Kinetics of the Hydrochloric Acid-catalysed Hydrolyses of Benzoic Anhydrides in Various Dioxan–Water Mixtures

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Kinetic studies on the hydrolysis of some benzoic anhydrides in the presence of 0.100M-hydrochloric acid have been performed in various dioxan–water mixtures over the temperature range 50—70 °C. The kinetic data indicate that the hydrolysis of *p*-methoxybenzoic anhydride proceeds by an *A*1 mechanism, whereas benzoic anhydride and its *p*-t-butyl and *p*-chloro-derivatives hydrolyse by an *A*2 mechanism in the water-rich mixtures, but a shift of the reaction mechanism towards the *A*1 type occurs when the water content in the solvent mixture decreases.

IN extension of previous studies [1-4] on the factors affecting the mixed mechanism (*A*1 and *A*2) involved in the acid-catalysed hydrolysis of some *para*-substituted benzoic anhydrides, the present paper deals with results

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[1] G. Calvaruso and F. P. Cavasino, *J. Chem. Soc.* (*B*), 1971, 483.

[2] G. Calvaruso, F. P. Cavasino, and E. Di Dio, *Ann. Chim.* (*Italy*), 1973, **63**, 663.

[3] G. Calvaruso, F. P. Cavasino, and E. Di Dio, *J.C.S. Perkin II*, 1974, 1108.

[4] G. Calvaruso and F. P. Cavasino, *Ann. Chim.* (*Italy*), 1968, **58**, 1039.

obtained for the hydrolysis of these anhydrides in various dioxan–water mixtures containing 0.100M-HCl over the temperature range 50—70 °C. The aim was to obtain information about the effects of changes in the solvent composition on the mechanism of the hydrochloric acid-catalysed hydrolysis of the anhydrides examined. Evidence for the reaction mechanism was obtained from evaluation of the activation parameters, from use of acidity functions, and from substituent effects.

TABLE 1

Kinetic data for the spontaneous and acid hydrolysis of *para*-substituted benzoic anhydrides in dioxan–water ([HCl] = 0.100M)

Dioxan–water (v/v)	t/°C	10^5k_0/s^{-1}	10^5k_{obs}/s^{-1}	10^4k_H/ l mol^{-1} s^{-1}
p-Methoxybenzoic anhydride				
20 : 80	50.0	3.2	9.5	6.3
	60.0	6.5	23.7	17.2
	70.0	12.0	65	53
40 : 60	50.0	0.68	3.08	2.40
	60.0	1.36	8.8	7.4
	70.0	2.69	23.7	21.0
60 : 40	50.0	0.172 [a]	0.93	0.76
	60.0	0.38 [a]	2.90	2.52
	70.0	0.83 [a]	8.2	7.4
75 : 25	50.0		0.60	0.60
	60.0		2.07	2.07
	70.0		5.8	5.8
90 : 10	50.0		1.22	1.22
	60.0		4.1	4.1
	70.0		11.8	11.8
p-t-Butylbenzoic anhydride				
40 : 60	50.0	1.93	3.5	1.57
	60.0	3.6	6.8	3.2
	70.0	6.2	12.0	5.8
60 : 40	50.0	0.49 [a]	1.05	0.56
	60.0	1.09 [a]	2.33	1.24
	70.0	2.07 [a]	4.5	2.43
75 : 25	50.0	0.150	0.47	0.32
	60.0	0.34	1.13	0.79
	70.0	0.80	2 57	1.77
90 : 10	50.0		0.38	0.38
	60.0		1.07	1.07
	70.0		2.52	2.52
Benzoic anhydride				
40 : 60	50.0	7.5	10.8	3.3
	60.0	12.7	18.7	6.0
	70.0	21.7	34	12.3
60 : 40	50.0	1.42 [a]	2.43	1.01
	60.0	2.85 [a]	4.9	2.05
	70.0	5.5	9.6	4.1
75 : 25	50.0	0.47 [b]	1.13	0.66
	60.0	0.95 [b]	2.33	1.38
	70.0	2.20 [b]	5.5	3.3
90 : 10	50.0	0.258 [b]	0.75	0.49
	60.0	0.58 [b]	1.78	1.20
	70.0	1.27 [b]	4.2	2.93
p-Chlorobenzoic anhydride				
40 : 60	50.0	39 [c]	48	9.0
60 : 40	50.0	9.7 [c]	12.8	3.10
75 : 25	50.0	2.30 [b]	3.9	1.60
90 : 10	50.0	1.58 [b]	2.18	0.60

[a] Ref. 4. [b] Ref. 2. [c] In the presence of 0.100M-LiCl.

EXPERIMENTAL

All materials and the solvent mixtures used in this work were prepared as described previously.[1–4] The rates of hydrolysis were followed spectrophotometrically with the apparatus and procedure described.[1–4] The observed first-order rate constants were reproducible within ±3%.

RESULTS AND DISCUSSION

Table 1 assembles the observed first-order rate constants, k_{obs}, for the overall hydrolysis in acid solution together with the first-order rate constants, k_0, for spontaneous hydrolysis and the second-order rate constants, k_H, for acid hydrolysis. The latter rate constants have been obtained [1–3] by dividing the difference $(k_{obs} - k_0) = k_c$ by the concentration of the catalyst acid ([HCl] = 0.100M). The activation parameters given in Table 2 have been calculated [1–3] by the least-square method from linear plots of log (k_H/T) against $1/T$.

TABLE 2

Activation parameters [a] for the acid hydrolysis of *para*-substituted benzoic anhydrides in dioxan–water

Dioxan–water (v/v)	Substituent					
	MeO		Bu^t		H	
	ΔH_H^*	ΔS_H^*	ΔH_H^*	ΔS_H^*	ΔH_H^*	ΔS_H^*
20 : 80	22.7	−3				
40 : 60	23.1	−3	13.7	−33	13.8	−32
60 : 40	24.3	−2	15.4	−30	14.7	−31
75 : 25	24.2	−3	18.1	−23	17.0	−25
90 : 10	24.3	−1	20.1	−16	19.0	−20

[a] ΔH_H^* in kcal mol^{-1} and ΔS_H^* in cal mol^{-1} K^{-1}.

For the estimate of the salt effect of the catalyst on the spontaneous hydrolysis in acid solution a procedure similar to that adopted previously [1–3,5] was employed. Since the salt effect of 0.100M-lithium chloride upon the spontaneous hydrolysis of benzoic anhydride and its *p*-methoxy and *p*-t-butyl derivatives has been found to be negligible (*cf.* also ref. 3), the k_0 values obtained in the absence of salt were used, when necessary, to make allowance for its contribution in acid solution. For *p*-chlorobenzoic anhydride, on the other hand, the salt effect of added lithium chloride is significant and k_0 appreciable relative to k_{obs}. For this anhydride the rate constant k_0 was thus estimated in the presence of 0.100M-LiCl for hydrolysis in 40 : 60 and 60 : 40 (v/v) dioxan–water. For the other two solvent mixtures, the very low solubility of lithium chloride did not allow us to perform measurements at this salt concentration and the k_0 values obtained in the absence of salt were hence used. Owing to this approximation, the rates of hydrolysis were followed only at 50 °C.

It can be seen from Table 1 that for benzoic anhydride and its *p*-chloro-derivative the rate constant for acid hydrolysis (k_H) decreases continuously at the temperatures investigated as the water content in the solvent mixture decreases. In the case of the *p*-methoxy and *p*-t-butyl derivatives the reaction rate decreases with decreasing water concentration until it reaches a minimum value in 75 : 25 (v/v) dioxan–water and then in-

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[5] C. A. Bunton and J. H. Fendler, *J. Org. Chem.*, 1966, **31**, 3764 and references therein.

creases again in mixtures of lower water content. A similar trend with a minimum at about the same solvent composition is observed[6] with the negative value of Hammett's acidity function ($-H_0$). However for *p*-methoxybenzoic anhydride only the plot of log k_c against $-H_0$ is linear with a slope of about unity (Figure 1; slope 0.92), indicating an *A*1 mechanism for the acid hydrolysis of this compound in the solvent mixtures examined. The values of the activation entropy (Table 2) also support[1–3] the occurrence of *A*1 hydrolysis.

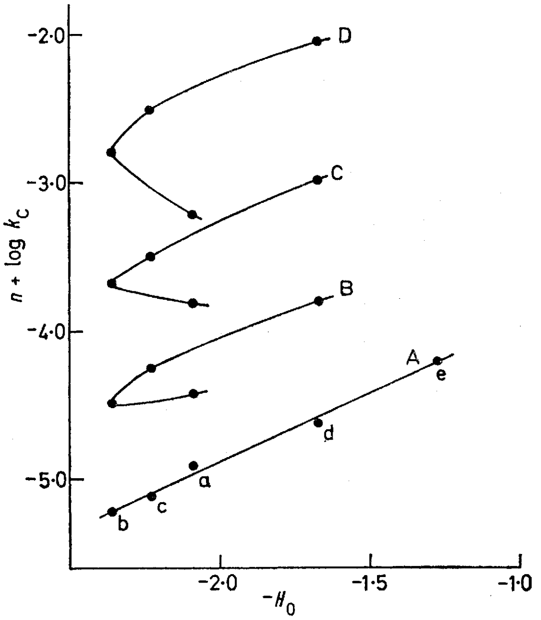

FIGURE 1 Plots of log k_c against $-H_0$ at 50 °C and [HCl] 0.100M in dioxan–water mixtures: a, 90 : 10 (v/v); b, 75 : 25 (v/v); c, 60 : 40 (v/v); d, 40 : 60 (v/v); e, 20 : 80 (v/v); A, MeO, $n = 0$; B, Bu^t, $n = 1$; C, H, $n = 1.5$; D, Cl, $n = 2$

For benzoic and its *p*-t-butyl derivative the large negative activation entropies found in 40 : 60 and 60 : 40 (v/v) dioxan–water are consistent[1–3] with a reaction mechanism of the *A*2 type, whereas the increases in ΔS_H^* with decreasing water concentration would indicate some contribution of the *A*1 mechanism to the acid hydrolysis in dioxan-rich mixtures. The observed ΔS^*_H increase should not be ascribed to solvation effects since the entropy of activation for *A*2 hydrolysis of benzoic anhydrides in the presence of perchloric acid was found[2] to be almost unaffected by the water content in dioxan–water mixtures.

Analysis of the effects of substituents upon the rate of acid hydrolysis provides additional support to these findings. The order of reactivity of the anhydrides in all mixtures studied (*cf.* Figure 2) is $\text{MeO} > \text{Bu}^t < \text{H} < \text{Cl}$ and the difference in the hydrolysis rate of benzoic anhydride and its *p*-t-butyl and *p*-chloro-derivatives becomes smaller as the amount of water in dioxan is diminished. The observed trends of the reactivities indicate[1–3] that *p*-methoxybenzoic anhydride is always hydrolysed by the *A*1 mechanism, whereas the other anhydrides undergo mainly *A*2 hydrolysis in water-rich mixtures, but a shift of the reaction mechanism towards the *A*1 type occurs when the concentration of water is decreased. The change in mechanism is favoured by an electron-releasing group.

The hydrochloric acid-catalysed hydrolysis of *p*-methoxybenzoic anhydride in 60 : 40 (v/v) dioxan–water was previously found[3] to proceed at [HCl] = 0.260M by a mixed mechanism (*A*1 and *A*2) in the temperature range 25—40 °C, whereas above 50 °C the only mechanism involved is *A*1. The results of the present work show that the reaction mechanism is not affected either by the increase in the water content in the solvent mixture or the decrease in the catalyst acid concentration, which are two factors favouring[1–3] the shift of the reaction mechanism towards the *A*2 type. Therefore the temperature appears to be the main factor affecting the mechanism of hydrolysis of this anhydride.

As for the other anhydrides, the present data indicate that even at the low hydrochloric acid concentration used the mechanism of the acid hydrolysis is affected to some extent by the change of water content in the dioxan–water mixtures.

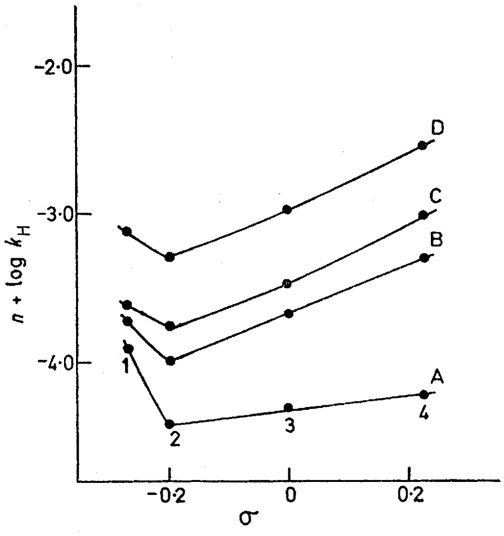

FIGURE 2 Plots of log k_H against Hammett substituent constants σ at 50 °C in dioxan–water mixtures: A, 90 : 10 (v/v), $n = 0$; B, 75 : 25 (v/v), $n = 0.5$; C, 60 : 40 (v/v), $n = 0.5$; D, 40 : 60 (v/v), $n = 0.5$; 1, MeO; 2, Bu^t; 3, H; 4, Cl

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[5/1994 *Received, 13th October*, 1975]

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[6] E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1948, 1976.