Kinetic and Mechanistic Studies of the Acid-Catalysed Hydrolysis of Di*tert.*-butyl Malonate in Dioxane-Water Media

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A kinetic investigation of the consecutive acid-catalysed hydrolysis of di*tert.*-butyl malonate in dioxane-water mixtures is given. The rate constants of the first and second hydrolysis steps decrease by addition of the organic solvent, and both steps proceed concurrently by $A_{Al}1$ and $A_{Ac}2$ mechanisms. The kinetic ratio k_I/k_{II} depends on the solvent composition. The results are compared with those obtained previously for di*tert.*-butyl succinate in many aspects such as rate, percentage $A_{Al}1$ fission and the role of the inductive as well as steric effects. The maximum concentration of the intermediate, halfester, decreases with decrease in the ionising power of the solvent and has nearly the same value for malonate and succinate in isocomposition media. The effect of the dielectric constant on the rate constant and the activation thermodynamic parameters are discussed.

Introduction

Kinetic studies of the acid-catalysed hydrolysis of simple esters led to the firm elucidation of an $A_{Ac}2$ mechanism for such reactions [1]. Tertiary esters, however, are known to undergo acid hydrolysis via a mixed $A_{Al}1$ and $A_{Ac}2$ mechanism whose relative amounts depend on the reaction conditions such as temperature and solvent composition [2–6]. On the other hand, dicarboxylic esters, which involve a consecutive reaction, produce complications by the fact that each step comprises two hydrolysis rate constants relevant to the different mechanisms. The sensitivity of these four rate constants as well as the percentage of bond-fission *contributing* to the different factors controlling the reaction is a point of real interest. The present investigation was undertaken in order to study the orientation caused by the presence of two *tert.*-butyl groups to the mode in which the respective rate constants are affected by such factors. For this study, the acid-catalysed hydrolysis of di*tert.*-butyl malonate in a series of dioxane-water mixtures was chosen.

Experimental

Di*tert.*-butyl malonate was prepared and purified as described before [7]. 1,4-Dioxane was carefully purified [8]. The kinetic procedure involved the hydrolysis of 0.02 M di*tert.*-butyl malonate with 0.05 M hydrochloric acid in a series of dioxane-water mixtures with a composition range varying from 30 to 95% by weight of the organic solvent. The reaction was followed titrimetrically by analysis of samples of the reaction mixture at different time intervals with respect to the acid produced [9].

Results and Calculation

The first-order rate constants k_I and k_{II} of the two consecutive steps of the acid-catalysed hydrolysis of di*tert.*-butyl malonate under different conditions of temperature and solvent composition are depicted in Table 1. These constants were calculated by the Swain's time ratio procedure [10, 11]. The maximum concentration of the halfester, $C_{B_{max}}$, and the corresponding time t_{max}, were calculated according to the standard expressions [11]. The separate rate constants k_{I1} and k_{I2} for the unimolecular and bimolecular mechanisms, respectively, of the first step of the reaction as well as k_{II1} and k_{II2} corresponding to those of the second step, were calculated according to the procedure described before [9]. A statistical least squares treatment [12] of the Arrhenius equation was used to calculate the activation energies. The enthalpies ($\Delta H^{\neq}$), entropies ($\Delta S^{\neq}$) and Gibbs energies ($\Delta G^{\neq}$) of activation were calculated using the absolute reaction rate equation

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[13]. The dielectric constants of the dioxane-water mixtures were determined by interpolation from the results reported by Åkerlof [14].

Discussion

The specific rate constants k_I and k_{II} of the individual consecutive steps of the reaction decrease largely with decreasing water concentration in the solvent, cf. Table 1. At a water content of about 10% the rate passes through a minimum and then increases with further addition of the organic solvent. The latter minimum corresponds to the maximum in the acidity function of the mixed solvent within the same range of composition [15]. The ratio k_I/k_{II} is less than 2.0, the value expected in the case of symmetric dicarboxylic esters based on the statistical calculation by Ingold [16, 17], regardless of the type of solvent. However, this ratio is not independent of solvent composition, it rather decreases with decrease in water content. This can be explained if one considers the fact that the overall rate constant for each step results from two components, the $A_{Al}1$ and $A_{Ac}2$ mechanisms, which are affected differently by the solvent composition, such that the $A_{Al}1$ mechanism is more evident at a higher ionising power of the solvent than the $A_{Ac}2$ mechanism [18]. The relatively larger steric effect of the bulky *tert.*-butyl groups in the first than in the second hydrolysis steps will be responsible for this change in k_I/k_{II}.

Figure 1 represents the variation of the calculated maximum concentration ($C_{B_{max}}$) of the halfester, *tert.*-butyl hydrogen malonate, with solvent composition at 40 °C. The value of $C_{B_{max}}$ shows interestingly that it decreases with increasing dioxane content of the medium and reaches a minimum at 90% (w/w) dioxane. The coexistence of the $A_{Al}1$ mechanism along with the $A_{Ac}2$ one in the second hydrolysis step, with the former largely sensitive to the ionising power of the solvent [18], will cause the rate of consumption of the halfester to be larger than its rate of accumulation. The net result is that $C_{B_{max}}$ decreases continuously with addition of dioxane. This is evidenced by the fact that when the points representing another tertiary ester of similar structure like, e.g., di*tert.*-butyl succinate [9] were plotted, they were found to fall on the same line. However, for primary dicarboxylic esters like, e.g.,

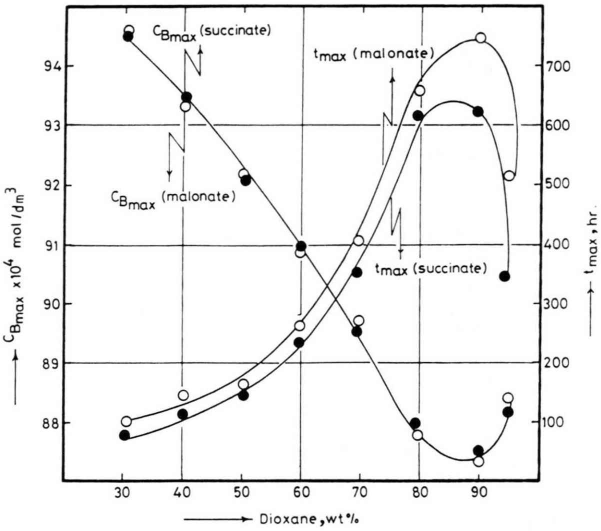

Fig. 1. Dependence of $C_{B_{max}}$ and t_{max} on dioxane content of the medium at 40 °C for di*tert.*-butyl malonate (○) and di*tert.*-butyl succinate (●).

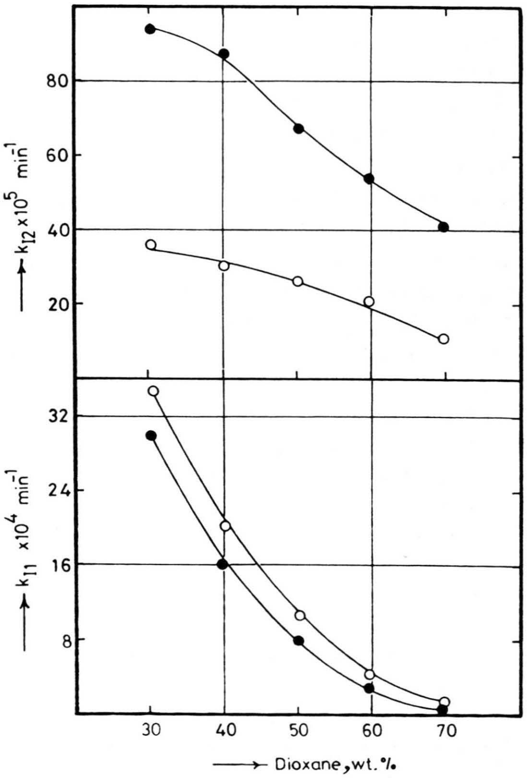

Fig. 2. Comparative plots of k_{11} and k_{12} against the weight per cent of dioxane at 60 °C for di*tert.*-butyl malonate (○) and di*tert.*-butyl succinate (●).

Table 1. Observed rate constants for the acid-catalysed hydrolysis of Di*tert*.-butyl malonate in dioxane-water mixtures [a]

t, °C	k 10^6 min^{-1}	Dioxane, wt%							
		30.6	40.1	50.1	59.8	69.7	79.5	89.7	94.7
		$[H_2O]$, mol/dm^3 38.7	33.9	28.4	22.9	17.3	11.7	5.9	3.0
30	k_I	79.2	53.4	34.4	23.3	13.3	12.6	10.0	11.9
	k_{II}	45.6	31.8	21.1	15.1	9.1	8.7	7.0	8.2
	k_I/k_{II}	1.737	1.679	1.630	1.543	1.462	1.448	1.429	1.451
35	k_I	154.9	97.7	67.6	43.7	32.4	22.9	17.4	27.5
	k_{II}	89.1	58.1	41.4	28.0	21.4	15.7	12.1	18.6
	k_I/k_{II}	1.738	1.682	1.633	1.561	1.514	1.459	1.438	1.478
40	k_I	215.2	148.1	130.1	78.8	50.1	30.3	26.4	39.4
	k_{II}	123.7	87.9	79.6	49.9	32.8	20.8	18.3	26.6
	k_I/k_{II}	1.740	1.685	1.634	1.579	1.527	1.457	1.443	1.481
45	k_I	537.0	331.1	213.8	138.0	91.2	60.2	44.7	67.6
	k_{II}	308.4	196.4	130.2	87.2	59.7	41.1	30.9	45.6
	k_I/k_{II}	1.741	1.686	1.642	1.583	1.528	1.465	1.447	1.482
50	k_I	1032.0	659.1	372.4	203.9	115.1	99.3	75.9	113.2
	k_{II}	592.1	390.0	227.4	128.6	75.1	67.4	52.3	76.2
	k_I/k_{II}	1.743	1.690	1.638	1.586	1.533	1.473	1.451	1.486
55	k_I	1819.0	1045.0	660.7	416.9	275.4	190.5	138.0	263.0
	k_{II}	1043.0	618.4	402.9	262.7	179.4	128.8	94.7	176.9
	k_I/k_{II}	1.744	1.693	1.640	1.587	1.535	1.479	1.457	1.487
60	k_I	3887.0	1948.0	1402.0	815.8	543.6	377.6	239.9	446.9
	k_{II}	2227.0	1149.0	853.4	512.8	353.4	254.3	163.8	299.7
	k_I/k_{II}	1.745	1.695	1.643	1.591	1.538	1.485	1.465	1.491
65	k_I	7079.0	3631.0	2344.0	1445.0	891.3	588.8	398.1	707.9
	k_{II}	4052.0	2141.0	1425.0	907.0	578.1	395.4	271.3	473.5
	k_I/k_{II}	1.747	1.696	1.645	1.593	1.542	1.489	1.467	1.495
70	k_I	13402.0	6404.0	4173.0	2782.0	1483.0	1023.0	645.7	1148.0
	k_{II}	7669.0	3774.0	2533.0	1743.0	960.0	685.1	439.1	767.3
	k_I/k_{II}	1.748	1.697	1.647	1.596	1.545	1.493	1.471	1.496

[a] Average deviation from these values is $\leqq \pm 3\%$ for replicate determination.

diethyl malonate [19] and diethyl succinate [20], in which hydrolysis takes place purely via the $A_{Ac}2$ mechanism, $C_{B_{max}}$ of the halfester is found to be completely independent of solvent composition. Figure 1 shows also the corresponding dependence of the t_{max} at which the halfester concentration is maximum, on solvent composition. It is noteworthy that in isocomposition mixtures the rate of the acid hydrolysis of di*tert*.-butyl malonate is lower than that of di*tert*.-butyl succinate, and vice versa for t_{max}, where $t_{max} = 6052$ and 5126 min, respectively, for di*tert*.-butyl malonate and di*tert*.-butyl succinate in 30.6% dioxane (w/w). This observation follows directly from the fact that the rate of reaction is influenced by the chain length between the two functional groups and is definitely larger when the chain is longer.

The Arrhenius equation is not strictly followed in the present work and a slight deviation above 50 °C takes place which depends on solvent composition. This deviation must mainly be due to the occurrence of two concurrent mechanisms whose activation energies differ widely [21]. The calculated rate constants for each type of mechanism gave good Arrhenius plots, and the corresponding activation energies were found to be typical for those experimentally determined for other esters hydrolysing purely via each mechanism [5]. As expected, the percentage contribution of the $A_{Al}1$ mechanism to the overall reaction in each step increases with temperature and decreases with increasing dioxane content. This percentage is also higher in the first step compared to the second one, since the steric effect enhancing the alkyl-oxygen fission [16] is larger.

Moreover, as evident in Fig. 2, the rate constants $k_{\mathrm{I}1}$ and $k_{\mathrm{I}2}$ corresponding to the $A_{Al}1$ mechanism of the first and second hydrolysis steps, respectively, are observed to be slower for succinate [9] than malonate. This trend is reversed, however, for the $A_{Ac}2$ mechanism in which the rate constants $k_{\mathrm{I}2}$ and $k_{\mathrm{II}2}$ are larger for succinate than malonate. The first observation can be rationalised on the basis of the step of the $A_{Al}1$ reaction involving the unimolecular heterolysis of the protonated ester molecule to yield a carbenium ion. This step is faster in the case of malonate than succintate because the shorter chain strengthens the inductive as well as the steric effects, which mainly govern the ease with which the carbenium ion ($^{+}C(CH_3)_3$) is removed.

On the other hand the higher $A_{Ac}2$ rate constants $k_{\mathrm{I}2}$ and $k_{\mathrm{II}2}$ for succinate relative to malonate may be explained as in the case of primary dicarboxylic esters [19], where the removal of the alcohol molecule, *tert.*-butanol, from the tetrahedral intermediate is determined mainly by the magnitude of the positive charge on the carbon of the carbonyl group, being inversely proportional to it, and leading to a higher rate for this step in succinate than malonate. Furthermore, the attack of the water molecule as a nucleophile in the $A_{Ac}2$ mechanism will suffer some difficulty due to the steric effect caused by the second *tert.*-butyl group [16], and hence produces an additional factor to influence the readiness with which the water molecule attacks the center of reaction, the attack being easier in case of succinate than malonate.

Application of the electrostatic ion-dipole interaction theory [22–24] to the present data gives a linear plot of $\log k_{\mathrm{I}}$ and $\log k_{\mathrm{II}}$ against $1/\varepsilon$ in the high range of dielectric constant (ε). Estimation of the radii of the activated complexes, according to the mentioned theory, gave values of 4.6 and 4.4 Å for the first and second hydrolysis steps, respectively, which are fairly lower than 4.8 and 4.9 Å for di*tert.*-butyl succinate [9] under similar conditions.

The thermodynamic parameters show that the enthalpies of activation, ΔH^{+}, for the overall reaction decreases considerably, from 100 to 80 kJ mol^{-1}, with increasing dioxane content. No such change is observed for the unimolecular ($\Delta H^{\ddagger}_{\mathrm{I}1} \sim \Delta H^{\ddagger}_{\mathrm{II}1} = 120 \pm 4$ kJ mol^{-1}) and bimolecular ($\Delta H^{\ddagger}_{\mathrm{I}2} \sim \Delta H^{\ddagger}_{\mathrm{II}2} = 65 \pm 2$ kJ mol^{-1}) reactions. However, ΔS^{+} acquires the values between − 24.0 to − 115.0 J mol^{-1} deg^{-1} for the first hydrolysis step and −30.0 to −120.0 J mol^{-1} deg^{-1} for the second one. This significant change is a further indication of the continuous transformation of the reaction mechanism of the two steps from $A_{Al}1$ to $A_{Ac}2$. The values of ΔS^{+} for the separated unimolecular and bimolecular reactions are all in good agreement with the range assigned for each mechanism [25]. ΔG^{+}, for both steps varies much less than does ΔH^{+} or ΔS^{+}. This weak dependence on solvent is due largely to a linear compensation between ΔH^{+} and ΔS^{+}.

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