Kinetics of Hydrolysis of Sulphamic Acid in Concentrated Perchloric Acid Solutions

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The kinetics of hydrolysis of sulphamic acid have been studied in perchloric acid solutions (0.2—10.2 mol dm^{-3}) at 48.5—80 °C. The measured first-order rate constant increases up to [H$^+$] = *ca.* 2.0 mol dm^{-3} and then gradually decreases with increasing acidity. The rate law for the acid-catalysed hydrolysis of sulphamic acid (as distinct from that of the sulphamate ion) is Rate = $k_2[H^+][\overset{+}{N}H_3SO_3^-]a_w$ (where a_w is the activity of water) and an *A*-2 mechanism is suggested.

THE hydrolysis of sulphamate ion to ammonium and sulphate ions in fairly dilute mineral acid has been studied previously.[1,2] Candlin and Wilkins[2] showed that the rate of hydrolysis increases with [H$^+$] at low acidities and becomes constant at [H$^+$] = *ca.* 2 mol dm^{-3}. These results have been interpreted in terms of a rate-determining hydrolysis of sulphamic acid rather than the sulphamate ion, and allow a calculation of K_a = 0.266 dm^3 mol^{-1} at 95 °C for NH_2SO_3H. We now report the first detailed study of the hydrolysis reaction at much higher acidities as relevant background work[3] to the study of other reactions of sulphamic acid at high acidity. Our results at lower acidity are in general agreement with the data previously published.[2]

EXPERIMENTAL

All the reagents were AnalaR grade, except for NH_2SO_3H which was organic analytical standard grade. Kinetic runs were started by adding a solution of sulphamic acid to the other components of the reaction thermostatted in an oil thermostat. Samples were withdrawn at appropriate times and analysed for sulphate.[4] Rate constants were obtained from plots of log ($C_\infty - C_t$) against time, where C_∞ and C_t are the concentrations of sulphate at infinity and time *t* respectively.

RESULTS

The hydrolysis reaction was studied over the perchloric acid concentration range 0.2—10.2 mol dm^{-3}. The reaction was always first order in the sulphamic acid concentration, first-order rate constants being independent of [NH_2SO_3H] over a six-fold concentration range. The rate of hydrolysis increased with increasing [H$^+$] until 2 mol dm^{-3}, and then remained constant before decreasing as the acidity was increased further, as shown in the Figure and Table 1. The decrease in $k_{obs.}$ may be readily interpreted in terms of a decrease in water activity, a_w. Values of $k_{obs.}/a_w = k_1$ increased with [H$^+$] as shown in the Figure. Extrapolation of the linear portion of this plot to zero acidity gives the k_1 value corresponding to the non-acid-catalysed decomposition of sulphamic acid (k_0). Rate constants for the acid-catalysed reaction are given by $k_1 - k_0$. Values of $(k_1 - k_0)/[H^+]$ were constant, showing the reaction to be first order with respect to [H$^+$]. The overall rate law is Rate ∝ $[H^+][\overset{+}{N}H_3SO_3^-]a_w$. Some uncertainty may arise from the fact that a_w values at 80 °C are not available.

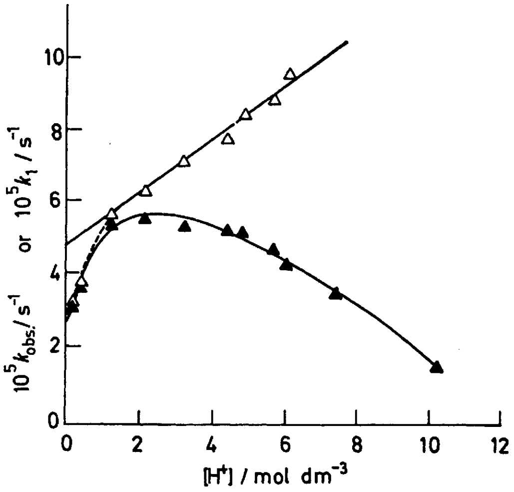
Rate constants were measured at several temperatures at [H$^+$] = 3.27 mol dm^{-3} (Table 2), values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ being 127 kJ mol^{-1} and 81.7 J K^{-1} mol^{-1}, respectively.

TABLE 1

Hydrolysis of sulphamic acid in perchloric acid at 80 °C

[HClO$_4$] / mol dm^{-3}	$10^5k_{obs.}$ [a] / s^{-1}	10^5k_1 [b] / s^{-1}	$10^5(k_1 - k_0)/[H^+]$ [c] / dm^3 mol^{-1} s^{-1}
0.204	3.12	3.14	
0.409	4.33	4.40	
1.267	5.30	5.61	0.639
2.141	5.42	6.06	0.589
3.271	5.39	6.70	0.581
4.500	5.19	7.70	0.644
4.906	5.19	8.33	0.719
5.315	4.80	8.50	0.696
5.724	4.30	8.60	0.663
6.133	4.08	9.27	0.728
7.36	3.38	(12.6) [d]	
10.2	1.37	(34.3) [d]	

[a] The mean of several runs with [NH_2SO_3H] between 0.02 and 0.1 mol dm^{-3}. [b] $k_1 = k_{obs.}/a_w$. Values of a_w were taken from J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4967. [c] $k_0 = 4.8 \times 10^{-5}$ s^{-1} (see text). [d] The values of a_w are very small.



Dependences of $k_{obs.}$ (▲) and k_1 (△) on [H$^+$] at 80 °C

TABLE 2

Temperature dependence at [HClO$_4$] = 3.27 mol dm^{-3}

θ_c/°C	48.5	69.0	80.0
$10^6k_{obs.}$/s^{-1}	0.566	9.88	48.0

DISCUSSION

The results at low acidity are easily understood in terms of the hydrolysis of sulphamic acid, the increase

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[1] S. H. Maron and A. R. Berens, *J. Amer. Chem. Soc.*, 1950, **72**, 3571.

[2] J. P. Candlin and R. G. Wilkins, *J. Chem. Soc.*, 1960, 4236.

[3] M. N. Hughes and J. R. Lusty, unpublished work.

[4] E. E. Archer, *Analyst*, 1957, **82**, 308.

in rate reflecting the increasing protonation of the sulphamate ion. Values of $k_{obs.}$ level off as the conversion of the anion into the acid becomes stoicheiometrically complete. Candlin and Wilkins [2] interpreted their results in terms of an *A*-1 acid-catalysed reaction of the sulphamate anion. The decrease in $k_{obs.}$ as $[H^+]$ is increased further is most easily understood in terms of the decrease in water activity, as has been well characterised for the acid hydrolysis of amides.[5] However, values of $k_{obs.}/a_w$ are not constant but increase with acidity, following $[H^+]$, not the Hammett acidity function H_0. This clearly implies the existence of an additional path involving the acid-catalysed hydrolysis of sulphamic acid, which occurs in addition to the previously characterised acid-catalysed hydrolysis of the sulphamate ion. This additional path involving sulphamic acid appears to involve an *A*-2 mechanism, in which a molecule of water is involved in the transition state, as indicated by the dependence of the rate on $[H^+]$.

$$\overset{+}{N}H_3SO_3^- + H^+ \rightleftharpoons \overset{+}{N}H_3SO_3H$$

$$\overset{+}{N}H_3SO_3H + H_2O \xrightarrow[\text{slow}]{} [NH_4]^+ + H_2SO_4$$

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[5] J. T. Edward and S. C. R. Meacock, *J. Chem. Soc.*, 1957, 2000.