Further the role of added polymer *i.e.*, polyethylene glycol during the hydrolysis also has been studied. In the present study, the variation of the rate of hydrolysis of ethyl acetate and ethyl benzoate in varying solvent medium has been studied.

Addition of surface-active materials in the solvent exhibit unusual variation in the physical properties such as surface tension, osmotic pressure, *etc*[3]. In dilute solutions, the surfactant acts as a normal solute. At fairly high concentration abrupt changes in physical properties have been observed. McBain pointed out that this anomalous behaviour could be explained in terms of organized aggregates, or micelles of the surfactant ions in which the lipophilic hydrocarbon chains are oriented towards the interior of the micelle, having the hydrophilic groups in contact with the aqueous medium.

EXPERIMENTAL

AnalR sample of polyethylene glycol was purchased and used as such. Ethyl acetate and ethyl benzoate were distilled over acetic anhydride and sulphuric acid and the distillate is collected and used. Deionized water is double distilled in the presence of potassium permanganate and a pellet of sodium hydroxide and pure distillate obtained at 100 ºC is used by storing in air proof containers. Acetone is distilled and pure distillate is used. Acetonitrile is distilled over phosphorous pentoxide and pure distillate obtained is used.

Concentrated sodium hydroxide was prepared in degassed conductivity water and allowed to stand for 24 h. The clear supernatant liquid was decanted carefully and quickly into a pyrex glass bottle and stoppered. The solution is standardized using a standard oxalic acid solution. From the standardized sodium hydroxide solution, the solution of required composition is prepared in degassed conductivity water and used for studying kinetics.

The kinetic study of the hydrolysis of the esters were followed conductometrically. The solution of the ester in organic solvent and sodium hydroxide in water are added in definite equal proportions as required. The conductance of the solution has been measured at various time intervals using a conductivity bridge. The balancing length l_1 for minimum sound as found out by dipping a conductivity cell in the solution and connecting terminals to the bridge. The resistance of the solution at each interval of time was calculated using the formula:

$$\text{Resistance of solution} = (l_1/l_2) \times \text{external resistance in ohms}$$

where l_1 is the balancing length in mm and l_2 is $(250\text{-}l_1)$ mm. From the resistance, the conductance of the solution, C_t at time 't' s was determined by taking its reciprocal. Conductance of the blank solution, C_0 and the conductivity of the reaction mixture at infinite time, C_∞ was also determined. From these values the second order rate constant for the hydrolysis of the esters were determined according to the equation:

$$k_2 = (1/at)(Co\text{-}C_t)/(C_t\text{-}C_\infty)\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

where 'a' is the initial concentration of the ester in mol dm^{-3}.

Rate constants were also determined graphically by dividing the slope of the plot $(C_0\text{-}C_t)/(C_t\text{-}C_\infty)$ against time in seconds by the initial concentration of the reactant.

RESULTS AND DISCUSSION

The kinetic data obtained during the study of the hydrolysis of different ester by hydroxide ion at 303 K (Tables 1 and 2).

TABLE-1
KINETIC DATA FOR THE HYDROLYSIS OF ETHYLBENZOATE IN VARIOUS SOLVENT MEDIA
$[OH^-]$ = [ethyl benzoate] = 2×10^{-2} mol dm^{-3}, Temperature 303 K

Solvent composition: (% v/v)		k_2/dm^3 mol^{-1} s^{-1}
Acetonitrile	Water	
20	80	0.08
30	70	0.13
50	50	0.14
60	40	0.19
Acetone	Water	
20	80	0.08
30	70	0.10
50	50	0.12
60	40	0.12

TABLE-2
KINETIC DATA FOR THE HYDROLYSIS OF ETHYLACETATE IN VARIOUS SOLVENT MEDIA
$[OH^-]$ = [ethyl acetate] = 2×10^{-2} mol dm^{-3}, Temperature 303 K

Solvent composition: (% v/v)		k_2/dm^3 mol^{-1} s^{-1}
Acetonitrile	Water	
20	80	0.035
40	60	0.038
60	40	0.045
Acetone	Water	
20	80	0.091
40	60	0.101
50	50	0.123

As the percentage of organic solvent increases the rate of hydrolysis of the ester increases. This may be due to the solvation of metal ion by the organic solvent resulting in OH^- ion which attacks in a facile manner.

The kinetic data obtained during the hydrolysis of the above two esters in the presence of the added polyethylene glycol by hydroxide ion in different solvent mixtures at 303 K (Tables 3 and 4).

It is found that the rate of hydrolysis of ethyl benzoate increases linearly as the concentration of the polymer increases. This may be as due to the decrease in the polarity of the medium (Table-3). As the concentration of the polymer increases it is found that the rate of hydrolysis of ethyl

TABLE-3
KINETIC DATA FOR THE HYDROLYSIS OF ETHYLBENZOATE AND ETHYLACETATE IN THE PRESENCE OF PEG
$[OH^-]$ = [ethylbenzoate] = 2×10^{-2} mol dm^{-3};
$[OH^-]$ = [ethylacetate] = 2×10^{-2} mol dm^{-3}
Temperature: 303 K, Solvent: AcCN:H_2O (1:4) (v/v)

[PEG] mol dm^{-3}	k (dm^3 mol^{-1} s^{-1})	
	Ethyl benzoate	Ethyl acetate
1×10^{-6}	0.0556	0.09
5×10^{-6}	0.0796	–
1×10^{-5}	–	0.10
5×10^{-5}	0.0836	0.13
1×10^{-4}	–	0.12
5×10^{-4}	0.0894	0.09

PEG = Polyethylene glycol

TABLE-4
KINETIC DATA FOR THE HYDROLYSIS OF ETHYLBENZOATE AND ETHYLACETATE IN THE PRESENCE OF PEG
$[OH^-]$ = [ethylbenzoate] = 2×10^{-2} mol dm^{-3};
$[OH^-]$ = [ethylacetate] = 2×10^{-2} mol dm^{-3}
Temperature: 303 K, Solvent: CH_3COCH_3:H_2O (1:4) (v/v)

[PEG] mol dm^{-3}	k (dm^3 mol^{-1} s^{-1})	
	Ethyl benzoate	Ethyl acetate
5×10^{-6}	–	0.11
1×10^{-5}	0.04	0.30
5×10^{-5}	0.05	–
1×10^{-4}	–	0.41
5×10^{-4}	0.09	0.20

PEG = Polyethylene glycol

acetate increases and then decreases. This may be attributed to the change in the role of the polymer at higher concentrations when it may solvate the ester (being smaller than ethyl benzoate) thereby retards the hydrolysis step (Table-4).

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(*Received*: 21 November 2006; *Accepted*: 14 September 2007) AJC-5851