Effects of Hydrochloric Acid upon the Kinetics and Mechanism of Hydrolysis of *para*-Substituted Benzoic Anhydrides in Dioxan–Water

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Kinetic data on the title reaction lead to conclusions similar to those obtained previously for hydrolyses catalysed by perchloric acid, namely a change in the reaction mechanism from *A*2 to *A*1 occurs as the acidity and the temperature increase. The two acids however catalyse the hydrolyses to different extents and their specific effects on the reaction rate depend upon the nature of the substituent group, the temperature, and the hydrolysis mechanism involved.

PREVIOUS studies[1,2] on the perchloric acid catalysed hydrolysis of *para*-substituted benzoic anhydrides in various dioxan–water mixtures showed that a change from the *A*2 ($A_{\rm AC}2$) to the *A*1 ($A_{\rm AC}1$) mechanism occurs as the acidity and the temperature increase and the water content decreases.

The present work is concerned with the kinetics of hydrolysis of some *para*-substituted benzoic anhydrides in 60 : 40 (v/v) dioxan–water in the presence of hydrochloric acid. It has been undertaken to investigate the effect of this acid upon the hydrolysis rate and upon the change in the reaction mechanism with increasing acidity. Since the catalytic powers of perchloric and hydrochloric acids appear to depend[3-6] on the nature of the substrates and on the type of mechanism involved in the acid hydrolyses, it was also of interest to ascertain what differences existed in the catalytic behaviour of these acids in the case of the carboxylic anhydrides examined.

EXPERIMENTAL

The carboxylic anhydrides examined in this work, *i.e.*, benzoic anhydride and its *p*-methoxy-, *p*-t-butyl-, and *p*-chloro-derivatives, were those used before.[1,2,7] The preparation of the various solutions containing hydrochloric acid was analogous to that described previously[1] for perchloric acid. The solutions containing lithium chloride were obtained by using a saturated solution of salt (Schuchardt water-free) and were standardised with silver nitrate. Owing to the limited solubility of lithium chloride in 60 : 40 (v/v) dioxan–water, the maximum salt concentration employed for the spontaneous hydrolyses was 1·00M. Moreover, hydrolyses in the presence of 1·00M-LiCl were studied at temperatures up to 50 °C because of separation of the solution into two liquid phases.

The hydrolyses were followed spectrophotometrically with the apparatus and the procedure described before.[1,2,7]

RESULTS

The observed first-order rate constant $k_{\rm obs}$ for the hydrolyses in acid solution is given[1,2] by $k_{\rm obs} = k_{\rm c} + k_0$, where $k_{\rm c}$ is the first-order rate constant for the catalysed hydrolysis and k_0 the first-order rate constant for the spontaneous hydrolysis corrected for the electrolyte effect of hydrochloric acid, which is assumed to be similar[1,2,5,6] to that of lithium chloride. Table 1 lists the rate constants k_0 in the presence and in the absence[7] of lithium chloride, and the rate constants $k_{\rm obs}$ are reported in Tables 2—5. The uncertainties in both k_0 and $k_{\rm obs}$ are[1,2] within ±3%.

TABLE 1

Rate constants, $10^6\,k_0/\mathrm{s}^{-1}$, for spontaneous hydrolysis of *para*-substituted benzoic anhydrides in the presence and in the absence of lithium chloride

		Substituent group			
T/°C	[LiCl]/M	MeO	Bu$^{\rm t}$	H	Cl
25·0	0 [a]			2·03 [b]	23·0
	0·260				17·7
	0·500			2·00	15·5
	1·00			1·68	11·8
40·0	0 [a]			6·7	70
	0·260				49
	1·00			5·4	34
50·0	0 [a]	1·72	4·9	14·2	122
	0·260			13·8	92
	1·00	1·40	3·3	10·2	63
60·0	0 [a]	3·8	10·9	28·5	
	0·260				168
70·0	0 [a]	8·3	20·7		
	0·260				297

[a] Ref. 7. [b] Extrapolated value.

For *p*-methoxy- and *p*-t-butyl-benzoic anhydrides the rate constants k_0 in the presence or in the absence of salt are small with respect to $k_{\rm obs}$ at low acidities and negligible at acid concentrations above 2·00M. Therefore for these anhydrides the k_0 values obtained in the absence of lithium chloride were used when necessary. For benzoic anhydride the contribution of spontaneous hydrolysis to the over-all reaction is relatively small at the lowest acidities studied and it is negligible at [HCl] > 3·00M. Since the variations in k_0 with added lithium chloride are very small up to [LiCl] = 0·500M (*cf.* Table 1), the rate constants k_0 in the absence of salt were used at [HCl] ⩽ 0·500M, whereas in the acidity range 1·00—3·00M the k_0 values obtained at [LiCl] = 1·00M were used. In the case of *p*-chlorobenzoic anhydride the salt effect of lithium chloride upon spontaneous hydrolysis is more significant than for the other anhydrides and k_0 is appreciable relative to $k_{\rm obs}$ (*cf.* Tables 1 and 5). Therefore the k_0 values used were those properly

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corrected for the salt effect of lithium chloride. However at 25 °C and [HCl] $\geqslant$ 2·00M the rate constants k_0 obtained in the presence of 1·00M-LiCl were always used. Owing to this approximation, kinetic measurements using acid concentration >1·00M were not performed at other temperatures. For all the anhydrides the rate constants k_0 were, when necessary, extrapolated from the experimental values at other temperatures.

TABLE 2

Kinetic data for the acid hydrolysis of *p*-methoxybenzoic anhydride

T/°C	[HCl]/M	10^4k_{obs}/s^{-1}	10^4k_H/ l mol^{-1} s^{-1}
20·0	5·00	48	9·6
25·0	0·260	0·0150	0·051
	0·500	0·0270	0·050
	1·00	0·067	0·065
	2·00	0·45	0·225
	3·00	2·48	0·83
	4·00	15·3	3·8
	5·00	90	18·0
30·0	5·00	163	33
35·0	3·00	8·8	2·93
40·0	0·260	0·085	0·300
	1·00	0·49	0·48
	3·00	16·2	5·4
45·0	1·00	0·93	0·92
	3·00	28·2	9·4
50·0	0·260	0·275	0·99
	1·00	1·65	1·63
	3·00	49	16·3
60·0	0·260	0·85	3·12
	1·00	5·3	5·3
	3·00	147	49
70·0	0·260	2·60	9·7
	1·00	15·0	15·0

TABLE 3

Kinetic data for the acid hydrolysis of *p*-t-butylbenzoic anhydride

T/°C	[HCl]/M	10^4k_{obs}/s^{-1}	10^4k_H/ l mol^{-1} s^{-1}
25·0	0·260	0·0250	0·072
	0·500	0·043	0·073
	1·00	0·082	0·076
	2·00	0·200	0·097
	3·00	0·54	0·178
	4·00	1·85	0·46
	5·00	8·8	1·76
	5·83	34	5·8
35·0	5·00	29·0	5·8
40·0	0·260	0·085	0·239
	1·00	0·307	0·284
	3·00	2·48	0·82
	5·00	52	10·4
50·0	0·260	0·182	0·51
	1·00	0·75	0·70
	3·00	6·5	2·17
	5·00	163	33
60·0	0·260	0·40	1·12
	1·00	1·53	1·42
	3·00	17·2	5·7
70·0	0·260	0·77	2·17
	1·00	3·3	3·09
	3·00	47	15·7

The second-order rate constants k_H for acid hydrolyses, obtained by dividing the k_c values by the concentrations of the catalyst acid, are also given in Tables 2—5. The activation parameters of Table 6 were obtained from plots of log (k_H/T) against $1/T$ by the least-square method.[1,2]

TABLE 4

Kinetic data for the acid hydrolysis of benzoic anhydride

T/°C	[HCl]/M	10^4k_{obs}/s^{-1}	10^4k_H/ l mol^{-1} s^{-1}
25·0	0·260	0·055	0·135
	0·500	0·092	0·144
	1·00	0·157	0·140
	2·00	0·293	0·138
	3·00	0·57	0·184
	4·00	1·18	0·295
	5·00	3·4	0·68
	5·83	8·2	1·41
35·0	5·00	10·7	2·14
	5·83	26·2	4·5
40·0	0·260	0·197	0·50
	1·00	0·57	0·52
	3·00	2·33	0·76
	4·00	5·6	1·40
	5·00	19·3	3·9
	5·83	47	8·1
50·0	0·260	0·41	1·03
	1·00	1·22	1·12
	3·00	5·7	1·87
	4·00	14·5	3·6
	5·00	52	10·4
60·0	0·260	0·88	2·29
	1·00	2·58	2·38
	3·00	13·7	4·5
	4·00	42	10·5
	5·00	148	29·6
70·0	0·260	1·73	4·5
	1·00	5·4	5·0
	3·00	33	10·9
	4·00	113	28·2

TABLE 5

Kinetic data for the acid hydrolysis of *p*-chlorobenzoic anhydride

T/°C	[HCl]/M	10^4k_{obs}/s^{-1}	10^4k_H/ l mol^{-1} s^{-1}
25·0	0·260	0·295	0·45
	0·500	0·37	0·43
	1·00	0·57	0·45
	2·00	0·95	0·42
	3·00	1·30	0·39
	4·00	1·55	0·36
	5·00	2·23	0·42
	5·83	2·62	0·43
40·0	0·260	0·85	1·38
	1·00	1·77	1·43
50·0	0·260	1·58	2·54
	1·00	3·3	2·67
60·0	0·260	2·98	5·0
70·0	0·260	5·4	9·3
	1·00	12·0	9·9

DISCUSSION

The diagnostic criteria [1] which will be used in this study are the effect of the substituent on the hydrolysis rate, the entropies of activation, and the acidity correlation of the reaction rate.

The effects of the substituent groups upon the rate of the acid hydrolysis of the anhydrides examined depend on the acidity of the solution. The trends of the plots of log k_c against Hammett's substituent constant[8] σ or against Brown's substituent constant[9] σ^+ at 25 °C (Figure 1) indicate[1,2,10,11] that a change in the reaction mechanism from $A2$ to $A1$ occurs as the acidity increases and that the $A1$ mechanism becomes predominant at an acid concentration which is lower for an electron-releasing group than for the electron-withdrawing one. It can be deduced from the plots of log k_c against σ at 25 °C (Figure 1) that, for instance, in the case of p-methoxybenzoic anhydride the $A1$ mechanism would be significant at [HCl] $> 1{\cdot}00$M, whereas for the p-chloro-derivative the mechanism, as suggested by the linear plot of log k_c against σ^+, would be mainly of the $A1$ type only at [HCl] $\geqslant 5{\cdot}00$M.

TABLE 6

Activation parameters[a] for the acid hydrolysis of *para*-substituted benzoic anhydrides at different acidities

	Substituent group							
	MeO		Bu^t		H		Cl	
[HCl]/M	ΔH_H^*	ΔS_H^*	ΔH_H^*	ΔS_H^*	ΔH_H^*	ΔS_H^*	ΔH_H^*	ΔS_H^*
0·260	21·2[b]	−11[b]	14·8	−32	15·2	−30	12·9	−35
	24·3[c]	−2[c]						
1·00	23·9	−2	16·1	−28	15·4	−29	13·2	−34
3·00	22·3	−2	18·2[b]	−19[b]	16·8[b]	−24[b]		
			21·0[c]	−10[c]	18·7[c]	−18[c]		
4·00					18·6[b]	−17[b]		
					21·9[c]	−7[c]		
5·00	20·9	−1	21·7	−3	20·5	−9		
5·83					20·9	−6		

[a] ΔH_H^* in kcal mol^{-1}, ΔS_H^* in cal mol^{-1} K^{-1}. [b] Values estimated for the temperature range 25—40 °C. [c] Values estimated for the temperature range 50—70 °C.

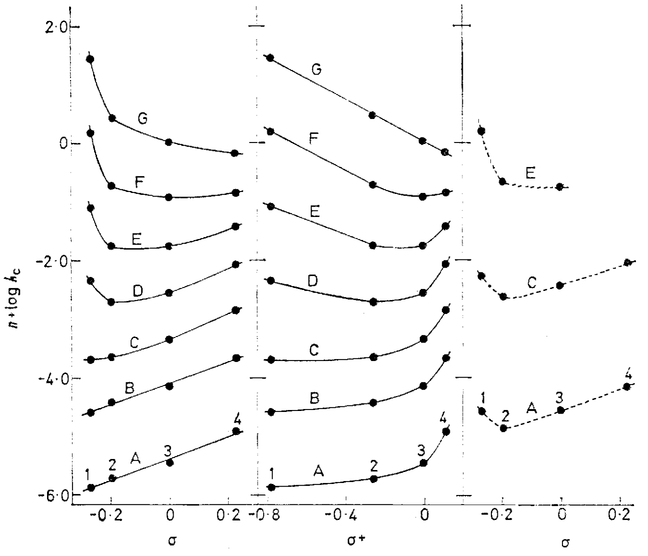

FIGURE 1 Plots of log k_c against σ and σ^+ at 25 °C (full lines) and of log k_c against σ at 50 °C (broken lines) and at different acidities: 1, MeO; 2, Bu^t; 3, H; 4, Cl; A, [HCl] = 0·260M, $n = 0$; B, [HCl] = 0·500M, $n = 1$; C, [HCl] = 1·00M, $n = 1{\cdot}5$; D, [HCl] = 2·00M, $n = 2$; E, [HCl] = 3·00M, $n = 2{\cdot}5$; F, [HCl] = 4·00M, $n = 3$; G, [HCl] = 5·00M, $n = 3{\cdot}5$

The observed order of the hydrolysis rates is modified when the temperature of the solution is increased (*cf.* Tables 2—5 and Figure 1), indicating[1,2] that the $A1$ mechanism is favoured by a temperature increase.

The entropies of activation (Table 6) provide additional support for the above conclusions. The temperature dependence of the hydrolysis rates has been investigated at various acid concentrations (*cf.* Tables 2—5). The plots of log (k_H/T) against $1/T$ are linear (Figure 2), in accord with Eyring's equation, over the whole temperature range covered, except at the following acidities at which the plots are curved (*cf.* Figure 2): MeO, [HCl] = 0·260M; Bu^t, [HCl] = 3·00M; H, [HCl] = 3·00 and 4·00M.

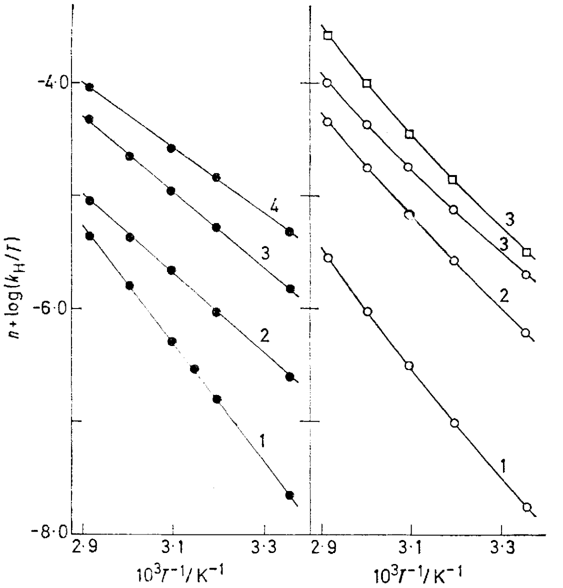

FIGURE 2 Typical plots of log (k_H/T) against $1/T$: ● [HCl] = 1·00M; 1, MeO, $n = 0$, ○ [HCl] = 0·260M; 2, Bu^t, $n = 1$, ○ [HCl] = 3·00M; 3, H, $n = 1{\cdot}5$, ○ [HCl] = 3·00M, □ [HCl] = 4·00M; 4, Cl, $n = 1{\cdot}5$

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[9] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979; P. R. Wells, *Chem. Rev.*, 1963, **63**, 171.

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The entropies of activation found for the hydrolysis of benzoic anhydride and its *p*-t-butyl- and *p*-chloro-derivatives at [HCl] $\leqslant$ 1·00M are markedly negative and in the range associated with the *A*2 mechanism.[1,2,6,11,12] Considerably less negative ΔS_H^* values (by *ca.* 30 cal mol^{-1} K^{-1}) are, on the contrary, observed for *p*-methoxybenzoic anhydride at [HCl] $\geqslant$ 1·00M, *i.e.*, at the acid concentrations where the log (k_H/T) against $1/T$ plots are linear. These ΔS_H^* values, which are independent of the acidity, are consistent with the *A*1 mechanism.[1,2,6,11,12]

The entropies of activation for the other anhydrides (Table 6) increase rapidly as the acidity increases, taking at high acidities values close to those found for the *A*1 mechanism in the case of *p*-methoxybenzoic anhydride. Therefore a change in the reaction mechanism from *A*2 to *A*1 occurs when the acid concentration is increased.

The observed deviations from Eyring's equation are ascribed [1,2,13] to the fact that the two reaction mechanisms, *A*1 and *A*2, contribute simultaneously to the acid hydrolysis, the *A*1 mechanism being predominant at higher temperatures. This is a consequence of the larger heat of activation associated with the *A*1 hydrolysis [1,3] (*cf.* Table 6).

It has been found previously [1] in the case of the perchloric acid catalysed hydrolyses of the anhydrides under study that the Zucker–Hammett criterion is useful in providing information only on the main mechanism involved in the acid hydrolyses and that independent evidence is necessary for the complete understanding of the reaction mechanism.

A linear relationship between log k_c and $-H_0$ [14] is found in the present work (Figure 3) for *p*-methoxybenzoic anhydride (slope 0·97), indicating that an *A*1 mechanism is operative; however the *A*2 mechanism has been also found to contribute significantly to the hydrolysis at the lowest acidities. For the other anhydrides S shaped curves are, on the contrary, observed.

The linear plot of log k_c against log [HCl] for *p*-chlorobenzoic anhydride (Figure 3; slope 0·96) would indicate an *A*2 mechanism over the whole acidity range investigated. However, according to suggestions above, this anhydride would hydrolyse by the *A*1 mechanism at the higher acidities examined. For benzoic anhydride and its *p*-t-butyl-derivative the initial parts of the log k_c against log [HCl] plots are linear in accord with an *A*2 mechanism (Bu^t, slope 1·1; H, slope 1·0), but the plots show an upward curvature at high acidities. In the light of the conclusions drawn above from the other mechanistic criteria, the deviations from the linear trend can be attributed to the change from the *A*2 to the *A*1 mechanism, as also suggested previously [1] for hydrolyses catalysed by perchloric acid. In fact, the deviations occur approximately at the acid concentrations where the contribution of the *A*1 mechanism to the hydrolysis reaction begins to be significant.

Conclusions.—The conclusions of the present work are analogous to those obtained previously [1] for the perchloric acid catalysed hydrolyses. However, the catalytic powers of perchloric and hydrochloric acids and their effects on the mechanisms of acid hydrolysis are different. In fact, the change from the *A*2 to the *A*1 mechanism with increasing acidity occurs at an acid concentration which is higher for hydrochloric acid than for perchloric acid. Moreover at 25 °C the hydrolyses of benzoic anhydride and its *p*-methoxy- and *p*-t-butyl-derivatives are faster in the presence of $HClO_4$ than in the presence of HCl (Figure 3) both when the *A*2 or a mixed mechanism is operative (low acidities) and when the reaction mechanism is exclusively of the *A*1 type (high acidities). In the latter case, however, the differences in the hydrolysis rates are larger than in the former. For *p*-chlorobenzoic anhydride the hydrolysis is slightly faster with hydrochloric acid (Figure 3) in the low acidity range where the *A*2 mechanism is involved, but it becomes much more rapid in the presence of $HClO_4$ at higher acidities when the perchloric acid catalysed hydrolysis proceeds by the *A*1 mechanism. In addition, at temperatures above 40 °C the hydrolyses are always faster in the presence of $HClO_4$ than in the presence of HCl (*cf.* Tables 2—5 and ref. 1).

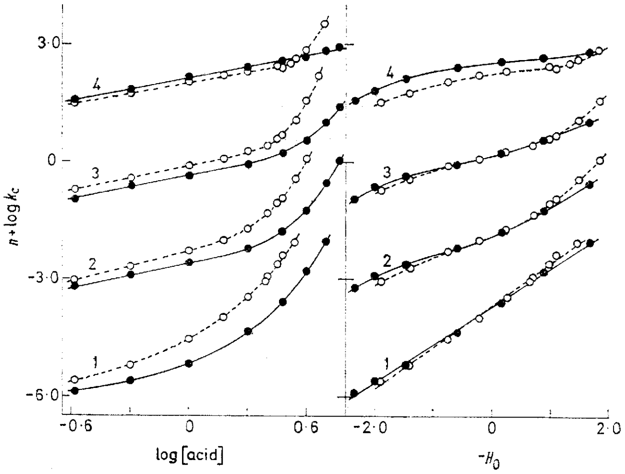

FIGURE 3 Plots of log k_c against log[acid] and $-H_0$ at 25 °C: ● HCl, ○ $HClO_4$ (ref. 1); 1, MeO, $n = 0$; 2, Bu^t, $n = 2{\cdot}5$; 3, H, $n = 4{\cdot}5$; 4, Cl, $n = 6{\cdot}5$; the H_0 values are known up to [$HClO_4$] = 4·00M and [HCl] = 5·00M (ref. 14)

These findings suggest that for the carboxylic anhydrides examined perchloric acid is a much more effective catalyst than hydrochloric acid in the *A*1 hydrolyses, whereas if the *A*2 mechanism is operative, it may be more or less effective than hydrochloric acid depending not only on the nature of the substituent group but also on the temperature.

If the protonating powers of the two acids as measured by the Hammett acidity function H_0 [14] are now taken

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[14] B. Torck, M. Hellin, and F. Coussemant, *Bull. Soc. chim. France*, 1962, 1664.

into account, it is possible to observe from the log k_c against $-H_0$ plots (Figure 3) that the hydrolyses are faster with hydrochloric acid when only the $A2$ mechanism is operative, whereas for the $A1$ hydrolyses the reaction rates are similar (for the *p*-methoxy-derivative at relatively low acidities) or higher in the presence of perchloric acid.

We can then conclude that the observed differences in the catalytic effectiveness of perchloric and hydrochloric acids are to be ascribed to the different protonating powers of these acids and to their specific electrolyte effects upon the $A1$ and $A2$ hydrolyses.[1,3-6]

[4/001 *Received, 2nd January,* 1974]