Kinetics and Mechanism of the Acid-catalysed Hydrolysis of Sodium *N*-1-Naphthylsulphamate

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The kinetics of the acid-catalysed hydrolysis of sodium *N*-1-naphthylsulphamate have been measured in hydrochloric, perchloric, and sulphuric acids over a wide range of acid strengths. Rate maxima are observed for hydrolysis in each acid. On the basis of Bunnett ω^* plots, the solvent isotope effect, and salt effects, the mechanism is seen as involving a pre-equilibrium protonation followed by a rate-determining *A*-2 type nucleophilic attack by water at sulphur. Entropy data, however, suggest that in the rate-determining step considerable nitrogen–sulphur bond rupture may occur prior to bond formation with the nucleophile. The pK_{BH^+} value for *N*-1-naphthylsulphamate is $-1{\cdot}45$ (based on the H_0 scale).

ON heating in aqueous acid, *N*-arylsulphamic acids are hydrolysed rapidly to the parent amine and sulphuric acid.[1] *N*-Alkylsulphamates also undergo hydrolysis, though not as rapidly as their aromatic analogues.[2,3] We have found that *N*-alkyl- (including the controversial sweetener, *N*-cyclohexyl-) and *NN*-dialkyl-sulphamates undergo hydrolysis mainly by an *A*-2 type mechanism,[4] and we have favoured a similar mechanism in the hydrolyses of *N*-phenylsulphamic acid and its *para*-substituted derivatives.[5] Simultaneously with our studies a Russian group [6,7] have been studying the kinetics of hydrolysis of phenylsulphamic acid and its *para*-substituted derivatives. In their studies they measured rate constants for hydrolysis in 2—62% perchloric acid and established that the rate profiles go through maxima in the range 40—50% acid. The Russian group view the hydrolysis reaction as involving an equilibrium protonation of the arylsulphamate ion to give a zwitterion, followed by its rate-determining decomposition, in a step that ‘ may or may not involve water ’.

We have now examined the kinetics and mechanism of the cleavage of the nitrogen–sulphur bond in the acid-catalysed hydrolysis of sodium *N*-1-naphthylsulphamate. In investigating the mechanism we have examined our kinetic data with reference to four different diagnostic criteria: the effects of acid and of added salt, the solvent isotope effect, and the effect of temperature. We have also examined the protonation equilibrium shown in the Scheme.

$$\mathrm{ArNH}\overset{-}{\mathrm{SO}_3} + \mathrm{H}^+ \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \mathrm{Ar}\overset{+}{\mathrm{N}}\mathrm{H_2SO_3}^- \xrightarrow[\mathrm{H_2O}]{\text{slow}} \mathrm{Ar}\overset{+}{\mathrm{N}}\mathrm{H_3HSO_4}^-$$

SCHEME

EXPERIMENTAL

Materials.—Hydrochloric acid (1—5M) was prepared from Volucon standards; stronger acid was made up from either AnalaR or Pronalys grade hydrochloric acid. Perchloric and sulphuric acid solutions of the required strength

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[4] W. J. Spillane, F. L. Scott, and C. B. Goggin, *Internat. J. Sulfur Chem. (A)*, 1971, **1**, 223.

[5] F. L. Scott and W. J. Spillane, *Chem. and Ind.*, 1967, 1999; W. J. Spillane, C. B. Goggin, N. Regan, and F. L. Scott, *Internat. J. Sulfur Chem. (A)*, in the press.

[6] E. Yu Belyaev, L. I. Kotlyar, B. A. Porai-Koshits, and K. A. Serkova, *Reakts. spos. org. Soedinenii*, 1968, **5**, 1033.

[7] E. Yu. Belyaev, L. I. Kotlyar, and L. M. Timokhina, *Reakts. spos. org. Soedinenii*, 1970, **7**, 294.

were prepared by dilution of the appropriate AnalaR grade acids. AnalaR grade sodium chloride and sodium perchlorate (the latter was dried at 40 °C for 24 h *in vacuo*) were used. Deuteriochloric acid (38%; Prochem) was diluted with deuterium oxide (Koch–Light) to obtain solutions of the required strength. In all cases, the exact strengths of the acid solutions were checked by titration with standard base. Sodium *N*-1-naphthylsulphamate was prepared and characterized as previously described.[8]

pK_{BH^+} *Determination.*—Ionization ratios (I) were calculated from the equation $I = ([BH^+]/[B])[(\varepsilon_B - \varepsilon)/(\varepsilon - \varepsilon_{BH^+})]$, where ε_B is the absorbance of the unprotonated substrate, measured at 25 °C in water or very dilute acid at 305 nm and ε_{BH^+} the absorbance of the protonated substrate at the same wavelength in $HClO_4 > 10$M.

Kinetic Measurements.—The decrease in naphthylsulphamate concentration ($\lambda_{max.}$ 305 nm) or the increase in 1-naphthylamine (λ 266 nm) was followed with either a Perkin-Elmer 124 or a Unicam SP 800 spectrophotometer. Good isobestic points were obtained; in general, rate constants were determined in duplicate with an accuracy of ±3%. In some of the runs in strong acid, the rate constants were less accurate and, in these cases, at least four runs were averaged to give constants with an accuracy of ±7%.

RESULTS AND DISCUSSION

Basicity Constant.—In order to find the correct acidity function to describe the protonation of the sulphamate, plots of $\log_{10} I$ *vs.* $-H_X$ were made, according to equation (i), where $H_X = H_0$, H_A, or H_0'''. If the

$$\log_{10} I = -\mathrm{m}H_X + \mathrm{p}K_{BH^+} \qquad \text{(i)}$$

pK_{BH^+} values are to be true thermodynamic basicity constants, it is necessary that m should be equal to $1 \pm 0{\cdot}05$.[9] The data in Table 1 show that none of the three acidity functions correctly describes the protonation behaviour of the naphthylsulphamate. The Bunnett and Olsen method[10] of calculating pK_{BH^+} was applied. This involves plotting $\log_{10} I + H_0$ *vs.* $H_0 + \log_{10} [H^+]$; pK_{BH^+} may then be obtained from the intercept according to equation (ii). The values of pK_{BH^+} obtained by

$$\log_{10} I + H_0 = \phi(H_0 + \log_{10} [H^+]) + \mathrm{p}K_{BH^+} \qquad \text{(ii)}$$

this method are in excellent agreement with those obtained by application of equation (i) (Table 1). The positive ϕ values obtained (0·36 and 0·45) are in agreement with the fact that $\log_{10} I$ increases less rapidly than $-H_0$ as shown by the m values of 0·76 and 0·79.

Since application of either equation (i) or the more general Bunnett and Olsen equation (ii) gives the same values of pK_{BH^+} for 1-naphthylsulphamate, we feel that the values obtained are reliable, despite the fact that the protonation behaviour of this compound is inadequately described by the various acidity functions used for nitroanilines (H_0), amides (H_A), or tertiary amines (H_0'''). Interestingly, the Russian group[7] have obtained a pK_a for *N*-*p*-methoxyphenylsulphamic acid (using the H_0 scale), and the m value which may be calculated from their data is *ca.* 0·80, in close agreement with ours when H_0 or H_A is used. When the substrate under study is not a true Hammett base the problem of which acidity function to use arises. In the present case, it appears that either H_0 or H_A may be used. However, in correlating the effect of acid on rate (below) we have used H_0 because we favour protonation on nitrogen for the sulphamates[4] (see Scheme). The acidity function H_A has been established as the best for amides,[9,11] which are generally considered to undergo protonation on oxygen in most media. In fact, H_A has been shown to be applicable when ionization or protonation at oxygen was occurring. Two recent examples are the ionization of arenesulphonic acids[12] (the benzophenone acidity function, H_0^a, is also applicable), and the protonation of various phosphoryl and sulphonyl groups.[13]

TABLE 1

Ionization data and pK_{BH^+} values for *N*-1-naphthylsulphamate at 25 °C

Acid	H_X	Slope (m) of $\log_{10} I$ *vs.* $-H_X$ m	$-\mathrm{p}K_{BH^+}$	Correln. coefft.	Method of equation
$HCl + HClO_4$ [a]	H_0	0·75	1·45 ± 0·1	0·993	(i)
	H_0	*c*	1·44 ± 0·1	0·990	(ii)
	H_A [b]	0·83	1·48 ± 0·1	0·999	(i)
	H_0'''	0·55	1·46 ± 0·1	0·999	(i)
$HClO_4$	H_0	0·79	1·45 ± 0·2	0·983	(i)
	H_0	*d*	1·45 ± 0·2	0·968	(ii)
	H_A	0·84	1·49 ± 0·2	0·978	(i)

[a] HCl was used up to 11·0M and $HClO_4$ was then used from 9M to achieve further protonation. There were medium effects on ε_B and on $_{BH^+}$. The method of A. R. Katritzky, A. J. Waring, and K. Yates (*Tetrahedron*, 1963, **19**, 465) was used to calculate pK_{BH^+} values. [b] Values of H_A and H_0''' for perchloric acid were taken from K. Yates, H. Wai, G. Welch, and R. A. McClelland, *J. Amer. Chem. Soc.*, 1973, **95**, 418. [c] The Bunnett and Olsen ϕ value is 0·36. [d] $\phi = 0{\cdot}45$.

Effect of Acids.—The data in Table 2 for the catalytic effects of hydrochloric, perchloric, and sulphuric acids show that the observed first-order rate constant *vs.* acid concentration profiles go through a maximum. Similar rate maxima have been observed for the perchloric acid-catalysed hydrolysis of several *p*-substituted phenylsulphamic acids.[6,7] These maxima are similar to those observed in the acid-catalysed hydrolysis of amides.[14] As in the case of amides, the position of the maximum depends on the catalysing acid (see Table 2) and on the basicity of the arylsulphamate.[6,7] These maxima are a consequence of the opposing effects of increasing protonation and decreasing water activity; the position of the maximum does not necessarily correspond to the point

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[11] K. Yates and J. C. Riordan, *Canad. J. Chem.*, 1965, **43**, 2328; C. A. Bunton, S. J. Farber, A. J. G. Millbank, C. J. O'Connor, and T. A. Turney, *J.C.S. Perkin II*, 1972, 1869.

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[13] R. Crevis, A. Levi, V. Lucchini, and G. Scorrano, *J.C.S. Perkin II*, 1973, 531.

[14] C. J. O'Connor, *Quart. Rev.*, 1970, **24**, 553.

of complete protonation. For example, the naphthylsulphamate will be half-protonated in hydrochloric acid of H_0 —1·94, *i.e.* 5·5M (18·5%), and will not be fully protonated in hydrochloric acid, since the point of 99% protonation corresponds to H_0 —4·59, whereas the data in Table 2 indicate that the maximum in hydrochloric acid occurs at about 10—11M-acid. In perchloric acid half-protonation occurs at 4·3M-acid (34·7%) and 99% protonation at 8·5M (57·2%); the maximum in the rate–acid profile is at *ca.* 6M-perchloric acid.

TABLE 2

Observed first-order rate constants (10^3k/s^{-1}) for the hydrolysis of sodium *N*-1-naphthylsulphamate at 40 °C

Acid strength (M)	HCl	$HClO_4$	H_2SO_4
1·0	0·35	0·35	0·27
2·0	0·71	0·93	
3·0	1·42	1·97	
4·0	2·81	3·10	2·41
5·0	4·04	4·55	
5·5	4·72	5·22	
6·0	6·5	6·12	4·65
6·0 [a]	10·15		
6·5	6·9		
7·0	8·84	6·0	
7·5		4·4	
8·0	10·7	3·8	4·65
9·0	11·6	1·5	4·48
10·0	12·0	0·82	2·05
11·0	12·0		
11·4 [a]	7·32		
11·4	8·8		
12·0		0·2	

[a] DCl in D_2O.

Using the data from hydrolyses in hydrochloric and perchloric acids we have carried out Bunnett (ω and ω*) and Bunnett and Olsen treatments.* Using Yates' method, we have defined the most appropriate acidity function as $H_S = 0.75\ H_0$ and the function plotted was thus $\log\{10^4h_0^{0.75}/(K_{BH^+}^{0.75} + h_0^{0.75})\}$ *vs.* $\log s_{H_2O}$. The Bunnett ω* plots gave the best results in that it was possible to correlate satisfactorily data over the whole range from 1 to 11·4M-HCl and from 1 to 10M-$HClO_4$. In HCl, ω* = 4·5 (correln. coefft. 0·98 for 14 points), and in $HClO_4$, ω* = —3·14 (correln. coefft. 0·96 for 12 points). Those plots did show some curvature, especially when the points at higher acidities were included, but considering the wide range of acidities involved (the spread of acidities is as large or larger than any of those included by Bunnett in his original papers), the number of points, and the reasonable correlation coefficients, we feel that the ω* values defined from the slopes of those plots are significant. These large negative ω* values are consistent with water playing the role of a nucleophile in the rate-determining step of the reaction. Similar ω* values (—2·5 to —3·8) have been obtained by Bunton *et al.*[15] for the acid-catalysed hydrolysis of various open and cyclic dialkyl sulphites, which, on the basis of other evidence, undergo hydrolysis *via* nucleophilic attack of water on the sulphur atom of the conjugate acids.

The Bunnett ω and the Bunnett and Olsen plots for hydrolyses in both acids were far less satisfactory and showed a scattering of points which could only be resolved into straight lines by omitting certain points and considering limited acid concentration ranges. For example, the Bunnett and Olsen plot for hydrolysis in $HClO_4$ over the limited range 4—10M gave a slope $\phi = +0.28$ (correln. coefft. 0·97) which is consistent with water involvement in the rate-determining step. In the Yates' plots the points could be grouped into two separate segments. Thus, the slope, *r*, changed sharply in hydrochloric acid of 10M from —1·59 (correln. coefft. 0·97, 10 points) to +0·8 (correln. coefft. 0·99, 4 points). In perchloric acid, *r* changed from —0·72 (correln. coefft. 0·99, 6 points) to +1·1 (correln. coefft. 0·98, 5 points) at *ca.* 6·5M-acid. Those changes in the magnitude of *r* suggest a changeover in mechanism[16] from *A*-1 to *A*-2 type as the maxima in the rate–acidity profiles are passed. However, since the activity of water is greatly reduced with increasing acid strength, the incursion of an *A*-2 process in unlikely in such strong acid and we feel that in the present instance these results from the Yates' plots represent a fortuitous and physically non-significant fit.

Solvent Isotope Effects.—The solvent isotope effects (k_{D_2O}/k_{H_2O}) of 1·55 (6M-HCl) and 0·83 (11·4M-HCl) (Table 2) are consistent with a reaction involving a pre-equilibrium protonation at lower acidities followed by a rate-determining nucleophilic attack of D_2O or H_2O.[14]

Salt Effects.—Bunton *et al.*[17] have shown that the salt effect of perchlorates is negligible or slightly negative in *A*-2 acid-catalysed ester hydrolysis, whereas chlorides assist the hydrolysis slightly. For esters reacting by an *A*-1 mechanism both perchlorates and chlorides assist hydrolysis, the former producing the greater acceleration. Three of the four sets of data (at 1, 2, 3, and 7M acidities) in Table 3 support an *A*-2 type process in terms of this

TABLE 3

Salt effects on the hydrolysis of sodium *N*-1-naphthylsulphamate in perchloric acid at 40 °C

Acid strength (M)	Added salt (M)	10^3k/s^{-1}
1·0		0·35
1·0	3·0 [a]	0·579
1·0	3·0 [b]	0·488
2·0		0·93
2·0	2·0 [a]	1·2
2·0	2·0 [b]	0·97
3·0		1·97
3·0	1·0 [a]	2·25
3·0	1·0 [b]	1·88
7·0		6·0
7·0	1·4 [a]	6·56
7·0	1·4 [b]	4·06

[a] Added NaCl. [b] Added $NaClO_4$.

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* *N*-1-Naphthylsulphamate may be regarded as a moderately basic substrate (pK_{BH^+} — 1·45). Thus, in the Bunnett plots the functions plotted were $\log 10^4k - \log\{10^4h_0/(h_0 + K_{BH^+})\}$ (ω plot) and $\log 10^4k - \log\{10^4[H^+]/(h_0 + K_{BH^+})\}$ (ω plot) *vs.* $\log a_{H_2O}$. In the Bunnett and Olsen plot, $\log 10^4k - \log\{10^4[BH^+]/([BH^+] + [B])\}$ *vs.* $-(H_0 + \log[H^+])$ was plotted.

[15] C. A. Bunton, P. B. D. de la Mare, and J. G. Tillett, *J. Chem. Soc.*, 1958, 4754; 1959, 1766.

[16] K. Yates, *Accounts Chem. Res.*, 1971, **4**, 136.

[17] C. A. Bunton, J. H. Crabtree, and L. Robinson, *J. Amer. Chem. Soc.*, 1968, **90**, 1258.

diagnostic criterion. Thus, at 2, 3, and 7M acidities, added chloride clearly assists the hydrolysis whereas added perchlorate has either a negligible or retarding effect. The data for hydrolysis in 1M-acid are anomalous in that both salts produce some acceleration. This might appear to suggest an *A*-1 mechanism, but, in fact, a far greater acceleration would be expected for a substrate undergoing reaction by an *A*-1 mechanism in the presence of such quantities of added salt.[17]

TABLE 4

Effect of temperature and activation parameters for the hydrolysis of sodium *N*-1-naphthylsulphamate

Temp. (K) [a]	298	305	313	318·5	327·5	330
10^3k/s^{-1}	0·45	0·95	3·1	5·1	13·1	16·9
$\Delta H^‡$/kJ mol^{-1} = 90·8			$\Delta S^‡$/J mol^{-1} K^{-1} = −5·0			
Temp. (K) [b]	298	313	322	331·5		
10^3k/s^{-1}	0·94	6·01	14·4	32·8		
$\Delta H^‡$/kJ mol^{-1} = 86·2			$\Delta S^‡$/J mol^{-1} K^{-1} = −16·8			
Temp. (K) [c]	299	304·5	313	320·5	331	
10^3k/s^{-1}	1·66	3·04	8·8	19·2	49·1	
$\Delta H^‡$/kJ mol^{-1} = 86·2			$\Delta S^‡$/J mol^{-1} K^{-1} = −13·4			

[a] Hydrolyses carried out in 4·0M-HCl. [b] Hydrolyses carried out in 7·0M-$HClO_4$. [c] Hydrolyses carried out in 11·4M-HCl.

Thermodynamic Data.—The heats and entropies of activation for the acid-catalysed hydrolysis are given in Table 4. We would have expected rather larger negative entropies for a true bimolecular nucleophilic process. The $\Delta S^‡$ value for hydrolysis in 4·0M-hydrochloric acid will be a composite value since protonation is not complete. However, the entropy data for hydrolysis is 7·0M-perchloric and 11·4M-hydrochloric acids should be only slightly influenced by the protonation equilibrium (Scheme) since this will lie substantially to the right in these strong acid media and thus it should be possible to relate these entropy values to the rate-determining step of the hydrolysis.

Conclusion.—The Bunnett ω* plots, the solvent isotope effect, and the salt effects support an *A*-2 type mechanism, preceded by a rapid equilibrium protonation (on nitrogen) for the hydrolysis of sodium *N*-1-naphthylsulphamate (see Scheme). Entropy data however suggest that in the rate-determining step considerable nitrogen–sulphur bond-breaking may occur prior to bond-formation with the nucleophile. Entropy data had also indicated partial *A*-1 character in the predominantly *A*-2 type hydrolysis of several *N*-alkylsulphamates.[4] We have similarly rationalized [18] a Taft steric sensitivity parameter (δ) of unity for the acid-catalysed hydrolysis in dioxan of a number of aliphatic, aromatic, and alicyclic sulphamates in terms of bond-lengthening prior to cleavage in the transition state.

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[18] W. J. Spillane, C. B. Goggin, N. Regan, and F. L. Scott, *Internat. J. Sulfur Chem.* (*A*), 1973, **8**, 281.