

The Kinetics and Mechanism of the Hydrolysis of 2,3-(Phenylmethylenedioxy)benzene (*OO'*-Benzylidenecatechol) and Benzaldehyde Diphenyl Acetal

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General-acid catalysis has been detected in the hydrolysis of *OO'*-benzylidenecatechol with a Brønsted α -value of 0.47 for catalysis by carboxylic acids. There is also a relatively fast spontaneous hydrolysis with $k(\text{H}_2\text{O})/k(\text{D}_2\text{O}) = 1.61$ and $\Delta S^\ddagger = -21.1 \text{ cal deg}^{-1} \text{ mol}^{-1}$ at 75°. The entropy of activation for the hydronium-ion catalysed reaction is $-8.78 \text{ cal deg}^{-1} \text{ mol}^{-1}$ and the isotope effect $k(\text{H}_3\text{O}^+)/k(\text{D}_3\text{O}^+) = 0.92$ at 75°. These reactions are thought to proceed via *A-S_E2* mechanisms.

The hydrolysis of benzaldehyde diphenyl acetal is much faster than that of benzylidenecatechol and in 20% (w/w) dioxan-water mixtures is also general-acid catalysed with α approximately 1 and $k(\text{H}_3\text{O}^+)/k(\text{D}_3\text{O}^+) = 0.67$ at 15°. An *A-S_E2* mechanism was also favoured for this reaction.

UNTIL recently the hydrolyses of acetals were considered to be specific-acid catalysed.¹ Since 1968 however investigations of a wider range of acetals have shown that their hydrolyses are sometimes general-acid catalysed.²⁻⁷ We now report two additional examples, the hydrolyses of *OO'*-benzylidenecatechol and benzaldehyde diphenyl acetal.

RESULTS

The rate constants for the hydrolysis of *OO'*-benzylidenecatechol in aqueous buffers of constant pH increase with

¹ See B. Capon and M. C. Smith, *J. Chem. Soc. (B)*, 1969, 1031.

² T. H. Fife and L. K. Jao, *J. Amer. Chem. Soc.*, 1968, **90**, 4081.

³ E. Anderson and B. Capon, *Chem. Comm.*, 1969, 390; *J. Chem. Soc. (B)*, 1969, 1033.

⁴ E. Anderson and T. H. Fife, *J. Amer. Chem. Soc.*, 1969, **91**, 7163.

increasing concentration of buffer when the ionic strength is held constant at 0.5M (see Tables 1-3). The hydronium-ion concentration of the phosphate-, chloroacetate-, and the most acidic of the formate buffers changed appreciably on dilution and the results were corrected by Gold and Waterman's method (Table 1).⁸ The plots of k_{obs} or k_{corr} against concentration of undissociated acid are sometimes curved with the experimental values of k_{obs} or k_{corr} at the higher concentrations falling below the straight line defined by the results for the lower concen-

⁵ T. H. Fife and L. H. Brod, *J. Amer. Chem. Soc.*, 1970, **92**, 1681.

⁶ A. Kankaanpera and M. Lahti, *Acta Chem. Scand.*, 1969, **23**, 2465, 3266.

⁷ E. Anderson and T. H. Fife, *J. Amer. Chem. Soc.*, 1971, **93**, 1701.

⁸ V. Gold and D. C. A. Waterman, *J. Chem. Soc. (B)*, 1968, **839**, 849.

TABLE 1

The hydrolysis of *OO'*-benzylidencatechol at 65° in buffers requiring correction for changes in $[H_3O^+]$

$[HA]_{\text{stoich}}$ (M)	$10^5 k_{\text{obs}}$ (s ⁻¹)	$10^3 [H_3O^+]$ (M)	$10^4 \Delta [H_3O^+]$ (M)	$[HA]$ (M)	$10^5 k_{\text{corr}}$ (s ⁻¹)	$10^5 k_{\text{calc}}$ (s ⁻¹)
(A) Formic acid ($I = 0.50M$) ($K_{HA} = 1.493 \times 10^{-4}$, $K'_{HA} = 3.875 \times 10^{-4}M$ $[HCO_2Na]_{\text{stoich}} = [HCO_2H]_{\text{stoich}}/9$; pH = 2.71 – 2.79)						
0.450	8.44, 8.51	3.25	5.80	0.447	7.92, 7.99	8.88
0.360	8.08, 7.91	3.20	5.30	0.357	7.61, 7.44	7.72
0.270	6.98, 7.01	3.12	4.51	0.267	6.58, 6.61	6.56
0.180	5.64, 5.61	2.98	3.14	0.177	5.36, 5.33	5.40
0.090	4.17, 4.37	2.67	(0)	0.087	4.17, 4.37	4.24
Slope = $1.29 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$, s.d. 3.8%. Intercept = $3.11 \times 10^{-5} \text{ s}^{-1}$, s.d. 3.0%; $r = 0.997$. Only the results for the three over concentrations were used.						
(B) Chloroacetic acid ($I = 0.50M$) ($K_{HA} = 9.16 \times 10^{-4}$, $K'_{HA} = 2.38 \times 10^{-3}$) $[ClCH_2CO_2Na] = [ClCH_2CO_2H]/5$ pH = 2.25 – 2.10						
0.500	28.4, 28.4	10.5	26.7	0.490	26.3, 26.3	25.9
0.400	24.5, 24.2	10.3	24.0	0.390	22.6, 22.3	22.4
0.300	20.4, 20.9	9.87	20.1	0.290	18.8, 19.3	18.8
0.200	16.4, 16.5	9.22	13.5	0.191	15.3, 15.4	15.2
0.100	11.6, 11.7	7.86	(0)	0.092	11.6, 11.7	11.7
Slope = $3.67 \times 10^{-4} \text{ s}^{-1}$; s.d. 1.1%. Intercept $8.34 \times 10^{-5} \text{ s}^{-1}$; s.d. 1.6%; $r = 0.9995$						
(C) Phosphoric acid ($I = 0.50M$) ($K_{HA} = 4.256 \times 10^{-3}$, $K'_{HA} = 1.105 \times 10^{-2}M$) $[H_2PO_4Na] = [H_3PO_4]/4$ pH = 1.80 – 1.56						
0.402	97.1, 95.3	31.1	131.1	0.371	85.4, 83.6	84.6
0.322	80.7, 79.5	29.4	113.9	0.293	70.5, 69.3	70.7
0.241	66.9, 65.5	27.1	90.5	0.214	58.8, 57.4	56.7
0.161	49.1, 47.2	23.7	57.0	0.137	44.0, 42.1	43.0
0.080	28.7, 29.5	18.0	0	0.062	28.7, 29.5	29.6
Slope = $1.78 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$; s.d. 1.9%. Intercept = $1.86 \times 10^{-4} \text{ s}^{-1}$; s.d. 4.5%; $r = 0.9985$						
(D) Chloroacetic acid [$I = 0.05M$] ($K_{HA} = 9.16 \times 10^{-4}$, $K'_{HA} = 1.39 \times 10^{-3}$) $[ClCH_2CO_2Na] = 2 \times [ClCH_2CO_2H]$ pH = 3.03 – 2.97						
0.025	1.89, 1.95	0.670	0.875	0.0243	1.82, 1.88	1.83
0.020	1.69, 1.75	0.664	0.810	0.0193	1.63, 1.69	1.65
0.015	1.49, 1.54	0.653	0.706	0.0144	1.44, 1.49	1.47
0.010	1.33, 1.33	0.633	0.509	0.0094	1.29, 1.29	1.29
0.005	1.14, 1.10	0.582	(0)	0.0044	1.14, 1.10	1.11
Slope = $3.67 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$; s.d. 3.5%. Intercept = $9.48 \times 10^{-6} \text{ s}^{-1}$; s.d. 2.1%; $r = 0.9952$						

TABLE 2

The formic-acid-catalysed hydrolysis of *OO'*-benzylidencatechol at 65.10° ($I = 0.50M$)

pH 3.10 $[HCO_2Na] = [HCO_2H]/4.90$						
$[HCO_2H]$ (M)	0.083	0.166	0.249	0.332	0.415	
$10^5 k_{\text{obs}}$ (s ⁻¹)	2.67, 2.74	3.77, 3.81	4.97, 4.95	5.91, 5.95	6.99, 7.03	
$10^5 k_{\text{calc}}$ (s ⁻¹)	2.73	3.80	4.88	5.95	7.03	
Slope = $1.29 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$; s.d. 1.1%. Intercept = $1.65 \times 10^{-5} \text{ s}^{-1}$, s.d. 2.3%; $r = 0.999$						
pH 3.54 $[HCO_2Na] = [HCO_2H]/1.5$						
$[HCO_2H]$ (M)	0.060	0.120	0.180	0.240	0.300	
$10^5 k_{\text{obs}}$ (s ⁻¹)	1.60, 1.61	2.40, 2.35	3.07, 2.97	3.88, 3.81	4.45, 4.44	
$10^5 k_{\text{calc}}$ (s ⁻¹)	1.63	2.34	3.06	3.77	4.49	
Slope = $1.19 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$; s.d. 1.9%. Intercept = $9.13 \times 10^{-6} \text{ s}^{-1}$; s.d. 4.9%; $r = 0.999$						
pH 3.76 $[HCO_2Na] = 1.5 \times [HCO_2H]$						
$[HCO_2H]$ (M)	0.040	0.080	0.120	0.160	0.200	
$10^5 k_{\text{obs}}$ (s ⁻¹)	1.60	2.08	2.67	3.06	3.74	
$10^5 k_{\text{calc}}$ (s ⁻¹)	1.58	2.10	2.62	3.14	3.76	
Slope = $1.31 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$; s.d. 4.3%. Intercept = $1.05 \times 10^{-5} \text{ s}^{-1}$, s.d. 7.1%; $r = 0.997$						

TABLE 3

The acetic-acid-catalysed hydrolysis of benzylidencatechol at 65.10° ($I = 0.50M$)

pH 3.58 $[AcONa] = [AcOH]/10$						
$[AcOH]$ (M)	0.200	0.400	0.600	0.800	1.000	
$10^5 k_{\text{obs}}$ (s ⁻¹)	2.09, 2.09	3.11, 3.11	4.06, 3.99	4.69, 4.66	5.53, 5.45	
$10^5 k_{\text{calc}}$ (s ⁻¹)	2.11	3.08	4.04	5.01	5.97	
Slope $^a = 4.84 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$; s.d. 2.0%. Intercept $^a = 1.14 \times 10^{-5} \text{ s}^{-1}$; s.d. 3.7%; $r = 0.999$						
pH 4.08 $[AcONa] = [AcOH]/4$						
$[AcOH]$	0.080	0.160	0.240	0.320	0.400	
$10^5 k_{\text{obs}}$ (s ⁻¹)	1.08, 1.09	1.50, 1.52	1.88, 1.84	2.17, 2.21	2.37, 2.44	
$10^5 k_{\text{calc}}$ (s ⁻¹)	1.10	1.49	1.87	2.26	2.65	
Slope $^a = 4.84 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$; s.d. 3.5%. Intercept $^a = 7.10 \times 10^{-6} \text{ s}^{-1}$; s.d. 2.9%; $r = 0.998$						

^a Calculated from the results for the three lowest concentrations.

trations. This kind of behaviour has been observed in other general-acid catalysed reactions⁸ and because of this complication the constants were also measured at low buffer concentrations ($< 0.03M$) and with $I = 0.05M$ (Tables 1 and 4). Under these conditions the slight curvature in the plot of k_{obs} against concentration of acid was still found

arise from a property of the reaction rather than from the pK_a of the hydronium ion being wrongly assigned. The positive charge could lead to it being a less effective catalyst than expected from the Brønsted relationship for neutral catalysts and the extent of the deviation may depend on the structure of the transition state.

TABLE 4

The hydrolysis of benzylidene catechol in buffers with ionic strength 0.05M at 65.0°

AcOH pH 3.74 [AcONa] = [AcOH]/9							
[AcOH] (M)	0.00562	0.01125	0.0225	0.0450	0.0900	0.135	0.180
$10^5 k_{obs}$ (s ⁻¹)	0.625, 0.628	0.663, 0.659	0.732, 0.729	0.872, 0.854	1.10, 1.12	1.27, 1.31	1.48, 1.50
$10^5 k_{calc}$ (s ⁻¹)	0.627	0.661	0.729	0.864	1.13	1.40	1.67

Slope $a = 6.00 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$; s.d. 2.2%. Intercept $a = 5.94 \times 10^{-6} \text{ s}^{-1}$, s.d. 5.7%. $r = 0.999$

HCO ₂ H pH 3.68 [HCO ₂ Na] = 1.11 × [HCO ₂ H]							
[HCO ₂ H] (M)	0.009	0.018	0.027	0.036	0.045		
$10^5 k_{obs}$ (s ⁻¹)	0.794, 0.794	0.901, 0.912	1.03, 1.05	1.14, 1.12	1.26, 1.26		
$10^5 k_{calc}$ (s ⁻¹)	0.795	0.910	1.03	1.14	1.26		

Slope = $1.28 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$; s.d. 2.3%. Intercept = $6.79 \times 10^{-6} \text{ s}^{-1}$; s.d. 1.3%. $r = 0.998$

^a Calculated from the results at the four lowest concentrations.

with acetic acid and k_{cat} was evaluated from the linear portion of the plot. The values of k_{cat} are similar under the two sets of conditions.

The slopes of the plots k_{obs} or k_{corr} against the concentration of the buffer acid are within experimental error independent of pH. Therefore they are equal to the catalytic constants for general-acid catalysis (Table 5)

TABLE 5

Catalytic constants for the hydrolysis of *OO'*-benzylidene catechol at 65.0°

<i>I</i> = 0.50M	$10^5 k_{cat}$ (l mol ⁻¹ s ⁻¹)	pK_a
Acetic acid	4.84, 4.84	4.827
Formic acid	12.9, 12.9	3.826
	11.9, 13.1	
Chloroacetic acid	36.7	3.038

$\alpha = 0.470$ (s.d. 0.028); $\log G = 2.221$ (s.d. 0.107); $r = 0.991$

<i>I</i> = 0.05M	$10^5 k_{cat}$ (l mol ⁻¹ s ⁻¹)	pK_a
Acetic acid	6.00	4.827
Formic acid	12.6	3.826
Chloroacetic acid	36.7	3.038

$\alpha = 0.43$ (s.d. 0.07); $\log G = -2.290$ (s.d. 0.278); $r = 0.978$

and there is no general-base catalysis. The catalytic constants are related to the dissociation constants of the acids by the Brønsted equation [equation (1)], with p and

$$\log(k_{HA}/p) = a \times \log(q \times K_{HA}/p) + \log G \quad (1)$$

and q taken as 1 and 2 respectively. The value of a for the results at $I = 0.50$ was 0.47 and for the results at $I = 0.05$ was 0.43 (Table 5). The catalytic constant for the hydronium ion predicted from equation (1) on the assumption that $K(H_3O^+) = 55.5M$, $p = 3$, and $q = 2$ is $9.8 \times 10^{-2} \text{ l mol}^{-1} \text{ s}^{-1}$, 11 times greater than the experimental value $8.93 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$. Alternatively $K(H_3O^+)$ would have to be 0.336M ($pK_a^{calc} = 0.47$) to bring the point for catalysis by H_3O^+ on the line generated by the carboxylic acids. This value differs from the similarly derived values from the Brønsted relationship for the hydrolysis of vinyl ethers ($pK_a^{calc} = 0.21 + 0.1$)⁹ and for the hydrolysis of cyanoketen dimethyl acetal ($pK_a^{calc} = +1.53$).⁸ It therefore seems that these deviations

The pH-rate profile for the hydrolysis of *OO'*-benzylidene catechol in the absence of buffer was constructed from the intercepts of the plots of k_{obs} in buffers against the concentration of the buffer acid. The results (Table 6) fitted

TABLE 6

The pH-dependence of the rate of hydrolysis of *OO'*-benzylidene catechol at 65.10° ($I = 0.50M$)

Buffer	pH	$10^5 k_{obs}$ or $10^5 k_{int}$	$10^5 k_{calc}$ ^a
1.00M HCl ^b	0.09	1190, 1250, 1240	
0.10M HCl	1.19	90.6, 89.3	
0.010M HCl	2.11	9.72, 9.58	
CICH ₂ CO ₂ H	2.10	7.88	7.45
HCO ₂ H	2.71	2.97	2.56
"	3.10	1.65	1.51
"	3.54	0.913	1.03
AcOH	3.58	1.14	1.01
HCO ₂ H	3.76	1.05	0.925
AcOH	4.08	0.745	0.840
Phosphate	7.27	0.366, 0.376	
0.10M NaOH ^c	13	0.517	

^a The values of k_{int} for the carboxylic acid buffers were plotted against 10^{-pH} to give a straight line with slope $[k(H_3O^+)] = 9.45 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$ (s.d. 7.9%), intercept $[k(H_2O)] = 7.62 \times 10^{-6} \text{ s}^{-1}$ (s.d. 29%), $r = 0.982$; k_{calc} was calculated from these values. The value of the intercept is not well defined and a more accurate value for the rate constant for the spontaneous hydrolysis is obtained from the results in phosphate buffer. ^b $I = 1.00M$. ^c $I = 0.10M$.

the equation $k_{obs} = k_0 + k_H \times 10^{-pH}$ with $k_0 = 7.62 \times 10^{-6} \text{ s}^{-1}$ and $k_H = 9.45 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$. The plot of log

TABLE 7

The kinetics of hydrolysis of *OO'*-benzylidene catechol in aqueous perchloric acid at 25.14°

[HClO ₄]	-H ₀	$10^4 k_{obs}$
1.000	0.32	2.94, 2.95
2.000	0.82	11.1, 11.3
2.995	1.32	36.1, 37.3
3.947	1.78	116, 115
5.021	2.34	439, 446

k_{obs} for the hydrolysis in aqueous perchloric acid against $-H_0$ is a straight line with slope 1.07 (Table 7).

⁹ A. J. Kresge, H. L. Chen, Y. Chiang, E. Murrill, M. A. Payne, and D. S. Sagatys, *J. Amer. Chem. Soc.*, 1971, **93**, 413.

TABLE 8

The hydrolysis of benzaldehyde diphenyl acetal in 20 : 80 (w/w) dioxan-water mixtures at 65.0° ($I = 0.50M$)

HCO ₂ H pH* 3.53 [HCO ₂ Na] = [HCO ₂ H]/3						
[HCO ₂ H] (M)	0.114	0.228	0.343	0.457	0.571	
10 ³ k _{obs} (s ⁻¹)	2.60, 2.66	2.86, 2.92	3.20, 3.26	3.53, 3.48	3.67, 3.72	
10 ³ k _{calc} (s ⁻¹)	2.62	2.91	3.21	3.51	3.80	
Slope ^a = 2.59 × 10 ⁻³ l mol ⁻¹ s ⁻¹ ; s.d. 4.1%. Intercept ^a = 2.32 × 10 ⁻³ s ⁻¹ ; s.d. 1.4%. $r = 0.995$						
AcOH pH* 4.64 [AcONa] = [AcOH]/3						
[AcOH] (M)	0.133	0.266	0.533	0.799	1.066	1.332
10 ⁴ k _{obs} (s ⁻¹)	2.30, 2.28	2.59, 2.63	3.17, 3.19	3.65, 3.62	4.12, 4.09	4.35, 4.39
10 ⁴ k _{calc} (s ⁻¹)	2.30	2.59	3.19	3.78	4.37	4.96
Slope ^b = 2.21 × 10 ⁻⁴ l mol ⁻¹ s ⁻¹ ; s.d. 2.4%. Intercept ^b = 2.00 × 10 ⁻⁴ s ⁻¹ ; s.d. 1.0%. $r = 0.999$						
ClCH ₂ CH ₂ CO ₂ H pH* 3.66 [ClCH ₂ CH ₂ CO ₂ Na] = [ClCH ₂ CH ₂ CO ₂ H]/3						
[ClCH ₂ CH ₂ CO ₂ H] (M)	0.107	0.214	0.321	0.428	0.534	
10 ³ k _{obs} (s ⁻¹)	1.24, 1.22	1.37, 1.40	1.53, 1.55	1.65, 1.68	1.83, 1.79	
10 ³ k _{calc} (s ⁻¹)	1.24	1.38	1.52	1.67	1.81	
Slope = 1.33 × 10 ⁻³ l mol ⁻¹ s ⁻¹ ; s.d. 3.5%. Intercept = 1.10 × 10 ⁻³ s ⁻¹ ; s.d. 1.5%. $r = 0.995$						

^a Calculated from the results at the four lowest concentrations. ^b Calculated from the results at the three lowest concentrations.

The hydrolysis of benzaldehyde diphenyl acetal was studied in 20% (w/w) dioxan-water as it was not sufficiently soluble in water. This reaction is 10³–10⁴ times faster than the hydrolysis *OO'*-benzylidenecatechol in water. It shows buffer catalysis (Table 8) and again the plot of k_{obs} against concentration of the undissociated acid is curved at high concentrations of acetic acid. The α -value is 0.998 (d , 0.071) (Table 9).

TABLE 9

Catalytic constants for the hydrolysis of benzaldehyde diphenyl acetal at 65° in 20% w/w aqueous dioxan ($I = 0.50$)

	10 ⁴ k _{cat} (l mol ⁻¹ s ⁻¹)	pK _a
CH ₃ CO ₂ H	2.21	5.373
ClCH ₂ CH ₂ CO ₂ H	13.3	4.65 ^a
HCO ₂ H	25.9	4.287

$\alpha = 0.998$ (s.d. 0.071); $\log G = 1.42$ (s.d. 0.32); $r = 0.997$.

^a Estimated value.

DISCUSSION

pH-Independent Hydrolysis of OO'-Benzylidenecatechol.

—This reaction appears to follow a different mechanism from the pH-independent hydrolyses of *p*-nitrophenoxytetrahydropyran,^{2,5} benzaldehyde *S*-(2,4-dinitrophenyl) methyl thioacetal,¹⁰ and tropone diethyl acetal.⁴ These reactions have isotope effects which are *ca.* 1 and the entropy of activation for the hydrolysis of *p*-nitrophenoxytetrahydropyran is +2.2 cal deg⁻¹ mol⁻¹ at 50°. In contrast ΔS^\ddagger for the pH-independent hydrolysis of *O'*-benzylidenecatechol is -21.5 cal deg⁻¹ mol⁻¹ at 65° and $k_0(\text{H}_2\text{O})/k_0(\text{D}_2\text{O}) = 1.61$ at 75° (Table 10). This suggests that the latter reaction is not a spontaneous uncatalysed ionisation as proposed for the other reactions, which is reasonable since the intermediate carbonium ion should not be excessively stable nor the leaving group particularly good.

A mechanism involving attack of hydroxide ion on the conjugate acid also seems unlikely as the rate constant for this process would have to be very high to account for the experimental value of k_0 . This is seen from a steady-state analysis of equation (2) which yields the relationship given in equation (3). If it is

assumed that $k_{-1}[\text{H}_2\text{O}] \gg k_2[\text{OH}^-]$ and $k_1/k_{-1}[\text{H}_2\text{O}] = 10^{-5}$, which is a conservative estimate since the pK_a

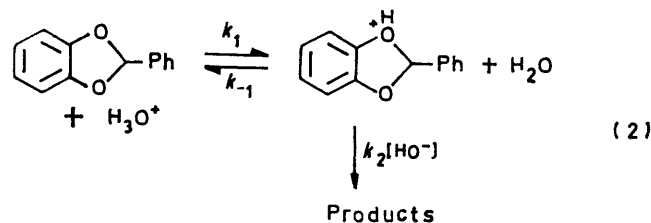
TABLE 10

Temperature dependence and isotopic effect for the hydrolysis of *OO'*-benzylidenecatechol in phosphate buffer pH 7.85 ($I = 0.028M$)^a

Temperature (°C)	85.24	75.17	65.00	75.17 ^b
10 ⁶ k _{obs} (s ⁻¹)	23.8, 23.9	9.95, 9.99	3.80, 3.84	6.15, 6.25

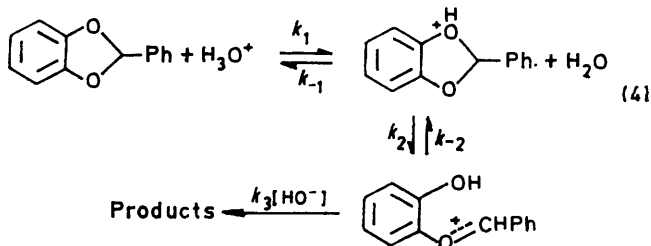
^a The logarithms of k_{obs} were plotted against the reciprocals of the absolute temperature to yield E_a 21,660 cal mol⁻¹ (s.d. 0.41%). The following activation parameters were calculated from this: $\Delta H^\ddagger = 20,999$ (cal mol⁻¹) (s.d. 80 cal mol⁻¹) $\Delta S^\ddagger = -21.49$ cal mol⁻¹ (s.d. 0.35 cal mol⁻¹) at 65°. ^b In D₂O, pD = 7.90.

of anisole is -6.5,¹¹ substitution of the experimental value of k_{obs} at 65° (4.9×10^{-6} s⁻¹) leads to a value of $k_2 = 5 \times 10^{13}$ l mol⁻¹ s⁻¹. This is much larger than



$$k_{obs} = k_1 k_2 [\text{H}^+][\text{HO}^-] / (k_{-1} + k_2[\text{HO}^-]) \quad (3)$$

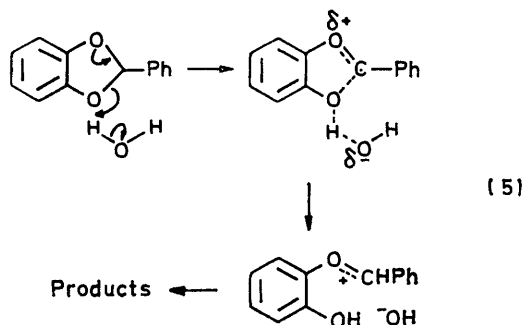
the second-order constant for a diffusion-controlled reaction and hence this mechanism can be excluded. The mechanism of equation (4) can be excluded on



¹⁰ T. H. Fife and E. Anderson, *J. Amer. Chem. Soc.*, 1970, **92**, 5464.

¹¹ E. M. Arnett, *Progr. Phys. Org. Chem.*, 1963, **1**, 325.

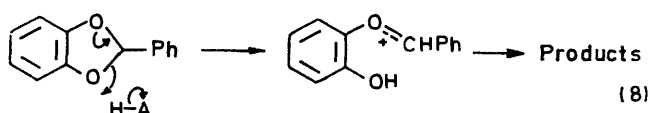
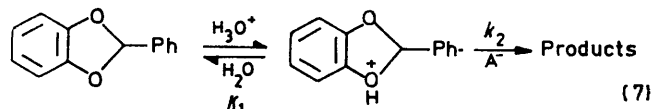
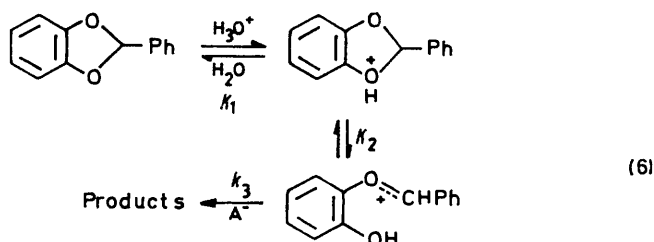
similar grounds. If k_{-2}/k_2 were taken as 1 a value of 5×10^{13} can be calculated for k_3 and if this process occurred k_{-2}/k_2 would be expected to be much smaller than one leading to an even higher value. This leaves a general acid-catalysed (S_E2) hydrolysis as the most likely mechanism [equation (5)]. This is consistent



with the isotope effect $k(\text{H}_2\text{O})/k(\text{D}_2\text{O}) = 1.61$ at 75° and the entropy of activation -21.47 cal deg^{-1} mol^{-1} at 65° (Table 10). The second-order constant for this process, $5 \times 10^{-6}/55.5 = 9 \times 10^{-8}$ l mol^{-1} , is larger than that calculated from the Brønsted equation for catalysis by carboxylic acids, *ca.* 5×10^{-10} , but such behaviour is not unusual.¹² Thus a positive deviation for general-acid catalysis by water from the Brønsted plot for carboxylic acids has been noted in the dehydration of acetaldehyde hydrate.¹² In contrast when the pH-independent hydrolysis involves an uncatalysed ionisation the difference between the experimental and calculated values of k_0 is much larger. Thus k_0 for the hydrolysis of 2-(nitrophenoxy)tetrahydropyran is *ca.* 10^5 times greater than the value estimated from the α -coefficient for catalysis by carboxylic acids (calculated from results in references 2 and 5).

Catalysis by Carboxylic Acids, Phosphoric Acid, and the Hydronium Ion.—It is difficult to be certain of the mechanism of hydrolysis of *OO'*-benzylidene catechol catalysed by carboxylic acids. Three mechanisms were considered [equations (6)—(8)]. That of equation (6) leads to the following expression for the catalytic constant $k_{\text{HA}} = k_3 K_1 K_{\text{HA}}$ where K_{HA} is the dissociation constant of HA. On substitution of the known values of k_{HA} and K_{HA} and an assumed value of 10^{-5} l mol^{-1} for K_1 values of 10^4 — 10^5 l mol^{-1} s $^{-1}$ are obtained for $k_3 K_2$ when HA is acetic, chloroacetic, or formic acid. So unless K_1 has been underestimated by several powers of 10 and/or K_2 were very small it is not necessary for k_3 to take a value greater than the rate constant for diffusion 10^{10} — 10^{11} l mol^{-1} s $^{-1}$. Kinetic analysis of equation (7) leads to a similar conclusion. Now $k_{\text{HA}} = k_2 K_1 K_{\text{HA}}$ and substituting the experimental values of k_{HA} and K_{HA} and an estimated value of K_1 (10^{-5} l mol^{-1}) leads to a value of k_2 of 10^4 — 10^5 l mol^{-1} s $^{-1}$ much less than the diffusion controlled limit. These

two mechanisms are therefore possible as well as the one involving mechanistic general-acid catalysis [equation



[8)]. The mechanism of equation (6) involves recyclisations of the initially formed carbonium ion, a process which has been demonstrated to occur concurrently with hydrolysis of the 2,3-*OO*-benzylidene-norbornane-*exo*-3-diols.¹³ However with *OO'*-benzylidene catechol recyclicalion would involve an intramolecular attack by a phenolic hydroxy-group instead of an alcoholic hydroxy-group. This is much less likely to occur since a phenolic hydroxy-group is much less basic than an alcoholic hydroxy-group; *e.g.* $\text{p}K_{\text{a}}(\text{methanol}) = -2$ and $\text{p}K_{\text{a}}(\text{phenol}) = -6.5$.

A mechanism similar to that of equation (7) has been proposed for the formic-acid-catalysed hydrolysis of 2-(*p*-methoxyphenyl)-4,4,5,5-tetramethyl-1,3-dioxolan.^{14,5} An *A-2* mechanism was also considered likely for the hydronium-ion-catalysed 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolan for which $\Delta S^\ddagger = 14.2$ cal deg^{-1} mol^{-1}

TABLE 11

The temperature dependence of the rate constant for the hydrolysis of *OO'*-benzylidene catechol in 1M-HClO₄^a

Temperature ($^\circ\text{C}$)	$10^4 k_{\text{obs}}$ (s^{-1})
65.00	173, 167, 164
55.00	65.4, 65.4, 65.8
45.00	24.8, 25.0, 25.1
35.00	8.79, 8.75, 8.88
25.14	2.98, 2.94, 2.95

^a The logarithms of k_{obs} were plotted against the reciprocals of the absolute temperature to yield $E_{\text{a}} = 20,242$ cal mol^{-1} (s.d. 0.36%). The following activation parameters were calculated from this: $\Delta H^\ddagger = 19,570$ cal mol^{-1} (s.d. 70 cal mol^{-1}), $\Delta S^\ddagger = -8.95$ cal deg^{-1} mol^{-1} (s.d. 0.2 cal deg^{-1} mol^{-1}) at 65.0° .

and $k(\text{H}_3\text{O}^+)/k(\text{D}_3\text{O}^+) = 0.42$.¹⁴ The entropy of activation for the hydronium-ion catalysed hydrolysis of *OO'*-benzylidene catechol is also negative (-8.95 cal deg^{-1} mol^{-1} at 65° , Table 11) and hence consistent with an

¹² See R. P. Bell, 'Acid-Base Catalysis,' Oxford University Press, Oxford, 1941, p. 92.

¹³ B. Capon and M. I. Page, *Chem. Comm.*, 1970, 1443.

¹⁴ T. H. Fife, *J. Amer. Chem. Soc.*, 1967, **89**, 3228.

A-2 mechanism but the solvent isotope effect [$k(\text{H}_3\text{O}^+)/k(\text{D}_3\text{O}^+) = 0.92$ at 65° , Table 12] does not appear to be so since $k(\text{H}_3\text{O}^+)/k(\text{D}_3\text{O}^+)$ normally falls in the range 0.3–0.7 for an *A-2* mechanism.¹⁵ The entropy of

activation for the formic-acid catalysed reaction seems to be most reasonable for the water-catalysed reaction we therefore favour this mechanism for the carboxylic acid-catalysed reaction. The entropy of activation for the formic-acid catalysed reaction

TABLE 12

Compound	Medium	Temp. ($^\circ\text{C}$)	$10^3k(\text{H}_3\text{O})$	$10^3k(\text{D}_3\text{O}^+)$	$k(\text{H}_3\text{O}^+)/k(\text{D}_3\text{O}^+)$
Benzylidene catechol	Aqueous 1.04M HCl and DCl	65.0	14.1, 14.1, 14.4	12.9, 13.0, 12.6	1.11
Benzaldehyde diphenyl acetal	0.102M-HCl and DCl in water dioxan mixtures with mole fraction of dioxan 0.0519	15.0	6.65, 6.75	9.81, 9.80	0.68

TABLE 13

The temperature dependence of the rate constant for the hydrolysis of *OO'*-benzylidene catechol catalysed by formic acid ($I = 0.05\text{M}$)^a

65.25° $[\text{HCO}_2\text{Na}] = [\text{HCO}_2\text{H}]/5$ pH 3.18

$[\text{HCO}_2\text{H}]$ (M)	0.010	0.020	0.030	0.040	0.050
10^6k_{obs} (s^{-1})	1.13, 1.10	1.26, 1.28	1.39, 1.43	1.53, 1.56	1.69, 1.65
10^6k_{calc} (s^{-1})	1.13	1.26	1.40	1.54	1.68

Slope = $1.38 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$; s.d. 3.3%. Intercept = $9.87 \times 10^{-6} \text{ s}^{-1}$; s.d. 1.5%. $r = 0.996$

60.50° $[\text{HCO}_2\text{Na}] = [\text{HCO}_2\text{H}]/5$ pH 3.17

$[\text{HCO}_2\text{H}]$ (M)	0.010	0.020	0.030	0.040	0.050
10^6k_{obs} (s^{-1})	0.870	0.995	1.12	1.22	1.32
10^6k_{calc} (s^{-1})	0.880	0.993	1.11	1.22	1.33

Slope = $1.12 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$; s.d. 3.4%. Intercept = $7.68 \times 10^{-6} \text{ s}^{-1}$; s.d. 1.7%. $r = 0.998$

55.18° $[\text{HCO}_2\text{Na}] = [\text{HCO}_2\text{H}]/5$ pH 3.16

$[\text{HCO}_2\text{H}]$ (M)	0.010	0.020	0.030	0.040	0.050
10^6k_{obs} (s^{-1})	5.55, 5.44	6.23, 6.37	7.02, 7.04	7.73, 7.89	8.55, 8.46
10^6k_{calc} (s^{-1})	5.52	6.28	7.03	7.78	8.53

Slope = $7.53 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$; s.d. 2.1%. Intercept = $4.77 \times 10^{-6} \text{ s}^{-1}$; s.d. 1.1%. $r = 0.998$

50.48° $[\text{HCO}_2\text{Na}] = [\text{HCO}_2\text{H}]/5$ pH 3.14

$[\text{HCO}_2\text{H}]$ (M)	0.010	0.020	0.030	0.040	0.050
10^6k_{obs} (s^{-1})	3.16, 3.11	3.74, 3.82	4.30, 4.35	4.68, 4.76	5.17, 5.20
10^6k_{calc} (s^{-1})	3.22	3.73	4.23	4.73	5.24

Slope = $5.04 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$; s.d. 1.8%. Intercept = $2.72 \times 10^{-6} \text{ s}^{-1}$; s.d. 2.3%. $r = 0.995$

^a The logarithms of the slope were plotted against the reciprocals of the absolute temperatures to yield $E_a = 14,758 \text{ cal mol}^{-1}$ (s.d. 5.5%). The following activation parameters were calculated from this: $\Delta H^\ddagger = 14,085 \text{ cal mol}^{-1}$ (s.d. 750 cal mol^{-1}), $\Delta S^\ddagger = -34.79 \text{ cal deg}^{-1} \text{ mol}^{-1}$ (s.d. 2.3 $\text{cal deg}^{-1} \text{ mol}^{-1}$) at 65.25° .

TABLE 14

The deuterioacetic-acid-catalysed hydrolysis of *OO'*-benzylidene catechol

pD 3.92 $I = 0.50\text{M}$ $[\text{AcONa}] = [\text{AcOD}]/10$ 65.10°

$[\text{AcOD}]$ (M)	0.204	0.408	0.612	0.816	1.019
10^6k_{obs} (s^{-1})	1.21, 1.20	1.88, 1.91	2.45, 2.52	2.94, 3.00	3.33, 3.30
10^6k_{calc} (s^{-1})	1.22	1.86	2.50	3.14	3.78

Slope ^{a,b} = $3.13 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$; s.d. 3.09%. Intercept ^a = $5.82 \times 10^{-6} \text{ s}^{-1}$. $r = 0.998$

pD 4.06 $I = 0.05\text{M}$ $[\text{AcONa}] = [\text{AcOD}]/10$ 65.00°

$[\text{AcOD}]$ (M)	0.010	0.020	0.030	0.040	0.050
10^6k_{obs} (s^{-1})	4.06	4.52	4.92	5.28	5.62
10^6k_{calc} (s^{-1})	4.07	4.50	4.93	5.36	5.79

Slope ^{a,c} = $4.30 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$; s.d. 4.0%. Intercept ^a = $3.64 \times 10^{-6} \text{ s}^{-1}$; s.d. 1.0%. $r = 0.999$

^a Calculated from the results at the three lowest concentrations. ^b This was combined with the results in Table 2 to yield a value for $k(\text{AcOH})/k(\text{AcOD}) = 1.5$. ^c This was combined with the results in Table 5 to yield a value for $k(\text{AcOH})/k(\text{AcOD}) = 1.4$.

activation and solvent-isotope effect for the hydronium-ion-catalysed reaction would therefore be most simply explained by an *A-S_B-2* mechanism. As this also

($-34.8 \text{ cal deg}^{-1} \text{ mol}^{-1}$, Table 13) and the solvent isotope effect [$k(\text{AcOH})/k(\text{AcOD}) = 1.4$ – 1.5 , Table 14] are consistent but not uniquely consistent with this mechanism.

The plot of $\log k_{\text{obs}}$ against H_0 for the hydrolysis of benzylidene catechol in aqueous perchloric acid using

¹⁵ Cf. P. M. Laughton and R. E. Robertson in 'Solute-Solvent Interactions,' J. F. Coetzee and C. D. Ritchie, eds., M. Dekker, New York, 1969, p. 440.

the data in Table 7 is a straight line with slope -1.07 and the ϕ -value is 0.11 . It is interesting that these values are very similar to those reported for another $A-S_E2$ reaction, the hydrolysis of α -phenylvinyl diethyl phosphate (slope = 1.15 , $\phi = -0.2$).¹⁶ The hydrolysis of benzylidenecatechol is 30% faster in 1M-perchloric acid ($k_{\text{obs}} = 1.65 \times 10^{-2} \text{ s}^{-1}$ at 65°) than in 1M-hydrochloric acid ($k_{\text{obs}} = 1.25 \times 10^{-2} \text{ s}^{-1}$ at 65°) the opposite of the behaviour reported for the hydrolysis of formaldehyde dimethyl acetal.¹⁷ When potassium bromide was used instead of sodium chloride to maintain the ionic strength constant the rate constant was only slightly affected (see Table 15).

TABLE 15

The effect of sodium bromide on the rate of hydrolysis of *OO'*-benzylidenecatechol in formate buffers at 65° ($I = 0.50\text{M}$)

[HCO ₂ H] (M)	[NaCl] (M)	[NaBr] (M)	pH	$10^5 k_{\text{obs}}$
0.083	0.483	0	3.09	2.70
0.083	0	0.483	3.08	2.59
0.332	0.432	0	3.10	5.91
0.332	0	0.483	3.08	6.02

The catalytic constant for phosphoric acid ($1.78 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$ at 65°) is slightly larger than that predicted from equation (1) with $p = 3$, $q = 2$, and $pK_a = 2.371$, viz. $1.15 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$. This behaviour is commonly found with reactions thought to follow an $A-S_E2$ mechanism.¹⁸

The hydrolysis of benzaldehyde diphenyl acetal was also studied in order to find how significant the presence of the ring in benzylidenecatechol is for general-acid catalysis. Unfortunately this compound was not sufficiently soluble in water and its hydrolysis was studied in 20% aqueous dioxan. The α -value for reaction under these conditions is 0.998 ± 0.14 (95% confidence limits) and the isotope effect $k(\text{H}_3\text{O}^+)/k(\text{D}_3\text{O}^+) = 0.67$. The smaller α -value in the reaction of benzylidenecatechol suggests that there is less proton transfer in its transition state than in that for the reaction of benzaldehyde diphenyl acetal. According to Hammond's postulate the oxygen of the benzylidenecatechol should therefore be more basic in the transition state than that of benzylidene diphenyl acetal in its transition state. This in turn suggests a greater amount of bond breaking in the transition state for the reaction of benzylidenecatechol than in that for the reaction of benzaldehyde diphenyl acetal. Viewing these reactions at their microscopic reverses, this implies that O-C bond in the transition state for the intramolecular general-base catalysed attack of a phenolic group on a carbonium/oxonium ion is longer than that for intermolecular attack.

¹⁶ C. A. Bunton and L. Robinson, *J. Amer. Chem. Soc.*, 1969, **91**, 6072.

¹⁷ D. McIntyre and F. A. Long, *J. Amer. Chem. Soc.*, 1954, **76**, 3240; C. A. Bunton, J. H. Crabtree, and L. Robinson, *ibid.*, 1968, **90**, 1258.

¹⁸ J. M. Williams and M. M. Kreevoy, *Adv. Phys. Org. Chem.*, 1968, **6**, 63.

EXPERIMENTAL

OO'-Benzylidenecatechol.—Catechol (0.1 mol) was dissolved in dry pyridine (100 ml) and freshly distilled benzylidene chloride (0.1 mol) in pyridine (50 ml) was added to the mixture. This was then heated under a reflux condenser in an atmosphere of nitrogen for 12 h and the pyridine was evaporated (rotary evaporator). The residue was dissolved in methylene chloride and washed successively with water, 0.01M-hydrochloric acid, 0.5M-sodium hydroxide (5 times), and water. The solution was dried, evaporated, and the product recrystallised twice from aqueous ethanol; yield 50%; m.p. $49-50^\circ$ (Found: C, 79.1; H, 5.3. $\text{C}_{13}\text{H}_{10}\text{O}_2$ requires C, 78.8; H, 5.1%), δ (CDCl_3) 6.83 (s, 4), 6.03 (s, 1), and 7.54 p.p.m. (m, 5); mass spec. parent ion 198, 197 (equal intensity to parent ion), 196 (metastable), 121, 105, 77.

Benzaldehyde Diphenyl Acetal.— α -Dibromotoluene (0.02 mol) prepared from the photobromination of toluene was allowed to react with phenol (0.10 mol) in pyridine under similar conditions to those described in the last section. Thin-layer chromatography (t.l.c.) of the crude product showed the presence of at least 12 compounds. This mixture was chromatographed on a large plate and the fraction collected having R_F 0.35 in 3% diethyl ether-light petroleum (b.p. $40-60^\circ$). This was distilled ($100^\circ/0.8$ mm) and the residue was recrystallised from light petroleum (b.p. $40-60^\circ$), m.p. $55-56^\circ$; yield 0.7% (Found: C, 82.8; H, 6.0. $\text{C}_{19}\text{H}_{16}\text{O}_2$ requires C, 82.6; H, 5.8%); δ (CDCl_3) 6.66 (s, 1) and 7.3 p.p.m. (m, 15); mass spec. parent ion 276, very intense PhCHOPh peak at 183, 165, 155, 106 ($\text{C}_6\text{H}_5\text{CHO}$), 105 ($\text{C}_6\text{H}_5\text{CO}$).

Kinetic Procedure.—All the reactions were followed by measuring the formation of aldehyde spectrophotometrically at 250 nm. A Cary-14 spectrophotometer in which the pen-recorder drive wire drove a transmitting potentiometer was used. A constant voltage from a Mallory battery was fed across the ends of this potentiometer and a voltage proportional to pen travel was obtained from the wiper. This was fed to a Solatron data-logger equipped with a Creed tape punch thus enabling voltages proportional to the absorbance to be punched at constant time intervals. Rate constants were calculated from the results on an KDF9 computer using a generalised least-squares method which treated the absorbances at time zero and infinity and the first-order rate constant as disposable parameters.^{19,20} The most satisfactory results were obtained when the reaction was followed for 4–5 half-lives. It has been reported that a generalised least-squares method which treats the infinity value as a disposable parameter does not give satisfactory results²¹ but this is probably because the reactions were not followed for more than 2 half-lives. In our experience when this is done a satisfactory estimate of the infinity value is not obtained and the standard deviation is high. Some of the slower runs were carried out in a five-sample cell compartment. The movement of this and the rate of punching were controlled by the digital clock of the data-logger. The program used to calculate the results first sorted them and then carried out generalised least-squares calculation on each run.

¹⁹ W. E. Deming, 'Statistical Adjustment of Data,' Dover Publications Inc., New York, 1964.

²⁰ W. E. Wentworth, *J. Chem. Educ.*, 1965, **42**, 96, 162.

²¹ J. P. Klinman and E. R. Thornton, *J. Amer. Chem. Soc.*, 1968, **90**, 4390.

The cell compartment of the spectrophotometer was thermostatted by circulating water from a Lauda thermostat. The temperature was measured in the cell with a thermometer which had been calibrated against an N.P.L. standardised thermometer. It was constant to ± 0.03 °C. 10 mm. Spectrosil cells were used. The buffer (2.5 ml) was placed in the cell and allowed to equilibrate for 30 min. A stock solution of the substrate in dioxan (25 μ l) was added from a Hamilton syringe. The cell was then removed, vigorously shaken, and returned to the cell holder. For fast runs [$t(1/2) < 10$ min] the solutions were stirred with a glass rod equilibrated at the same temperature.

The values of k_{obs} for the reactions in phosphate, chloroacetate, and the most acidic formate buffer were corrected for variations in the concentration of hydrogen ion. The method of Gold and Waterman was followed except that the results were corrected to the hydrogen-ion concentration of the most dilute buffer (Table 1). The value of $k(\text{H}_3\text{O}^+)$ at $I = 0.5\text{M}$ was calculated from the results in 0.1 and 0.01M-hydrochloric acid to be $8.93 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$ at 65° and

at $I = 0.05\text{M}$ from the values of k_{obs} in buffers extrapolated to zero buffer concentration and the calculated hydrogen-ion concentration to be $7.78 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$. The values of k_{obs} or k_{corr} were plotted against the concentration of undissociated acid using a linear least-squares method. The variation of k_{obs} or k_{corr} with buffer concentration for each set of data was tested for curvature by checking if the plot for the three lowest concentrations gave a lower standard deviation of the slope and a greater coefficient of correlation than that for all the concentrations in the set (generally 5), and if the slope of the plot for the three lowest concentrations differed by more than three standard deviations from that for three highest concentrations. When this was found the slope and intercept of the plot for the three lowest concentrations was used. The calculation of k_{corr} and the least-squares calculations were performed using the Cotan on-line desk system of the Glasgow University KDF9 computer. The programs were written in Algol.

[1/1845 Received, October 11th, 1971]