

Kinetic Solvent Effect on Hydrolysis of Ethylchloroformate in Binary Aqueous Mixtures

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Summary: The kinetics of the neutral hydrolysis of ethylchloroformate have been studied in water-acetonitrile and in water-tetrahydrofuran mixtures in the temperature range of 30-50°C. The hydrolysis reaction follows a first-order rate law. The rates of the hydrolysis showed maxima at 0.9 and at 0.92 water mole fraction in water-acetonitrile and in water-tetrahydrofuran mixtures, respectively. The activation parameters ΔH^\ddagger and ΔS^\ddagger showed minima at nearly the same solvent composition range. The significance of these results from the viewpoint of the changing of solvent structure in such mixture is discussed.

Introduction

In the last three decades considerable effort has been expended on developing suitable models to describe the nature of liquids and the way in which the structure of the bulk liquid is modified by introduction of a solute, i.e., a neutral molecule, dissociated ion or other solvent [1-6], acting as structure maker or breaker. Mixed solvents in which water was frequently one component, provided a graded series of the highly intensive investigated solvolytic media in which to explore relation between rates, mechanisms and the effect of changing solvent properties [6-12].

In order to investigate further how far the solvent and thermodynamic properties of aqueous binary mixtures are reflected on kinetic parameters, we report in this work the results of the study of the kinetics of the hydrolysis of ethylchloroformate in water-tetrahydrofuran solutions. These co-solvents interact with water [13,14], so that the relative importance of structural changes in solvents can be put into evidence.

Results and Discussion

The rate of the hydrolysis were determined for a range of mixtures containing water-acetonitrile and water-tetrahydrofuran solutions at four temperatures in the temperature range 30-50°C. Three determinations were done for each composition at each temperature and the reproducibility was found to be good. Constant in-

tegrated values for the first order rate constant, k , were obtained throughout each run. The k -values at each composition at 30°C are collected in Table 1. The obtained data were analysed by the least-squares procedure using a computer program which produces values for ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger , the enthalpy, entropy and free energies of activation at 30°C together with their standard deviations. These activation parameters are also given in Table 1.

As shown in Table 1, there is large sensitivity of the rate constant to solvent composition. The ratio of the highest to the lowest value at 30°C is *ca.* 100. The observed changes can be seen clearly when representing (k_x/k_1) versus water mole fraction x , as shown in Fig. 1. k_x and k_1 are values of k at x and 1 respectively. At the other temperatures, the curves obtained are similar. In both solvent mixtures the ratios k_x/k_1 tend to increase slightly with increasing water mole fraction and reach maxima at the rich water solvent composition and then decrease. The similarity in the profiles of k_x/k_1 curves indicate that the hydrolysis mechanism is not altered with changing the co-organic solvents, i.e. acetonitrile and tetrahydrofuran solvents having the same effect on the rate of the reaction.

In order to explain the effect of solvent on the hydrolysis rate of ethylchloroformate, it is necessary to throw light on the mechanism of the reaction. The first order kinetic data suggest the following mechanism [16,17].

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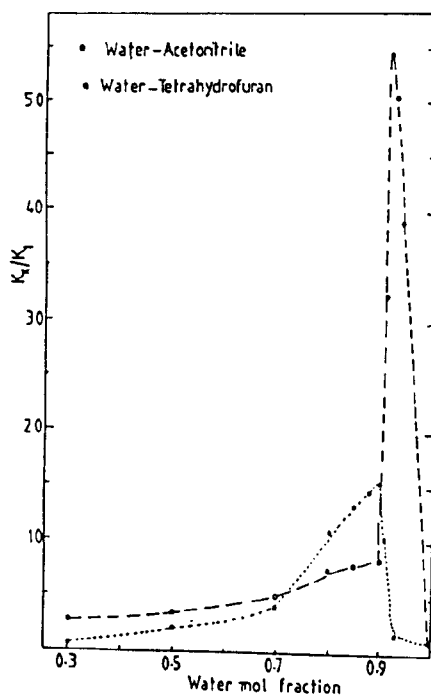
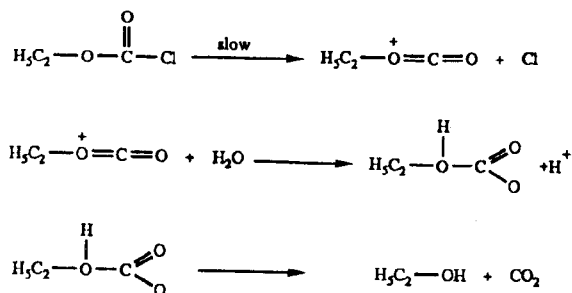


Fig. 1: Variation of k_2/k_1 vs. water mole fraction (x) at 30°C for the hydrolysis of ethylchloroformate in binary aqueous mixtures.

According to the above mechanism it is expected that as the solvent polarity increases, the reaction rate increases [7]. However, data in Table 1 show that this is only satisfied at solvent composition less than 0.9 water mole fraction. It reveals that the dielectric constants of the solvent media can not be the only solvent parameters involved which affects the kinetics of our solvolysis reaction.

It is believed that the hydrolytic reactions in water reflect and indeed are to some considerable extent determined by the properties of liquid water

Table 1: Kinetic and thermodynamic data for the hydrolysis of ethylchloroformate in water-acetonitrile and in water-tetrahydrofuran solutions at 30°C.

Water fraction	$k \cdot 10^5$ (s^{-1})	ΔH^\ddagger (k.cal/mol)	ΔS^\ddagger (cal/mol.K)	ΔG^\ddagger (k.cal/mol)
Water-Acetonitrile Solutions				
0.30	0.42 ± 0.02	21 ± 1	15.2 ± 0.7	25 ± 1
0.50	2.25 ± 0.03	19.4 ± 0.7	15.5 ± 0.2	24.1 ± 0.8
0.70	3.2 ± 0.1	17.2 ± 0.6	22.0 ± 0.7	24 ± 1
0.80	8.6 ± 0.3	13.3 ± 0.4	33 ± 1	23.3 ± 0.7
0.85	10.3 ± 0.3	11.5 ± 0.4	39 ± 1	23.0 ± 0.7
0.88	11.3 ± 0.3	10.0 ± 0.3	43 ± 2	23.0 ± 0.9
0.90	11.9 ± 0.3	9.7 ± 0.3	44 ± 1	23.1 ± 0.6
0.91	8.1 ± 0.5	9.9 ± 0.2	44 ± 2	23.3 ± 0.8
0.93	1.25 ± 0.06	10.0 ± 0.5	48 ± 2	24 ± 1
1.00	0.77 ± 0.02	11.2 ± 0.3	45 ± 1	24.7 ± 0.6
Water-Tetrahydrofuran Solutions				
0.30	2.1 ± 0.1	17.71 ± 0.6	21.5 ± 0.7	24.2 ± 0.8
0.50	2.7 ± 0.1	16.9 ± 0.4	23.6 ± 0.9	24.0 ± 0.7
0.70	4.3 ± 0.1	14.0 ± 0.3	32.0 ± 0.6	23.7 ± 0.5
0.80	5.8 ± 0.2	13.5 ± 0.4	33 ± 1	23.5 ± 0.7
0.85	6.2 ± 0.2	13.3 ± 0.4	34 ± 1	23.5 ± 0.7
0.90	6.5 ± 0.2	12.9 ± 0.4	35 ± 1	23.5 ± 0.7
0.91	25.0 ± 0.8	11.0 ± 0.5	39 ± 2	23 ± 1
0.92	42 ± 1	6.5 ± 0.2	52 ± 2	22.3 ± 0.8
0.93	39.0 ± 0.8	6.3 ± 0.1	53 ± 1	22.4 ± 0.4
0.94	30.0 ± 0.8	8.1 ± 0.3	48 ± 1	22.6 ± 0.6
1.00	0.77 ± 0.02	11.2 ± 0.3	45 ± 1	24.7 ± 0.6

[18]. Water consists of a mixture of fluctuating regions of three-dimensional hydrogen bonded polymers in equilibrium with randomly arranged water monomer molecules. A considerable fraction from acetonitrile and tetrahydrofuran molecules joined in chains and rings, but they do not seem to participate in the formation of three-dimensional clusters that are characteristic of water [1,13]. On the basis of this solvent structure, the maxima in k -values appearing on adding co-organic solvents to water could be attributed to the effect of the release of water monomers by possible breakdown of three dimensional hydrogen bonded water structure by adding the co- organic solvents [19-21] and or due to the effect of initial and transition state solvation. The polar transition state (II) is presumably preferentially solvated by water. On the other hand, the ester probably is preferentially solvated by co-organic solvent, tetrahydrofuran and acetonitrile [22]. Thus a reorganization of solvent molecules occurs on going from the initial state to the transition state. The solvent reorganization undoubtedly becomes more radical in solvent mixtures in which the breaking of the three dimensional water structures has occurred.

The behaviour of activation parameters towards solvent variation reflects to a large extent the changes occurring in the structural features surrounding the reactant and the transition state molecules as well the breaking of solvent structure during the attainment of the transition state [24-27]. In our case, the variation of the activation parameters with solvent composition is listed in Table 1 and represented for ΔH^\ddagger and ΔS^\ddagger in Fig. 2. From which, it is seen that the values of the entropy, ΔS^\ddagger , are negative in all the solvent mixtures investigated. It indicates that in all of these solvent compositions the activated complex structure is relatively more ordered than the structure of the reactants. Fig. 2 shows also minimum in each of ΔH^\ddagger and ΔS^\ddagger profiles at nearly the same solvent

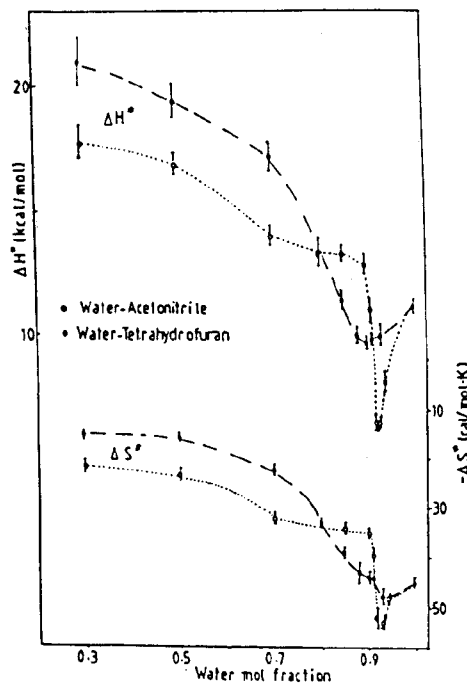


Fig. 2: Dependence of the activation parameters on solvent composition at 30°C.

composition range in which the maxima in rate constants were observed (Table 1). These minima in the activation parameters could be also attributed to the change in the structure stability of the solvent with changing the composition, as discussed above. Hence, the behaviour of ΔH^\ddagger and ΔS^\ddagger is interpreted on the basis that the breakdown of solvent structure, as a consequence of charge separation in

the activation process, parallels the sensitivity to changes in the solvent composition [1,18]. It is also seen from Fig. 2 that in the water rich solvent composition, the minima in the values of the activation parameters (ΔH^\ddagger and ΔS^\ddagger) relative to those obtained in pure water are lower in water-tetrahydrofuran as compared to that found in water-acetonitrile solutions. It indicates that the addition of small increments of tetrahydrofuran to water causes more fluctuation in solvent structure during the activation process than that obtained from the addition of acetonitrile.

The free energies of activation, ΔG^\ddagger , listed in Table 1 do not change much with solvent composition. This is attributed to a linear compensation between ΔH^\ddagger and ΔS^\ddagger . This compensation phenomenon was observed for many solvolysis reactions [27,28] and takes place because the freedom of movement of molecules (which affects ΔS^\ddagger) is related to the bond strength (which affects ΔH^\ddagger). The isokinetic relationship was found with values of 338 and 352 K for water-acetonitrile and water-tetrahydrofuran solutions, respectively.

Experimental

Pure ethylchloroformate (Cambrian) was redistilled before use. Acetonitrile (Merck; Max. H₂O 0.03%) tetrahydrofuran (Merck; Max H₂O 0.06%) and doubly distilled water were used to prepare all the solutions. All solvent mixtures used throughout the investigation were mixed by weight, and mole fractions were then calculated. Attempts to extend the range of solvent mixtures were thwarted by low solubility.

The rate of hydrolysis reaction was followed by conductance measurements in the temperature range 30 - 50°C. Conductance *versus* concentration calibration curves were constructed, using completely reacted solutions whose chloride ion contents were determined by a titrimetric method using Volhard's technique [15]. Successive dilutions of these solutions were made to cover the complete range of the conductance observed in the kinetic experiments. Large scale calibration curves were obtained at several experimental temperatures in the various solvent mixture, and they were used to convert the measured conductivity to molar con-

centrations. The range of initial concentration suitable for the kinetic studies on the halide was determined by trial and error. In the concentration range 0.01 to 0.1 molar ethylchloroformate, kinetic results were reproducible and exhibited strictly first order behaviour with small random experimental error.

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