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Studies of Rate of Solvolysis Reaction of Some Aromatic Esters

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ABSTRACT

Rate and mechanism of solvolysis reaction of aromatic ester depends upon various features of solvent like dipole moment, H – bonding, viscocity, dileotric constant, protic or aprotic nature of solvent, protogenic, protophitic, amphiprotic or amphoteric nature of solvent. It also depends upon temperature, pressure and electron donar or electron acceptor group present in the aromatic ester.

1. INTRODUCTION

Parker and his coworkers showed in a more detailed investigation, that most of the anions in dipolar aprotic solvents are much less solvated than in protic solvents. But, polarisable charges transition states in dipolar aprotic solvents are more solvated than in protic solvents. The result is that the bimolecular reactions of anion, which pass through a large polarisable transition states containing that anions are much faster in dipolar aprotic solvents than in protic solvents. Reactions of small anions are most accelerated in solvents.

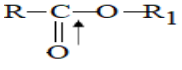
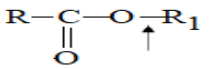
According to the theory of Hughes and Ingold "the creation and concentration of charges is accelerated and destruction and diffusion of charges is inhibited by increase in ion solvating power of the medium".

On the basis of this theory, the expected effect of ionising media on the rate of some charge type of reactions may be tabulated

Table Solvent effect on rates of Nucleophilic Substitution Reaction

Reaction Mechanism increase Type	Products		Effect of charges on activation	Effect of in solvent polarity on Reaction rate
$Y^- + R - X$	S_N2	$Y - R - X^-$	Dispersed	Small decrease
$Y + R - X$	S_N2	$Y - R^+ + X^-$	Increased	Large Increase
$Y^- + R - X^+$	S_N2	$YR + X$	Dispersed	Large Increase
$Y + R - X^+$	S_N2	$YR^+ + X$	Dispersed	Small decrease
$R - X$	S_N1	$R + X$	Increased	Large Increase
$R - X^+$	S_N1	$R^+ + X$	Dispersed	Small decrease

The activation parameters for many reactions have been evaluated by a large number of workers involving the formation of ions from neutral molecules in a variety of solvents.

The hydrolysis of the ester is considered to be one of the most important ion-dipole type of reaction and the hydrolysis of carboxylic esters is the reverse of the esterification. It can be catalysed by both acids and bases. Usually, the hydrolysis of esters are catalysed by acid, base or enzymes. The acid and base catalysed hydrolysis of esters in aqueous solutions are carried out in presence of H^+ (Hydrogen) ion and OH^- (Hydroxyl) ion respectively and are largely of specific types. There is generally a nucleophilic attack on the carbonyl carbon atom and an electrophilic attack on the alcoholic oxygen atom in both the acid and base catalysed hydrolysis of esters in aqueous medium. The special feature of the hydrolysis reaction is that the products may be formed either by the cleavage of an acyl oxygen  or an alkyl oxygen  bond. Both of these mode of fissions have been observed under proper conditions in appropriate systems.

Ingold and his coworkers suggested a general description of the different mechanism of esterification in 1939. A total of eight different mechanisms were recogonised from their work depending on whether:

(i) an alkyl oxygen (AL) cleavage or an acyl oxygen (AC) cleavage take place,

(ii) catalysis is accompanied by a acid (A) or a base (B) or

(iii) The water molecules does not take part in slow step of reaction in hydrolysis, i.e., the reaction is unimolecular (1) or the water does participate in the reaction, i.e., the reaction is bimolecular.

Thus, as for example a A_{AC}^{2} hydrolysis means this hydrolysis is a bimolecular reaction involving acyl-oxygen bond cleavage carried out in acidic medium.

Among these pathways, only B_{AC}^{1} and A_{AL}^{2} have not

(i) the acivation energy (Ea) depends on the type of reaction but does not depend upon the nature of the solvent and

(ii) the entropy of activation ($_{\Delta}s^{*}$) changes with the nature of the solvent.

The $_{\Delta}S^{*}$ (entropy of activation) is negative and becomes more negative as the polarity of the medium decreases. It is clear from this, that the rates of reactions producing ions in solution increase with the polarity of the solvent and that increase is governed largely by the change in the entropy of activation.

The reaction in which the solvent plays an important role is controlled by the electrostatic forces between the solvent and the solute molecules. Different types of reaction in which the electrostatic effect imposed by the solvent.

Table Mechanism of Ester Hydrolysis

Types of Hydrolysis	Form Attacked	Fission	Symbol of mechanism	Remarks
Basic	$R^{1}CO_{2}R$	Acyl	B_{AC}^{1}	Not observed to date
Basic	$R^{1}CO_{2}R$	Acyl	B_{AC}^{2}	Very common for all esters
Basic	$R^{1}CO_{2}R$	Alkyl	B_{AL}^{1}	Quite general for esters of tertiary alcohol
Basic	$R^{1}CO_{2}HR+$	Alkyl	B_{AL}^{2}	Extremely rare for b - lactones
Acidic	$R^{1}CO_{2}HR+$	Acyl	A_{AC}^{1}	Rare (in very strong acidic solution)
Acidic	$R^{1}CO_{2}HR+$	Acyl	A_{AC}^{2}	Very common for primary and secondary alcohol
Acidic	$R^{1}CO_{2}HR+$	Alkyl	A_{AL}^{1}	Quite general for esters of tertiary alcohols.
Acidic	$R^{1}CO_{2}HR+$	Alkyl	A_{AL}^{2}	Not observed to-date

The kinetics of alkali catalysed hydrolysis of Ethyl cinnamate were studied in water-EG media having varying composition ranging from 30% to 80% (v/v) of organic co-solvent at different temperatures i.e. at $20^{o}C$, $25^{o}C$, $30^{o}C$, $35^{o}C$ and $40^{o}C$. The reaction was found to follow second order kinetic equation. Hence, its specific rate constant values were calculated using this equation and have been tabulated. In order to highlight the variation of specific rate constant values with gradual addition of organic co-solvent in the solvent mixtures. The values of log k were plotted against mol % of the organic co-solvent (EG).

2. Results and Discussion

It is clear that variation of log k with mol % of organic co-solvent follows decreasing trends. Up to approximately 25.0 mol % of organic co-solvent, the decrease is of higher degree whereas after 25.0 mol % of the organic co-solvent, the depletion is comparatively slower at all the five temperatures. The trend of variation in the values of specific rate constant may be discussed in the light of Hughes and Ingold theory. According to the theory, increase in dielectric constant values of the reaction media results in increase in the rate when there is concentration of charges on the transition state and causes a decrease in the rate when there is diffusion or destruction of charges on the transition state.

With a view to study the variation in specific rate constant with dielectric constant of the media, the values of log k with change in dielectric constant of the media have been tabulated ahead. From this table, it is clear that there is decrease in dielectric constant value of media with gradual addition of EG in the reaction media. In the alkali catalysed hydrolysis of Ethyl cinnamate, due to participation of OH^{-} ion (negative ion).

Specific rate constant values of Alkali catalysed hydrolysis of Ethyl cinnamate in water-EG media

k x 10^2 in $(dm)^3$ $mole^{-1}$ min^{-1}

Temp. in ^OC	(v/v)% of Ethylene glycol (EG)					
	30%	40%	50%	60%	70%	80%
20^0C	62.46	55.22	51.51	47.44	45.82	43.34
25^0C	125.86	1.7.25	95.10	84.76	71.70	67.75
30^0C	254.16	207.92	170.06	147.98	125.49	107.80
35^0C	466.77	37.92	315.94	245.64	216.32	170.06
40^0C	897.64	732.66	348.02	446.58	347.54	243.33

Table

Variation of log k values of the reaction with mol % of Ethylene glycol in water-EG media.

% of (v/v)	Mol % of EG	Temperature				
		20^0C	25^0C	30^0C	35^0C	40^0C
30%	12.16	1.7956	2.0999	2.4051	2.6691	2.9531
40%	17.73	1.7521	2.0304	2.3179	2.5751	2.8649
50%	24.42	1.7119	1.9782	2.2306	2.4996	2.7388
60%	32.64	1.6761	1.9282	2.1702	2.3903	2.6499
70%	42.94	1.6611	1.8904	2.0986	2.3351	2.5410
80%	56.34	1.6369	1.8309	2.0326	2.2306	2.3862

Using Arrhenius formula,

$$k = A \cdot e^{-E_{exp}/RT}$$

the iso-composition activation energy for alkali catalysed hydrolysis of Ethyl cinnamate in aquo-EG media were evaluated from the values of slopes of the linear plot of log k values against 1/T. From the value of slopes of the straight lines, the values of the iso-composition activation energy have been calculated and are enlisted.

After making observation of the values of E_{exp}, it is clear that there is depletion in the E_{exp} values with increase in the concentration of organic co-solvent (EG) in the reaction media. The E_{exp} values decrease from 101.97 kJ/mol to 67.39 kJ/mol. It has been established that changes in the values of activation energy are obviously noticeable only when the solvation changes take place either at the initial state level or at the transition state level or at both the levels. The decrease in the activation energy of the reaction with decrease in the specific rate constant values does not seem to be quite natural, rather it is of specific type. The following three possibilities may be held responsible for the depletion in the values of E_{exp}.

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