Hydrolysis of Ethyl Benzoate in Nitrogenous and Non-Nitrogenous Medium

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Abstract:The current study shows that all parameter was calculated using Wynne-jones and Eyring equation. In ethyl Benzoate ester, H^0 and $S°$ were found to decrease in water - ethylene glycol mixture. This may be due to greater desolation of initial state compared to the transition state. $H°$ and $S°$ were found to increase in water dioxan mixture whereas free energy was found to increase in both cases with increasing composition of organic co solvent. the values of potential energy decrease due to activation were also calculated in each case. The values of functions discussed here is found to be positive in each case. A comparative chart for the variation of different kinetic parameters of ethyl Benzoate and ethyl benzoate in ethylene glycol - water dioxan water and ethylene glycol water systems are well-discussed and explained.

Background: The solvent influence on the salt effect is a secondary effect arising from the dielectric constant modification of the activity coefficients of the reactant particles. Theoretical treatments of the influence of neutral salts or ionic strength, on the rates of reaction between ions in solution were given by Bronsted and Bjerrum, Christiansen and Scatchard, the suggestion made by lamer has also been considered for the mathematical derivation of the required relation.

Materials and Methods: The desired constancy of the temperature during the course of study was achieved with the help of a water - thermostat. To achieve and to maintain the temperature of the thermostat above that of the surroundings, metal incursion heater and glass heating lamp (electric bulbs) were made. A toluene - mercury thermo regulator heated with an electronic relay and connected with the heating lamp was employed to achieve the accuracy in temperature of the order of +1.

Results: It was concluded from the second order rate constants for the ester is checked. It is reproducible for all sets of repeated experiments are reflected in terms of the average deviation and the standard deviation in the value of 'k'. The rate constant value of alkaline hydrolysis ethyl benzoate were found to decrease ethylene glycol water media. The rate of hydrolysis of ethyl Benzoate was found to decrease in dioxan water media. this observation that during the hydrolysis process either metal state is more solvated or the transition state is desolated to a greater extent than the initial state. But in ethyl benzoate ester, all these parameters were found to increase in water ethylene glycol solvent system with increasing composition of organic co solvent.

Conclusion:The current study shows that all parameter was calculated using Wynne-jones and Eyring equation. In ethyl Benzoate ester, H^0 and $S°$ were found to decrease in water - ethylene glycol mixture. This may be due to greater desolation of initial state compared to the transition state. $H°$ and $S°$ were found to increase in water dioxan mixture whereas free energy was found to increase in both cases with increasing composition of organic co solvent. the values of potential energy decrease due to activation were also calculated in each case. The values of functions discussed here is found to be positive in each case. A comparative chart for the variation of different kinetic parameters of ethyl Benzoate and ethyl benzoate in ethylene glycol - water dioxan water and ethylene glycol water systems are well-discussed and explained.

***Key Word***: Hydrolysis, Ethyl Benzoate, Nitrogenous, Non-Nitrogenous Medium

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I. Introduction

The solvent influence on the salt effect is a secondary effect arising from the dielectric constant modification of the activity coefficients of the reactant particles. Theoretical treatments of the influence of neutral salts or ionic strength, on the rates of reaction between ions in solution were given by Bronsted and Bjerrum[1], Christiansen and Scatchard[2], the suggestion made by lamer has also been considered for the mathematical derivation of the required relation.

For reactions between ions of unlike sign, there is generally an entropy increase from reactants to activated complex, while for ions of like sign, there is an entropy decrease. In terms of solvation of ions, the explanation of the entropy factor is that two ions coming together to form a neutral molecule will become partially desolated in the transition state. Laidler and Landskroner[3] used Kirkwood's equation for the activity coefficient f, of a solute with an arbitrary distribution of charges embedded in a sphere of radius b and dielectric constant D, submerged in a medium of
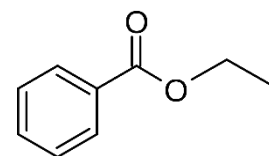
dielectric constant D. Laidler and Lanskroener evaluated free energy on the basis of construction of specific activated complex model of constantfree energy· It are bound to vary with the change in solvent composition. For knowing b. and G. of ion-dipolar reactions, without having any assumption for the model of the activated complex, Jha, Singh and Das[36] proposed a pair of equations, which were further improved by Singh et. al.[37] which give better result than that reported on previous occasions.Accordingto Hughes and lngold theory,an increase in the ion-solvating power of the medium accelerates the creation and concentration of charges and inhibit their destruction and diffusion". Their theory is able to predict the rate of reaction in solution. For predicting the rate, they have made certain assumptions about the expected solvation of reactants and transition state and also about the ion-solvating power of the solvent. The following three assumptions have been made as to the amount of solvation to be expected in the presence of electric charges: (i) Solvation will increase with the magnitude of the change. (ii) Solvation will decrease with increasing dispersal of a given charge. (iii) The decrease of solvation due to dispersal of a charge will be less than due to sits destruction. Experimentally it is observed that solvent in some cases enhance a reaction considerably, while in other cases the effect is smaller. while studying the hydrolysis of amides i. e. ion-polar reactions, has evaluated a· for the hydrolysis of certain amides in water-dioxan and water- isopropanol solvents a. differs from b·, as the former is the sum of the radius of the activated complex and a certain constant.

Anandakrishnan and Radhakrishnamurti, Nayak and Raut, Rakshit and Sarkar have studied the solvent effect on reaction rates of ion-dipolar reactions and concluded that higher the dielectric constant of the medium, the faster is the rate of reaction.A quite different observation was noted by D.D. Robert while studying the alkaline hydrolysis of ester in dimethyl sulphoxide at different temperatures. He noted that the rate increases with increasing concentration of DMSO in the solvent mixture, i.e. decreasing dielectric constant of the medium. From the experimental values of the activation energy and entropy of activation, for many reactions involving the formation of ions from neutralmolecules in a variety of solvents, two generalizations were made:(i) the activation energy Exp depends on thetype of reaction but does not depend on the nature of the solvent and(ii) the entropy of activation changes with the nature of the solvent. If it is generally negative, and becoming more negative as the polarity of the solvent decreases. The rate of reactions producing ions in solution increases with the polarity of the solvent and that the increase is governed largely by the change in the entropy of activation. Regarding the relation of the entropy decrease in going from reactants to activated complex with the freezing of the solvent molecules around the incipient ions, it has been found that the activated complex is almost an ion pair at its distance of closest approach, or at least exceedingly a polar complex approaching an ion pair. Each end of the polar complex has already accumulated a layer of solvent molecules, whose presence is necessary to allow the

II. Material and Methods

The desired constancy of the temperature during the course of study was achieved with the help of a water - thermostat. To achieve and to maintain the temperature of the thermostat above that of the surroundings, metal incursion heater and glass heating lamp (electric bulbs) were made. A toluene - mercury thermo regulator heated with an electronic relay and connected with the heating lamp was employed to achieve the accuracy in temperature of the order of +1. A metal paddle stirrer driven by a small electric motor stirred the water of the thermostat regularly and vigorously throughout the experiment to keep the temperature uniform. The thermostat thus described was found capable of achieving temperature control. Baryta set, the main apparatus in use, was all glass class A° type of corning brand and consisted of a burette with automatic zero mounted on a reservoir of capacity inters. It contained baryta solution of known strength for studying the kinetics of the reaction adopting titration process. Many other glass apparatuses, such as burettes, pipettes, conical flasks, measuring flasks, watch glass, beakers etc. were also in frequent use during the course of experimental investigation: they were all of corning registered grade. Before being used all of them were cleansed with chromic acid followed by repeated rinsing with distilled water. They were steamed out' and dried by passing a current of air while they were still warm.
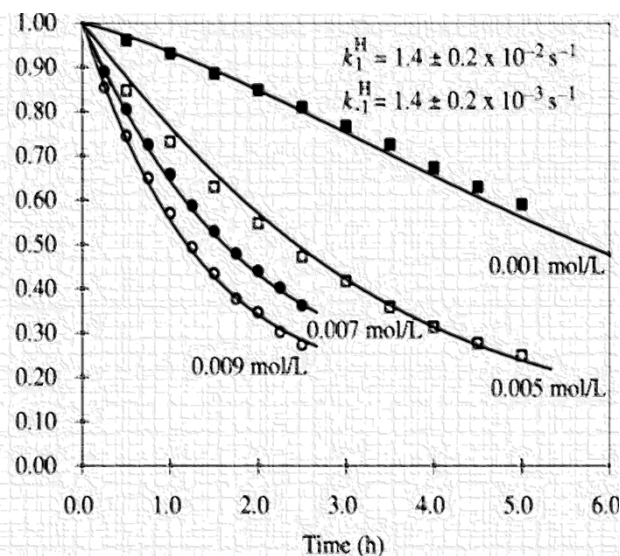
III. Resultand Discussion

The second order rate constants for the ester is checked. It is reproducible for all sets of repeated experiments are reflected in terms of the average deviation and the standard deviation in the value of 'k'. The rate constant value of alkaline hydrolysis of ethyl| Benzoate and ethyl benzoate were found to decrease ethylene glycol water media the rate of hydrolysis of ethyl Benzoate was found to decrease in dioxan water media. The above nature of change in k value[8] was in agreement with the predictions of Hughes-lngold theory where the rate is expected to decrease with decreasing dielectric constant of the medium. In case of hydrolysis of ethyl

benzoate in pyridine water media, the specific rate constant values were found to increase with increasing proportion of pyridine in the media.The Ethyl Benzoate manufactured by W.J. Bush and Co. Ltd.; London was used. For its purification, 200 ml of the ethyl Benzoate was withdrawn from the sealed bottle containing it and taken in a 500 ml glass stoppered corning containing 40 grams of BDH grade sodium hydrogen carbonate. After being stoppered the flask was left for four hours with occasional shaking. Then the ester was decanted into a dry clean flask having 20 g of BDH grade magnesium sulphate. The flask was stoppered, shaken for five minutes and allowed to stand for two hours. The ester was filtered and distilled using all Pyrex glass distillation apparatus having quick-fit interchangeable joints with an efficient fractionating column. All precautions were made to protect the receiver from atmospheric moisture? The constant boiling middle fraction at 137-140°C under the reduced pressure of 50 mm of mercury-column was created and stored for the study of the kinetic behavior.

To check and to calculate the value of precision, i. e. reproducibility of kinetic runs and rate constants, the hydrolysis of ethyl Benzoate was repeated four times separately at 50% composition of dioxan (organic co-solvent). The concentration of the alkali, the amount of ester added and percentage of co-solvent were kept same for each repetition.

Thereby the rate increases as observed experimentally. But pyridine also a weak base, is unable to affect the dissociation after a certain limit. Therefore, the increase in rate becomes less appreciable after a certain time. The slight increase in rate thereafter might be due to the effect of dielectric constant alone which is also simultaneously operative and is of smaller magnitude. However, the understanding of these effects will be clearer later on with the study of the effect on activation parameter. Experimental value[6] of is compotation activation energy (E.,) were determined using Arrhenius equation. It was concluded from this observation that during the hydrolysis process either metal state is more solvated or the transition state is desolated to a greater extent than the initial state. But in ethyl benzoate ester, all these parameters were found to increase in water ethylene glycol solvent system with increasing composition of organic co solvent.

IV. Conclusion

The current study shows that all parameter was calculated using Wynne-jones and Eyring equation. In ethyl Benzoate ester, H^0 and $S°$ were found to decrease in water - ethylene glycol mixture. This may be due to greater desolation of initial state compared to the transition state. $H°$ and $S°$ were found to increase in water dioxan mixture whereas free energy was found to increase in both cases with increasing composition of organic co solvent. the values of potential energy decrease due to activation were also calculated in each case. The values of functions discussed here is found to be positive in each case. A comparative chart for the variation of different kinetic parameters of ethyl Benzoate and ethyl benzoate in ethylene glycol - water dioxan water and ethylene glycol water systems are well-discussed and explained.

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