

Kinetics and Binary-Solvent Effect on Acid Catalysed Hydrolysis of Butyl Formate

Abstract

The rate of the acid catalysed hydrolysis of butyl formate has been investigated in presence of dimethyl sulfoxide (DMSO) in the temperature range of 20 to 40^o c. The reaction rate was decreased with progressive addition of dimethyl sulfoxide. The iso-composition activation energies, iso dielectric activation energies and activation parameters like enthalpy of activation, entropy of activation and Gibbs free energy of activation, were also calculated and discussed in term of solvent effect. A mechanism was also proposed to account for the solvent effect on reaction rate.

Keywords: Butyl Formate, specific rate, hydrolysis, kinetic solvent effect,. Water-DMSO

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Introduction

The rate of chemical reaction is changed with the change of solvent composition of reaction mixture which has great importance in laboratory as well as in chemical industry. Sometimes , it is found that the rate is increased by a factor 10⁹ with change of solvent (Cram D. J, et.al., 1961). The solvent affects the reaction- rate in two ways. One through static or equilibrium solvent effect and another through dynamic or fractional solvent effect (Reichardt C, 2003, Rose S et.al, 1995, Singh AK., 2015, Herodes K., et.al. 1999). The static solvent effect on reaction- rate can be understood in terms of Transition State Theory. The second method influences the rate of fast reaction. The solvent effect is also closely related to nature and extent of solvent-solute interaction. Solvent-solute interaction are very much complex in mixture of the solvent than pure solvent due to the possibility of specific solvation of any solvent present in the mixture. In this investigation, studies of solvent effect in hydrolysis of butyl formate has been reported, which has greater use as polar aprotic solvent, a flavouring agent and fragrance.

Experimental Section: *Material and method*

Butyl formate is a formate-ester which is formed by condensation of formic acid with hydroxyl group of butanol-1. It is found in apple strawberries, sherry and parmesan cheese. It has a fruity plum-like odour and taste. Its molecular formula is C₅ H₁₀ O₂. The reaction kinetics of the formate ester has been studied under first order condition and the entire chemical used are from Pub Chem. NIH. Calculated amount of organic solvent (DMSO) water and stock acid (HCl) has been mixed in 250 ml conical flask in such a way that total volume of the solution was 50 mL and its strength became 0.5M. The conical flask containing the solution and small stoppard bottle containing pure Butyl formate has been thermostated for 30 minutes. Then 0.60 ml of ester has

been withdrawn and added quickly to the acidic solution of water-solvent mixture. Now the strength of solution in terms of ester becomes 0.1M. Immediately 2 mL of aliquot of the reaction mixture was withdrawn and allowed to run into a conical flask containing 25mL of ice cold water so that the reaction may be arrested quickly. The acid of the solution was titrated as soon as possible by means of standard baryatha solution using phenolphthalein as indicator. The moment, at which half of the aliquot was added into the ice cold water, the stop clock was started. This time has been considered as the starting time or zero time. Taking into account of zero time, kinetics of reaction was studied by estimating the amount of remaining ester at definite desired interval of time. This reading was recorded as T_t .

RESULTS AND DISCUSSION

Solvent Effect Dependence and Rate Constant

The rate of hydrolysis of Butyl formate has been measured in water-DMSO medium by the slope of $\log k$ against time (Table-2 and Fig-1). The plot of $\log k$ against reciprocal of time has been found to be linear. The retardation of rate with increase solvent composition may be explained on the basis of the fact that the formation of polarised transition state is favoured with increased proportion of DMSO. This fact is also supported by Hugh and Ingold (Hughes E.D, Ingold C.K., 1935) qualitative theory. The rate determines the step of hydrolysis of ester is an addition of hydroxyl ion to the carbon of carbonyl group and after which rapid reaction with water is followed. Hence, if the activity of hydroxyl ion decreases, the reaction-rate must be decreased as suggested by Tommila et al. 1935. The lower the rate in water-ethanol mixture suggested that interaction between water and DMSO increases with increased concentration of free water available for solvation of hydroxyl ion. The curve of $\log k$ against mole fraction represents smooth decrease (fig-1), which implies that solvation of hydroxyl ion is stronger and hence the values of rate constant decreases (M.S. Metwally, 1992, Singh, AK, 2021).

Table 1. Bimolecular rate constant $k \times 10^4 (\text{dm}^3/\text{mole}/\text{min})$

Temp in °C	% of DMSO				
	30%	40%	50%	60%	70%
20°C	74.98	64.56	53.70	41.68	32.35
25°C	162.18	137.72	116.14	94.40	77.62
30°C	330.36	316.22	242.66	206.53	175.79
35°C	653.13	568.85	489.77	436.51	380.18
40°C	1318.25	114.15	1000.00	931.10	860.99

Table 2.log k values with different mole %

Percentage of DMSO	Mole%	4+ log k				
		20°C	25°C	30°C	35°C	40°C
30	9.77%	1.875	2.210	2.519	2.815	3.12.
40	14.40%	1.810	2.139	2.500	2.755	3.060
50	20.17%	1.730	2.065	2.385	2.690	3.000
60	27.49%	1.620	1.975	2.315	2.640	2.969
70	37.09%	1.510	1.890	2.245	2.580	2.935

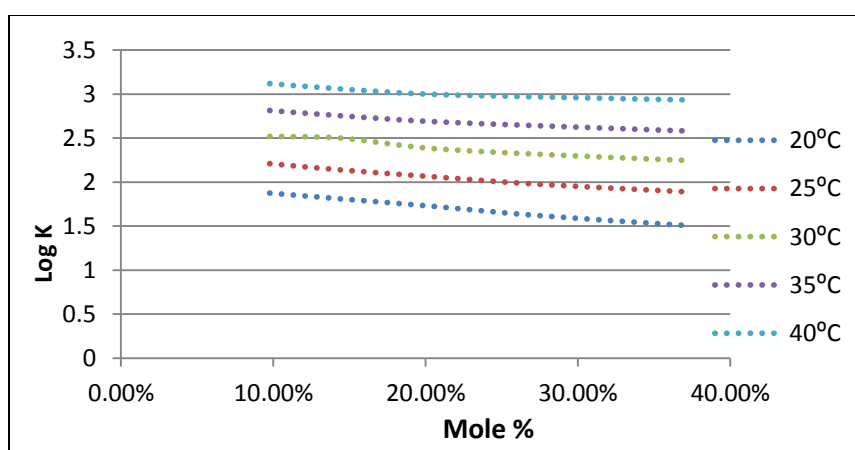


Fig. 1.Plots of log k with mole %

Activation Energy (E_c) and Rate of Reaction

Arrhenius plots (Log k against $1/T$) has been used to calculate value of activation energy (E_c). Table-4, collects the obtained values of activation energies under different solvent composition. The increase in (E_c) values with increase in solvent composition has been noticeable because it will only happen when there is solvation change taking place either in initial level or transition level or both.

The increasing value of (E_c) as a function of solvent composition indicates that solvation occurs at initial level whereas desolvation takes place at transition level(Singh A.K..et.al, 1984) .

Table 3. Different log k values as a function of temperature

Temp in °C	$10^3/T$	4 + Log k				
		30%	40%	50%	60%	70%
20°C	3.412	1.875	1.810	1.730	1.620	1.510
25°C	3.355	2.210	2.139	2.065	1.975	1.890
30°C	3.300	2.519	2.500	2.385	2.315	2.245
35°C	3.247	2.815	2.755	2.690	2.640	2.580
40°C	3.195	3.120	3.060	3.000	2.969	2.935

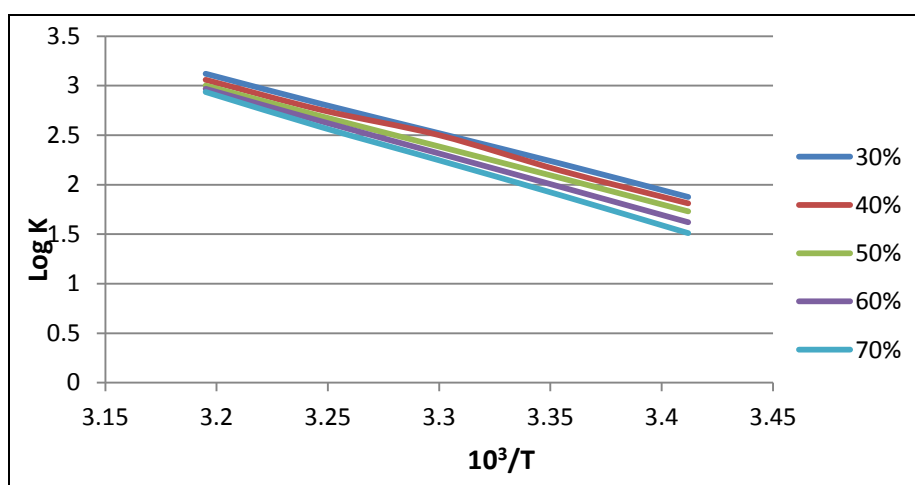
Fig- 2. Plots of log k with $10^3/T$

Table 4. Iso- Composition activation energy at different solvent fraction

% of E_c	30%	40%	50%	60%	70%
E_{exp} in KJ/mole	109.60	110.65	113.02	119.79	124.92

Table 5. The values log k_{DPT} at different D

Temp in °C	$10^3/T$	D=68	D=70	D=72	D=74	D=76
20°C	3.413	1.380	1.460	1.560	1.650	1.740
25°C	3.356	1.820	1.905	1.990	2.075	2.160
30°C	3.300	2.240	2.315	2.390	2.465	2.530
35°C	3.247	2.620	2.680	2.740	1.790	2.859
40°C	3.195	2.990	3.055	3.120	3.175	3.230

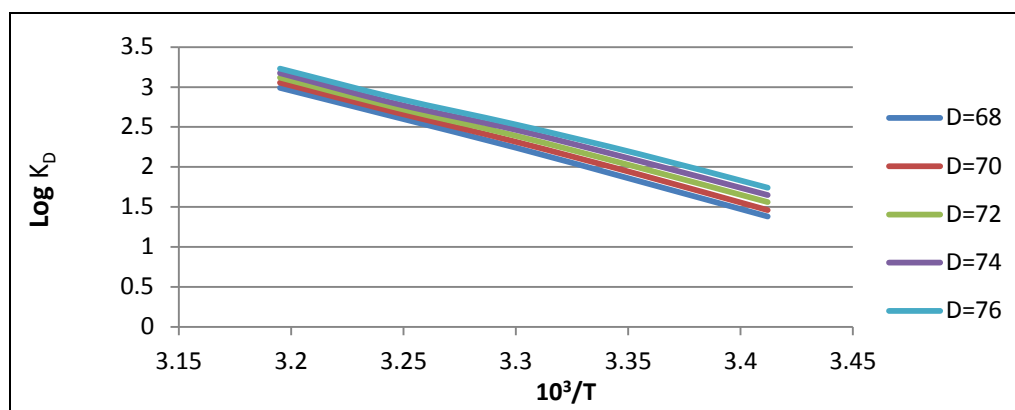


Fig. 3. Variation of $\log k_d$ with $10^3/T$

Dielectric Effect on reaction rate

The another aspect of effect solvent may also be considered by observing the effect of dielectric constant D on reaction rate. If there is an increase in rate, it is found to increase in D whereas the rate decreases with decrease in D . The dielectric constant values are obtained by interpolation of Akerlof data (Akerlof G., 1932). Linear relationships are obtained between $\log k$ and $D-1/2D+1$ for dipole-dipole interaction as given by Laidler (Laidler K.J. and Landskroener P. A., 1956). However, for ion-dipole linear relations are obtained by plotting $\log k$ and $\log D$ or $\log k$ against $1/D$. With the help of slopes of plots of $\text{Log } k_D$ against reciprocal of absolute temperature, the iso-dielectric values has been calculated [Table-5, Fig-3] with the help of slope of different linear line. The depletion in (E_D) with decreasing D [Table-6], showed that depletion in (E_D) values followed similar trend as (E_c) values with increasing proportion of solvent composition (RK. Wolfod. 1964, Bano Arjuman, Singh AK., 2017, Singh A K. Bano Arjuman. 2019).

Table 6. Calculated values of (E_D) at constant D

Dielectric constant(D)	D=68	D=70	D=72	D=74	D=76
E_D in kJ/mole	137.28	136.53	133.20	130.33	125.22

CONCLUSION

The gradual decrease of rate is constantly found with increased proportion of solvent composition due to increased concentration of free water available for solvation of hydroxyl ion. The increase of activation energy with increasing composition of solvent indicates desolvation in transition state and solvation in initial state. Dielectric value follows similar trend as iso-composition activation energy.

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