

A Kinetic Investigation of the Effect of Solvent Ethanol on Hydrolysis of Acetic Anhydride by Conductivity Method

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ABSTRACT

Hydrolysis is an important and significant chemical degradative process in the environment, since many hydrolysable chemicals including pesticides and plasticizers find their way into ground water through leaching and run-off. The rates of hydrolysis are greatly dependent on environmental factors such as solvent composition, temperature and ionic strengths of salts present. In this study, kinetic investigation on the hydrolysis of Acetic Anhydride (used in the manufacture of dyes and pesticides etc) has been undertaken conductometrically. To determine the effect of solvent ethanol on the hydrolysis of Acetic Anhydride, a series of reactions was conducted in different ethanol-water mixtures, keeping all other reaction conditions identical. The pseudo first order rate constants obtained in different ethanol-water mixtures increase with increasing percentage of water in the medium. In each solvent composition, the kinetics of hydrolysis of Acetic Anhydride was followed at varying substrate concentration, keeping all other experimental parameters identical. In all cases the reactions were followed under pseudo first order conditions. The constancy of the rate constant values indicate that the order of the reaction with respect to Acetic Anhydride in different ethanol-water mixtures is one. Solvation is an electrostatic phenomenon. Since increasing proportion of ethanol retard the rate of reaction, it is concluded that reaction proceeds faster in a more polar medium. Thus, we conclude that decrease in hydrolysis rate of acetic anhydride by addition of a less polar solvent ethanol is due to progressive increase in the solvation of the reactant compared to that of the transition state.

Keywords: Kinetics, Hydrolysis, Conductivity, dipole-dipole reaction, solvation.

INTRODUCTION

Hydrolysis reactions have been extensively used in degradation of complex substances to produce harmless eco-friendly products. Solvent effect constitutes an interesting study in nucleophilic displacement reactions. So, in the present study, the kinetics of hydrolysis of Acetic Anhydride was investigated in ethanol-water system. A change of solvent may change the rate of a chemical reaction by many orders of magnitude¹. The relationship between the nature of the solvent and the reaction rate is very complex. Depending on the many possible interactions between the solvent and the reactants and solvent and the Transition State^{2,3}.

In the present study, effect of substrate concentration in various ethanol-water mixtures at 308 K was studied. To determine the effect of solvent on hydrolysis, a series of reactions was conducted in different ethanol-water mixtures, keeping all other reaction conditions identical at 308 K. The pseudo first order rate constants increased with increasing percentage of water in the medium.

EXPERIMENTAL

Purified and analar samples of Acetic Anhydride were used. Ethanol was shaken with quick lime and allowed to stand overnight. The supernatant liquid was decanted and fraction distilling at 350.9 K was collected. All solutions and reaction mixtures were prepared in conductivity water.

Kinetic Techniques

The kinetics of the hydrolysis was followed by continuous monitoring of the reaction mixture. The instrument used for this was a Systronics Digital Direct Reading Conductivity Meter which is designed for measuring the specific conductivity of a solution using a conductivity cell. The accuracy and reproducibility of the readings are $\pm 0.5\%$. The rate of hydrolysis was followed by noting the specific conductance of the solution at suitable intervals of time. As hydrolysis proceeded, weakly ionized acetic acid was produced which contributed to the increase in specific conductance of the solution. An electrically operated thermostat was used. Temperatures were recorded by means of an accurate, sensitive thermometer reading to tenths of a degree.

RESULTS AND DISCUSSION

The observed first order rate constants were obtained by plotting $\log (K_{\infty} - K_t)$ versus time based on the expression

$$K = 2.303/t \log K_{\infty}/(K_{\infty} - K_t)$$

Log K values were also plotted against $\epsilon - 1/(2\epsilon + 1)$ values. This plot is linear which indicates that the reaction is of dipole-dipole type.

Effect of Substrate on Reaction Rate in Ethanol – Water mixture

To find out the order of the reaction in Acetic Anhydride in Ethanol – water, experiments were conducted in 10% Ethanol at 305 K, by varying the initial Anhydride concentration, keeping all other experimental parameters identical. In all cases, reactions were followed under pseudo first order conditions, using large excess of solvent over substrate. For each reaction, satisfactory $\log (K_{\infty} - K_t)$ versus temperature plot was obtained, showing that reaction exhibits first order dependence with respect to Acetic Anhydride. The pseudo first order rate constant k_1 was obtained from the slope of this plot. The constancy of k_1 values indicate that order of reaction with respect to Acetic Anhydride is one.

Table 1

S.No	10^2 [substrate]/M	$10^3 / K_1$
1.	0.85	1.80
2.	1.06	1.79
3.	1.70	2.07
4.	2.12	2.15
5.	4.23	2.15
6.	10.59	2.21

Effect of varying [Ethanol] on rate of hydrolysis of Acetic Anhydride at 308 K

To determine the effect of medium on hydrolysis, a series of reactions was conducted in different ethanol-water mixtures, viz., 10%, 25%, 50%, 75%, 90% and 100% Ethanol. The pseudo first order rate constants were obtained in different Ethanol-Water mixtures. These K_1 values increased with increasing percentage of water in the medium. [Table 2].

Since solvation is an electrostatic phenomenon, an ion or polar molecule in a polar solvent, gets oriented and attracts the solvent molecules. Since the rate of hydrolysis is found to be highest in 100% water and increasing proportion of Ethanol retard the rate of the reaction, it is clear that reaction proceeds faster in a more polar medium. This leads to the conclusion that the Transition State is more polar than the reactants. If so, the rate of the reaction increases with increasing dielectric constant of the medium. The actual values of the dielectric constants for different percentages were collected. The plot of $\log K_1$ versus $\epsilon^{-1}/(2\epsilon + 1)$ is linear which indicates that the reaction is of dipole-dipole type. Dipolar Acetic Anhydride molecule and dipolar water are assumed as the reactants in the rate determining step.

Table 2: Effect of solvent Ethanol on the rate of hydrolysis of Acetic Anhydride at 308 K.

[Ac₂O] = 0.1059

S.No	Percentage of Ethanol	$10^3 K_1 / \text{sec}^{-1}$
1.	10	3.21
2.	25	3.10
3.	50	0.65
4.	75	0.40
5.	90	0.15
6.	100	0.03

The change in rate with the change in solvent composition can also be explained on the basis of solvent – reactant interaction and solvent – transition interaction according to Hughes and Ingold⁴,

- 1) Solvation will increase with the magnitude of the charge
- 2) Solvation will decrease with the increasing dispersal of a given charge.

This would mean that the transition state is more solvated than the reactants because of an increased magnitude of charge in the former. Therefore decrease in hydrolysis rate of Acetic Anhydride by the addition of a less polar solvent is due to the progressive increase in the solvation of the reactant compared to that of the transition state.

CONCLUSION

The hydrolysis reaction of Acetic Anhydride exhibits first order dependence with respect to anhydride under pseudo first order conditions in 10% Ethanol- water mixture and 20% Ethanol-water mixture at 308 K. The rate of hydrolysis increased with increasing polarity or increasing dielectric constant of the medium. A plot of $\log K_1$ versus $\epsilon^{-1}/(2\epsilon + 1)$ is linear indicating that reaction is of dipole-dipole type. The change in rate with change in solvent composition can be also explained on the basis of solvent-reactant interaction and solvent-transition state interaction. According to Hughes and Ingold⁴, solvation will increase with the magnitude of the charge and will decrease with increasing dispersal of a given charge. This would mean that the transition state is more solvated than the reactants because of an increased magnitude of charge in the former. Therefore, decrease in hydrolysis rate of Acetic Anhydride by the addition of a less polar solvent ethanol is due to the progressive increase in the solvation of the reactant compared to that of the transition state.

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