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THE ACID CATALYSED HYDROLYSIS OF N-ACETYLSULPHANILIC ACID - A CHANGING MECHANISM.

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We recently reported[1] that acetanilide readily sulphonates in solutions of sulphuric acid > 70 per cent w/w to form N-acetylsulphanilic acid, and noted that the rate of hydrolysis of this latter compound increased with increasing acidity beyond 80 per cent w/w sulphuric acid. We have now prepared N-acetylsulphanilic acid and have followed its rate of hydrolysis to 4-aminobenzene sulphonic acid between 20 - 95 per cent w/w sulphuric acid at 80, 90 and 100°C and also at 25, 30 and 40°C and 86.3 and 95.3°C over limited ranges of acidity so that we measured 5 points on each Arrhenius plot. The rate of hydrolysis was calculated from the decrease in absorbance at 251 mμ.

At all temperatures there is a maximum in the rate profile between 30 - 35 per cent w/w followed by a local minimum at 77 per cent w/w sulphuric acid. This phenomenon has previously been observed for amides only in the case of the nitro derivatives of acetanilide.[2,3]

The table shows the rate data observed at 80°C together with the values of the activation energy calculated at each acidity. At acidities before the minimum in the profile the values of E_a show a small increase and are consistent with an A-2 mechanism. Before we could test the data on a rate-acidity correlation we had to evaluate pK_{SH^+}. Using the relationship

$$C_{SH^+}/C_S = (A - A_S)/(A_{SH^+} - A)$$

where A, A_S and A_{SH^+} are the absorbances of the solution, unprotonated, and fully protonated substrate, respectively at 251 mu and 25°C we found that a plot of $\log(C_{SH^+}/C_S)$ against $-H_A$[4] was linear (slope = 0.96) and the value of pK_{SH^+} (equal to H_A at half protonation) = -1.63 and we used this value in our calculations. A Bunnett and Olsen l.f.e.r. plot[5(a)] of the same data gave a value of $pK_{SH^+} = -1.36$, $\phi = 0.44$. The values of pK_{SH^+} thus obtained differ by 0.27 log units, in agreement with the hypothesis[5(a)] that the H_A acidity function is too negative by ca. 0.3 log units.

The rate data fit a Bunnett w plot[6] (at 80°C, w = 2.0, correlation coefficient = 0.998) and a Bunnett and Olsen l.f.e.r.[5(b)] (at 80°C, $\phi = 0.62$, correlation coefficient = 0.976). These correlations contrast with the results for benzamide, N-methylbenzamide and N,N-dimethylbenzamide whose hydrolysis rates did not fit these relationships[7] and for which a two term mechanism involving both O- and N-protonated transition states was postulated. Indeed, the results reported here are the first example where these relationships fit for an amide over such an extensive range of acidities.

Beyond the region of the minimum in the rate-acidity profile the values of E_a increase rapidly, consistent with a change in mechanism from A-2 to A-1. Similar, but less marked, increases in the values of E_a have been reported previously[2,3] for the hydrolysis of the nitroacetanilides changing from an A-2 to an A-1 mechanism.

Hydrolysis of N-acetylsulphanilic acid in sulphuric acid at 80°C.

H_2SO_4 (% $\underline{w}/\underline{w}$)	$10^5\underline{k}_\psi$ $\underline{s}^{-1}$	E_a kcal.mole^{-1}
20.0	174	16.7
25.1	223	16.3
30.1	255	16.1
35.0	255	16.5
40.0	249	17.1
44.9	187	18.1
50.0	160	18.8
55.0	77.2	19.8
60.0	34.2	20.9
65.1	10.2	22.6
70.0	1.81	28.2
75.7	0.472	38.7
80.0	1.78	28.2
85.0	1.82	28.1
90.0	4.05	31.8
96.6	6.43	35.6

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