

# Kinetics of the Alkaline Solvolysis of 3-chloropropionate Ion in Water-tert.butyl Alcohol Solution

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**Summary:** The rates of alkaline solvolysis of 3-chloropropionate ion at four different temperatures 30, 37, 43 and 57°C in water-tert. butyl alcohol have been measured. The rates of solvolysis were found to be second-order overall and first-order with respect to each 3-chloropropionic acid and hydroxide ions concentrations. There is no simple correlation between the dielectric constant "D" and the rate constant "k". The addition of tert. butyl alcohol to water causes an increase of the rate in a non-linear form. The activation parameters  $E_a$ ,  $\Delta H$ ,  $\Delta S$  for the solvolysis reaction pass through a minimum value at about 0.89 then followed by a maximum value at about 0.97 water mole fractions. The results and the obtained data were discussed.

## Introduction

For many solvolysis reactions carried out in aqueous-organic mixed solvents, the activation enthalpy and entropy pass through a maximum value followed by a minimum value as the solvent composition is varied[1-5]. The position and depth of the maximum and minimum are dependent upon the substrate and the non aqueous component of the solvent mixture. If the maximum-minimum behaviours in the various activation parameters are related to the same physical phenomena, it would be expected that the variation of these parameters with changes in the organic component of the solvent mixture should be parallel to one another[3]. For this reason, we have studied the alkaline hydrolysis of 3-chloropropionate ion in a series of water-tert. butyl alcohol in order to learn more about solvent effect upon reaction rates.

## Experimental

Aldrich chemical pure 3-chloropropionic acid was used after further recrystallisation from ether and kept dried in a desiccator. Tert.butyl alcohol

reagent grade was distilled (b.p. 82.9°C) and the middle fraction was used. Twice-distilled water and the purified alcohol were used to prepare all the solutions. All solvent mixtures used throughout this investigation were mixed by volume, and the mole fractions and weight percentage were calculated making use of the density of pure components[6]. Enough of each solvent mixture was to complete the series of studies. Apparatus, techniques and procedure were conducted as previously described[7].

The reaction mixtures were prepared by mixing known amounts of 3-chloropropionic acid, base, tert.butyl alcohol and/or water. Solutions of each reaction mixtures were kept in air thermostat adjusted at the desired temperature.

The solutions were then quickly mixed and the initial concentration of the base was then determined by titration with standardised hydrochloric acid solution.

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At higher alcohol concentrations, the reaction mixtures solutions are turbid due to phase separation which is more noticeable at higher hydroxide concentrations and lower temperatures. Thus, we limited our kinetic runs to solvent mixtures containing less than about 50% by volume tert.butyl alcohol. Under these conditions the reaction mixtures were clear and the results were reproducible giving rise to strictly second order behaviour.

### Results and Discussion

The rate of alkaline solvolysis of 3-chloropropionate ion in a series of water/tert.butyl alcohol mixtures in the investigated range of the mixed solvent was found to follow the second order expression

$$k = \frac{2.303}{(a-b)t} \log \frac{b(a-x)}{a(b-x)} \quad (a \neq b)$$

where "x" is the number of mole/L reacting in time "t", "a" is the initial concentration of 3-chloropropionic acid, "b" is the initial concentration of base and "k" is the specific reaction rate constant.

The rate constants were evaluated from the slopes of the straight lines obtained when  $\log b(a-x)/a(b-x)$  were plotted against time "t".

Fig. 1 shows typical plots obtained in water-tert. butyl alcohol solutions at 43°C. The calculated values of the rate constants in the various solvent mixtures and at the different temperatures are given in Table 1.

The rate constants represent the average of at least four determinations. For each solvent mixture, "D" was calculated from the experimental values for the pure solvents[6] assuming linear dependence of dielectric constant on composition. It is clear from Table 1 that the rate constant of the reaction increases as the dielectric constant of the medium decreases.

Fig. 2. shows a plot of the second-order rate constants versus solvent-composition. It can be seen that the rate of reaction increases in a non linear manner as the tert.butyl alcohol constant of the solvent mixture increases and that the rate first in-

creases slowly up to about 40% by weight tert.butyl alcohol and then more rapidly on further increase in the alcohol concentration. Suspension of tert.butyl alcohol in water at higher alcohol con-

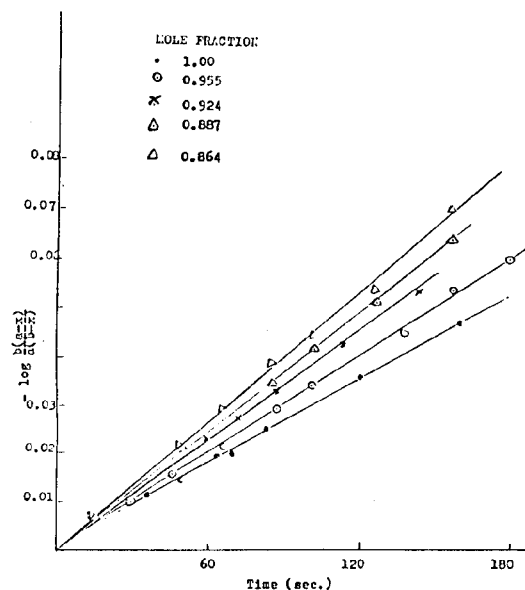


Fig. 1: Second-order plots at 43°C of chloropropionic acid in water/t.butyl alcohol solvent mixtures (mole fraction).

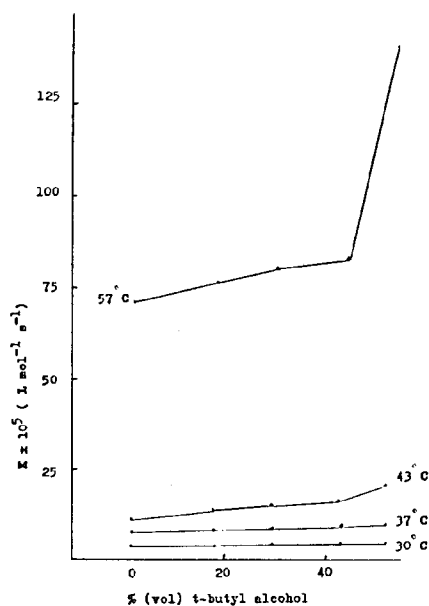


Fig. 2: Dependence of the second-order rate constant on solvent composition.

Table-1: Dependence of the rate constant K on the dielectric constant of the medium for the solvolysis of 3-chloropropionate ion in water/tert.butyl alcohol solutions.

T <sup>o</sup> C	Solvent Water/t.butyl alcohol (V/V)	Medium Dielectric Constant	Rate Constant K x 10 <sup>5</sup> 1 mol <sup>-1</sup> s <sup>-1</sup>
30 <sup>o</sup> C	Water	77.40	2.56
	80-20	66.05	2.61
	70-30	60.03	2.95
	60-40	54.35	3.40
	55-45	51.35	3.51
37 <sup>o</sup> C	Water	74.85	6.60
	80-20	63.95	7.40
	70-30	58.35	7.70
	60-40	52.50	7.85
	55-45	49.50	8.70
43 <sup>o</sup> C	Water	72.70	11.20
	80-20	62.15	12.80
	70-30	56.60	14.50
	60-40	50.90	15.80
	55-45	47.90	19.95
57 <sup>o</sup> C	Water	67.70	70.60
	80-20	57.95	76.00
	70-30	52.70	80.00
	60-40	47.25	83.10
	55-45	44.30	141.30

centration (above 40%) might have interfered the determination of the rates. Fig. 3 illustrates the plot of log k versus 1/D for each investigated temperature. These plots show that there is no simple correlation between the dielectric constant "D" and the rate constant k, and that the values are not even in the same manner predicted by simple electrostatic theory[8].

The prediction of the dielectric theory of medium effects sometimes fit and sometimes fail to fit the actual behaviour of polar reaction rates[9]. This failure of the electrostatic picture might be because its general postulates are too simplified and

also because specific solvation effects[10] other than those desirable in the electrostatic theory in terms of the dielectric constant can be expected to be of importance[10,11] in controlling the reaction rate.

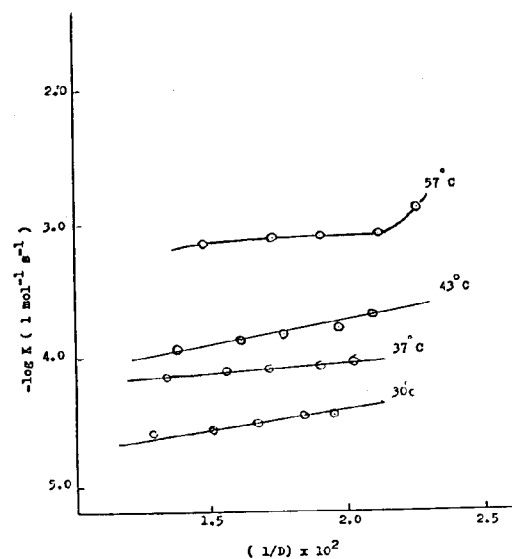


Fig. 3: Dependence of the second-order rate constant of 3-chloropropionate ion on the dielectric constant of the medium.

Difference in the degree and type of solvation of the reactants and activated complex in mixed solvent can change either the rate or the rate and mechanism of chemical reaction.

The Arrhenius equation was found to be obeyed satisfactorily since good straight lines were obtained on plotting the logarithm of the experimental reaction rate constant versus the reciprocal of the absolute temperature as shown in Fig. 4.

The thermodynamic parameters of activation  $E_a$ ,  $\Delta S$ ,  $\Delta H$  and  $\Delta G$  are usually taken as a measure of the solvation effects. Each of these thermodynamic properties represents the difference between the corresponding properties of the transition state and the ground state in the medium[11].

Various aspects of solvation, preferential solvation as well as a change in the solvent composition usually affects both the enthalpy and entropy of

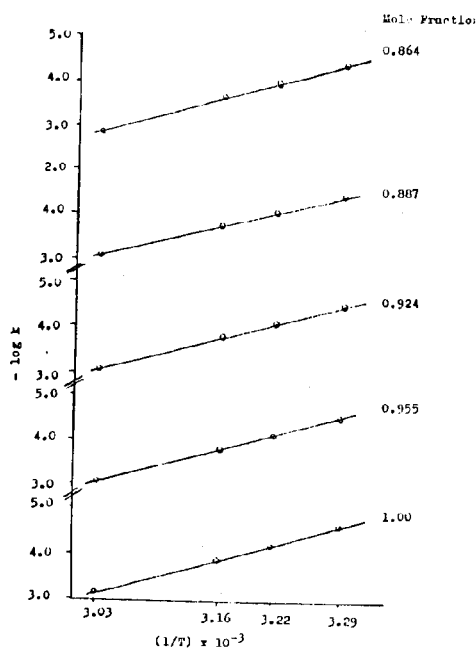


Fig. 4 Arrhenius plots of  $\ln Kvs 1/T$  for solvolysis of 3-chloropropionic acid in tert.butyl alcohol-water solvent mixtures.

activation[9]. The variation of the enthalpy of activation,  $\Delta H$  and the entropy of activation,  $\Delta S$  for the different solvent compositions at 30°C are given in Table 2 and shown in Fig. 5.

From this figure, it is seen that on increasing the concentration of tert.butyl alcohol in the solvent mixture each of the activation parameters  $E_a$ ,  $\Delta H$  and  $\Delta S$  first increases slightly to a maximum value at about 0.97 water mole fraction followed by a decrease to a minimum value at about 0.89 water mole fraction and then finally it increases again. The observed maxima-minima behaviour in the activation parameters lie near the pure water end of the composition scale.

It can also be seen that a large entropy change is associated with a large enthalpy change and a small entropy change with a small enthalpy change. This behaviour is characteristic of reactions involving moderate change in structure of solvent composition[9]. This characteristic behaviour of the activation enthalpy and entropy has been observed for many solvolytic reaction[7,12,13] and under a variety of conditions seems to reflect a common sol-

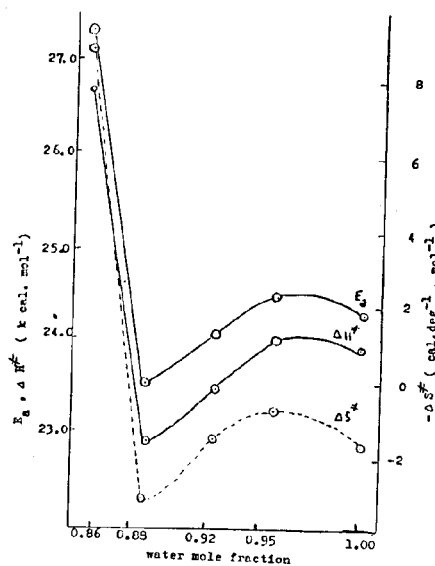


Fig. 5: Dependence of the activation parameters,  $E_a$ ,  $\Delta H$  and  $\Delta S$  on solvent composition for solvolysis of 3-chloropropionate ion in water/t.butyl alcohol solvent mixtures.

Table 2: The activation parameters for the solvolysis of 3-chloropropionate-ion in water/tert.butyl alcohol solvent mixtures at 30°C.

Water/tert.butyl alcohol Composition		$E_a$	$\Delta H$	$-\Delta S$	$\Delta G$
water-alc	water				
(V/V)	mole fraction				
water	1.000	24.19	23.59	1.78	24.13
80-20	0.955	24.47	23.87	0.72	24.09
70-30	0.924	24.12	23.52	1.66	24.04
60-40	0.887	23.57	22.97	3.27	23.96
55-45	0.864	27.36	26.76	9.04	24.02

$E_a$  : k cal mol<sup>-1</sup>  
 $\Delta H$  : k cal mol<sup>-1</sup>  
 $-\Delta S$  : cal deg<sup>-1</sup> mol<sup>-1</sup>  
 $\Delta G$  : k cal mol<sup>-1</sup>

vent behaviour, going from reactants to activated complex, solvent molecules are also involved in the activation process and their effects can dominate the effect that can be attributed to the reacting molecules themselves. The solvent molecules are to some extent oriented about solute and this orientation imposes a restriction on the motion of solvent molecules. This solvation effect is an appreciable factor in determining the activation parameter of the system. Changes in the thermodynamics of solvation process are included in the activation parameters.

There is an evidence [11,14,15] which further support the conclusion that the maximum-minimum behaviour may be related to the accompanying solvent reorganisation attending the activation process for solvolysis in binary alcohol-water system[16].

Aqueous-organic solvents are particularly interested because the organic component can interact strongly with the three-dimensional hydrogen bonded structure of water. This contradiction may increase or decrease the regularity of the solvent structure and hence effect the rate of reactions. This behaviour could be related to the accompanying solvent-reorganization attending the activation process for the system.

In such cases it is concluded that the partial breakdown of solvent structure as a consequence of charge separation in the activation process parallels the sensitivity to change in the solvent composition.

The results observed in this study indicate that in t.butyl alcohol/water solvent mixtures, the activation parameters show a great variation with changing solvent composition. The calculated values of  $\Delta G$  are also listed in Table (2) and it can be seen that they do not change much with solvent composition. This must be due to the linear compensation between  $\Delta H$  and  $\Delta S$ .

The plot of  $\Delta H$  versus  $\Delta S$  gave rise to a straight line as shown in Fig. 6. The linear  $\Delta H$ ,  $\Delta S$  relationships have also been observed for many systems [3,16].

However, this behaviour is expected if the solvents in a system performed closely similar roles in

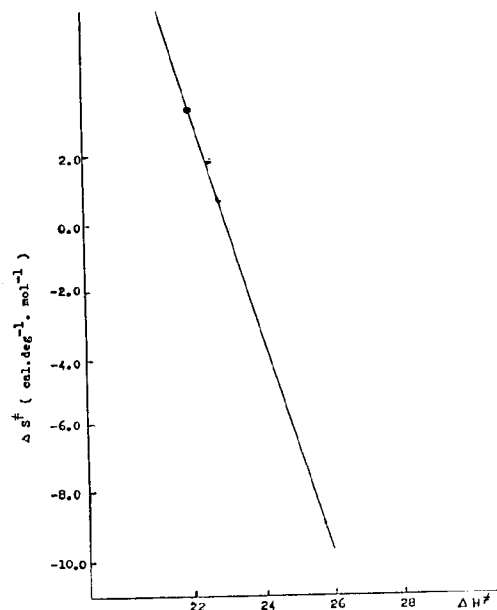


Fig. 6: Plots of  $\Delta H$  vs  $\Delta S$  for the alkaline solvolysis of 3-chloropropionate ion in t. butyl alcohol/water solvent mixtures.

the reaction[9]. This is a characteristic of reactions involving moderate changes in the substrate structure or solvent composition.

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