Kinetics of Acid-Catalysed Hydrolysis of Diethylsuccinate in Dioxane-Water Mixtures

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The specific rate constants k_1 and k_2 of the consecutive first-order acid-catalysed hydrolysis steps of diethylsuccinate in dioxane-water mixtures covering the range 0–95% (w/w) of dioxane are determined at 25–55 °C. As the concentration of dioxane increases, the rate of the reaction decreases to a minimum at about 90% (w/w) dioxane, after which it increases again. The ratio k_1/k_2 was found to be almost constant at the value 2.0. The activation energies of the reaction are independent of solvent composition. Available electrostatic theories regarding the effect of the dielectric constant on the rate are presented, from which the reaction is shown to be an ion-molecular dipole type of interaction. The thermodynamic parameters and the radii of the activated complex at different solvent compositions are calculated and discussed.

Introduction

Our knowledge about solvent effects on chemical reactions is well presented in [1]. Acid-catalysed consecutive ester hydrolyses have so far only been studied either in purely aqueous media or in mixed solvents of one composition [2–6]. In order to learn about the role of the dielectric constant of the solvent in such reactions, we have studied the acid catalysed hydrolysis of diethylsuccinate at various solvent compositions and temperatures. Water-dioxane was chosen as the solvent system. The kinetic and thermodynamic data obtained are compared to the solvent composition and its dielectric constant in order to get a full picture of the solvent effect on the reaction under investigation.

Experimental

Materials

Pure diethylsuccinate (B.D.H.) was distilled before use; b.p. 216.5 °C at 760 mm pressure, IR (film): 3000, 1760 (C=O), 1580 and 1180 cm^{-1}; H^1-NMR ($CDCl_3$): $\delta = 1.2$ (t, 6H, CH_3), 2.5 (s, 4H CH_2), 3.9–4.2 (q, 4H, CH_2).

Symmetrical 1,4 dioxane was purified as described in literature [7, 8]. The water used in kinetic experiments was freshly distilled from alkaline potassium permanganate.

Kinetic procedure

The rate of the reaction was determined using 0.02 M diethylsuccinate and 0.05 hydrochloric acid in a series of water-dioxane mixtures ranging from 0 to 95% (w/w) of dioxane. A titrimetric procedure involving analysis of the acid produced during the course of the reaction was followed using a screened indicator [6]. Completion of the reaction was ensured by heating samples in sealed ampules at 85 °C till a constant reading was obtained. The latter was always concordent with that theoretically calculated.

Results and Calculation

The rate constants k_1 and k_2 corresponding to the two steps of the acid-catalysed hydrolysis of the diethyl ester were computed using the time ratio procedure [9], involving a modification of the method adopted by Swain [10].

The values of k_1 and k_1/k_2 are collected in Table 1 at the indicated temperatures. A statistical least squares treatment [11] of the Arrhenius equation was used to calculate the activation energies E_1 and E_2 based on the rate constants k_1 and k_2, respectively. The values of activation energies E_1 and E_2 vary very little with the solvent composi-

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Table 1. The rate constant $k_1 \times 10^6$ in min^{-1} and the ratios k_1/k_2 for the acid hydrolysis of diethylsuccinate in dioxane-water mixtures.

t °C		Dioxane, wt%										
		0.000	10.227	20.198	27.660	40.133	50.023	59.827	69.692	79.450	89.392	94.566
		$[H_2O]$, mole/l										
		55.52	49.89	44.57	40.74	33.83	28.41	22.91	17.31	11.76	6.06	3.10
25	k_1	142.20	126.99	112.99	93.53	82.28	69.50	65.43	58.02	51.54	42.19	53.95
	k_1/k_2	1.989	1.996	1.988	1.984	1.988	1.995	1.976	1.992	1.992	1.976	1.968
30	k_1	226.20	206.73	179.37	149.75	127.31	112.84	111.68	90.77	84.28	68.55	85.95
	k_1/k_2	2.010	1.938	1.985	2.020	1.997	1.980	2.010	1.998	1.993	2.040	1.993
35	k_1	372.40	326.90	287.10	240.06	206.06	181.55	161.32	142.39	132.15	113.10	133.56
	k_1/k_2	1.960	2.004	1.996	2.004	1.996	2.010	2.000	2.000	2.006	1.997	2.000
45	k_1	862.04	761.65	669.12	571.34	490.43	468.46	380.68	343.28	313.29	271.36	330.03
	k_1/k_2	1.993	1.990	1.993	1.996	1.990	1.989	1.997	1.997	1.996	1.996	1.992
55	k_1	2003.5	1812.1	1454.0	1300.9	1105.7	970.3	862.8	789.3	678.6	614.7	717.5
	k_1/k_2	2.030	1.998	2.000	1.993	1.996	1.992	2.006	2.006	1.992	1.998	1.998

tion. The correlation coefficient values (r) of the linear plot of the Arrhenius equation lie in the range of 1.0 ± 0.05.

The entropies of activation $\Delta S^{\ddagger}$ were calculated using the expression

$$\log k/T = 10.3187 + \frac{\Delta S^{\ddagger}}{19.147} - \frac{\Delta H^{\ddagger}}{19.147\,T}$$

where $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and k are in J mole^{-1}, J mole^{-1} · deg^{-1} and sec^{-1} respectively. The resulting thermodynamic parameters are collected in Table 2.

Discussion

The rate constants k_1 and k_2 go through a minimum corresponding to about 90% dioxane (w/w), Figure 1. This minimum corresponds to the sharp increase of the acidity function of the mixed solvent in this range [13, 14]. The ratio k_1/k_2 is on the average equal to 2.0, as expected in cases of symmetric dicarboxylic esters, on the bases of the statistical calculations by Ingold [3, 6]. This ratio can be taken as representing the selectivity between the first and second steps, and $\log k_2$ as the reactivity. However, the application of the RSP (reactivity-selectivity principle) [15, 16] is limited here due to the constant selectivity at different reactivities. This arises from the fact that the mechanisms of the two steps of the reaction are the same for all solvent compositions studied*.

The values of E_1 and E_2 are almost equal (60.0 ± 4.5 kJ mol^{-1}) and lie within the range characteristic for most ester hydrolyses via $A_{Ac}2$ mechanism. The constancy of the E values indicates that the changes in solvation of the reactants and the transition states with the change in the solvating power of the medium outweigh each other such that the net change in activation energy of the reaction will be very small.

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* Details on the application of the RSP to consecutive dicarboxylic ester hydrolysis in general will be dealt with in a subsequent communication.

Table 2. Thermodynamic parameters of activation at 35 °C.

Parameter	Dioxane, wt%										
	0.000	10.227	20.198	27.660	40.133	50.023	59.827	69.692	79.450	89.392	94.566
$\Delta G_1^{\ddagger}$ kJ mol^{-1}	106.29	106.62	106.95	107.41	107.79	107.89	107.02	108.75	108.94	109.34	108.92
$\Delta H_1^{\ddagger}$ kJ mol^{-1}	56.44	56.96	56.80	56.61	56.82	56.74	58.15	55.95	56.15	57.70	56.45
$-\Delta S_1^{\ddagger}$ J mol^{-1} K^{-1}	161.78	161.16	162.76	164.85	165.40	166.75	163.18	171.36	171.31	167.60	170.27
$\Delta G_2^{\ddagger}$ kJ mol^{-1}	108.01	108.40	108.72	109.19	109.56	109.92	112.04	110.53	110.73	111.15	110.69
$\Delta H_2^{\ddagger}$ kJ mol^{-1}	58.28	56.95	56.88	56.59	56.50	56.74	54.91	54.98	56.18	57.77	56.38
$-\Delta S_2^{\ddagger}$ J mol^{-1} K^{-1}	161.34	166.98	168.24	170.71	172.19	172.58	179.47	180.27	177.02	173.10	176.24

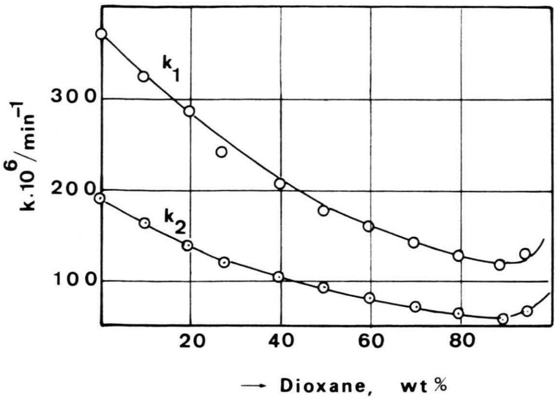

Fig. 1. Variation of the reaction rates with dioxane content of the mixed solvent at 35 °C.

The dependence of the rate constant on the water concentration of the mixed solvent is illustrated in Fig. 2, where it is seen that a linear relationship between the logarithm of the rate constant and log$[H_2O]$ is obtained at high water concentrations. The plots at all temperatures investigated are parallel and the slope of the linear part is unity, confirming the first-order nature of the reaction in which the A_{Ac^2} mechanism, incorporating one water molecule in the transition state, is followed.

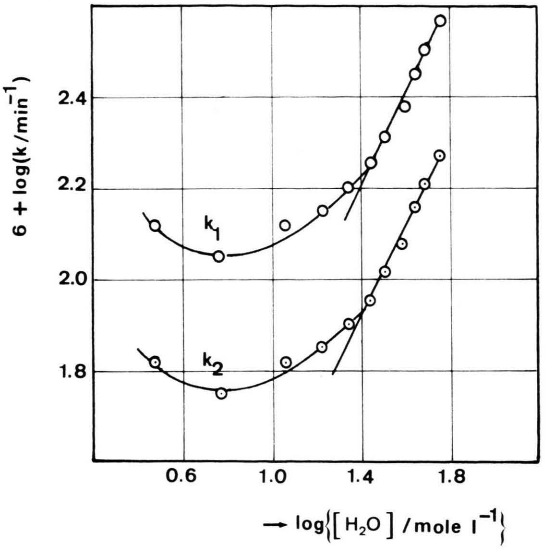

Fig. 2. Plots of log k against log $[H_2O]$ for the two steps of the reaction.

The deviation from linearity of the plots in Fig. 2 towards higher rates is again to be attributed to the increase in the acidity of the medium.

The variation of the concentrations of the reactant diethylsuccinate, the intermediate ethylhydrogensuccinate and the product succinic acid

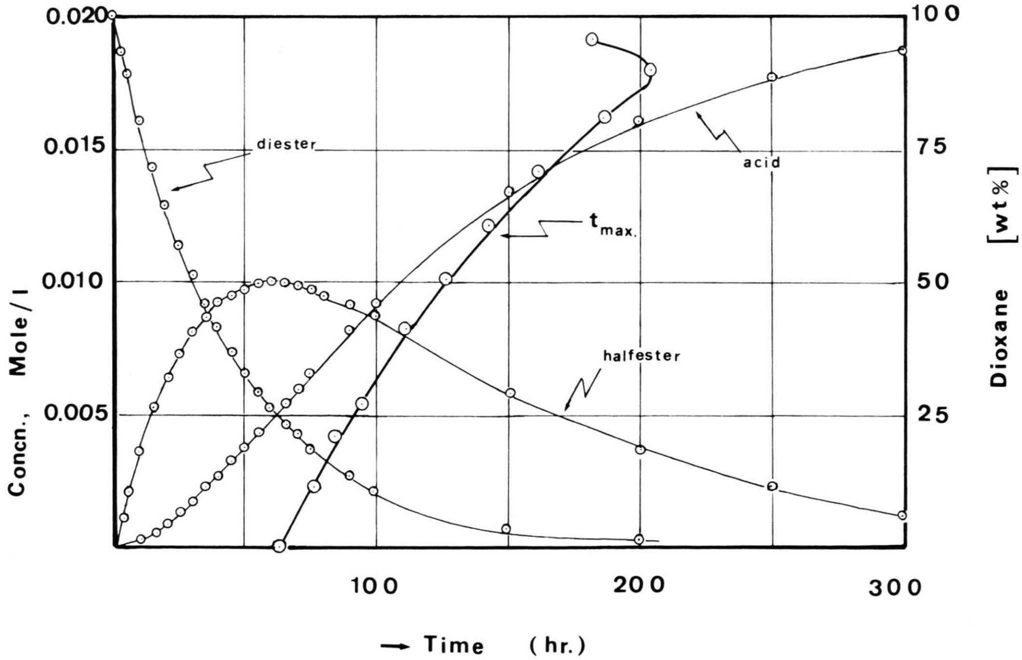

Fig. 3. Variation of the concentrations of reactant ester, intermediate half-ester and product acid with time; and the variation of t_{max} for the reaction with dioxane content of the medium.

during the course of the reaction in a purely aqueous medium are calculated at 35 °C and represented in Figure 3. The maximum concentration of the half-ester is reached at $t_{\max} = 3690$ min. The latter was similarly computed throughout the whole range of the solvent compositions, and the results are plotted in Fig. 3 vs. the dioxane content of the medium. A minimum in $t_{\max}$ near the 90% dioxane-water mixture is observed, which is consistent with the minima of k_1 and k_2 at this composition.

The dielectric constant values of the solvent mixtures were obtained by interpolation from the data of Åkerlof [17]. The reaction rate shows a remarkable decrease as the dielectric constant D of the medium is lowered. According to the electrostatic theories of Laidler and Landskroener [19], if the reaction is to be considered as a dipole-dipole interaction, a linear relationship between log k and $(D-1)/(2D+1)$ should be obtained. However, treatment of the reaction as an ion-dipole interaction should give a linear plot of log k against $1/D$. Other linear relationships between log k and D or log D [21—23] are described. Such plots are represented in Fig. 4 for the two rate constants k_1 and k_2. Deviation from linearity at low dielectric constants is observed and is attributed to solvent sorting or specific solvation effects [24]. From the slopes of the linear portions of log k_1 and log k_2 vs. $1/D$ the radii of the activated complexes were calculated to be 4.5 and 4.4 Å, respectively, which is in good agreement with the values previously calculated for many carboxylic esters undergoing acid hydrolysis in various solvents [25].

The values of the thermodynamic parameters of activation, i.e., the free energies $\Delta G^{\neq}$, the enthalpies $\Delta H^{\neq}$ and the entropies $\Delta S^{\neq}$ for the two consecutive steps are calculated and given in Table 2. The values of $\Delta G_1^{\neq}$ and $\Delta G_2^{\neq}$ show only a very slight change as the dioxane content of the solvent mixture is increased. As also $\Delta H^{\neq}$ and $\Delta S^{\neq}$ do not change much, the compensation effect between $\Delta H^{\neq}$ and $T\Delta S^{\neq}$, which plays an important role in keeping $\Delta G^{\neq}$ more or less constant in other cases [26, 27], is of no relevancy here. The values of $\Delta S^{\neq}$ show only a slight lowering as the organic component of the medium is increased, confirming the uniformity of the mechanism in the whole range of solvent compositions [28]. Moreover the values of

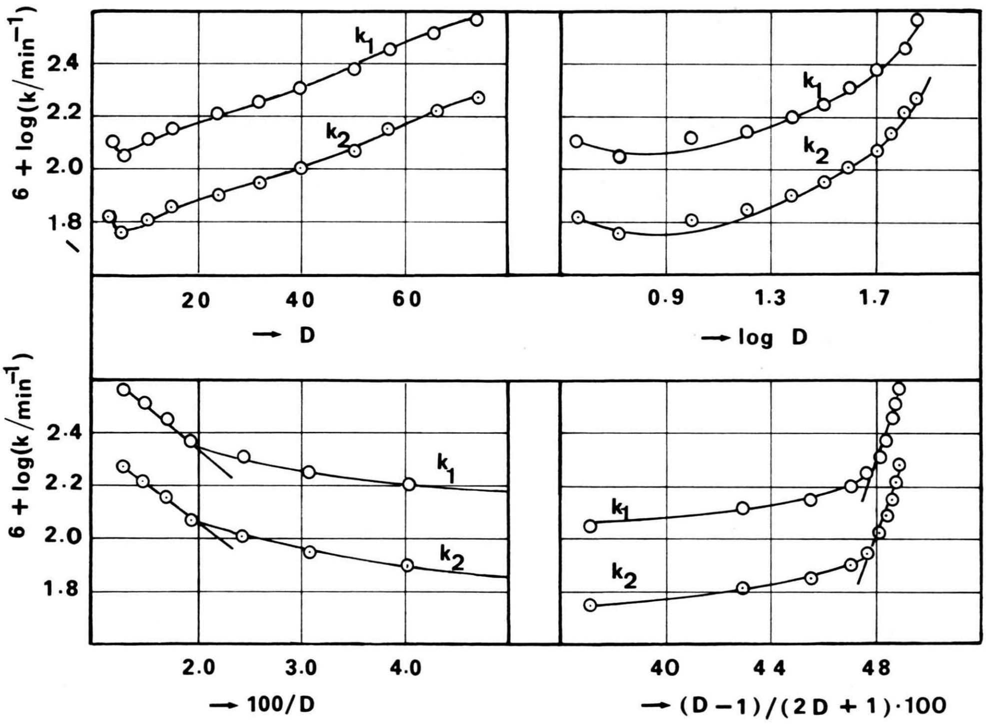

Fig. 4. Dependence of the reaction rates on the dielectric constant of the medium.

the entropy of activation of the second step, $\Delta S_2^{\ddagger}$, are lower than those for the first step, $\Delta S_1^{\ddagger}$, indicating that the activated complex produced during the hydrolysis of the halfester is more solvated than that formed during the ester hydrolysis. The former complex, with its free carboxylic group, is definitely more polar than the latter one and consequently will be more favourable for solvation through hydrogen bonding with water. That is why the difference $\Delta\Delta S^{\ddagger}$ is dependent on the solvent compositon and is largest in the dioxane-rich media, where the water available for solvation is limited and will preferably solvate the more polar activated complex, causing a large drop in $\Delta S^{\ddagger}$. In water rich media, however, the difference $\Delta S^{\ddagger}$ is smaller, since there is enough water to solvate both the activated complexes to the same extent.

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