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Kinetic Studies on the of Solvolysis Reaction of Aromatic Esters Which have Medicinal Properties

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Abstract

It has also been concluded that the dielectric constant, external pressure, internal cohesion (viscocity) and hydrogen bondings of the solvents mainly produce change in the rate where as the polarity of the solvent has been found responsible for change in the nature of the mechanism.It seems necessary to discuss about the different types of solvents

Introduction

After going through the kinetic study of various types of solvolysis reactions in aquo-organic co-solvent reaction media, the researchers of the past[1-3] and recent times[4-6] have reported that the organic solvents have been found to play a dominant as well as interesting role on the reactions by producing not only a significant but peculiar change in the rate of reaction as well as in the mechanism of the reaction.

A large number of kineticists have observed that study on the rates and mechanisms of chemical reactions, particularly in solutions, is one of the most important problems in the kinetic field of chemistry, so the studies on the kinetic effect of the solvent on the rates and mechanisms of various types of reactions have aroused much curiosity and enquiries for the hopeful researchers.

Though many researchers in the past[81-85] and in the recent years[86-92] have reported about the solvent effect on the rate and mechanism of solvolysis of various esters, but, the effect of solvent on the medicinal and biochemical properties of aromatic esters has not been paid even a little attention so far.

Hence in order to highlight the above noted useful but still untouched research problem, it has been thought essential to study the kinetics of solvolysis of cinnamate esters which are obtained from cinemon group of plants and possesses a large number of biochemical and medicinal uses for human beings.

In this scheme, it has been proposed to study the kinetics of alkali catalysedsolvolysis of ethyl cinnamate separately in presence of two different solvents having mono and dihydroxyl groups namely ethyl alcohol and ethylene glycol.

This is analogous to the $S_N{}^2$ reaction in saturated aliphatic nucleophilic displacement.

This pathway is reversible in principle, but, in practice it is completely driven to the right because of the proton transfer from the carboxylic acid to the alkoxide ion as shown above. Out of these two suggested pathways, the second one involving a tetrahedral intermediate (II) has adequately been supported by Bender[79], not only by the arguments based on stereochemical studies but lso on the basis of IR spectra, he was able to establish the existence of tetrahedral intermediate. Fedor and Bruice[80] have also put forward the kinetic evidences in favour of the second pathway. Since the tetrahedral intermediate has a negative charge and is crowded, hence, it is expected that alkali catalysed hydrolysis will be influenced both by polar and steric effects. Therefore, electron attracting group should enhance the rate.

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TYPES OF SOLVENTS.

On the basis of their polarising capacities the solvents are, generally, classified in the following three categories:

(i) Polar and weakly polar solvents

(ii) Dipolar aprotic solvents

(iii) Protic solvents

On the basis of their attachment with protons, Reutov[7], classified the solvents into the following four categories:

(i) Amphiprotic or Amphoteric Solvents:

Solvents which can attract ptotons or part readily with protons are called Amphiprotic or Amphoteric solvents, e.g. water and alcohol

(ii) Aprotic Solvents:

They are those solvents which are incapable of accepting or giving protons, e.g. benzene, cyclohexane, chlorohexane, chlorobenzene etc.

(iii) Protophilic Solvents:

The solvents which possess the great affinity for protons are called Protophilic solvents e.g. amines, pyridine and liquid ammonia etc.

(iv) Protogenic Solvents:

They are those solvents which can apart readily with protons e.g. anhydrous sulphuric acid, anhydrous formic acid.

From the point of view of predicting the solvent effect, various solvolysis reactions may be classified under the following three different broad headings:

(a) Dipole - Dipole Reactions:

These types of reactions are generally very slow. The electrostatic forces between the reactants are very small. Hence, the effect of ionic strength and dielectric constant of the medium is also very slow on such type of reactions. Examples of this type (dipole-dipole) of reactions are:

$C_5H_5N + CH_3I = C_5H_5NCH_3I$

$C_2H_5Cl + H_2O = C_2H_5OH + HCl$

$(C_2H_5)_3N + C_2H_5I = (C_2H_5)_4NI$

(b) Ion - Dipole Reactions:

These reactions are comparatively slow. Hence, they can be studied with more comfort. The rate determining step of such type of reactions takes place between ions and dipole. For example:

$CH_3Br + I^- = CH_3I + Br^-$

$CH_3Cl + OCH_3^- = CH_3OCH_3 + Cl^-$

$CH_2Cl_2 + 2OH^- = 2Cl + H\,CHO + H_2O$

(c) Ion - Ion Reactions:

Generally such type of reactions are abnormally fast. The rate of this type of reactions is diffusion controlled. Example of these type of reactions are:

$$H_2O_2 + 2H^+ + 2Br^- = 2H_2O + Br_2$$

$$CH_2BrCOO^- + S_2O_3^{--} = CH_2S_2O_3COO^{--} + Br^-$$

Effect of Selective solvation:

The phenomenon by which a solvent selectively solvates either the reactants or the transition state is known as selective or specific solvation. Either the rate or the rate and mechanism both of a chemical reaction taking place in a solution may be changed by selective or specific solvation. Laidler-Erying[10] and Chattaway[11] have described many reactions such as ammonium ion-cyanide ion, bromo acetate ion-thiosulphate ion etc. and they have shown that although the rate of these reactions vary with change in solvent with change of the value of dielectric constant of the mixed solvent system, the mechanism remains uneffected.

Boozer and Lewis[12], on the other hand, after studying the decomposition of secondary alkyl (2-butyl, 2-pentyl) chlorosulphites in dilute solution of dioxane and in isooctaneinferred that the selective solvation of reactants have been found responsible for the change in rate and mechanism of both of these reactions. Winstein and Fainberg[13] have reported that the effect of solvent changes on free energies, enthalpies and entropies of activation are quite complex and they often depend to the some extent in change in solvation of reactants and on solvation of transition state. Amis[14] and Goldernberget al.[15] have recorded the evidences of selective solvation. Goldenberg et al. have confirmed the selective solvation of ions from conductance data of perchloric acid in methanol, ethanol and their aqueous solutions. They have observed that 0.3% water (by weight) solvate selectively the proton forming $H_9O_4^+$ complex.

The effect of anion solvators on the rates of anion-neutral molecule reaction:

The solvents having very extra ordinary peculiar properties such as dimethyl sulphoxide (DMSO) and dimethyl formamide (ETOH) affect astonishingly the rates of reactions between anion and neutral molecule. It has been observed that bromobenzene reacts rapidly with potassium-t-butoxide even at room temperature when the solvent is DMSO where as the same reaction is negligible at temperature below 180°C when the solvent is tertiary butanol[16].

Such effects, which are recognizable as very general are explained by a hypothesis put forward by Parker et al.[17-18] which pictures the transition states of the reactions of this kind of reactions are bulky anions with a broadly distributed charge, and the such transition state anion interacts much less strongly with hydrogen bonding donors than do the compact reactant anions such as chloride, bromide orazide. The standard potential of the reactant ion is thus decreased much more than that of the transition state by the transfer from a weak anion solvator like dimethyl formamide (ETOH) to a strong one like methanol. The result of the transfer is consequently an increase in the DG* value for the reaction and a decrease in the specific rate.

The effect of specific cationsolvators on the rates of anion neutral molecule reactions.

In the non-availability of the strong solvators and specially in solvents of low dielectric constant cation-anion interaction has a significant influence on the rate of anion-neutral molecule reactions. Because this type of interaction is generally quite stronger with the reactant anion than with the transition state so that the reaction proceeds with low reaction rate. A solvent which is strong specific cationsolvator i.e. one which does not substitute solvent-anion interaction for cation-anion interaction can produce spectular increase in rate. Even relatively small proportions of the strong-cationsolvator have large effects. Zaugg[19] observed that high cation solvating potentials correlates with a calculated high electron density in a p-orbital such as that on oxygen in the amides. It does not correlates with the dipole moment of the molecule.

The intensity of the cation anion interaction has been found to be affected by the nature of the ions in much the same way as that either kind of ion solvent interaction i.e. for symmetrical ions it is greater the smaller the ion.

In dimethyl formamide which is better cationsolvator than Dimethyl Sulphoxide , the specific rates of the reaction of the lithium halide with methyl tolunesulphonate are in the proportion : iodide-1, bromide-3.4, chloride-9.1, when extrapolated to zero salt strength. The addition of five moles/litre of water reduces the specific rate of the reaction with chloride by a factor of 24, but reduces that of the reaction with iodide by a factor of 2 only.

EFFECT OF SOLVATION

As mentioned before, Parker and his coworkers[17] 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.

The cations are generally smaller and less polarisable than anions which are not hydrogen bond acceptors[19]. Some cations (transition) are Lewis acids and a few others (organic cations) are hydrogen bond donors, but the common interactions to be considered are cation dipole and structure making and breaking. Small "closed shell" cations like Na^+, K^+ etc. are more solvated by HMPT, ETOH and DMSO than by acetonitrile, formamide and water and much more solvated than by methanol. Structural effects are apparent in large organic cations. Non-electrolytes are considered less solvated by water than by methanol. This type of cations are more solvated by dipolar aprotic solvents than methanols. Reactions which proceed through a cationic transition state in which positive charge is dispersed were first investigated by Hughes and Gassar[20]. They have also concluded that transition states were very much more solvated by dipolar aprotic solvents than protic solvents like methanol etc. One of the important aspects of solvation on the reaction velocity is the variation of activation energy with respect of phenomenon. Glasstoneet al.[21] have given a vivid picture of phenomenon.

The curve I, represents the potential energy curve for a given reaction in a particular solvent, say water, in which non of the reactants or the activated complex is solvated. In another solvent, if the activated complex is solvated but the reactants are unaffected, the potential energy curve will be shown as II (fig.I A). However, the maximum of the curve will be lowered by an amount of DH equal to the heat of solvation of the activated complex. The activation energy, when the activated complex is solvated (E_{II}) is thus lowered than (E_1) for the reaction in a solvent in which there is no solvation. Therefore, apart from the influence of the other factors, solvation of the activated complex will tend to bring about in increase in the rate.

However, if only the reactants are solvated and not the activated complex, then the potential energy curves will have the form indicated in Fig. I.B. It is evident that the solvation of one or more reactants will result in an increase in the activation energy and the reaction will be retarded.

Further, it can be seen clearly that if both reactants and the activated complex are solvated, there may be little change in the activation energy and the reaction velocity will not be influenced on this account.

Result and Discussion

The kinetics of alkali cataysed hydrolysis of Ethyl cinnamatewere studied in aquo-EtOH media having 30 to 80% (v/v) of ethyl alcohol at temperatures ranging from 20°C to 40°C.

This trend is being observed at almost all the temperatures at which the kinetics has been studied.

In order to study the variation in k values with change in mol % of the organic co-solvent (EtOH), the logarithm of k values and mol % of EtOH have been tabulated in Table - III.15. The plots of log k against molar composition of ETOH have been shown in Fig.- 3.11, which shows that the rate of the reaction decreases linearly with increasing mol % of the organic co-solvent EtOH in the reaction media at all the temperatures. Such decrease in the rate constant with increasing proportion of the organic co-solvent like EtOH is not new in the kinetics of solvent effect. It is similar to the observations reported in previous chapter for aquo-EG media.

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