The Acid-catalysed Hydrolysis of Diaryl Carbonates

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The rates of hydrolysis of diphenyl and bis-(4-nitrophenyl) carbonates have been studied in aqueous acidic dioxan. The dependence of rate on acid concentration for the hydrolysis of diphenyl carbonate passes through a maximum in perchloric acid but not in hydrochloric or sulphuric acid. It is shown that the rate maximum in perchloric acid is not due to extensive protonation of the substrate as for amides but arises from specific electrolyte effects on the high neutral rate. All the acids studied decrease the rate of hydrolysis of bis-(4-nitrophenyl) carbonate. This decrease again reflects large negative salt effects on the neutral rate but rate measurements at constant ionic strength suggest the occurrence of very weak acid catalysis.

WILLIAMS and COOPER showed that the hydrolysis of diphenyl carbonate in dilute perchloric acid (50% aqueous dioxan) proceeds by both a neutral and an acid-catalysed pathway,[1] the neutral rate being about 40% of the rate in 0·1M-acid. It was also found that the rate of hydrolysis was strictly of the first order in acid over the concentration range 0—0·1M-perchloric acid. Quite different behaviour, however, has been reported for the hydrolysis of bis-(4-nitrophenyl) carbonate in aqueous acid.[2] There is a rapid pH-independent reaction as for diphenyl carbonate, but no apparent acid catalysis; the rate of reaction decreases as the hydrochloric acid concentration is increased over the range 1·0—5·29M. Fife and McMahon suggested that the apparent absence of acid catalysis arises from both the strong electron-withdrawing power of the nitro-substituent which reduces the equilibrium concentration of the conjugate acid to a very low level, and from the very rapid neutral hydrolysis pathway with which weak acid catalysis cannot complete.

In order to provide further evidence of the mechanism of hydrolysis of diaryl carbonates in the presence of acids, we have examined the effect of added acids and salts, at relatively high electrolyte strength, on the hydrolysis of diphenyl and bis-(4-nitrophenyl) carbonate.

EXPERIMENTAL

Materials.—The carbonates were prepared by standard methods.[3,4] Bis-(4-nitrophenyl) carbonate, twice recrystallised from carbon tetrachloride–cyclohexane, had m.p. 140—142 °C (lit.,[5] 140 °C) and diphenyl carbonate, a commercial sample recrystallised from absolute ethanol, had m.p. 78—80 °C (lit.,[6] 78 °C).

Acid-catalysed Hydrolyses.—The acids were of Analytical Reagent quality. Their concentrations were determined by titration with standard alkali. Lithium perchlorate was a recrystallised commercial sample. It was dehydrated at *ca.* 150 °C and kept in a vacuum for 24 h with a diffusion pump. Anhydrous lithium chloride and sodium salts were prepared similarly. Anhydrous dioxan was prepared by a standard method.

Kinetic Measurements.—The rates of hydrolysis were determined spectrophotometrically[7] by following the characteristic absorption of the phenolic products; diphenyl carbonate, 275 nm: bis-(4-nitrophenyl) carbonate, 330 nm. Spectrophotometric measurements were made on a Unicam SP 800 recording spectrometer operating on a constant wavelength scan mode and fitted with an external recorder and a thermostatically controlled cell holder (±0·1 °C). Diphenyl carbonate (50 µl of stock solution in dioxan) was injected into 3 ml of aqueous acidic solution in a 1 cm stoppered cell. In the case of bis-(4-nitrophenyl) carbonate, 25 µl of stock solution made up in dioxan were injected into 3 ml of acidic aqueous dioxan (3 : 2 v/v). The concentration of diphenyl carbonate used was *ca.* 10^{-4}M and of bis-(4-nitrophenyl) carbonate, $0·5 \times 10^{-4}$M.

Values of the first-order rate coneffiicent, k_1, were calculated from the usual equation and can be represented by equation (1), where k_W is the rate coefficient for the

$$k_1 = k_W + k_{H^+}[H^+] \qquad (1)$$

neutral reaction and k_{H^+} for the acid-catalysed reaction.

DISCUSSION

Hydrolysis of Diphenyl Carbonate.—The data for the hydrolysis of diphenyl carbonate are in Table 1. The rate of hydrolysis in both sulphuric and hydrochloric acid at first increases linearly with increase in acid concentration but above *ca.* 1·0M-acid begins to increase much less rapidly than stoicheiometric acidity. With perchloric acid, the rate of hydrolysis at first increases but then passes through a shallow maximum at *ca.* 1·5M-acid and then decreases. Such rate maxima can arise in two main ways: either because of extensive protonation of a basic substrate as in the hydrolysis of

TABLE 1

Hydrolysis of diphenyl carbonate in 5% (v/v) dioxan–water at 69·8 °C

(*a*) Effect of added acids

[Acid]/M *	0·500	1·00	1·50	2·00	3·00	4·00
$HClO_4$, 10^3k_1/min^{-1}	4·97	5·15	5·18	5·12	4·87	
H_2SO_4, 10^3k_1/min^{-1}	5·95	6·99		8·37	9·97	10·70
HCl, 10^3k_1/min^{-1}	6·49	8·07		10·40	11·9	13·60

(*b*) Effect of added salts

Salt/M	0·500	1·00	1·50	2·00	3·00	4·00
$NaClO_4$, 10^3k_1/min^{-1}		3·23		1·94	1·01	0·03
$NaHSO_4$, 10^3k_1/min^{-1}	5·68	5·94	6·08			

(*c*) With perchloric acid and sodium perchlorate ($[ClO_4^-]$ = 3·00M)

$[HClO_4]$/M	0·00	0·45	1·00	1·50	2·25	3·00
$[NaClO_4]$/M	3·00	2·55	2·00	1·50	0·75	0·00
10^3k_1/min^{-1}	1·01	1·87	2·72	3·36	4·22	5·07
$10^3k_{H^+}/[H^+]$/ l mol^{-1} min^{-1}		1·91	1·71	1·70	1·43	1·35

* $k_W = 4·86 \times 10^{-3}$ min^{-1}.

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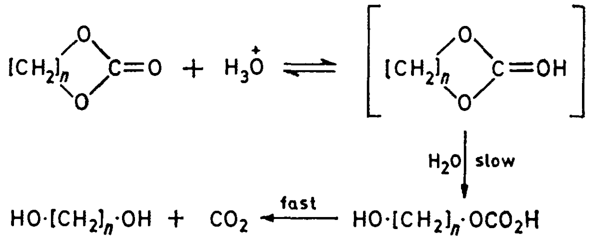
amides[8] and hydroxamic acids,[9] or from the superposition of a specific salt effect on an acid-catalysed reaction (often accompanied by a considerable effect on a concurrent neutral reaction) such as observed in the hydrolyses of some sulphites,[10] phosphates,[11] phosphinates,[12] and carboxylic esters.[13]

An explanation of different effects of various acids on the hydrolysis of diphenyl carbonate is provided by data for the effect of added salts [Table 1(*b*)]. Sodium hydrogen sulphate is moderately effective in catalysing the neutral hydrolysis whereas the addition of sodium perchlorate strongly slows down this reaction. The observed behaviour in perchloric acid could arise from combination of a negative salt effect on the neutral rate with positive acid catalysis. That this is indeed the case is shown by the fact that in mixtures of perchloric acid and sodium perchlorate at constant perchlorate ion concentration [Table 1(*c*)] the rate of hydrolysis increases continuously with increase of acid concentration. In such solutions the neutral rate should have a constant depressed value corresponding to the negative salt effect on it of 3·00M-perchlorate ion, and any increase above this will be due to acid catalysis. The values of $k_{\mathrm{H}^+}/[\mathrm{H}^+]$ in the solutions studied are not constant but fall as the acid concentration is increased and reflect the concave dependence of rate on acid concentration. It is generally assumed that, in such mixtures, the ionic strength effect will be approximately independent of the nature of the cation. A similar dependence of rate on the nature of the cation has been found, however, for other reactions, *e.g.*, the acid-catalysed hydrolysis of cyanamide.[14,15] The simple first-order dependence of rate on acid concentration observed by Cooper and Williams[1] at low acidity is masked at high acidities by complex electrolyte effects. The kinetic evidence therefore indicates that diphenyl carbonate hydrolyses by a similar mechanism in both dilute and concentrated acidic solution. The most probable mechanism is that established by Sarel and his co-workers[16,17] for the hydrolysis of cyclic carbonates in which a rapid pre-equilibrium protonation is followed by a slow bimolecular rate-limiting attack of the conjugate acid by a water molecule, and carbonyl–oxygen bond fission occurs.



Hydrolysis of Bis-(4-nitrophenyl) Carbonate.—The effect of added acids on the rate of hydrolysis of bis-(4-nitrophenyl) carbonate is quite different from that of diphenyl carbonate. Perchloric acid, sulphuric acid, and hydrochloric acid all depress the rate quite markedly [Table 2(*a*)]. This behaviour arises principally from the considerable negative salt effect exerted by the anion of the acid on the neutral rate as shown by the data in Table 2(*b*). Thus both perchloric acid and lithium perchlorate of the same concentration (2·00M) have an almost identical effect on the rate observed in the absence of added acids and salts ($k_{\mathrm{W}} = 13{\cdot}6 \times 10^{-3}$ min^{-1}) which is reduced to 2·40 and 2·06 × 10^{-3} min^{-1} respectively. Both hydrochloric acid and lithium chloride also exert approximately identical salt effects. The small increase in rate with increasing acid concentration [Tables 2(*c*) and 2(*d*)] in solutions of perchloric and hydrochloric acid in which the ionic strength was held constant by the addition of lithium perchlorate and lithium chloride respectively, suggests that very weak acid catalysis does in fact occur. Our conclusions on the hydrolysis of bis-(4-nitrophenyl) carbonate are therefore in general agreement with and provide further confirmation of those of Fife and McMahon.

TABLE 2

Hydrolysis of bis-(4-nitrophenyl) carbonate in 60% (v/v) dioxan–water at 39·4 °C

(*a*)

$[\mathrm{HClO_4}]$/M		0·24	0·58	1·15	1·73	2·00	2·30
10^3k_1/min^{-1}	13·6	8·64	7·12	4·50	2·82	2·40	1·76
$[\mathrm{HClO_4}]$/M	3·45	4·60					
10^3k_1/min^{-1}	0·75	0·43					
$[\mathrm{H_2SO_4}]$/M	0·271	1·09	1·63	2·17	2·71	3·26	5·43
10^3k_1/min^{-1}	12·3	9·91	6·79	5·42	4·58	3·58	1·15
$[\mathrm{HCl}]$/M	0·350	1·38	1·88	2·76	3·68	4·60	
10^3k_1/min^{-1}	12·0	10·5	7·87	5·77	3·85	2·73	

(*b*) Effect of added salts

$[\mathrm{LiClO_4}]$/M	0·300	0·600	0·900	1·20	1·50	1·80	2·00
10^3k_1/min^{-1}	10·0	7·63	5·61	3·97	3·05	2·41	2·06
$[\mathrm{LiCl}]$/M	0·200	0·400	0·800	1·00			
10^3k_1/min^{-1}	12·6	11·6	8·37	7·00			

(*c*) With perchloric acid and lithium perchlorate $[\mathrm{ClO_4^-}] = 2{\cdot}00$M)

$[\mathrm{HClO_4}]$/M		0·400	0·800	1·00	1·60	2·00
$[\mathrm{LiClO_4}]$/M	2·00	1·60	1·20	1·00	0·40	
10^3k_1/min^{-1}	2·06	2·08	2·23	2·25	2·42	2·40

(*d*) With hydrochloric acid and lithium chloride $[(\mathrm{Cl^-}] = 0{\cdot}500$M)

$[\mathrm{HCl}]$/M	0·100	0·200	0·300	0·400
$[\mathrm{LiCl}]$/M	0·500	0·400	0·300	0·200
10^3k_1/min^{-1}	11·0	11·3	11·7	11·6

We thank the S.R.C. for a studentship (to P. H. N.).

[2/1124 *Received*, 18*th May*, 1972]

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