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SOLVOLYSIS RATES AND ACTIVATION PARAMETERS OF PHENYLCHLOROFORMATE IN WATER-TETRAHYDROFURAN AND WATER-DIOXANE MIXED SOLVENTS

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ABSTRACT

The rates of hydrolysis of phenylchloroformate were measured over the temperature range 30-55 °C in water-tetrahydrofuran and water-dioxane mixtures of different compositions. The influence of solvent variation on reaction rate was examined in terms of changes in the activation parameters. The activation parameters $\Delta H^{\star}$ and $\Delta S^{\star}$ for the solvolysis reaction showed minima at a water mole fraction of about 0.5 in water-tetrahydrofuran solvent mixtures, whereas these parameters increased continuously with increasing concentration of water in water-dioxane solvent mixtures. The results are discussed in terms of the polarity of the medium and the change in the solvent structure.

INTRODUCTION

Kinetic solvent effects on reactions in different media are often rationalized in terms of solvent polarity, which sums up all the specific and non-specific interactions of the media with initial and transition states [1]. However, the interpretation of the kinetic results on the basis of the solvent polarity of the medium sometimes fails and sometimes succeeds.

Many works [2-7] have been published recently on the rationalization of kinetic solvent effects on various reactions using a thermodynamic approach. These essentially entail the determination of the kinetic solvent effects by splitting the activation parameters into contributions from initial and transition states, and hence attempting to correlate and to understand the behaviour of the activation parameters in terms of the relevant physicochemical properties of the solvents. In order to investigate further how far the thermodynamic properties of aqueous binary solvent mixtures are re-

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flected in the kinetic parameters, we report in this work the results of the hydrolysis of phenylchloroformate in water–tetrahydrofuran (THF) and water–*p*-dioxane solutions.

EXPERIMENTAL

Pure phenylchloroformate (Merck) was used for the kinetic measurements. Doubly distilled water was used throughout and the co-solvents tetrahydrofuran (THF) and *p*-dioxane were of AnalaR grade. The mixed solvents were prepared by mass dilution.

The rate of the hydrolysis reaction was followed conductimetrically at six equidistant temperatures over the temperature range 30–55 °C. The details of the procedure are described elsewhere [8]. The rate constants were determined by Guggenheim's method [9] with a maximum error estimated as ±5%. Activation enthalpies $\Delta H^\star$ and entropies $\Delta S^\star$ were calculated by a linear least-squares method, using Eyring's equations [9].

RESULTS

The kinetic results show that the rates of hydrolysis of phenylchloroformate ester in water–THF and water–dioxane solutions follow the first-order rate law. Table 1 shows the observed rate constants at 30 °C under the

TABLE 1

Rate constants and activation parameters (at 30 °C) for the hydrolysis of phenylchloroformate in water–tetrahydrofuran and water–dioxane solutions

Water mole fraction	$k \times 10^6$ (s^{-1})	$\Delta H^\star$ (kJ mol^{-1})	$-\Delta S^\star$ (J mol^{-1} K^{-1})	$\Delta G^\star$ (kJ mol^{-1})
Water–THF				
0.2	0.291 ± 0.008	62.97 ± 0.51	161.0 ± 1.2	111.71 ± 0.86
0.3	0.509 ± 0.002	61.30 ± 0.40	162.0 ± 0.9	110.45 ± 0.67
0.4	1.11 ± 0.04	55.10 ± 1.11	175.9 ± 4.5	108.40 ± 2.47
0.5	24.50 ± 1.11	32.51 ± 0.81	224.8 ± 3.1	100.62 ± 1.75
0.6	26.71 ± 1.06	35.19 ± 0.92	215.5 ± 3.9	100.45 ± 2.10
0.7	7.81 ± 0.23	43.51 ± 1.02	198.0 ± 5.1	106.27 ± 2.56
Water–dioxane				
0.4	3.34 ± 0.11	30.04 ± 1.20	249.5 ± 3.6	105.6 ± 2.29
0.5	1.22 ± 0.02	40.08 ± 1.32	224.7 ± 5.2	108.15 ± 2.90
0.6	1.41 ± 0.03	46.02 ± 1.14	203.8 ± 4.1	107.74 ± 2.38
0.7	22.11 ± 0.31	65.77 ± 1.41	115.9 ± 2.2	100.87 ± 2.08
0.8	24.90 ± 0.32	96.32 ± 2.11	14.1 ± 0.4	100.58 ± 2.23

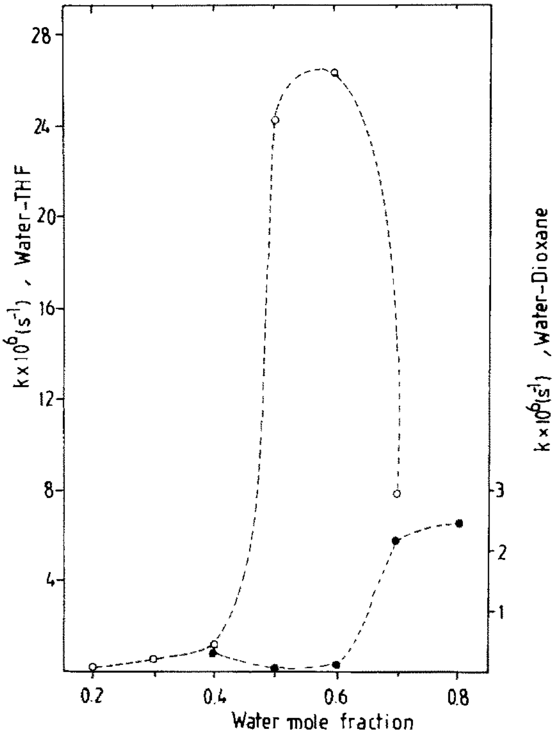


Fig. 1. Dependence of the first-order rate constants on solvent composition at 30 ° C: ○, water–THF; ●, water–dioxane.

limiting conditions used in this work for the chosen binary mixtures at different mole fractions. At least three kinetic runs were carried out for each composition at each temperature. The temperature dependence of the rate constants of the hydrolysis reaction was analysed by a least-squares procedure using a computer program which produces values for $\Delta H^{\star}$, $\Delta S^{\star}$ and $\Delta G^{\star}$, the enthalpy, entropy and free energy of activation at 30 ° C, together with their standard deviations. The results of the application of this procedure to our data are given in Table 1. The effects of solvent composition on the specific rate constants and on the activation parameters at 30 ° C are presented in Figs. 1 and 2, respectively. At other temperatures, the curves obtained are similar.

DISCUSSION

The results listed in Table 1 show that the rate constant of the hydrolysis reaction is sensitive to solvent composition. The ratios of the highest rate constant to the lowest rate constant are 91.7 and 20.4 in water–THF and water–dioxane solutions, respectively. The observed changes in the rate

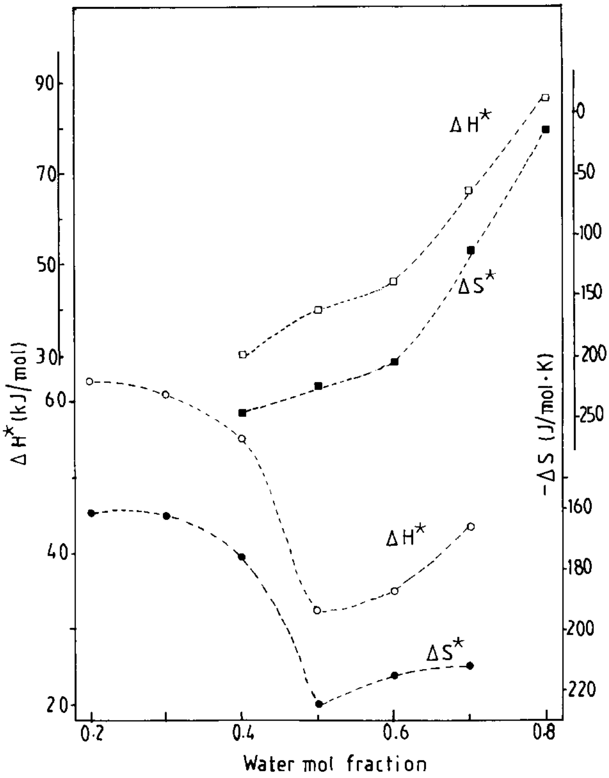
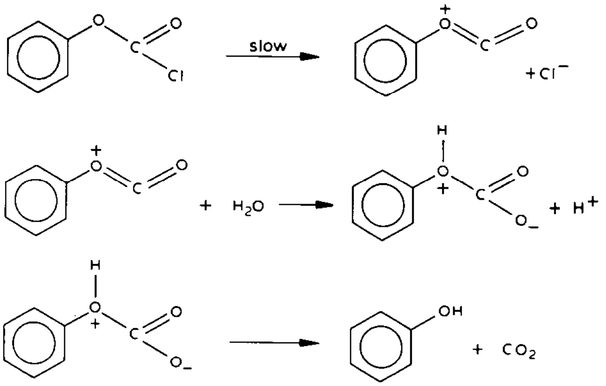


Fig. 2. Dependence of the activation parameters $\Delta H^{\star}$ and $\Delta S^{\star}$ on solvent composition at 30 ° C; □, $\Delta H^{\star}$ (water–dioxane); ■, $\Delta S^{\star}$ (water–dioxane); ○, $\Delta H^{\star}$ (water–THF); ●, $\Delta S^{\star}$ (water–THF).

constants k with solvent composition for the reaction under study are shown in Fig. 1. It can be seen that the rate constants increase with increasing water concentration in water–THF mixtures to a maximum at a water mole fraction of about 0.6; then they decrease. In water–dioxane mixtures the rate constants tend to decrease with increasing water concentration in the solutions to a minimum at a water mole fraction of about 0.5; then they increase. These results may indicate a change in the solvent structure of the binary solvent mixtures with a variation in solvent composition. Furthermore, the larger changes in the k values in water–THF relative to those in water–dioxane indicate that the structures of water–dioxane solutions may be more ordered than those of water–THF solutions, under the assumption that the mechanism is the same in both solvent mixtures.

The kinetics of the hydrolysis reaction suggest a mechanism [10,11] in which the rate-determining step is the ionization of the carbon–chlorine bond to give an acylium ion, which is stabilized by conjugation with the lone pair of electrons of the phenyl oxygen atom.



According to the suggested mechanism, the transition state is more polar than the ground state. Therefore, it is expected that as the solvent polarity increases the reaction rate increases. However, our results listed in Table 1 show that this is not the case in the investigated binary solvent mixtures. According to the electrostatic theory of the medium effect [12] the plot of $\ln k$ vs. $(D-1)(2D+1)^{-1}$ (where D is the dielectric constant of the medium) gives a straight line. However, this linear relation is not found for our data. The plots show non-linear curves with a maximum in the water–THF solutions and a minimum in the water–dioxane solutions. The use of $1/D$ instead of $(D-1)(2D+1)^{-1}$ does not improve the plot. This indicates that there is no simple correlation between the reaction rate constant and the dielectric constant of the medium [13]. In addition on application of the Grunwald Winstein relation [14] no correlation is found between the rate constants and the solvent ionizing power of the solvent mixtures. As indicated in the introduction, the usual approach of correlating the kinetic solvent effects with some of the widely used solvent polarity scales (which is thought to be feasible and useful for pure non-aqueous solvents) is difficult in most of the aquo-organic solvents because of scanty "solvent polarity" data. It is therefore better to analyze our data on the basis of solute–solvent interactions of the species involved and on the relevant physicochemical properties of the mixed solvents.

Table 1 shows that the values of the entropy of activation $\Delta S^{\star}$ are negative in all solvent mixtures investigated. This indicates that in all of these solvent mixtures the polar transition state is preferentially solvated by water molecules. Thus a reorganization of solvent molecules occurs on going from the initial state to the transition state. Although the transition state is obviously highly solvated relative to the initial state, the solvent reorganization is undoubtedly more radical in aqueous organic solvents where water is monomeric [15]. This explains the negative entropies of activation in the solvents investigated. It is seen in Fig. 2 that when the concentration of water is increased in water–THF mixtures $\Delta H^\star$ and $\Delta S^\star$ first decrease to a minimum at a water mole fraction of about 0.5 and then increase. The positions of the $\Delta H^\star$ and $\Delta S^\star$ minima appear to coincide. The changes in $\Delta H^\star$ and $\Delta S^\star$ amount to about 30.5 kJ mol^{-1} and 63.8 J K^{-1} mol^{-1}, respectively. In the water–dioxane solvent mixtures, the $\Delta H^\star$ and $\Delta S^\star$ values continuously increase with increasing concentration of water. The change in $\Delta H^\star$ amounts to 66.3 kJ mol^{-1} and that for $\Delta S^\star$ is 235.4 J K^{-1} mol^{-1} over the entire range of solvent composition. At high water concentrations, lower values of $\Delta H^\star$ are observed in water–THF mixtures compared with those observed in water–dioxane mixtures. However, at low water concentrations, the reverse behaviour is observed, i.e. $\Delta H^\star$ values in water–THF solutions are higher than those in water–dioxane solvent mixtures. These results may be due to a change in the stabilization of the transition state or the initial state with changing composition of the solvent mixtures. They possibly reflect the enhanced kinetic basicity of water molecules solvated by THF as compared with those solvated by dioxane in the higher water concentration region.

Dioxane is more inert and its interaction forces with water are less than THF. Taft–Kamlet parameters for hydrogen-bond acceptance (HBA) are 0.523 [16] and 0.386 [16] for THF and dioxane, respectively. The overall indices of polarity are 0.576 [16] and 0.553 [16] for THF and dioxane, respectively. These results may lead to the observed effects of the solvents on reactivity, which shows an almost regular increase in activation parameters with increasing mole fraction of water in the water–dioxane mixtures but an irregular variation in activation parameters with solvent composition with minima at a water mole fraction of 0.5 in water–THF solutions. In the latter system the higher polarity of the solvent molecules and the higher hydrogen bond acceptance (HBA) value lead to stronger interactions between the solvent molecules themselves and between the solvent molecules and the ground state and the transition state of the reactant. These interactions affect the solvent structure and lead to the extrema observed.

Significantly large changes in $\Delta H^\star$ and $\Delta S^\star$ with negligible change in $\Delta G^\star$ (Table 1) with varying solvent composition can normally be attributed to the enthalpy–entropy compensation effect [17]. Such a compensation effect generally results in a linear relationship between $\Delta H^\star$ and $\Delta S^\star$. The plots of $\Delta H^\star$ and $\Delta S^\star$ for the investigated ester are also essentially linear (Fig. 3). However, Peterson et al. [18] argued that the linear plots of $\Delta H^\star$ vs. $\Delta S^\star$ could be completely fortuitous for the following reason. Since both $\Delta H^\star$ and $\Delta S^\star$ are derived from the same equation with certain sets of data, then the random error in $\Delta H^\star$ is directly proportional to the random error in $\Delta S^\star$. Thus the measurements which involve a significant range of errors could lead to a linear relationship between $\Delta H^\star$ and $\Delta S^\star$. Our data show that the values of $\Delta H^\star$ change by 30.46 kJ mol^{-1} in water–THF and by

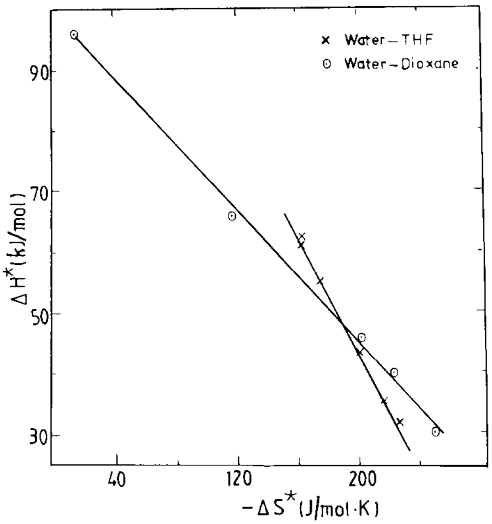


Fig. 3. Plot of $\Delta H^\star$ vs. $\Delta S^\star$ for the hydrolysis of phenylchloroformate in water–THF (×) and water–dioxane (⊙) solutions.

66.28 kJ mol^{-1} in water–dioxane. The $\Delta S^\star$ values change by 63.8 and 235.4 J K^{-1} mol^{-1} in water–THF and water–dioxane mixtures, respectively. These changes in $\Delta H^\star$ and $\Delta S^\star$ are much larger than the respective maximum standard deviations of these activation parameters. It is therefore difficult to believe that such large changes in $\Delta H^\star$ and $\Delta S^\star$ are due to random errors.

The behaviour of the activation parameters towards solvent change observed in this study is similar to that observed for many solvolytic reactions in aqueous–organic solvent mixtures under a variety of conditions [19–24]. The appearance of the minima in $\Delta H^\star$ and $\Delta S^\star$ values in water–THF mixtures is attributed to a change in structural stability with composition [25]. Hence, the behaviour of $\Delta H^\star$ and $\Delta S^\star$ 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 [25]. The disappearance of the extrema in the activation parameters in water–dioxane solvent mixtures is explained by the structural stability of these solvent mixtures compared with water–THF mixtures.

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