Temperature Dependence of the Rates of Hydrolytic Reactions in Concentrated Perchloric Acid Solutions

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The rates of the acid catalysed hydrolyses of phenyl, ethyl, t-butyl, and 4-nitrophenyl acetates and of diethyl sulphite have been determined as a function of perchloric acid concentration and temperature. Enthalpies and entropies of activation, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were deduced for the hydrolytic reactions as a function of perchloric acid concentration. The concentration dependences of the thermodynamic data are discussed in terms of reaction mechanism and the influence of hydration phenomena on reaction rates in concentrated acid solutions.

INFORMATION concerning the mechanisms of hydrolytic reactions catalysed by concentrated aqueous solutions of strong acids has been gained from empirical correlations between rate constants, water activities, and acid concentration or acidity functions.[1-3] Frequently such correlations have involved rate and water activity or acidity function data which refer to different temperatures and it has been emphasized that the resulting empirical parameters, used as criteria of mechanism, may be in error.[4] Knowledge of entropies of activation has also helped in the diagnosis of reaction mechanism.[5,6] However values of $\Delta S^{\ddagger}$ vary significantly with the concentration of catalysing acid for which the variation of rate of reaction with temperature has been determined.[4,7,8] A similar variation in enthalpies of activation has been reported particularly for reactions which *undergo* a change of mechanism as the concentration of strong acid is increased [7,8] For three reactions which did not undergo a change in mechanism Smith and Yates have shown that the dependence of $\Delta H^{\ddagger}$ on acid concentration largely resulted from the variation of the water activity of aqueous sulphuric acid solutions with temperature.[4] Consistent sets of $\Delta H^{\ddagger}$ values were calculated from the variation of rate constant with temperature for different sulphuric acid solutions with the same water activity. Further information concerning the mutual effects of acid concentration, temperature, and solvent activity on the rates of reactions in concentrated acid solutions is needed in order to test the generality of the conclusions of Smith and Yates.[4,7,8] Data are here reported for the hydrolyses of ethyl,[7,9,10] t-butyl,[10] phenyl,[7,9] and 4-nitrophenyl [7,9] acetates and of diethyl sulphite [11] in aqueous perchloric acid solutions as a function of temperature.

EXPERIMENTAL

The rates of hydrolysis of ethyl, t-butyl, phenyl, and 4-nitrophenyl acetates were deduced from the time dependences of absorbance values at 210, 211, 267, and 317 nm respectively, which were measured using Unicam SP 1800 and 8000 spectrophotometers fitted with thermostatted (± 0.13 K) cell compartments. Perchloric acid solutions were prepared by dilution with water of AnalaR aqueous 71—73 w/w % perchloric acid (Hopkin and Williams) and were determined volumetrically. Reaction solutions were prepared by volume from aqueous perchloric acid at the temperature under investigation and liquid ester. One run was performed for each perchloric acid concentration at each temperature. Concentrations of ester in reacting solutions were *ca.* 10^{-2} mol dm^{-3} for ethyl and t-butyl acetates and *ca.* 10^{-3} mol dm^{-3} for phenyl and 4-nitrophenyl acetates. All reactions exhibited pseudo-first-order kinetics and gave good linear first-order plots. First-order rate constants k_1/s^{-1} were evaluated from the slopes of plots of $\ln(A_\infty - A_t)$ against time, where A_t is the absorbance value at time t. Infinity readings A_∞ were taken after at least eight half-lives. First-order rate constants for the hydrolysis of diethyl sulphite (0.075 mol dm^{-3}) in aqueous perchloric acid were determined using the titration method described by Bunton *et al.*[11]

RESULTS

Pseudo-first-order rate constants k_1/s^{-1} for the hydrolyses of five esters in aqueous perchloric acid solutions are given in Tables 1—4. The activation parameters $\Delta G_{\mathrm{w}}^{\ddagger}$, $\Delta H_{\mathrm{w}}^{\ddagger}$, and $\Delta S_{\mathrm{w}}^{\ddagger}$ were calculated from k values at constant water activity as follows. The variation of water activity with perchloric acid concentration at each of the temperatures T/K for which rate data were measured was evaluated *via* equation (1) from water activities at 298 K[12,13] and relative partial molal enthalpies of water L_{w} in perchloric acid

$$\ln(a_{\mathrm{w}})_T = \ln(a_{\mathrm{w}})_{298} + \frac{L_{\mathrm{w}}}{R}\left(\frac{1}{T} - \frac{1}{298}\right) \qquad (1)$$

solutions.[14] Hence from plots of log k_1 against the concentration $C_{\mathrm{HClO_4}}$ of perchloric acid and of a_{w} against $C_{\mathrm{HClO_4}}$, values of log $(k_1/C_{\mathrm{HClO_4}})$ were deduced as a function of temperature at constant water activity. Enthalpies of activation $\Delta H_{\mathrm{w}}^{\ddagger}$ were calculated, in accordance with

$$\ln(k_1/TC_{\mathrm{HClO_4}}) = -(\Delta H_{\mathrm{w}}^{\ddagger}/RT) + (\Delta S_{\mathrm{w}}^{\ddagger}/R) + \ln(\boldsymbol{k}/h) \qquad (2)$$

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TABLE 1

Pseudo-first-order rate constants k_1/s,$^{-1}$ as a function of perchloric acid concentration C_{HClO_4}/mol dm^{-3} for the hydrolysis of two esters at four temperatures

20 °C		25 °C		30 °C		35 °C	
C_{HClO_4}	10^3k_1	C_{HClO_4}	10^3k_1	C_{HClO_4}	10^3k_1	C_{HClO_4}	10^3k_1
			Phenyl acetate				
0.96	0.04	0.94	0.06	0.94	0.11	0.94	0.17
1.98	0.07	1.86	0.12	1.94	0.19	1.87	0.31
2.89	0.11	3.01	0.19	2.85	0.27	2.88	0.49
2.97	0.11	3.85	0.25	3.75	0.43	3.87	0.71
3 85	0.14	4.81	0.32	3.84	0.45	4.23	0.82
3.91	0.14	5.83	0.46	4.83	0.54	4.73	0.94
4.97	0.23	6.35	0.51	5.73	0.70	5.70	1.04
5.40	0.24	6.72	0.55	6.73	0.92	6.58	1.48
5.59	0.25	7.27	0.62	7.63	1.18	7.63	1.93
6.63	0.33	7.62	0.69	8.51	1.57	8.51	2.30
7.66	0.43	8.58	0.93	9.06	1.80	9.49	3.73
8.99	0.51	9.28	1.00	9.57	2.74		
9.13	0.60	9.67	1.37				
9.42	0.98						
9.44	1.01						
			4-Nitrophenyl acetate				
1.25	0.04	1.00	0.05	1.28	0.07	1.31	0.15
2.34	0.06	2.39	0.11	2.30	0.12	2.31	0.19
3.58	0.08	3.81	0.14	2.46	0.13	3.64	0.39
4.73	0.12	4.62	0.22	3.57	0.28	4.87	0.48
5.93	0.17	5.95	0.35	4.76	0.29	6.05	0.79
7.11	0.46	6.86	0.47	6.02	0.64	7.10	1.18
8.37	0.52	8.36	0.79	6.87	0.84	8.26	2.27
8.74	0.56	8.80	1.28	8.43	2.06	9.02	4.58
9.13	1.24	9.40	2.18	9.53	5.85	9.65	8.58

TABLE 2

Pseudo-first-order rate constants k_1/s^{-1} as a function of perchloric acid concentration C_{HClO_4}/mol dm^{-3} for the hydrolysis of t-butyl acetate at four temperatures

15 °C		20 °C		25 °C		30 °C	
C_{HClO_4}	10^3k_1	C_{HClO_4}	10^3k_1	C_{HClO_4}	10^3k_1	C_{HClO_4}	10^3k_1
0.55	0.05	0.54	0.07	0.20	0.06	0.55	0.21
0.98	0.07	0.97	0.15	0.48	0.09	0.98	0.63
1.41	0.14	1.72	0.50	0.70	0.21	1.43	1.47
1.87	0.30	1.80	0.55	0.92	0.28	1.91	2.68
2.38	0.56	1.96	0.64	1.17	0.42	2.16	4.00
2.84	1.17	2.46	1.37	1.43	0.72	2.36	5.20
3.35	3.22	2.65	2.15	1.67	1.08	2.87	10.22
3.72	5.60	2.88	3.02	1.84	1.37	3.10	14.79
3.90	7.78	3.35	6.13	2.10	1.76	3.33	23.76
4.01	7.82	3.53	8.47	2.35	2.55	3.62	33.35
				2.60	4.38		
				2.79	5.75		
				3.11	9.79		
				3.46	20.90		
				3.50	21.33		

TABLE 3

Pseudo-first-order rate constants k_1/s^{-1} as a function of perchloric acid concentration C_{HClO_4}/mol dm^{-3} for the hydrolysis of ethyl acetate at five temperatures

15 °C		20 °C		25 °C		30 °C		35 °C	
C_{HClO_4}	10^3k_1	C_{HClO_4}	10^3k_1	C_{HClO_4}	10^3k_1	C_{HClO_4}	10^3k_1	C_{HClO_4}	10^3k_1
1.27	0.07	1.32	0.12	1.05	0.09	1.38	0.19	1.35	0.28
1.88	0.08	2.40	0.17	2.10	0.23	2.52	0.35	2.71	0.62
2.20	0.10	3.48	0.22	3.70	0.42	2.85	0.40	3.80	0.78
4.00	0.15	4.40	0.30	4.80	0.45	3.60	0.48	5.04	1.03
4.80	0.18	6.01	0.40	5.96	0.55	3.75	0.52	6.38	1.48
5.96	0.22	6.45	0.43	6.70	0.59	5.17	0.64	7.47	1.67
7.20	0.21	7.01	0.46	7.00	0.63	6.00	0.86	8.59	1.77
8.48	0.21	7.25	0.47	8.80	0.59	8.15	1.00	10.10	1.61
9.60	0.19	7.80	0.45	9.99	0.51	9.10	1.15	11.26	1.02
10.38	0.17	8.30	0.41	10.80	0.34	10.10	0.92	12.30	1.09
		9.05	0.37			10.90	0.68		
		10.00	0.26			11.30	0.62		
		10.25	0.23			11.80	0.68		

equation (2), from the slopes of plots of log (k_1/TC_{HClO_4}) against $(1/T)$. In equation (2) $\boldsymbol{k}$ and h are the Boltzmann and Planck constants respectively. Standard deviations σ/kJ mol^{-1} in $\Delta H_w^\ddagger$ differed for each plot within the ranges $\pm 0.002 \leqslant \sigma \leqslant \pm 0.02$ for phenyl acetate, $\pm 0.01 \leqslant \sigma \leqslant \pm 0.45$ for 4-nitrophenyl acetate, $\pm 0.002 \leqslant \sigma \leqslant \pm 0.13$ for diethyl sulphite, $\pm 0.006 \leqslant \sigma \leqslant \pm 0.06$ for t-butyl acetate, and $\pm 0.02 \leqslant \sigma \leqslant \pm 0.41$ for ethyl acetate. Free energies of activation $\Delta G_w^\ddagger$ were calculated using equation (3) from the rate constants at 298 K for each water activity.

TABLE 4

Pseudo-first-order rate constants k_1/s^{-1} as a function of perchloric acid concentration C_{HClO_4}/mol dm^{-3} for the hydrolysis of diethyl sulphite at four temperatures

5 °C		11 °C		15.4 °C		25 °C	
C_{HClO_4}	10^4k_1	C_{HClO_4}	10^4k_1	C_{HClO_4}	10^4k_1	C_{HClO_4}	10^4k_1
1.00	0.25	0.55	0.73	1.45	1.08	0.55	1.16
2.30	1.03	1.65	1.75	2.40	3.00	1.55	5.22
3.60	3.13	2.75	2.58	3.35	7.20	2.10	9.25
5.33	12.50	3.95	6.57	4.55	16.16	2.95	19.18
6.35	24.25	4.45	15.12	5.60	42.0	3.10	20.43
		5.75	30.01	6.70	76.5	4.00	36.76
						4.15	42.0
						5.75	106.8

$$\Delta G_w^\ddagger = -RT\ln(k_1h/\boldsymbol{k}TC_{HClO_4}) \qquad (3)$$

Hence $\Delta S_w^\ddagger = (\Delta H_w^\ddagger - \Delta G_w^\ddagger)/T$. The thermodynamic data are listed in Table 5.

TABLE 5

Thermodynamics of activation, based on rate data at constant water activity, for the hydrolysis of five esters in aqueous perchloric acid at 298 K

a_w	$\Delta G_w^\ddagger$/kJ mol^{-1}	$\Delta H_w^\ddagger$/kJ mol^{-1}	$-\Delta S_w^\ddagger$/J K^{-1} mol^{-1}	$\Delta G_w^\ddagger$/kJ mol^{-1}	$\Delta H_w^\ddagger$/kJ mol^{-1}	$-\Delta S_w^\ddagger$/J K^{-1} mol^{-1}
	Phenyl acetate			4-Nitrophenyl acetate		
0.9	97.1	77.6	65	98.1	69.0	98
0.8	96.9	76.8	67	98.0	69.0	97
0.7	96.8	76.3	68	97.7	67.4	102
0.6	96.6	76.0	69	97.5	68.3	98
0.5	96.5	75.9	69	97.1	68.2	97
0.4	96.4	75.5	70	96.9	67.7	98
0.3	96.1	75.1	70	96.5	68.3	95
0.2	95.9	74.7	71	96.0	68.2	93
0.1	95.6	76.3	65	95.5	67.0	96
	Ethyl acetate			Diethyl sulphite		
0.9	95.8	58.8	124	92.2	82.0	34
0.8	95.8	6.00	120	91.0	80.3	36
0.7	95.8	59.9	120	90.0	74.5	52
0.6	95.9	60.4	119	89.2	69.2	67
0.5	95.9	61.3	116	88.6	66.3	75
0.4	96.0	64.2	107	87.9	63.1	83
0.3	96.1	71.0	84			
0.2	96.4	78.5	60			
0.1	97.0	94.8	7			
	t-Butyl acetate					
0.95	92.3	108.2	−53			
0.90	90.3	107.3	−57			
0.85	88.4	107.6	−64			
0.80	86.4	109.2	−76			

Enthalpies of activation $\Delta H_c^\ddagger$ were deduced from the slopes of plots of $\ln(k_1/T)$ against $(1/T)$, based on values of k_1 as a function of temperature at constant concentration of perchloric acid. The values are given in Table 6.

Water activity and L_w data used in the present work are tabulated in Table 7. Data for other perchloric acid concentrations were read off from graphs of a_w and $\bar{L}_w$ as a function of C_{HClO_4}.

TABLE 6

Enthalpies of activation $\Delta H_c^{\ddagger}$/kJ mol^{-1}, based on rate data at constant acid concentration, for the hydrolyses of five esters in aqueous perchloric acid at 298 K

C_{HClO_4}/mol dm^{-3}	Phenyl acetate	4-Nitrophenyl acetate	t-Butyl acetate	Ethyl acetate	Diethyl sulphite
1			108.4	59.2	
2	77.2	68.2	107.7	58.5	81.5
3	76.7	65.6	108.8	60.0	80.5
4	76.1	68.0		60.8	75.1
4.5	76.1	66.9			
5	74.9	68.6		61.0	68.0
5.5	75.5	68.6			
6	74.9	67.5		63.4	63.7
6.5	74.4	66.4			
7	74.4	67.3		70.9	
7.5	73.8	67.3			
8	73.2	66.4		76.6	
8.5	73.7	67.3			
9		64.7		92.1	

TABLE 7

Water activities [12,13] and relative partial molal enthalpies of water [14] for aqueous perchloric acid solutions at 298 K

C_{HClO_4}/mol dm^{-3}	a_w	$\bar{L}_w$/kJ mol^{-1}	C_{HClO_4}/mol dm^{-3}	a_w	$\bar{L}_w$/kJ mol^{-1}
0.95	0.9632	0.008	6.48	0.3904	−0.979
1.84	0.9165	0.025	6.98	0.3195	−1.314
2.64	0.8590	0.042	7.48	0.2565	−1.732
3.39	0.7915	0.000	7.96	0.2030	−2.243
4.09	0.7153	−0.123	8.39	0.1583	−2.858
4.74	0.6343	−0.339	8.78	0.1223	−3.594
5.35	0.5508	−0.498	9.16	0.0931	−4.473
5.94	0.4687	−0.707	9.54	0.0702	−5.494

DISCUSSION

4-*Nitrophenyl and Phenyl Acetate*.—The hydrolyses of 4-nitrophenyl and phenyl acetate in aqueous sulphuric acid at 298 K followed $A_{Ac}2$ mechanisms in the acid concentration range 0—7 mol dm^{-3} and $A_{Ac}1$ mechanisms at acid concentrations >11.5 mol dm^{-3}.[9] The rates of the hydrolyses catalysed by perchloric acid were *ca.* 1.5—2.5 times slower, compared at equal molarities of acid, than the corresponding rates for sulphuric acid catalyst. A similar difference between the catalytic effects of perchloric and sulphuric acids has been reported for the $A_{Ac}2$ hydrolyses of methyl benzoate and ethyl acetate.[10] Plots of $\log_{10}$ (k_1/C_{HClO_4}) against $\log_{10}a_w$ were linear (Figures 1 and 2) over the perchloric acid concentration range 0—9.5 mol dm^{-3}, and in accord with equation (4),[1] enabled values of the parameter

$$\log_{10}(k_1/C_{HClO_4}) = w^*\log_{10}a_w + \text{constant} \quad (4)$$

w^* to be evaluated. The figures of −0.7 and −0.3 for the hydrolyses of 4-nitrophenyl and phenyl acetate respectively are consistent with the $A2$ reaction mechanism.[1] Plots of $\log_{10}(k_1/C_{H_2SO_4})$ against $-\log_{10}a_w$ for the reactions catalysed by sulphuric acid [9] were approximately parallel to the corresponding plots for perchloric acid catalyst. The mechanisms were unaffected by the change in catalysing acid. Plots of $(\log_{10}k_1 + H_0)$, where H_0 is the Hammett acidity function for aqueous perchloric acid,[3,14] against $\log_{10}a_w$ were curved. Slopes (w parameters [1]) ranged from *ca.* 7 for low to *ca.* 2.5 for high perchloric acid concentrations. Again the involvement of water in the rate-determining steps of the reaction is indicated [1] by these results. A change to an $A_{Ac}1$ mechanism, reported [9] to occur for sulphuric acid catalyst, was not clearly shown by the present results because the concentrations of perchloric acid studied were not as high as the concentrations of sulphuric acid for which the $A_{Ac}1$ mechanism became predominant. However evidence for a small partial change over from the $A_{Ac}2$ to the $A_{Ac}1$ mechanism was apparent from marked decreases which occurred in the slopes of the plots of $(\log_{10}k_1 + H_0)$ against $\log_{10}a_w$ for perchloric acid solutions at concentrations > *ca.* 9 mol dm^{-3}.

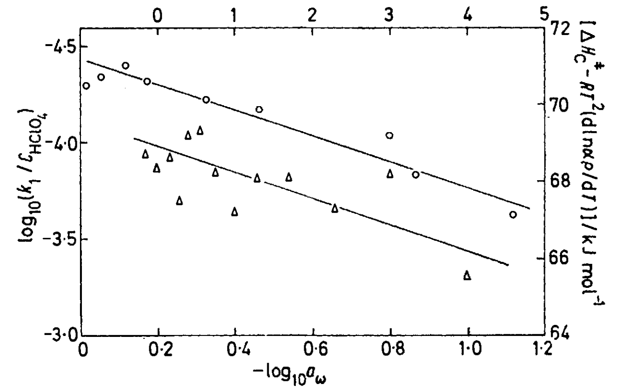

FIGURE 1 Test of ○ equation (4) (bottom and left hand axes) and △ equation (13) (top and right hand axes) for the hydrolysis of 4-nitrophenyl acetate

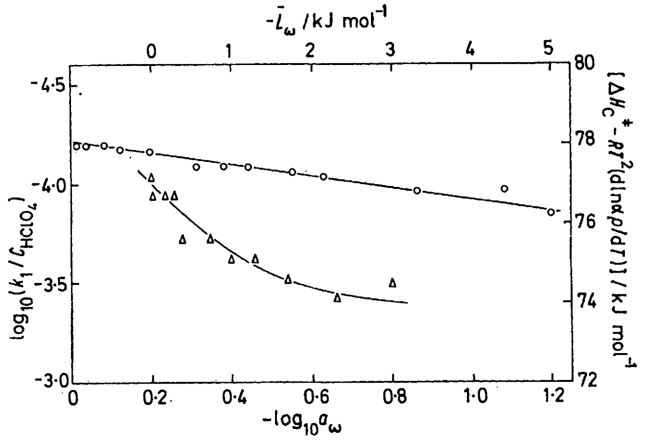

FIGURE 2 Test of ○ equation (4) and △ equation (13) for the hydrolysis of phenyl acetate

The enthalpies and entropies of activation for the hydrolyses of 4-nitrophenyl and phenyl acetate (Table 5) were consistent with the $A2$ hydrolysis mechanism for perchloric acid concentrations up to *ca.* 9 mol dm^{-3}.[5] The enthalpies of activation $\Delta H_c^{\ddagger}$ (Table 6), which refer to constant concentration of acid, varied by *ca.* 3—4 kJ mol^{-1} as the perchloric acid concentration was increased in the range 1—9 mol dm^{-3}. The enthalpies of activation $\Delta H_w^{\ddagger}$ (Table 5) showed a smaller variation with increasing acid concentration. The values for 4-nitrophenyl acetate were effectively constant whereas those for phenyl acetate exhibited a slight downward trend which was only marginally greater than the estimated experimental error. In general the results are similar to those reported by Smith and Yates[4] for the hydrolyses of benzamide, *N*-methylbenzamide, and *NN*-dimethylbenzamide catalysed by aqueous sulphuric acid. Their conclusions concerning the influence of variations of a_w with temperature on enthalpies of activation are therefore also applicable to the hydrolyses of 4-nitrophenyl and phenyl acetates. The constancy of the derived $\Delta H_w^{\ddagger}$ values for the hydrolysis of the two acetates confirms that the reactions proceeded by the $A_{Ac}2$ mechanism in all perchloric acid solutions with $a_w \geqslant 0.1$ ($C_{HClO_4} \leqslant 9.1$ mol dm^{-3}).

The influence of water activity on the reaction rate at a given temperature has been represented[1] by the empirical equation (4) and has been explained[15] in terms of changes in hydration which accompany the formation of the transition state from reacting substrates. Smith and Yates[4] drew attention to the corresponding influence of the variation of water activity with temperature on enthalpies of activation. The following treatment attempts to formalize this influence in terms of an empirical relationship between enthalpies of activation and $\bar{L}_w$. The $A2$ mechanism for the acid catalysed hydrolysis of an ester S may be represented by reactions (5) and (6) in which *s*, *n*, and *p* represent the hydration

$$S_s + H_n^+ \rightleftharpoons SH_p^+ + (s + n - p)H_2O \qquad (5)$$

$$SH_p^+ + (t - p)H_2O \rightleftharpoons \ddagger_t^+ \longrightarrow \text{products} \qquad (6)$$

numbers of S, H$^+$, and SH$^+$ and *t* is the number of water molecules, hydrating and reacting, with the transition state $\ddagger_t^+$.[3,15] If $C_{SH_p^+} \ll C_{S_s}$, then the resulting rate equation leads to (7) for the experimental pseudo-first-order rate constant as a function of acid concentration and water activity.[3,15] In equation (7) K_{SH^+} is the acid

$$\log_{10}(k_1/C_{H_n^+}) = (t - s - n)\log_{10}a_w + \log_{10}(k/K_{SH^+}) + \log_{10}(y_{S_s}y_{H_n^+}/y_{\ddagger_t^+}) \qquad (7)$$

ionization constant of SH$^+$, *k* is the rate constant for the rate-determining reaction (6), and y_i represents the activity coefficient of species *i*. Comparison of equations (4) and (7) suggested to Bunnett[15] that w^* may be equated with $(t - s - n)$ providing the activity coefficient term in equation (7) was a constant independent of acid concentration. The applicability of equation (4) to the hydrolyses of 4-nitrophenyl acetate (Figure 1) and phenyl acetate (Figure 2) over a wide range of perchloric acid concentration provided the incentive for testing whether a corresponding relationship existed between the enthalpies of activation $\Delta H_c^{\ddagger}$ and relative partial molal enthalpies of water $\bar{L}_w$ in perchloric acid solutions. Differentiation of equation (7) with respect

$$\frac{\mathrm{d}\log_{10}(k_1/C_{H_n^+})}{\mathrm{d}T} = (t - s - n)\frac{\mathrm{d}\log_{10}a_w}{\mathrm{d}T} + \frac{\mathrm{d}\log_{10}(k/K_{SH^+})}{\mathrm{d}T} + \frac{\mathrm{d}\log_{10}(y_{S_s}y_{H_n^+}/y_{\ddagger_t^+})}{\mathrm{d}T} \qquad (8)$$

to temperature leads to (8) which combined with equations (9)—(11) leads to equation (12) in which ρ is the density of aqueous perchloric acid and α is the degree of

$$(\mathrm{dln}k_1/\mathrm{d}T) = (\Delta H_c^{\ddagger} + RT)/RT^2 \qquad (9)$$

$$(\mathrm{dln}a_w/\mathrm{d}T) = \bar{L}_w/RT^2 \qquad (10)$$

$$(\mathrm{dln}C_{H_n^+}/\mathrm{dT}) = (\mathrm{dln}\ \alpha\rho/\mathrm{d}T) \qquad (11)$$

$$\Delta H_c^{\ddagger} - RT^2\frac{\mathrm{dln}\alpha\rho}{\mathrm{d}T} = -(t - s - n)\bar{L}_w + RT^2\frac{\mathrm{dln}(k/K_{SH^+})}{\mathrm{d}T} - RT + RT^2\frac{\mathrm{dln}(y_{S_s}y_{H_n^+}/y_{\ddagger_t^+})}{\mathrm{d}T} \qquad (12)$$

dissociation of perchloric acid in water. Values of RT^2 (dlnαρ/dT) are given elsewhere.[14] If the final term in equation (12) was medium independent then, taking $w^* = (t - s - n)$, equation (13) should be applicable. The tests of equation (13) are contained in Figures 1 and 2.

$$\Delta H_c^{\ddagger} = RT^2\frac{\mathrm{dln}\alpha\rho}{\mathrm{d}T} = -w^*\bar{L}_w + \text{constant} \qquad (13)$$

The axes for the plots of $\Delta H_c^{\ddagger} - RT(\mathrm{dln}\alpha\rho/\mathrm{d}T)$ against $-\bar{L}_w$ and of $\log_{10}(k_1/C_{HClO_4})$ against $\log_{10}a_w$ have been chosen such that lines of equal slope appear parallel. The enthalpy plot exhibited some scatter because of its extreme sensitivity to experimental error. The maximum deviation on the ordinate axis of any single point from the line was only *ca.* 1 kJ mol^{-1}.

The similarity between the slopes of the two plots in Figure 1 for the hydrolysis of 4-nitrophenyl acetate suggests that equation (13) gave an approximate fit of the data for this reaction. The applicability of the treatment for the hydrolysis of 4-nitrophenyl acetate is consistent with both the results and the conclusions of the study[4] of benzamide hydrolyses. Medium effects on enthalpies of activation or reactions in concentrated acid solutions are apparently governed, through $\bar{L}_w$ as representing the variation of water activity with temperature, by the relative hydration requirements of the reacting substrates ($S_s + H_n^+$) and the transition states in the reactions.

The tests of equations (4) and (13) for the hydrolysis of phenyl acetate are shown in Figure 2. The curves were not exactly parallel; the plot of equation (13) was curved with a slope of *ca.* −1.3 changing to *ca.* −0.2 with increasing perchloric acid concentration. These slopes may be compared with the w^* value of −0.3 from equation (4). Despite the lack of exact parallelism the slopes were in approximate agreement. The assumptions that the activity coefficient (final) terms in equations (7) and (12) were independent of acid concentration are

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[15] J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4973.

unlikely to be completely valid and exact parallelism would therefore be fortuitous. The conclusion that medium-induced variations of enthalpies of activation are primarily caused by the variation of a_w with temperature is therefore apparently not discounted by the results for the hydrolysis of phenyl acetate.

t-Butyl Acetate.—The rates of hydrolysis of t-butyl acetate at 298 K (Table 3) agree closely with previous results of Bunton *et al.*[10] A plot of $\log_{10}k_1 + H_0$ against $\log_{10}a_w$ had a slope w of -6.1 which is consistent with a predominantly $A1$ reaction mechanism.[1,3,10] The enthalpy of activation of *ca.* 108 kJ mol^{-1} and the positive entropies of activation (*cf.* previous value of 59.4 J K^{-1} mol^{-1})[5,6] are also in accordance with the $A1$ mechanism.[5] Adam *et al.*[16] deduced that t-butyl acetate is 85% hydrolysed by an $A_{Al}1$ mechanism (energy of activation 115 kJ mol^{-1}) and 15% by an $A_{Ac}2$ mechanism (E_a 72 kJ mol^{-1}) in aqueous hydrochloric acid at 298 K. This would give an overall apparent activation energy of *ca.* 109 kJ mol^{-1} which is closely similar to the present value of $E_a = (\Delta H_c^{\ddagger} + RT) \sim 111$ kJ mol^{-1}. Because of the fast rate of reaction, the hydrolysis of t-butyl acetate was only studied at low (<3.5 mol dm^{-3}) concentrations of perchloric for which the $\bar{L}_w$ values were small and showed little variation with acid concentration.[14] Hence, in accordance with the data in Table 5, the enthalpy of activation would not be expected to vary appreciably with increasing acid concentration. The medium effects on the rates of reaction were reflected in variations in the entropies and not the enthalpies of activation.

Ethyl Acetate.—Previous results for the rates of hydrolysis of ethyl acetate in aqueous perchloric acid at 298 K closely agree with the present data which have extended the earlier study to higher acid concentrations. The rate constant against acid concentration profile increased to a maximum rate (k_1 value) at moderate (*ca.* 7—8.5 mol dm^{-3}) acid concentrations then decreased appreciably before a further increase at high (>11.5 mol dm^{-3}) acid concentrations. A similar rate profile has been recorded for the hydrolysis of ethyl acetate in aqueous sulphuric acid solutions.[7,9]

Enthalpies of activation $\Delta H_c^{\ddagger}$ for ethyl acetate hydrolysis showed considerably greater variation with acid concentration than the corresponding enthalpy changes for the hydrolyses of 4-nitrophenyl and phenyl acetates. Although the plots of equations (4) and (13) were both linear (Figure 3) the slopes of 0.2 and 8.3 respectively were significantly different. The $\Delta H_w^{\ddagger}$ data also gave a trend to higher enthalpies of activation with increasing acid concentration. Similar results for the hydrolyses of some benzimidates[8] were interpreted in terms of the occurrence of changes in the rate determining steps as the concentration of the catalysing acid (H_2SO_4) was increased. The same explanation was given to account for increases in $\Delta H_c^{\ddagger}$ and $\Delta S^{\ddagger}$ from 70.7 to 99.2 kJ mol^{-1} and from -64 to $+10$ J K^{-1} mol^{-1} respectively for the hydrolysis of ethyl acetate in 40.2—98.4% sulphuric acid in water.[7] It was proposed that the mechanism of ethyl acetate hydrolysis changed from $A_{Ac}2$ to $A_{Ac}1$ as the H_2SO_4 concentration was increased.[7,9] This proposal would also be consistent with the results for the hydrolysis of ethyl acetate in aqueous perchloric acid solutions. A change over from an $A2$ to an $A1$ mechanism would be expected[5] to give an increase in $\Delta H_c^{\ddagger}$ of *ca.* 40 kJ mol^{-1} and to reverse the sign of $\Delta S^{\ddagger}$. The enthalpy of activation increased slowly up to a perchloric acid concentration of *ca.* 6.5 mol dm^{-3} suggesting that the $A_{Ac}2$ mechanism predominated at this acidity. At higher acidities $\Delta H_c^{\ddagger}$ and $\Delta S^{\ddagger}$ increased more rapidly until for $C_{HClO_4} > 9$ mol dm^{-3}, although the changeover was incomplete, the values showed that the $A1$ mechanism had probably become predominant. The change in mechanism apparently occurred at a lower acid concentration (mol dm^{-3}) with perchloric acid as catalyst than with sulphuric acid catalyst. This would be consistent with evidence that perchloric acid is less efficient than sulphuric acid as a catalyst for $A2$ ester hydrolyses and more efficient for $A1$ hydrolyses.[10] In general the results for ethyl acetate hydrolysis exemplify the conclusion[7,8] that large variations in enthalpy of activation with acid concentration must be associated with changes in reaction mechanism and cannot be explained solely in terms of medium effects involving a dependence on water activity.

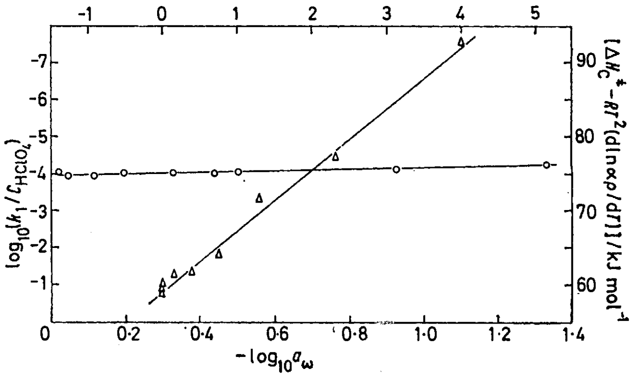

FIGURE 3 Test of ○ equation (4) and △ equation (13) for the hydrolysis of ethyl acetate

A change in mechanism may not be the only factor which contributes to the observed trends in $\Delta H_c^{\ddagger}$ and $\Delta S^{\ddagger}$ for ethyl acetate hydrolysis. At high acidities a fraction of the reacting ester will be protonated [equation (5)] and it is therefore relevant to consider the influence of the protonation on the activation parameters. In the extreme case of virtually complete protonation ($C_{SH_p^+} \gg C_{S_s}$) the first order-rate constant k_1 is given by equation (14).[3] Taking logarithms and differentiating with respect to temperature leads to equation (15)

$$k_1 = (C_{S_s}/C_{SH_p^+})(k/K_{SH^+})C_{H_n^+}a_w^{(t-s-n)}(y_{S_s}y_{H_n^+}/y_{\ddagger_t^+}) \quad (14)$$

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[16] K. R. Adam, I. Lauder, and V. R. Stimson, *Austral. J. Chem.*, 1962, **15**, 467.

[in which ΔH is given by equation (16)] which may be compared with the corresponding equation (12) for acid solutions in which negligible protonation of substrate occurs. The equations differ only by the inclusion of

$$\Delta H_c^{\ddagger} - RT^2 \frac{\mathrm{dln}\alpha\rho}{\mathrm{d}T} = \Delta H - (t - s - n)\bar{L}_{\mathrm{w}} + RT^2 \frac{\mathrm{dln}(k/K_{\mathrm{SH^+}})}{\mathrm{d}T} - RT + RT^2 \frac{\mathrm{dln}(y_{\mathrm{S}_s} y_{\mathrm{H}_n^+}/y_{\ddagger_t^+})}{\mathrm{d}T} \quad (15)$$

$$\Delta H = RT^2 \mathrm{dln}(C_{\mathrm{S}_s}/C_{\mathrm{SH}_p^+})/\mathrm{d}T \quad (16)$$

ΔH in equation (15). Values of ΔH for the protonation of primary amines[14] and amides[17] [the negative sign should be deleted from equation (6) in ref. 14 and equation (ii) in ref. 17] have been measured. For a single substrate the results were equivalent to an increase in ΔH of *ca.* 25 kJ mol^{-1} for amines and *ca.* 15 kJ mol^{-1} for amides as the perchloric acid concentration was raised from zero to *ca.* 9 mol dm^{-3}. Assuming similar behaviour for ethyl acetate leads to the conclusion that the onset of appreciable protonation [equation (5)] of the neutral ester would give a marked increase in the apparent activation enthalpy $\Delta H_c^{\ddagger}$ for the reaction even if the $A_{\mathrm{Ac}}2$ mechanism was still operating at all acid concentrations. The apparent activation enthalpy for ethyl acetate hydrolysis increased by 35 kJ mol^{-1} as the perchloric acid concentration was raised from zero to *ca.* 9 mol dm^{-3}. It appears probable that two major factors contributed to this increase; first the increasing fraction of ester which was protonated at higher acidities led to the progressive change over from the applicability of equation (12) to equation (15), and secondly a partial change from an $A_{\mathrm{Ac}}2$ to an $A_{\mathrm{Ac}}1$ mechanism also occurred.

Diethyl Sulphite.—The rates of hydrolysis of diethyl sulphite at 298 K were in good agreement with the results of Bunton *et al.*[11] who deduced an energy and entropy of activation of 84.9 kJ mol^{-1} ($\Delta H^{\ddagger}$ 82.4 kJ mol^{-1}) and -34.3 J K^{-1} mol^{-1} for the reaction in 1 mol dm^{-3} perchloric acid. The present values of enthalpies and entropies of activation were close to these figures for perchloric acid concentrations up to *ca.* 3 mol dm^{-3}. The data are typical of acid catalysed reactions proceeding by an $A2$ mechanism.[5] A plot of $\log_{10}k_1 + H_0$ against $\log_{10}a_{\mathrm{w}}$ for the results for 298 K gave a slope (w) of 3.0 which is also consistent with an $A2$ mechanism.[1,18] Bunton *et al.*[11] showed that the hydrolysis of diethyl sulphite in 3 mol dm^{-3} perchloric acid predominantly involved sulphur–oxygen bond fission.

As the concentration of perchloric acid was increased above *ca.* 3 mol dm^{-3} the enthalpy of activation for diethyl sulphite hydrolysis decreased and the entropy of activation became more negative. Calculation of $\Delta H_{\mathrm{w}}^{\ddagger}$ values (Table 5) only slightly altered the magnitude of these trends. A plot of $\log_{10}(k_1/C_{\mathrm{HClO_4}})$ against $\log_{10}a_{\mathrm{w}}$ [equation (4), Figure 4] was curved with slopes (w*) ranging from -8.3 at low acid concentrations to -2.8 at high concentrations. The corresponding plot involving enthalpy data [equation (13), Figure 4] also had a negative slope (-22) but was much steeper. The results differed significantly from those for the hydrolysis of the other esters studied here and elsewhere[7] and of benzamides[4] and benzimidates[8] for which $\Delta H_{\mathrm{w}}^{\ddagger}$ was either medium independent or increased with increasing acid concentration. However $\Delta H_c^{\ddagger}$ decreased and $\Delta S^{\ddagger}$ became more negative with increasing acid concentration for the H_2SO_4 catalysed tritiation of 2,6-lutidine and 2,4,6-collidine.[19] The results were explained in terms of the variation with temperature of activity coefficient ratios in the rate equations. In the present context this explanation would require that the final term in equation (12) decreases appreciably with acid concentration when S_s is diethyl sulphite, but is medium independent with 4-nitrophenyl acetate or phenyl acetate as substrate. The more negative value of w* for diethyl sulphite suggests that the term $-(t - s - n)\bar{L}_{\mathrm{w}}$ in equation (12) also contributed to the observed decrease in $\Delta H_c^{\ddagger}$. However this term alone is insufficient (Figure 4) to account for the enthalpy behaviour. The changes in $\Delta H_c^{\ddagger}$ and $\Delta S^{\ddagger}$ are in the wrong sense to be explicable in terms of a change over to an $A1$ mechanism: the activation parameters are consistent with an $A2$ mechanism at all acid concentrations.[5] It is also unlikely that the build up of an appreciable equilibrium concentration of protonated substrate [reaction (5)] in reacting solutions was responsible for the variations in $\Delta H_c^{\ddagger}$ and $\Delta S^{\ddagger}$. Speculative suggestions would be that at high perchloric acid concentrations the reactions remain $A2$ but that there is a change in the site of protonation of the substrate, in the nature of bond fission, or in the mode of involvement of the reacting water *molecule in* the rate-determining step. Any of these possibilities would influence the structure (but not the composition) of the transition state and would therefore also affect the apparent activation parameters for the reaction.

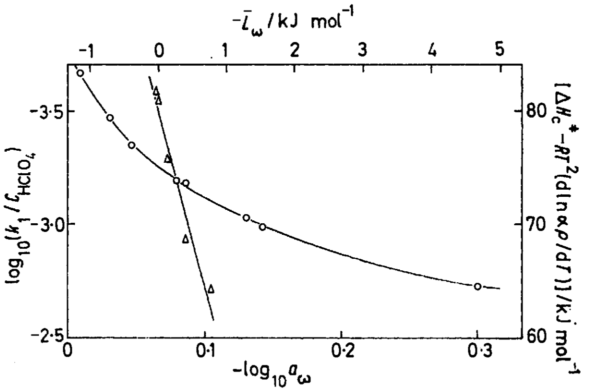

FIGURE 4 Test of ○ equation (4) and △ equation (13) for the hydrolysis of diethyl sulphite

[7/1281 *Received*, 18*th July*, 1977]

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