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Original Researcher Article

Kinetic Reaction, Mechanism and Activation Parameter of Alkali Catalyzed Hydrolysis for Propyl Caprate in Water- Acetone Solvent System.

Anil Kumar Singh.

Department of Chemistry, Teerthanker Mahaveer University, Moradabad, India
Email: dr.anilkumarsingh2009@gmail.com

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ABSTRACT

At temperatures ranging from 20 to 40 degrees Celsius, the rate of base-catalyzed hydrolysis of propyl caprate has been measured in a mixture of water and acetone that contains from 30 to 70 percent (v/v). The specific rate constant values decrease with the proportion of organic solvent, following second-order ki-netics. the number of water molecules linked to the activated complex has been determined at various temperatures using the slopes of logk plotted against different mole percentages of water. The iso-kinetic temperature was determined, and its values being lower than 300 indicate weak solvent-solute interactions during the ester hydrolysis process. Thermodynamic activation parameters were also determined using the Wynny Jones Equation.

Keywords: Activation parameter, Isokinetic temperaturepropyl caprate, Solvent effect, water-acetone mixture.

INTRODUCTION

A number of authours(Alaa.omer,2025),(Seliverstove, 2020),(Chhetri,2016,),(Reichardt,2003),(Tahani Saad, 2014,)has been trying to study about hydrolysis of acid and amide. In this report , here I am trying to explainthe result of base catalyzed hydroplysis of propyl caprate which has greater importance in cosmetics and personal care industry as emollient which help to soften and moisture the skin. It is also used in pharmacetutical, serving as recipient to improve the stability and bioavability of active ingredients. The solvent effect was introduced first by (Parker, 1962). According to this theory, the rate of reaction of aprotic solvent is greater than protic solvent in which the transition state passes through more polarization. This theory has been also supported by [Roberts]. However, this statement is against the qualitative predication of (Ingold, 1967) and also against the theoretical predication of (Laidler, 1956,). According to both authors, the rate of such reaction should be decreases with increasing dielectric constant of the media. Therefore, its needs more investigation to reach at definite conclusion, particularly in the case of propyl caprate. To study about activation parameter and mechanism of the rate process, here in this report, it has been decided to study about hydrolysis of caprate ester which have great importance in the chemical industry as well as also used as foodadditive. The molecular formula of propyl caprate is C13H16O2.Its structure is linear as CH3-(CH2)8-C(=O)-O-CH2-CH3. Acetone itself does not readily react with ester under neutral aqueous condition but in water, ester linkage in propyl caprate can undergoes hydrolysis. In basic medium(sponification) , giving deconate salt and propanol.

In this regard, the kinetic result of caprate ester in aqueous solvent has been examined through the study of activation parameters which result the solvent solute interaction. Kinetics model also calculated by the different plots of rate against log [H2O] which show the result of structure change of water molecule. Finally this study of the project also examine the effect of thermodynamic parameters on rate and mechanism of the reaction media.

EXPERİMENTAL

Second-order kinetics have been used to study the kinetics of the reactions. Merck grade or BDH (Analar) chemicals were used. Known procedure is followed for purifying the acetone. A conical flask containing capyarate ester has been heated for 30 minutes. Freshly distilled propyl caprate andN/10 mI HCI stand in seperate bottle in thermostate for half an hour, when they acquire the temperature of water bath, maximum 5 mI of propyl caprate and 10mI of N/10 mI HCI. Immediately withdrawn 10mI of reaction mixture with help of pipate. Now titrate the solution by adding N/10 NaOH from the burete using phenolphthaline as indicator. Similarlty again pipate out 5mI of reaction mixture after 5 minutes and repeate the procedure. Repeate the above procedure by withdrawing 5mI of reaction mixture after 15,30,45,60 minuite. This give the values of different timing(Vt) The V∞ reading indicate the complition of of hydrolysis calculated after 24 hours in same procedure.Specific rate has been calculated which is keeped in Table-1

RESULT AND DISCUSSION

Reaction rate:

The calculated rate of base-catalyzed hydrolysis propyl caprate using second-order kinetics has been listed in Table-1. The rate of reaction decreases with increasing proportion of solvent composition with increasing temperature. The decrease in rate of reaction may either due to solvent-solute interaction or due to the dielectric effect although both factors are equally important for the depletion of rate but, according to (Gelles, 1954), solvent-solute interaction is the more probable factor for influence the rate, and the dielectric constant is secondary factor which influence the rate. Depletion of rate with an increasing proportion of rate has been also found recently by different workers (Magda, 2019),(Sinha,2017)

Table– I Calculated values of rate constant [k x103(dm)3/mole/mint] at different solvent composition.

Temp in OC	% of acetone				
	30%	40%	50%	60%	70%
20OC	48.30	44.05	40.08	36.30	33.26
25OC	102.56	89.12	87.29	68.70	60.25
30OC	218.27	191.42	159.58	126.18	112.20
35OC	440.55	363.91	294.44	239.88	184.92
400C	889.20	706.31	571.47	423.64	337.28

Reaction rate and mechanism of reaction as a function of water concentration:

The rate can also been expressed as a function of water concentration by polting logk against- different concentrations of log [H_2O]. Table-2The rate of reaction shows a marked increase with increaseing concentration of water and the linear plots has been obtaion in more water rich midia[Fig-1]. TheSolvation number(water molecules associated with activated complex) can be dermined with help of different slopes obtaioned by plots logk against different concentration of log [H_2O] as suggested by (Tommilla,1959) & (Lane,1964) are inserted in [Table-3]. From the Table-3, it has been observed that the solvaion number increses with increasing temperature.From the values of Solvation numbers(Activated complex associated water molecules), shows that structure of water molecules changes from dense to bulky form with increasing temperature. (Sharma, 2013,), (Namami, 2020) and (Robertson, 1967)

$$[H_2O]\,d \leftrightarrow [H_2O]b$$

Table-2 Variation oflogk values with log [H_2O] at different temperature.

% of Aceone	% of H2O	log [H2O]	3 + log k				
			200C	250c	300c	350c	400c
30%	70%	1.569	1.684	2.011	2.339	2.644	2.949
40%	60%	1.522	1.644	1.950	2.282	2.561	2.849
50%	50%	1.4437	1.603	1.941	2.203	2.469	2.757
60%	40%	1.346	1.560	1.837	2.101	2.380	2.627
70%	30%	1.221	1.522	1.780	2.050	2.267	2.528

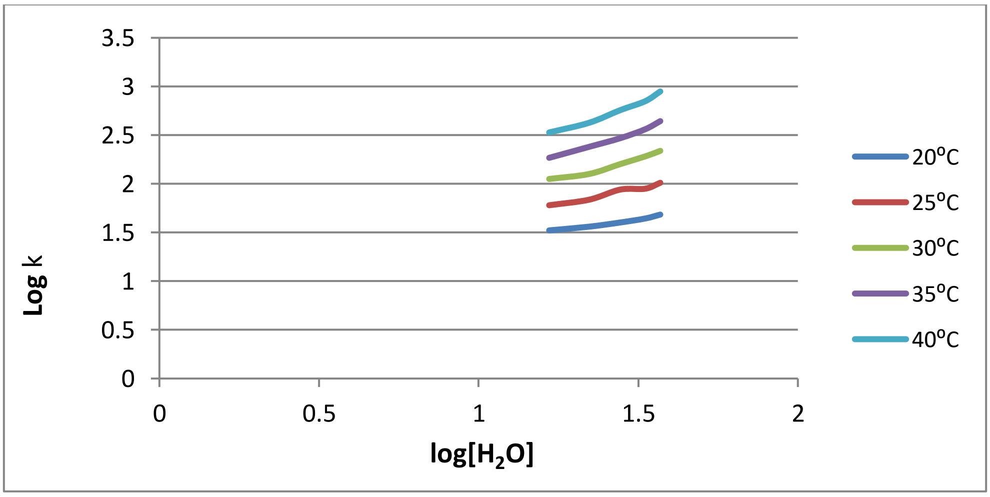

Fig. 1: Plot of log [H_2O] with logk

Table-3 Different values Slopes of log k against log $[H_2O]$ Water-DMF media.

Temp0C	Slope
200c	0.521
250c	0.785
300c	1.111
350c	1.119
400c	1.126

Activation parameters and its effect on rate and mechanism of the reaction:

Like iso composition activation energy and Iso-dielectric activation energy, some others thermodynamic parameters (enthalpy of activation, Gibb's free energy of activation and entropy of activation) also have better indicator of effects exerted by solvent on solvolysis reaction. Calculation of these parameters are obtained with help ofWynne-jones and Eyring equation (Wynne-jones,1953) and the values are placed in Table-4. By observing the different data arranged in Table-4, it has been found that, all the numerical values these three activation parameters are increase with increasing fraction of solvent composition in reaction media.

According to the fundamental relation of thermodynamic it has been observed that the increase in ΔG^*.valueswith simultinious decrease in both of $\Delta H^*$and ΔS^* value isonly possible when ΔS^* decreases more than ΔH^*. From this observation it has been inferred that in presence of acetone in reaction mixture for the solvolysis reaction of propyl caprate is entropy control and enthalpy stimulated reaction. (Singh,1984),(Mohamad,1989), (Singh,2021).However, linear variation of in ΔH^* and non-liner variation of ΔS^* and ΔG^*. with increasing mole % shown in Fig-2 and Fig-3&4 respectively, give the indication that specific solvation taking place in water- acetone solvent system as earlier report of (Saville,1955)

Iso-kinetic Temperature (Barclay-Butlar rule:

In order to study the Iso- kinetic temperature, ΔH^* values are plotted against ΔS^*(fig-5). The observation show that the variation is well-linear in accordance with the Barclay-Butlar rule [23]. The numerical value of the slope has been found to be less than 300. It is found in this case is 283.07. These lower values of slope indicate weak solute-solvent interaction in reaction media as alredy reported by(Laffler, 1955) and different workers(Namami Shanker,2020),(Magdh,2011)

Table-4 Numerıcal values of thermodynamics ActivatioParameters

$\Delta H^*$and ΔG^* in kJ/Mole, ΔS^*in J/K/Mole

% of Acetone	Mole %	ΔH^* in kJ/Mole	200C		250C		300C		350C		400C	
			ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*
30%	9.56	108.60	89.40	65.52	89.11	65.40	88.69	65.70	88.41	65.55	88.07	64.50
40%	14.11	108.30	89.62	63.75	89.46	63.22	89.02	62.19	88.90	62.98	88.67	62.71
50%	19.77	100.46	89.85	36.21	89.51	36.74	89.42	36.43	89.45	35.74	89.23	35.87
60%	26.99	99.86	90.10	33.31	90.10	32.75	90.08	32.27	89.97	33.73	90.01	31.46
70%	36.45	90.85	90.31	1.84	90.43	1.40	90.38	1.551	90.64	0.68	90.60	0.798

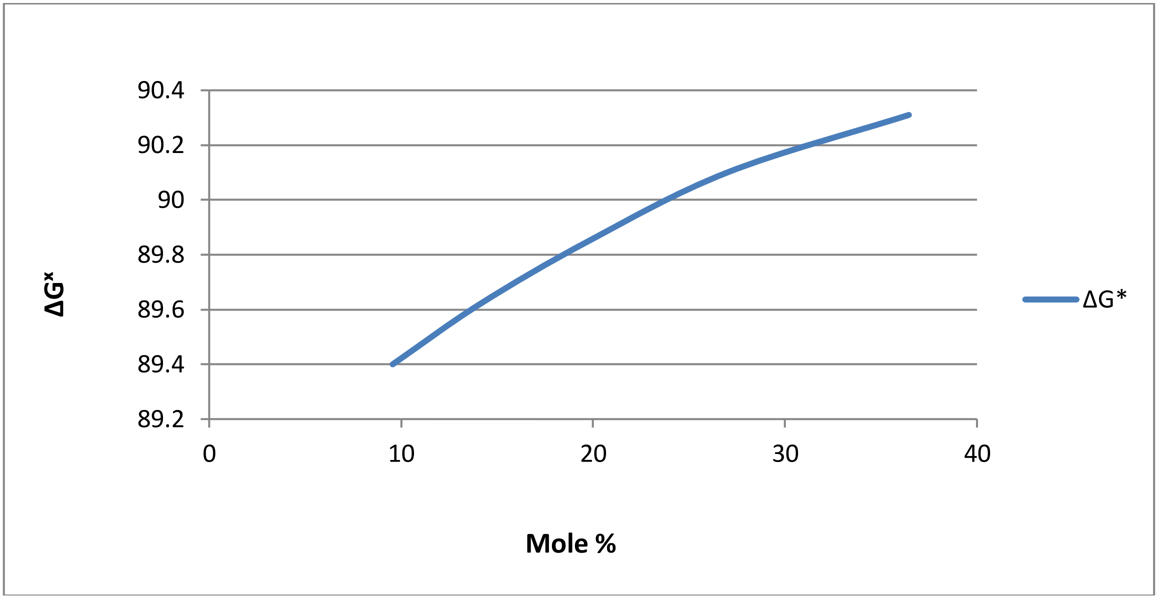

Fig (2)- Variation of ΔG* against mole % at 200C

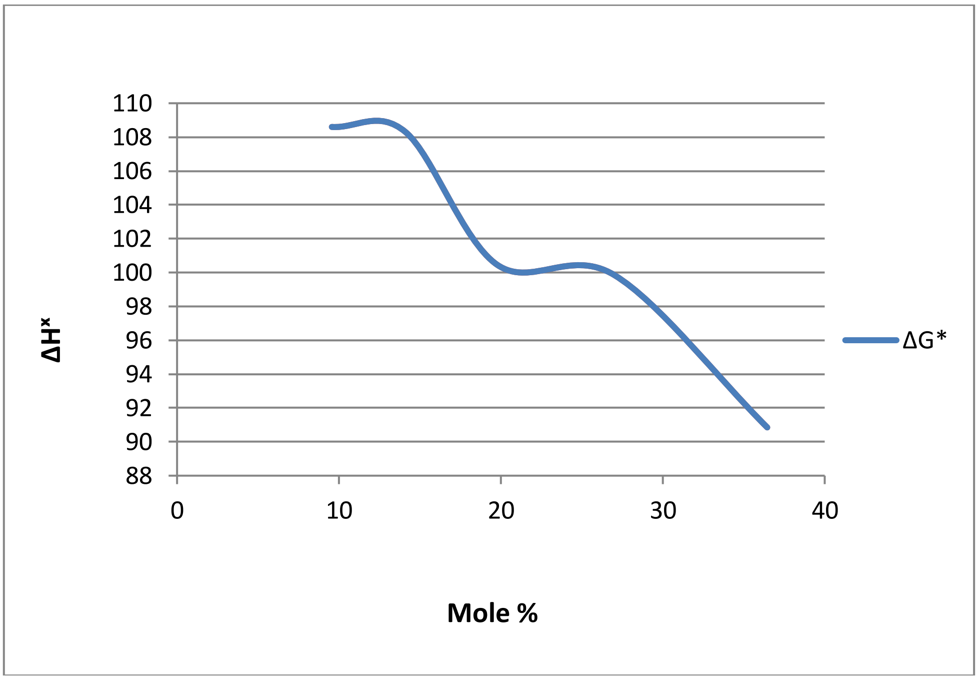

Fig (3)- plot of ΔH* against mole % at 200C

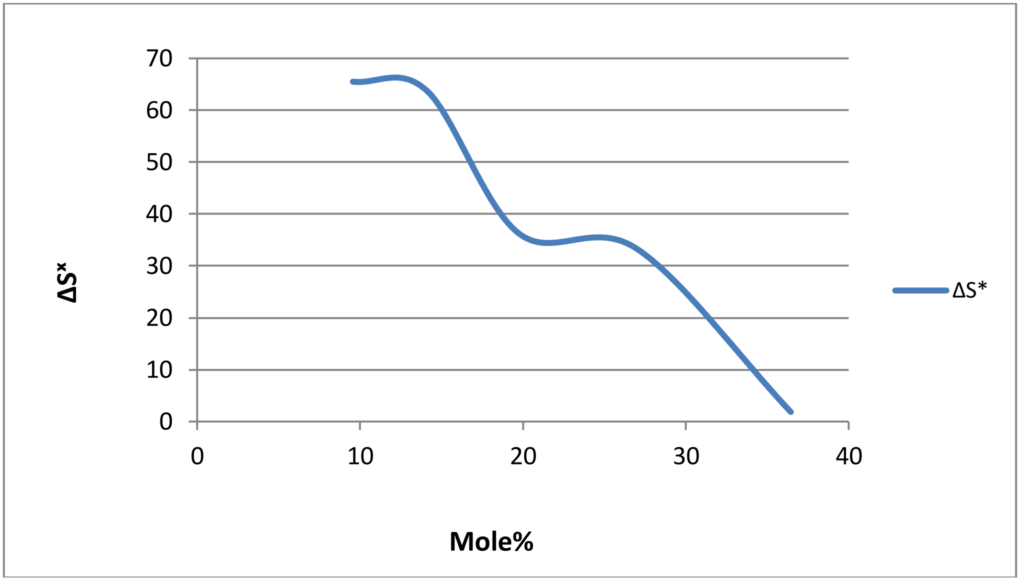

Fig (4)- Variation of ΔS^x versus mole % at 200C

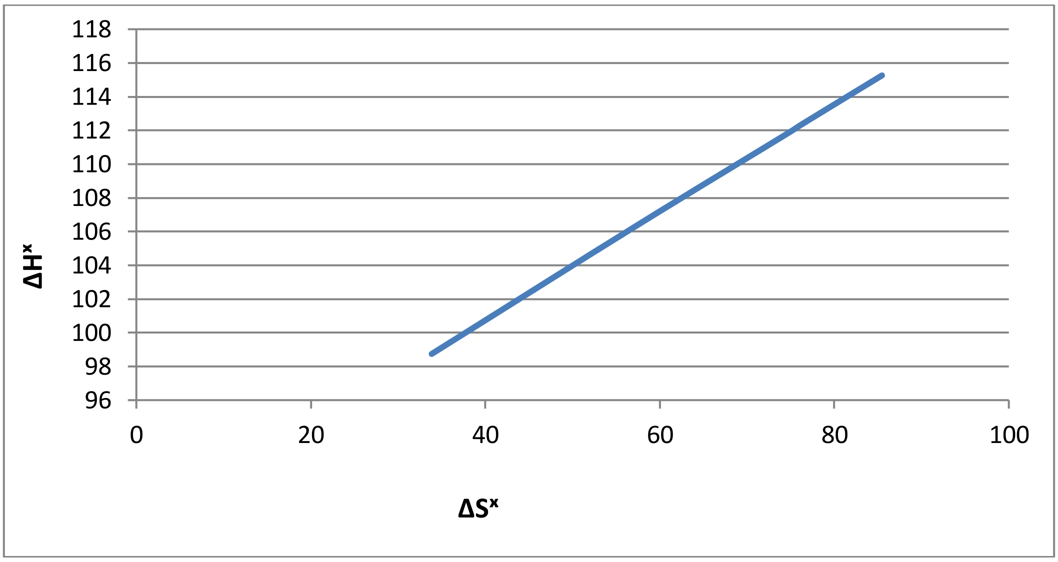

Fig. 5: Variation of ΔH* with ΔS* at 200C water-acetone media.

CONCLUSION:

On the basis of above discussion of this report, it has been found that in alkali catalysed hydrolysis of propyl caprate, the rate of reaction decreases proportionally with incresing fraction of solvent.The solvation numbers (number of water molecules associated in the activated complex) has been increseswith increasing temperature.The decrease in values of ΔG* together with ΔH* and ΔS* is possible only when the reaction entropy control and enthalpy stimulated reactionThe value of iso-kinetic temperature is approximate 283.07indicatingweak solvent- solute in reaction media.

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