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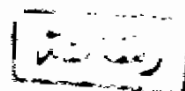
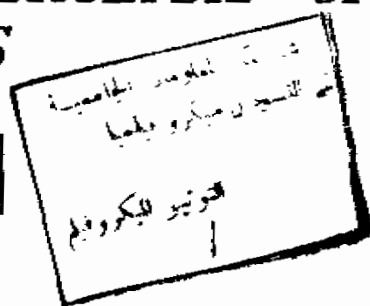
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KINETIC STUDIES OF HYDROLYSIS OF SOME ESTERS

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SUMMARY

Methyl 2-methylprop-2-enoic acid (methyl methacrylate) (2) is very important commercially, since it polymerizes to polymethyl methacrylate (perspex) under the influence of heat. This polymer is a typical thermoplastic, i.e., linear, can be softened on heating, moulded and cooled repeatedly so that the properties of plastic is hardly affected. Perspex is tough, transparent and soluble in many organic solvents. Methyl prop-2-enoic acid(methyl acrylate) (1) also polymerizes, but this polymer is soft than the former. Thus the rates of the alkaline hydrolysis of esters 1 and 2 were studied at temperatures ranging from 10° to 35° in two series of dioxane-water and acetone- water mixtures containing from 10 to 75% by volume of the organic component since the nature of the solvent is crucial in deciding which route will be energetically most favorable for a given substrate. Thus it was of great interest to study the electrostatic effects and to correlate the rate constants to the dielectric constant of the solvent. This is particularly true for bimolecular reactions where the solvent influence can be explained satisfactorily by treating the solvent as a continuous dielectric and by assuming the solvent to act solely by virtue of its dielectric effect.

Moreover, no much work on the hydrolytic cleavage of unsaturated esters in different aquo-organic solvents with different dielectric constants has been carried out in order to explore an additional sight into mechanisms which can serve as models for many biological systems, since it has been found that relatively little changes in structures can greatly affect the rates of reactions involving nucleophilic catalysis. Thus stability of esters 1 and 2 under the influence of specific solvent effects, dielectric constant of the medium and temperature change are studied due to their commercial importance.

The kinetic studies and application of the differential method show that the rate follows the second-order kinetic equation, first-order with respect to both the ester and hydroxide ion, and the reaction proceeds by $B_{AC}2$ mechanism.

Many equations have been derived to correlate the rate constant of a reaction to the dielectric constant of the solvent. It is applicable to reactions that are of such a character that the electrostatic interactions are more important than non-electrostatic ones such as ion-ion, ion-dipole and certain dipole-dipole interactions.

The theories are based on the Kirkwood expression for the activity coefficient of a spherical solute molecule bearing a particular distribution of charges. The resulting equations predict a linear dependence of the logarithm of the rate constant on the reciprocal of the dielectric constant. The proportionality constant depends on the net charges on the reactant molecules and also on the distribution of charges in the reactant molecules and the activated complex.

However the decrease in the rate of hydrolysis of esters by increasing the dielectric constant of the medium and the linear variation of the logarithm of specific constant with the reciprocal of the dielectric constant of the medium with positive slope in both aquo-organic solvents in the present study indicate the ion-dipolar interaction, in which the activated complex is less polar than the reactants.

Among these various theoretical expressions, the Laidler and Landskroener equation for ion-dipolar type of bimolecular reactions in which plots of $\log k$ versus $\frac{1}{D}$ are linear with negative slopes is most widely accepted. They proposed the transition state to be more polarized than the initial state. However, their equation could not be applied for ion-dipole reactions in which the linear plots of $\log k$ against $\frac{1}{D}$ yield positive slope. It also suffers from an arbitrary assumption

about the dielectric constant of ideal solution. Thus Lallan's et al. equation which is more general for computation of b^* , the size of activated complex, i.e., the distance of closest approach of solvent molecules to the activated complex in a bimolecular reaction, and G^* , the number proportional to the dipole moment of the activated complex, i.e., the distance of closest approach of solvent molecules to the transition state, is found to be more applicable in the present work, since no assumption about the dielectric constant of an ideal solution is needed and also is applicable to the bimolecular ion-dipolar reactions in which the $\log k - \frac{1}{D}$ correlation is linear with a positive slope.

Similar to the rate coefficient equation;

$$\ln k = \ln k_0 + \ln \frac{\nu_A \nu_B}{\nu_{AB^*}}$$

taking into consideration the dielectric constant of the solute, they expressed their equation as follows:

$$\log k = \log k_0 + \frac{1}{2.303} \frac{e^2}{2kT} \left[\left\{ \left(\frac{1}{b_A} - \frac{1}{b^*} + \frac{3}{2} \sum \frac{G}{b^3} \right) \frac{1}{D} \right\} - \left\{ \frac{1}{b_A} - \frac{1}{b^*} + \frac{3}{2(1+\alpha)} \sum \frac{G}{b^3} \right\} \right]$$

where α = half of the dielectric constant of the solute,

$$\sum \frac{G}{b^3} = \left[\frac{G_A}{b_A^3} + \frac{G_B}{b_B^3} - \frac{G^*}{b^{*3}} \right], \quad \text{and } b_A, \text{ size of } \bar{O}H \text{ ion} =$$

$$1.4 \times 10^{-8} \text{ cm.}$$

Thus the magnitude of the calculated b^* values obtained ($2.03\text{\AA}$) which is the effective radius of the solvated activated complex for both esters 1 and 2 at all temperatures in two series of aquo-organic solvents is in agreement with Lallan and coworkers and Roberts for the alkaline hydrolysis of ethyl acetate in DMSO-water and in the order of the magnitude of molecular dimensions (10^{-8} cm). However, since the size of the bare OH is $1.4\text{\AA}$, thus the value of b^* which is the closest approach of solvent molecule to the seat of reaction is reasonable. Also from the distance of C-O bond which is reported as $1.43\text{\AA}$, it is therefore quite reasonable that the new C...OH bond which is being formed in the transition state due to the attack of OH⁻ ion on the carbonyl group in the alkaline hydrolysis of esters is $2-3\text{\AA}$. These results along with the values of energy and entropy of activation and the Arrhenius frequency factor confirm that esters 1 and 2 hydrolyse by a bimolecular $B_{AC}2$ mechanism in which the transition state is much less polarized and preferentially solvated than the reactants. These results can be attributed to a non-electrostatic increasing forces where the solvent-solute interaction is a more influencing factor than the dielectric constant of the medium.

The small decrease in the rate by increasing the polarity of the solvent indicates dispersion of electric charge on the activated complex.

The two separate straight lines concerning the two regions 10-35% and 40-70% (v/v) of organic solvent compositions in both aquo-organic solvents with different magnitudes of slope in the linear relationship between $\log k$ and $\frac{1}{D}$ together with the identical value of b^* indicate the pronounced specific solvent effect on the rate of the reaction. The difference in slopes of $\log k$ versus $\frac{1}{D}$ can thus be attributed to selective solvation by the polar solvents. Thus in 10-35% organic solvent, solvation of transition state is considered to take place only by water molecules which are in excess, whereas organic solvent acts as a desolvating agent. The higher rates of hydrolysis of esters 1 and 2 in dioxane than in acetone in this limiting range of $\frac{1}{D}$ gives an evidence for sepecific solvent effect where the limiting value of radius of activated complex is smaller in dioxane than in acetone. It also indicates that transition state is much less polar than reactants and is preferentially solvated by acetone, the aprotic-polar solvent than in the aprotic nonpolar solvent, dioxane. This can be attributed to the fact that H_2O molecules are firmly bonded to the $\bar{O}H$ ion due to its

greater charge density in comparison to the transition state.

The increase in the rate by increasing addition of organic solvent is attributed to a drastic change in the liquid structure of water, either by promoting or disrupting its quasi-crystalline structure. As a result molecules of water which are setting free, provide the reactant ions by a higher immediate dielectric constant environment, thus help in increasing the rate of reaction inspite of the decrease in the bulk dielectric constant of the medium. The higher rate of reaction in 40-70% (v/v) acetone-water than in the corresponding dioxane-water mixtures can be attributed to the interaction between solvent dipoles in the mixed media as well as to selective solvation of the reacting ions and activated complex. In these solvent solutions where the forces associating the more polarisable acetone with water is stronger than with dioxane (0.71 vs. 0.27, respectively), due to hydrogen bonding, the reactant ions will be on average surrounded to a lesser extent and less solvated in acetone-water mixtures, leading to a higher rate in acetone-water mixtures. It can also be attributed to the substantial increase in the effective concentration of OH^- ions due to the higher basicity of acetone than dioxane.

The sensitivity, m , of a substrate to the organic solvent in the medium is obtained from the equation:

$$\log k_2 = m N_s + K$$

Thus on plotting $\log k_2$ versus the mole fraction of organic solvent, N_s , two intersecting linear correlations are obtained for both esters in both aquo-organic solvents. The deviation from continuous linearity is more pronounced in acetone than in dioxane.

The branched ester exhibits less deviation from linearity than the nonbranched ester. The ratio m_{II}/m_I (m_{II} and m_I represents region II, molar excess of organic solvent $N_s = 0.1007$ to 0.3840 and region I, molar excess of water, $N_s = 0.0226$ to 0.1007 , respectively, indicates the enhanced sensitivity of both nonbranched and branched esters to increasing organic solvent concentration in region II than is in region I. It is nearly constant for both esters in dioxane or acetone.

The linear plots between $\Delta H^\ddagger$ and $T\Delta S^\ddagger$ with slope equal to unity for the hydrolysis of both esters in different binary mixtures show that there is no variation of $\Delta G^\ddagger$ due largely to the generally compensation effect between $\Delta H^\ddagger$ and $\Delta S^\ddagger$. This is in agreement with the experimental results where the values of enthalpies

($\Delta H^\ddagger$) and entropies ($\Delta S^\ddagger$) change as the structures or binary mixtures are changed and the values of $\Delta G^\ddagger$ are more or less constant.

The higher rate of hydrolysis of methyl methacrylate than methyl acrylate in 40-75% by volume of organic solvent (region II) in contradiction to its lower rate in 10-35% by volume of organic solvent (region I) is a good indicative to the variable S_N2 mechanism where the strength of bonds in transition state depends on solvent. Thus in region I where water is in excess, the mechanism involves the formation of a tight transition state in which the ionisation of the carbonyl group is in the norm so that the α -methyl group destabilizes it by both its polar and steric effects, whereas in region II, it involves the formation of a loose transition state in which the partially positive carbonium ion is stabilized due to hyperconjugation ($+R^\ddagger$). The bimolecular mechanism is ascertained by the values of $\Delta S^\ddagger$ and frequency factor $\log A$. The change of solvent from dioxane to acetone affects markedly the rates of hydrolysis of branched ester 2 than nonbranched ester 1.

INTRODUCTION