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A Comparative Kinetic Study of Saponification of Industrially Important Esters

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Kinetics of saponification of seven 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 the 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 furthemore the stearates are more saponifiable than laurates and oleosterate in 72% alcohol-water moiety and in general these processes are much faster in acetone-water system than in alcohol-water.

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 diesters 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 study of alkaline hydrolysis of eight structurally related ethyl esters in 85% aqueous ethanol and 85% dimethyl sulphoxide with a special emphasis on the solvent effects and also polar, steric and hyperconjugative effects was reported by Roberts[9–11]. Meseller and Speiser[12] made a detailed survey of

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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 rates, the prime requisites of the optimum solvent composition for a reaction was developed by Wong *et al.*[14] Balkrishnan *et al.*[15–20] studied the influences of dipolar aprotic protic solvents in the saponification of diol monoesters, $\alpha:\beta$ unsaturated esters and their corresponding saturated esters and also aliphatic di-carboxylic esters. Holba *et al.*[21] investigated the kinetics of alkaline hydrolysis of semi esters of dicarboxylic acids 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.

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 values and values are noted from Swain's modified table for series first order reactions. From the relation, $\tau = B_0k_1t$ the value of k_1 and from relation $K = k_2/k_1$, the values 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 the semisolid esters employed in the present work were of extra pure variety (BDH/Amrut Industries) 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 the esters employed are in agreement with the data collected from the literature. The rate studies were carried out for 0.3 to 0.7 of the life period of the saponification reaction. Requisite amounts of the reaction mixture (diesters and an 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, solvents and the whole system was kept during the reaction as well as titration in a stream of nitrogen. The sodium hydroxide solutions employed in the saponification process as well as in the titrations were prepared carbonate free by the reaction of metallic sodium with conductivity water. The solvents ethanol and acetone used in the saponification process were purified by repeated distillation with CaO and also by azeotropic distillation methods.

Treatment of data

Percentages of a saponification reaction for a particular kinetic run are plotted as a 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 'K' values and 'τ' values are noted from the standard tables furnished by Swain[1]. Using the following relations

$$\tau = B_0 k_1 t$$

$$K = k_2/k_1$$

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.

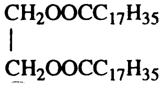
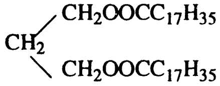
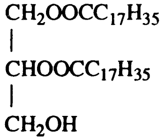
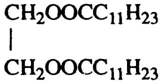
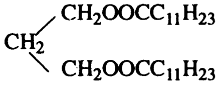
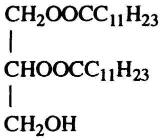
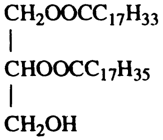
RESULTS AND DISCUSSION

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, this aliphatic hydroxyl group is found to facilitate the alkaline hydrolysis of the ester without participating itself as a nucleophile. Such anchimeric assistances are also encountered in a variety of biochemical transformations and this has prompted 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 monoester/half ester is more than that of monoester/half ester hydrolytic reaction. This strange finding could be rationalised by invoking the concept of Kumuira *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

TABLE-1
SERIES FIRST ORDER REACTION
SAPONIFICATION OF DISTEARATES, DILAURATES OF GLYCOL, PROPYLENE GLYCOL AND GLYCEROL AND ALSO GLYCERYL OLEOSTEARATE

$[OH^-] = 0.02$ M
$[Cl^-] = 0.02$ M
Temp. 50° ± 0.05°C
[Ester]= 0.001 M
Alcohol-Water = 0.5546 mole fraction
Acetone-Water = 0.612 mole fraction
(v/v : 72/28) EtOH-Water and Acetone-Water System

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	
		(EtOH-Water)	(Acetone-Water)	(EtOH-Water)	(Acetone-Water)
Ethylene glycol distearate	 $\begin{array}{l} CH_2OOCC_{17}H_{35} \\ \vert \\ CH_2OOCC_{17}H_{35} \end{array}$	11.18	98.43	0.0522	0.7450
Propylene glycol distearate	 $CH_2\begin{array}{l} \diagup CH_2OOCC_{17}H_{35} \\ \diagdown CH_2OOCC_{17}H_{35} \end{array}$	32.58	39.65	0.6840	0.7668
Glyceryl distearate	 $\begin{array}{l} CH_2OOCC_{17}H_{35} \\ \vert \\ CHOOCC_{17}H_{35} \\ \vert \\ CH_2OH \end{array}$	72.82	104.05	0.1600	4.510
Ethylene glycol dilaurate	 $\begin{array}{l} CH_2OOCC_{11}H_{23} \\ \vert \\ CH_2OOCC_{11}H_{23} \end{array}$	35.90	112.00	0.0502	0.2800
Propylene glycol dilaurate	 $CH_2\begin{array}{l} \diagup CH_2OOCC_{11}H_{23} \\ \diagdown CH_2OOCC_{11}H_{23} \end{array}$	28.11	29.90	0.9296	2.472
Glyceryl dilaurate	 $\begin{array}{l} CH_2OOCC_{11}H_{23} \\ \vert \\ CHOOCC_{11}H_{23} \\ \vert \\ CH_2OH \end{array}$	75.12	120.65	0.0150	0.3575
Glyceryl oleostearate	 $\begin{array}{l} CH_2OOCC_{17}H_{33} \\ \vert \\ CHOOCC_{17}H_{35} \\ \vert \\ CH_2OH \end{array}$	109.0	57.20	0.0130	12.34

the relative enthalpies of reactant and transition states. In the alkaline hydrolysis of esters 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.

TABLE-2
SERIES FIRST ORDER REACTION
SAPONIFICATION OF DISTEARATES, DILAURATES OF GLYCOL, PROPYLENE GLYCOL AND GLYCEROL AND ALSO GLYCERYL OLEOSTEARATE: THEROMODYNAMIC PARAMETERS OF 1st STEP AND 2nd STEP

$[OH^-] = 0.02$ M [Ester] = 0.001 M
$[Cl^-] = 0.02$ M Alcohol-Water = 0.5546 mole fraction (v/v : 72/28)

S No.	Name of ester	ΔE_a	kcal/mole	$-\Delta H$	kcal/mole	ΔS	e.u.	ΔG	kcal/mole	log A_1	log A_2
		ΔE_{a_1}	ΔE_{a_2}	$-\Delta H_1$	$-\Delta H_2$	ΔS_1	ΔS_2	ΔG_1	ΔG_2		
1.	Ethylene glycol distearate	16.510	17.280	16.230	17.400	–16.160	–19.400	–10.840	–10.940	8.762	9.459
2.	Propylene glycol distearate	7.710	9.597	8.070	8.730	–8.680	–10.530	–5.170	–5.220	7.121	7.514
3.	Glyceryl distearate	6.930	7.380	7.910	8.100	–6.470	–9.480	–5.808	–4.990	7.242	7.284
4.	Ethylene glycol dilaurate	20.420	28.960	18.090	29.170	–19.950	–20.300	–11.330	–22.410	9.593	9.657
5.	Propylene glycol dilaurate	12.250	16.080	12.620	18.340	–12.210	–21.300	–8.530	–12.720	7.896	9.876
6.	Glyceryl dilaurate	9.120	15.200	4.980	5.700	–9.160	–9.630	–1.770	–2.496	7.227	7.317
7.	Glyceryl oleostearate	8.730	17.190	8.580	17.610	–13.670	–19.610	–4.050	–10.080	8.216	9.506

TABLE–3

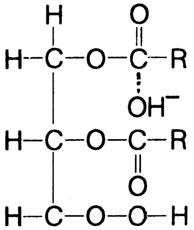
SERIES FIRST ORDER REACTION SAPONIFICATION OF DISTEARATES, DILAURATES OF GLYCOL, PROPYLENE GLYCOL AND GLYCEROL AND ALSO GLYCERYL OLEOSTEARATE: THEROMODYNAMIC PARAMETERS OF 1st STEP AND 2nd STEP

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

$[Cl^-] = 0.02$ M　　Alcohol-Water = 0.612 mole fraction (v/v : 72/28)

S.No.	Name of ester	ΔE_a	kcal/mole	$-\Delta H$	kcal/mole	ΔS	e.u.	ΔG	kcal/mole	log A_1	log A_2
		ΔE_{a_1}	ΔE_{a_2}	$-\Delta H_1$	$-\Delta H_2$	ΔS_1	ΔS_2	ΔG_1	ΔG_2		
1.	Ethylene glycol distearate	6.520	12.050	5.079	12.570	–8.830	–7.200	–5.076	–12.567	12.710	12.800
2.	Propylene glycol distearate	5.420	8.020	7.220	8.120	–6.120	–7.840	–7.220	–8.120	12.190	12.370
3.	Glyceryl distearate	4.470	6.360	6.598	7.150	–5.270	–6.490	–6.600	–7.140	12.420	12.430
4.	Ethylene glycol dilaurate	10.140	16.470	17.860	6.870	–13.170	–13.740	–17.850	–6.870	12.184	12.185
5.	Propylene glycol dilaurate	6.020	9.093	3.056	9.215	–7.607	–10.350	–6.662	–9.212	12.841	12.841
6.	Glyceryl dilaurate	4.824	7.907	3.247	4.950	–5.253	–8.048	–3.245	–4.947	12.950	12.760
7.	Glyceryl oleostearate	4.670	7.180	7.500	12.210	–11.730	–14.540	–7.490	–12.200	12.250	12.380

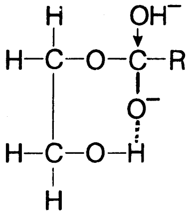
In our present study, particularly in the saponification of distearates, dilaurates and also oleosterates of glycerol, the –ve charge on the carbonyl oxygen atom in the transition state decreases by difussion through intramolecular hydrogen-bond formation as shown in the following structure.



Where 'R' stands for
laury = $C_{11}H_{23}$
Stearic = $C_{17}H_{35}$
Oleo = $C_{17}H_{33}$

Structure I

As mentioned earlier, the rate of saponification of a diester is more than that of a monoester could further be explained on the basis that the transition state (Structure I) which is also formed from the intramolecular hydrogen bond formation of the monoester is less solvated by aqueous ethanol or aqueous acetone



Where 'R' stands for
laury = $C_{11}H_{23}$
Stearic = $C_{17}H_{35}$
Oleo = $C_{17}H_{33}$

Structure II

and therefore responsible for the lowering of the rate of saponification of the monoester.

A perusal of thermodynamic parameters (Tables 2 and 3) indicates that in general the energies of activation are higher for laurates while the enthalpies of activation, entropies of activation and free energies of activation of dilaurates of ethylene glycol and propylene glycol are relatively lower than the values of the corresponding individual esters of distearates of glycols and glycerol, however, with a few exceptions of glyceryl dilaurate. Such a behaviour may be attributed due to the presence of a lauryl unit ($C_{11}H_{23}$) which is a shorter alkyl group than the oleic/stearic unit ($C_{17}H_{33}/C_{17}H_{35}$) and, moreover, the vicinal hydroxyl groups formed in the saponification process also play a prominent role in the internal stabilization of the transition state causing lower saponification rates. These thermodynamic parameters are also in consonance with any type of ion-dipole reaction.

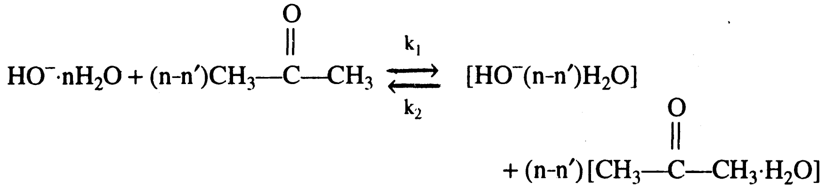
The results of the present work also show that systems which involve a high degree of internal stabilization of the transition state are susceptible to the solvent influence and therefore much variance in the thermodynamic parameters and also in the value of the rate constants for both the steps.

The variable susceptibility to polar effects suggests an increased importance of transition state solvation in acetone. If ρ^* is equated with the degree of negative 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 aqueous acetone than in aqueous ethanol.

While it is not permissible to make a quantitative assessment of the contribution of transition state solvation to the $-\Delta F$ term, the importance of the contribution shows that substitution of aqueous acetone for aqueous ethanol leads to an enhanced rate of reaction.

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

The state of the anion solvation is frequently mentioned by Benson[26] and Tommila *et al.*[27] as a contribution cause of reactivity. Thus in aqueous acetone, the activity of the hydroxide ion is dependent upon the following equilibrium.



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

where 'n' equals the maximum number of water molecules hydrogen-bonded to hydroxide ion. With increasing acetone content, the equilibrium would be shifted to right, resulting in a less solvated 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 concentration does not explain the dependency of medium effect upon substrate steric substituent constants 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 dissolvation mechanism were operative this would imply decreasing size of the nucleophile with increasing acetone content in the solvent medium. Such a charge in the steric bulk of the attacking reagent should be reflected by variation in the reaction constant parameter "δ". However, such responses are not generally recorded in "δ" at higher mole fractions of acetone.

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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REFERENCES

1. C.G. Swain, *J. Am. Chem. Soc.*, **66,** 1096 (1944).
2. S.V. Anantkrishnan and P.S. Radhakrishnamurthy, *Proc. Ind. Acad. Sci.*, **436A,** 249 (1962).
3. _______, *Indian J. Chem.*, **3,** 336 (1965).
4. S.V. Anantkrishnan and R.V. Venkatratnam, *Indian J. Chem.*, **4,** 379 (1966).
5. _______, *Proc. Indian Acad. Sci.*, **65A,** 188 (1967).
6. _______, *Proc. Indian Acad. Sci.*, **65A,** 298 (1967).
7. C. Bruice Thomas and Thomas Fife, *J. Am. Chem. Soc.*, **84,** 1973 (1962).
8. G. Sorsaro, *Chem. Ind. (Lond.)*, **2,** 75 (1964).
9. D.D. Roberts, *J. Org. Chem.*, **9,** 2714 (1964).
10. _______, *J. Org. Chem.*, **29,** 2039 (1964).
11. _______, *J. Org. Chem.*, **30,** 3516 (1965).
12. F. Messeller and P. Speiser, *Pharma. Acta. Helv.*, **40,** 449 (1965).
13. C.K. Kumuira, Murai, Koichi and Y. Hidetoshi, *Kogya Keguka Zasshi,* **71,** 1569 (1968).
14. Wong, Kin Fal and Ecker, *Ind. Eng. Chem. Proc. Dec. Develop.*, **8,** 568 (1969).
15. M. Balkrishnan, G.V. Rao and N. Venkatasubramanian, *Tetrahedron Lett.*, **45,** 4617 (1972).
16. _______, *Int. J. Chem. Kinetics*, **6,** 103 (1974).
17. _______, *J. Chem. Soc., Perkins Trans.*, **2,** 6 (1974).
18. G.V. Rao and N. Venkatasubramanian, *Aust. J. Chem.*, **24,** 201 (1971).
19. _______, *Indian J. Chem.*, **10,** 178 (1972).
20. _______, *Polymer*, **14,** 332 (1973).
21. V. Holba, J. Benko and P. Komadel, *Z. Phys. Chem. (Leipzig)*, **262,** 445 (1981).
22. P. Kiltl and E. Donoso, *J. Mater. Sci.*, **16,** 533 (1981).
23. A.J. Parker, *Chem. Revs.*, **69,** 1 (1969).
24. P. Haberfield, J. Friedman and M.F. Pinkston, *J. Am. Chem. Soc.*, 94, 71 (1972).
25. C.K. Ingold, Structure and Mechanism in Organic Chemistry, Cornell University Press, Ithaca, New York, 345–350 (1953).
26. S.W. Benson, The Foundation of Chemical Kinetics, McGraw-Hill Book Co. Inc., New York, pp. 535–536 (1960).
27. E. Tommila and M.L. Murto, *Acta Chem. Scand.*, **17,** 1947 (1963).

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