

Alkaline Hydrolysis of Ethyl Salicylate in Aquo-Dioxan Mixture Medium

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Abstract: The current study shows that 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 salicylate and ethyl benzoate in ethylene glycol - water dioxan water and ethylene glycol water systems are well-discussed and explained.

Background: A qualitative prediction of rate in solution with the help of transition state theory has been made by Hughes and Ingold in case of reactions of known mechanism. According to Hughes and Ingold 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 charge. (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 its destruction.

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 use of. 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 and more. 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.

Results: It was concluded from this observation that during the hydrolysis process either metal state is more solvated or the transition state is desolvated 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 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 salicylate and ethyl benzoate in ethylene glycol - water dioxan water and ethylene glycol water systems are well-discussed and explained.

Key Word: Alkaline Hydrolysis, Ethyl Salicylate, Aquo-Dioxan Mixture

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I. Introduction

Experimentally it is observed that solvent in some cases enhance a reaction considerably, while in other cases the effect is smaller. The study of the mechanizing as to how a solvent alters the specific rate of reaction has been fascinating branch of physical chemistry. The need of such study was not only for theoretical interest but also in account of its practical utility. Many reactions that we perform in the laboratory or in the industry take place in some solvent media. Further, biological reactions also take place in solution. In laboratory as well as industry, we want to enhance the rate of desired reactions and try to retard the rate of desired one. For a successful attempt for such changes, a knowledge of the role of solvent as well as their properties. is very essential.

As regards the theoretical interest, the study started with the advent of collision theory. Kineticists became interested in comparing the rates of different reactions in solution as well as in gas phase and from the data, they compared the collision number obtained experimentally in two cases. For example, the thermal decomposition of nitrobenzoic acid was studied in a variety of solvents and it was observed that though there was thousand-fold variation in rate with solvent used but that the value of E and log A are scattered. One expected a rate of reaction in solution compared to gas phase. But the study failed to show such generalization. An attempt to predict solvent effect on the basis of transition state theory was also made. However, in recent years, it has been felt that the study of reaction rates in binary aquo-organic media, have great potentiality to understand the transition state structure. Therefore, a large number of different types of reactions have been repeated in aquo-organic media and a number of empirical as well as theoretical equations for the affect. of

solvent in such reaction rates have been suggested. Besides this, the role of solvent in the salvation of transition state have been predicted.

Here it is thought essential to discuss some of the concepts that were developed on the basis of these studies. A qualitative prediction of rate in solution with the help of transition state theory has been made by Hughes and Ingold in case of reactions of known mechanism. According to Hughes and Ingold 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 charge. (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 its destruction.

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 immersion heater and glass heating lamp (electric bulbs) were made use of. 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 and more. 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 3 liters. 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. Result and Discussion

The Ethyl salicylate manufactured by W.J. Bush and Co. Ltd.; London was used. For its purification, 200 ml of the ethyl salicylate 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.

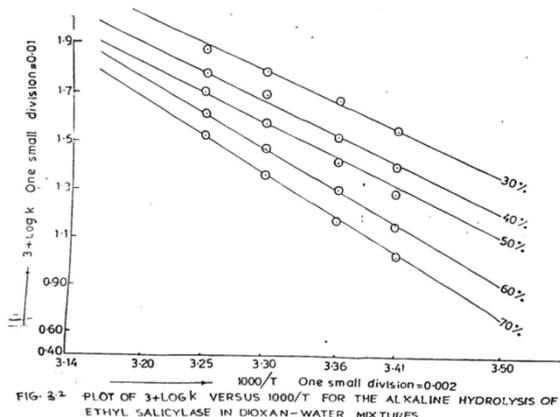
To check and to calculate the value of precision, i.e. reproducibility of kinetic runs and rate constants, the hydrolysis of ethyl salicylate was repeated four times separately at 50% composition of dioxan (organic co-solvent). The concentration of the alkali, the amount of ester added and percentage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

The second order rate constants for the ester tabulated in Table. Precision that 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 salicylate and ethyl benzoate were found to decrease in ethylene glycol water media. The rate of hydrolysis of ethyl salicylate was found to decrease in dioxan water media. The above nature of change in k value⁸ was in agreement with the predictions of Hughes-Ingold 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.

VALUES OF $3 + \log k$ vs $10^3/T$ FOR THE ALKALINE HYDROLYSIS OF ETHYL SALICYLATE IN AQUO - DIOXAN MIXTURES

Temp. (°C)	Values of $10^3/T$	Values of $3 + \log k$ at different compositions (v/v)				
		30%	40%	50%	60%	70%
20	3.413	1.550	1.401	1.282	1.149	1.086
25	3.356	1.670	1.519	1.477	1.301	1.168
30	3.300	1.784	1.682	1.580	1.470	1.357
35	3.247	1.872	1.777	1.699	1.612	1.519



Thereby the rate increases as observed experimentally. But pyridine also a weak base, is unable to effect 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 value⁶ of its computation activation energy (E_a) were determined using Arrhenius equation. All parameter was calculated using Wynne-jones and Eyring equation. In ethyl salicylate ester, H^\ddagger and S^\ddagger 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^\ddagger and S^\ddagger 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. 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 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 salicylate and ethyl benzoate in ethylene glycol - water dioxan water and ethylene glycol water systems are well-discussed and explained.

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