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Kinetic and Mechanistic Study of Saponification of a Few Industrially Important Esters, *viz.*, Glyceryl Dilaurate and Glyceryl Oleostearate

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Kinetics of saponification of two structurally related and industrially important diesters have been investigated. Time ratio method and Swain's standard data for series first order reactions have been utilised for evaluation of rate data and thermodynamic parameters, *viz.*, $\Delta E^{\neq}$,– $\Delta H^{\neq}$, $\Delta G^{\neq}$, $\Delta S^{\neq}$ and log A for both the steps which involve the competitive and consecutive saponification reactions which also indicate that the first step of saponification process is quite faster than the second step and further more the oleostearate is less saponifiable than dilaurate in 72% dioxane-water, DMSO-water moiety and in general these processes are much faster in DMSO-water system than alcohol-water, acetone-water and dioxane-water systems.

INTRODUCTION

In a saponification process, the concentration of alkali is relatively in large excess over the ester concentration; the process is exemplified as a series first order reaction. The practical solution for the determination of the rate constants from the experimental data in series first order reactions was first explored in great detail by Swain[1]. A comparative kinetic study of the alkaline hydrolysis of mono and di esters of different carboxylic acids in protic and aprotic solvents was carried out by Anantkrishnan and co-workers[2, 3] and separately by Anantkrishnan and Venkatratnam[4–6].

A study of hydroxyl group catalysis in the alkaline hydrolysis of the ester bond was investigated by Bruice and Fife[7] and these studies revealed that the faster alkaline hydrolysis is due to the internal solvation of the transition state followed by the attack of the hydroxyl ion (OH^-) at the ester carbonyl group. Sorsaro[8] carried out a detailed investigation on the reaction rates of the saponification processes in mixed solvents and finally presented a relation between the acidity functions and reaction rates.

A detailed kinetic sudy of alkaline hydrolysis of two structurally related ethyl esters in 85% aqueous ethanol and 85% dimethyl sulphoxide with a

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special emphasis on the solvent effects and also polar, steric and hyperoconjugative effects was reported by Roberts[9–11]. Messeller and Speiser[12] made a detailed survey of literature and presented forty references on the kinetics and kinetic laws, influence of temperature, variance of thermodynamic parameters in respect of substituents, solvents and their dielectric constants, structure and reactivity especially in ester hydrolytic reactions. The saponification reactions with regard to six alkyl adipates were carried out in dioxane-water mixtures by Kumuira *et al.*[13] and noticed that the k_1 was quite larger than k_2 and that the longer the carbon chain in alkyl group the smaller the difference between the two rate constants. Furthermore the rate constants of secondary and branched alcohols were nearly equal to each other but smaller than those of the esters of normal alcohol.

From the study of thermodynamic parameters, transition state theory and also the effects of solvents on reaction rate, the prime requisites of the optimum solvent composition for a reaction were developed by Wong *et al.*[14] Balkrishnan *et al.*[15–20] studied the influences of dipolar-aprotic protic solvents in the saponification of diol mono esters, $\alpha : \beta$ unsaturated esters and their corresponding saturated esters and also aliphatic dicarboxylic esters. Holba *et al.*[21] investigated the kinetics of alkaline hydrolysis of semi-esters of dicarboxylic acid in electrolyte solutions. Kiltl and Donoso[22] have developed a new mathematical approach for the evaluation of kinetic parameters in respect of many competitive, consecutive reactions with a broad consideration of the whole experimental points on the curve rather than the individual data points.

A number of experimental studies of saponification of diethyl adipates was undertaken by Lee *et al.*[28] and they observed that a forced cycling of feed composition produces significant yield, which had also increased the intermediate product relative to the optimal steady state operation. Debis *et al.*[29] made a detailed study of the effect of polar-aprotic solvent nature on the trimerisation of aliphatic isocyanates by organometallic catalysis and finally concluded that the trimerisation rates were very much enhanced on the addition of DMSO or DMF.

Attempts were made by Moseles and Ohag[30] to determine second order rate constants (k_2) for ethyl isocyanates and $EtO_2CC_6H_4NO_2$-p saponification in aq. methol at 35°C using unmonitored conductomeric techniques of Iskander *et al.* Second order rate constants and activation parameters along with LFER relationships systematically determined for the hydrolysis of $Ph_2P(S)OC_6H_4R$ ($R = 4\text{-}NO_2$, 3-Br, 4-Me) by Istomin, Eliseeva and Kalabina[31]. Further they observed that the 'ρ' values decreased with increased temperature and were irregularly altered by the composition of the aq. ethanol solvent and they failed to make any interpretation for such irregular observations. Singh, Singh and Jha[32] have observed that the transition state formed in acid hydrolysis of ethyl formate in DMSO-water medium becomes more solvated with increase in DMSO concentration.

The kinetics of saponification of ROAc (R = Me, Et, Pr) was conductometrically followed in acetone-water or DMSO-water systems at 0–0.06 mole fraction organic solvent by Mata and Crespo[33] and they observed a second order kinetics. Further the effect of solvent composition on the activation parameters and rate constants indicated that the mechanism involved attack by a solvated OH^- on a solvated ROAc and finally an exchange process took place where one of the solvent molecules was replaced by water to give a hydrated-solvated complex which proved to be a rate determining step.

A detailed study of the influence of steric effects upon the rate constants for competing B_{ac}^2 and E_{CB}^1 ester hydrolysis was undertaken by Inoux *et al.*[34] and they concluded that the steric hindrance brought about by α-tertbutylation of cyanoacetate ester results in an increase in pH dependent rates observed at basic pH for ester saponification by both the mechanisms. However, in the case of B_{ac}^2 mechanism an increase in the pKa value is due to α-proton dissociation while in the E_{CB}^1 mechanism the increase in the rates is due to release of ground state strain at the transition state.

Rate constants and activated parameters were determined for the basic and acid hydrolyses of the several alkyl acetates in acetone-water system by Mitzner and Lenke[35] and further they have shown necessary correlation with substituents and substituent constants as well as steric constants. They have observed in both the above reactions two different correlations one for straight chain esters and the other for branched chain esters and the resulting difference was mostly from solvation effects. An elaborate study on the effect of DMSO on the kinetic behaviour of alkali catalysed hydrolysis of methyl salicylate was undertaken by Singh *et al.*[36] and they concluded that the DMSO dependence of the title saponification kinetics at 15–35°C in 10–70% (V/V) DMSO-water was mostly that the rate constants decrease as the DMSO composition in the aq. system increases and further the transition state hydrated by water is the rate determining step.

Kinetics of saponification of poly(vinyl acetate) in methnol-water and ethanol-water mixtures using NaOH as a catalyst was studied by Bakht and Mohammod Feroz[37] and their observations were that the saponification followed second order kinetics and the rate was enhanced by a closer cooling of poly(vinyl acetate) and this was further revealed by viscosity measurements. Kenkyu *et al.*[38] investigated into the alkaline hydrolysis of carboxylic acid esters catalysed by nucleic acid bases and polymers containing them and concluded that the large negative activation entropies for the catalysed *vs.* the uncatalysed reactions supported a more restricted transition state in the catalysed reactions by hydroxide ion and further they are absorbed on the adjacent sides of a catalyst surface. Studies on the rates and activation parameters of alkaline hydrolysis of the 3-methoxycarbonyl propionate ion in aq. mixtures of DMSO was undertaken by Biswas *et al.*[39] and they proposed that the activtion parameters and thermodynamic quantities were related to the transfer of transition state in a more solvated form. Dixon and Andrew[40] made detailed investigations on the base hydrolysis of a series of α-cyano thiophospho esters and drew conclusions that the classic Hammett functions σ, ρ are related to the hydrolysis in a more bimolecular nature.

Kinetic and mechanistic studies of the acid kinetic hydrolysis of the di, tert-butylmalonate in dioxane-water system was investigated by Khalil *et al.*[41] and they showed that the rate constants and activation parameters had a correlation with the slowing down of the steps of the hydrolysis and further the rate constant ratio was dependent on solvent composition and both these steps preceded concurrently A_A^1 and A_{ac}^2 mechanisms and also the maximum concentration of intermediate half ester decreased with decrease of ionising power of solvent and these observations are also related to the dielectric constant of the medium. Vibha *et al.*[42] studied the rates of alkaline hydrolysis of diethyl phthalates in dioxane-water system at different temperatures and at various compositions and finally concluded that the rates decreased with rise in percentages of dioxane. However, the iso-composition decreased the activation energy and further the variation in thermodynamic parameters $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were explained on the basis of solvation of species. They also suggested that at iso-kinetic temperature there was a weak solvent-solute interaction and they also calculated the solvation number of the reaction in the above solvent system.

A detailed kinetic study of the effect of aq. 2-propanol and aq. dioxane on the hydrolysis of amyl salicylate was carried out by Sing *et al.*[43] and their results showed the variation in dielectric constant values of the above solvent systems and they were correlated with the size of the transition state, and further they proposed a plausible mechanism on the basis of kinetic analysis and experimental details and conversions at each stage of the hydrolysis. Marsh *et al*[44]carried out a detailed kinetic study of hydrolysis of aryl esters by the pH-Stat method and further the pseudo first order and second order rate coefficients for the above title reactions were also evaluated. Catalysis of the hydrolysis of the trimethyl-*o*-benzoate by absorbed sodium docylsulphate was undertaken by Wong and Lobban[45] and they suggested a mechanism on the basis of (a) observed kinetics at various water concentrations, (b) the measured deuterium solvent isotopic effects, (c) the measured activation parameters, and (d) the observed kinetics with enolisation with the formation of enolate anion which is low.

Unterhalt *et al.*[46] studied the alkaline hydrolysis of pharmocologically important esters in DMSO at room temperature within a short time and established a quantitative relationship between structure of the ester and reaction rates. Xia and Xia[47] investigated into the intramolecular reaction and intramolecular catalysis solvent effects on the alkaline hydrolysis of ethyl 2-(2′-benzimidazolyl) acetate and ethyl 3-(2′-benzimidazolyl) propionate in DMSO-water and 1,4-dioxane-water mixtures and suggested the observed hydrolysis rate constants of these two esters with an irregular bell-shape involving intermolecular and intramolecular catalysis. A study of the effect of cationic micelles on the intramolecular general base catalysed hydrolysis of ionised phenyl salicylate at different temperatures in presence of acetyl trimethyl ammonium bromide was undertaken by Khan and Arifin[48] and they observed that the ester hydrolysis included both the intermolecular specific base catalysis of the hydroxide ion and the intramolecular general base catalysis of benzimidazolyl group.

An effective and convenient procedure for quantitative estimation with quantitative yields for ester hydrolysis in DMF was developed by Khurana and Sehgal[49] in a single stage saponification process. Khan and Arifin[50] made a detailed study of the effects of cationic micelles as rates and activation parameters of intramolecular general base-catalysed hydrolysis of ionised salicylate esters and they explained the micelles inhibition of hydrolysis of the above esters in terms of the pseudo phase model of the micelles and further increased values in both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were attributed to the miceller bond formations with the above said esters. Evans *et al.*[51] made a detailed study of microgels with trialkyl ammonium side chain function as catalyst for the alkaline hydrolysis of substituted phenyl laurate esters and concluded that the reaction of microgel solution with laurate esters is quite similar to that of the analogous miceller system from CTAB and further the rate constant in the hydrolysis of laurate esters obeys Bronsted correlation. The reaction between ethyloxalate and hydroxide ions was studied in a series of ethanol-water mixtures at 25° ± 0.01°C by Uddin and Shahid[52] and they concluded from the experimental values an activated complex existing as a double-sphere model. Numbert and Pirsalu[53] made a detailed study of alkaline hydrolysis of substituted phenyl benzoates in 80% DMSO at various temperatures and established a relation between reaction rate and substituted constants of the above phenyl benzoates. Verma *et al*[54] investigated into the kinetic study of solvent effect on alkaline hydrolysis of ethyl nicotinate in aquo-protic and aquo aprotic solvent media and observed that the rate decreases with increase in amount of aprotic solvent and further the activation parameters were interpreted on the basis of specfic solvation and dielectric properties of the media. Hu *et al.*[55] made a study on solvent effect and activation thermodynamics of saponification of ethylbenzoate at 25°C in ethanol-water mixtures and evaluated the necessary activation energies, frequency factors and three activation thermodynamic parameters and finally suggested a mechanism in consonance with the above thermodynamic data. A valuable review article entitled "Saponification kinetics-revisited" by Wheeler *et al.*[56] was published and the experimental details incorporated in this article were found most suitable for the classical undergraduate students.

An investigation into the kinetics and mechanism of the alkaline hydrolysis of 2,4-dinitophenyl 4-hydroxyphenyl propionate in 40% dioxane-water system (v/v) was undertaken by Cevasco *et al.*[57] and they concluded that the activation parameters are in consonance with the occurrence of the dissociative E^1_{CB} pathway although participation associated mechanism cannot be definitely ruled out.

EXPERIMENTAL

Theoretical treatment

In our investigations, the time ratio method is adopted rather than Powell's graphical method since time ratio method yields comparatively more precise rate constants. In this method, times for 15%, 35% and 70% of the reaction are recorded from a graph drawn on a large scale and the corresponding τ and κ values are noted from Swain's modified table for series first order reactions. From the relation $\tau = \beta_0 k_1 t$ the value of k_1 and from relation $\kappa = k_2/k_1$ the value of k_2 are evaluated. Thus the rate constants k_1 and k_2 for the two consecutive steps involved in a saponification process at different temperatures are calculated.

Materials and methods

The liquid esters and semisolid esters employed in the present work were of extra pure variety (BDH/E. Merck) and were further purified by distillation or by crystallization from a suitable solvent before use. The physical data, *viz.*, m.p., saponification value and IR spectra for esters employed are in agreement with the data collected from literature. The rate studies were carried out over 0.3 to 0.7 of the life period of the saponification reaction. Requisite amounts of the reaction mixture (diesters and excess of alkali which is twenty times over and above the stoichiometric equivalent concentration) were pipetted out at noted time intervals into a solution containing a known excess of potassium hydrogen phthalate which served to arrest the reaction. Carbon dioxide was carefully removed from the original reactants; the solvents and the whole system was kept during the reaction as well as titration in a stream of nitrogen. The sodium hydroxide solution employed in the saponification process as well as in the titration were prepared carbonate-free by the reaction of metallic sodium with conductivity water. The solvents ethanol/acetone/dioxane/DMSO used in the saponification process were purified by repeated distillation with CaO and also by azeotropic distillation methods.

Treatment of data

Percentage of a saponification reaction for a particular kinetic run are plotted as function of time 't' on a large scale. From a smooth curve drawn through these experimental points, the times for 15%, 35% and 70% of the reaction are recorded. From the time ratios, *e.g.*, t_{35}/t_{15} or log t_{35}/t_{15} the corresponding κ values and τ values are noted from the standard tables furnished by Swain[1] using the following relations:

$$\tau = \beta_0 k_1 t$$

$$\kappa = k_2/k_1$$

The rate constants for the consecutive, competitive steps are evaluated. The rate constants obtained in these investigations represent an average of at least three kinetic runs and are accurate within ±3%. Thermodynamic parameters, *viz.*, energy of activation $\Delta E^{\neq}$, enthalpy of activation $-\Delta H^{\neq}$, entropy of activation $\Delta S^{\neq}$, Gibb's free energy $\Delta G^{\neq}$ and frequency factor (A) with respect to these individual steps are calculated employing the necessary formulae. A summary of the rate constants and also the thermodynamic parameters are presented in Tables 1–3.

TABLE-1: SERIES FIRST ORDER REACTION SAPONIFICATION OF GLYCERYL DILAURATE AND GLYCERYL OLEOSTEARATE

$[OH^-] = 0.02$ M $[Cl^-] = 0.02$ M [Ester] = 0.001 M Temp: 50° ± 0.05°C
Alcohol-water = 0.5546 mole fraction Acetone-water = 0.612 mole fraction Dioxane-water = 0.648 mole fraction
(V/V: 72/28) Ethanol-water, acetone-water and dioxane-water systems

Name of Ester	Structure	Pseudo first order rate constant $K_1 \times 10^2$, sec^{-1} 1st step		Pseudo first order rate constant $K_2 \times 10^2$, sec^{-1} 2nd step		Pseudo first order rate constant $K_1 \times 10^2$, sec^{-1} 1st step	Pseudo first order rate constant $K_2 \times 10^2$, sec^{-1} 2nd step
		(Ethanol-water)	(Acetone-water)	(Ethanol-water)	(Acetone water)	(Dioxane-water)	(Dioxane-water)
Glyceryl dilaurate	$CH_2—OOCC_{11}H_{23}$ $CHOOCC_{11}H_{23}$ CH_2OH	75.12	120.65	0.0150	0.3575	187.0	1.18
Glyceryl oleostearate	$CH_2—OOCC_{17}H_{33}$ $CHOOCC_{17}H_{35}$ CH_2OH	109.00	57.20	0.0130	2.3400	115.0	5.10

TABLE-2: SERIES FIRST ORDER REACTION SAPONIFICATION GLYCERYL DILAURATE AND GLYCERYL OLEOSTEARATE

$[OH^-] = 0.02$ M $[Cl^-] = 0.02$ M DMSO-water = 0.602 mole fraction [Ester] = 0.001 M Temp: 30° ± 0.05°C (V/V: 72/28) DMSO-watersSystem

Name of ester	Structure	Pseudo first order rate constant $K_1 \times 10^2$, sec^{-1}, 1st step	Pseudo first order rate constant $K_2 \times 10^2$, sec^{-1} , 2nd step
Glyceryl dilaurate	$CH_2—OOCC_{11}H_{23}$ $CHOOCC_{11}H_{23}$ CH_2OH	450.0	45.0
Glyceryl oleostearate	$CH_2—OOCC_{17}H_{33}$ $CHOOCC_{17}H_{35}$ CH_2OH	511.0	4.60

TABLE-3
SERIES FIRST ORDER REACTION SAPONIFICATION OF GLYCERYL DILAURATE AND GLYCERYL OLEOSTEARATE

$[OH^-] = 0.02$ M [Ester] = 0.001 M $[Cl^-] = 0.02$ M

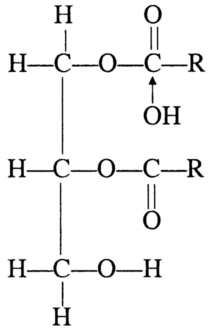
Parameters	Glyceryl dilaurate				Glyceryl oleostearate			
	Ethanol water (Mole fraction 0.5546)	Acetone water (Mole fraction 0.612)	Dioxane water (Mole fraction 0.648)	DMSO water (Mole fraction 0.602)	Ethanol water (Mole fraction 0.5546)	Acetone water (Mole fraction 0.612)	Dioxane water (Mole fraction 0.648)	DMSO water (Mole fraction 0.602)
ΔE_a(kcal/mole)								
ΔE_{a1}	9.120	4.824	2.974	2.059	8.730	4.670	3.889	3.432
ΔE_{a2}	15.200	7.907	5.582	4.804	17.190	7.180	5.720	4.804
$-\Delta H$ (kcal/mole)								
$-\Delta H_1$	4.980	3.247	1.596	1.084	8.580	5.500	5.569	1.330
$-\Delta H_2$	5.700	4.950	2.306	1.377	17.610	12.210	10.840	1.841
ΔS (e.u.)								
ΔS_1	–9.160	–5.253	–3.959	–2.876	–13.670	–11.730	–3.256	–1.563
ΔS_2	–9.630	–8.048	–6.175	–3.631	–19.610	–14.540	–4.625	–2.064
ΔG (kcal/mole)								
ΔG_1	–1.770	–3.245	–8.958	–10.850	–4.050	–7.490	–9.568	–13.310
ΔG_2	–2.496	–4.947	–12.990	–13.730	–10.080	–12.200	–18.840	–18.410
$\log A_1$	7.227	12.95	21.590	22.650	8.216	12.250	18.560	20.140
$\log A_2$	7.317	12.76	21.890	22.830	9.506	12.380	18.750	20.170

RESULTS AND DISCUSSION

A number of instances concerning anchimeric assistance are encountered in the literature. However, very little work is on record in respect of the saponification of diesters of glycols and glycerol. In the saponification process of these esters, anchimeric assistance is provided by the neighbouring hydroxyl group located in close proximity to an ester bond. Further, the aliphatic hydroxyl group is found to facilitate the alkaline hydrolysis of the ester without participating itself as a nucleophile. Such anchimeric assistances are also enocountered in a variety of biochemical transformations and this has promoted us to study in detail the saponification of the above said industrially important diesters.

A meticulous critical analysis of the rate data furnished in Table-1 shows that the reactivity pattern in respect of saponification process of diesters into monoesters/half-esters is more than that of monoester/half-ester hydrolytic reaction. This strange finding could be rationalised by involving the concept of Kumuria *et al.*[13] that the longer carbon chains present in the alkyl groups of the fatty acid units of the diester provide such a difference in rates. A survey of literature also reveals that the transition state formed from the saponification of an ester has a –ve charge localised on the carbonyl oxygen atom making this a good proton acceptor through a hydrogen bond formation[23]. This explanation of the transition state was also supported by Haberfield *et al.*[24] by calorimetric determination of the relative enthalpies of reactant and transition states. In the alkaline hydrolysis of ester the transition state resembles a species such as an alkoxide ion much more than a delocalised anion having a weak hydrogen-bonding interaction with the solvent.

In our present study, particularly in the saponification of oleostearates and dilaurates of glycerol the –ve charge on the carbonyl oxygen atom in the transition state decreases by diffusion through intramolecular hydrogen bond formation as shown in the following structure.



Where 'R' stands for

laury = $C_{11}H_{23}$

Stearic = $C_{17}H_{35}$

Oleo = $C_{17}H_{33}$

(Structure 1)

As mentioned earlier the rate of saponification of diester is more than that of monoester could further be explained on the basis that the transition state (str. 1) which is also formed from the intramolecular hydrogen bond formation of the monoester is less solvated by aq. ethanol or aq. acetone or aq. dioxane or aq. DMSO and, therefore, responsible for the lowering of the rate of saponification of the monoester.

A perusal of the thermodynamic parameters (Table-3) indicates that in general the energies of activation are higher for glyceryl oleostearate than glyceryl dilaurates, while the enthalpy of activation, free energies of activation and frequency factors of oleostearates of glycerol are relatively lower than the values of the corresponding dilaurates. The entropies of activation of dilaurates are marginally lower for glyceryl dilaurates than glyceryl oleostearates. Such a behaviour may be attributed due to the presence of Lauryl unit $C_{11}H_{23}$ which is a shorter alkyl group than oleic/stearic unit $C_{17}H_{35}$ and moreover the vicinal hydroxyl groups formed in the saponification process also play a prominent role in the internal stabilisation of transition state causing lower saponification rates, particularly in the case of glyceryl oleostearate. These thermodynamic parameters are also in consonance with any type of ion-dipole reactions.

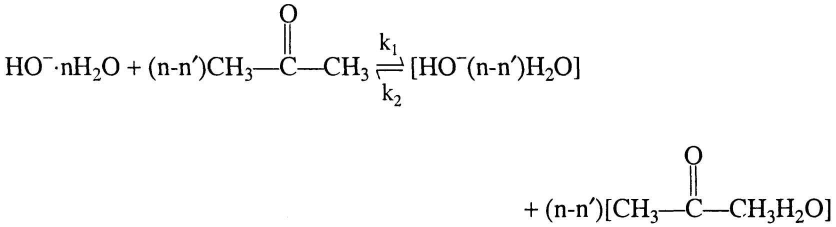
The results of the present work also show that systems which involve a high degree of internal stabilisation of the transition state are susceptible to the solvent influence and there is much variance in the thermodynamic parameters and also in the value of the rate constants for both the steps.

The variable susceptibility to polar effects suggests an increased importance of transition state solvation in acetone/dioxane/DMSO. If pK value is equated with the degree of –ve charge developed in the transition state or alternatively the degree of 'tightness' of the transition state complex, implies that the attacking hydroxide ion and the carbonyl carbon are separated by a greater distance in aq. DMSO than in aq. dioxane, aq. acetone and aq. alcohol.

While it is not permissible to make a quantitative assessment of the contribution of transition state solvation to the –ΔF term, the importance of the contribution shows that substitution of aq. DMSO/aq. dioxane/aq. acetone than in aq. alcohol leads to an enhanced rate of reaction.

However, more importantly, as per the Hughes-Ingold theory[25], both the reduced enthalpy entropy of activation support the involvent of a more highly solvated transition state of diester in aq.DMSO.

The state of anion solvation is frequently mentioned by Benson[26] and Tommila *et al.*[27] as a contribution cause of reactivity. Thus in aq. acetone, aq. dioxane and aq. DMSO systems of the present study show that the reactivity of hydroxide ion is dependent upon the following equilibrium:



$$HO^{-}\cdot nH_2O + (n\text{-}n')CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [HO^{-}(n\text{-}n')H_2O] + (n\text{-}n')[CH_3-\overset{\overset{O}{\|}}{C}-CH_3H_2O]$$

Where 'n' equals the maximum number of water molecules hydrogen-bonded to hydroxide ion. With increasing acetone, dioxane and DMSO content the equilibrium would be shifted to right, resulting in a less solvating hydroxide ion.

The effect of anion desolvation as the major contributing cause for the increase of rate constant is also to some extent unlikely for the following reasons:

(1) The activity of the hydroxide ion with increasing acetone/dioxane and DMSO concentrations does not explain the dependency of medium effect upon substrate steric substituent constant or the presence of medium effect discontinuities.

(2) With a small ion such as hydroxide, it is more realistic to treat the ion plus the hydrogen-bonded water molecules as a single kinetic unit. If the anion desolvation mechanism were operative this would imply decreasing size of the nucleophile with increasing acetone/dioxane/DMSO content in the solvent medium. Such a charge in the steric bulk of the attacking reagent should be reflecting by variation in the reaction constant parameter "δ". However, such responses are not generally recorded in "δ" at higher mole fractions of acetone/dioxane/DMSO.

It is also obvious that systems which involve a high degree of internal stabilization of the transition state are susceptible to pronounced dipolar aprotic solvent influences. Further, on the basis of this observation, it would seem that one can use di-polar aprotic solvent influences on reaction rates as a criterion in the assessment of anchimeric assistance in reactions involving internally stabilized transition states.

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