828. *Sulphur–Nitrogen Compounds. Part I. The Hydrolysis of Sulphamate Ion in Perchloric Acid.*

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The rate (R) of hydrolysis of sulphamate ion in 10^{-3}M- to 6M-perchloric acid at 95° obeys the relation: $R = 139 \times 10^{-4}[H^+]$[sulphamate + sulphamic acid]/($0{\cdot}266 + [H^+]$), units in minutes and moles l.$^{-1}$. A mechanism involving a pre-equilibrium between sulphamate ion and sulphamic acid, followed by slow hydrolysis of the acid, previously proposed by Maron and Berens,[1] is supported. The kinetic expression arises from the fact that sulphamate and sulphamic acid are the predominant species at the extremes of the acid range studied. The mechanism is supported by work in deuterium perchlorate and a kinetic value for the dissociation constant of sulphamic acid is obtained. The energy and entropy of activation in dilute and more concentrated acids are compared and interpreted.

Maron and Berens [1] found the rate of hydrolysis of sulphamate ion in dilute acid at 80—98° to be of first order with respect to sulphamate and hydrogen-ion concentrations. They proposed a mechanism:

$$H_2N{\cdot}SO_3^- + H_3O^+ \rightleftharpoons X \xrightarrow{k_1} NH_4^+ + HSO_4^-$$

and suggested that the intermediate X might be the zwitterion form of sulphamic acid, which would then react with water to form ammonium hydrogen sulphate.

Since the ionisation constant of sulphamic acid has been determined, subsequently to that work, as approximately 0·1 at 25°,[2,3] it is apparent that, at pH values above about 2, significant concentrations of both sulphamate and sulphamic acid will be present in solution and the first-order rate dependence on hydrogen ion will probably not persist.[4a] Maron and Berens did not investigate this region, and furthermore their kinetic analysis was complicated by the partial regeneration of hydrogen ions by dissociation of product bisulphate in dilute acid.

We have now examined the kinetics of hydrolysis in 10^{-3}M to 6M-perchloric acid and by using dilute solutions of sulphamic acid ($5{\cdot}0 \times 10^{-5}$M) have avoided significant changes in the medium during the hydrolysis. The only feasible method then, probably, for estimating the very low concentrations of sulphate formed as hydrolysis proceeds, is by using [^{35}S]sulphamic acid and (after dilution with a standard amount of inactive sulphate as carrier) following the specific activity of $^{35}SO_4^{2-}$.

Experimental

Materials.—Sulphamic acid was purified by crystallisation.[5] [^{35}S]Sulphamic acid was prepared from urea (0·5 g.) and 100% sulphuric acid containing ^{35}S (2·5 c.c. of sulphuric acid mixed with 4 mc of dried $Na_2{}^{35}SO_4$, supplied by Radiochemical Centre, Amersham). The procedure [6] was adapted to a small scale. The material obtained by this method was 96—97% pure and contained only traces of sulphate. [^{35}S]Deuterosulphamic acid resulted from evaporating, at reduced pressures, [^{35}S]sulphamic acid (4 mg.) twice with deuterium oxide (0·5—1·0 ml.; 99·8% D_2O). Deuterium perchlorate was prepared from chlorine heptoxide and deuterium oxide.[7] Sodium perchlorate was dried at 140° for 4 days and stored over silica gel in a desiccator.

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

[2] King and King, *J. Amer. Chem. Soc.*, 1952, **74**, 1212.

[3] Taylor, Desch, and Catotti, *J. Amer. Chem. Soc.*, 1951, **73**, 74; Spiro, *Trans. Faraday Soc.*, 1959, **55**, 1746.

[4] Bell, " Acid-Base Catalysis," Oxford, 1941, (*a*) pp. 122—127, (*b*) p. 145.

[5] " Inorganic Syntheses," Vol. II, ed. Fernelius, McGraw-Hill, New York, 1946, p. 178.

[6] Palmer, " Experimental Inorganic Chemistry," Cambridge, 1954, p. 349.

[7] Baddeley and Nield, *J.*, 1954, 4684.

Analytical Methods.—Two chemical methods for determining sulphate were used for following the hydrolysis rates. Direct estimation with lead nitrate with dithizone as indicator[8] ("dithizone" method) gave excellent first-order kinetic plots and was undoubtedly superior to the ethylenediaminetetra-acetate[9] and radiochemical methods. Unfortunately, it could not be used satisfactorily in high electrolyte concentration (>1M-perchlorate) because the end-point became sluggish, and it was inconvenient with low sulphamic acid concentrations because of the large volumes of solution involved. Sulphamic acid was determined[10] in certain runs for comparison with the other methods and for the experiments in which barium ions were also present. The radiochemical method was employed in most of the runs. The amount of $^{35}SO_4^{2-}$ produced increased as the hydrolysis of $NH_2{\cdot}{}^{35}SO_3H$ proceeded. This released sulphate was diluted with a constant large excess of inactive sulphate and precipitated with lead ions in weakly acid solution. (Radiochemical experiments indicated that barium ions completely co-precipitated sulphamate and sulphate.) The lead sulphate was radio-assayed as "infinitely thick" discs ($\sim$35 mg. cm.$^{-2}$ for ^{35}S).[11] With these conditions radioactivity count is a measure of specific activity, x, of the sample where [total sulphate] = [added sulphate + sulphate produced by hydrolysis]:

$$x = \frac{[^{35}SO_4^{2-}]}{[\text{total sulphate}]} \approx \frac{[^{35}SO_4^{2-}]}{[\text{added sulphate}]} \approx f(^{35}SO_4^{2-})$$

and hence a measure of the extent of reaction. The "zero-time" value indicated 4—8% reaction, which arose from some co-precipitation of lead sulphamate with sulphate and from $\sim$3% $^{35}SO_4^{2-}$ present in the labelled sulphamic acid. The method gave reasonable first-order curves but the rate constants of identical runs could vary by about ±4%. The reaction was usually followed up to the second half-life.

Kinetic Procedure.—Solutions were prepared at room temperature and an allowance made in the concentration values for the expansion of water in reaching water-thermostat temperatures of 80° and 95° (±0·1°). $NH_2{\cdot}{}^{35}SO_3H$ (0·0125 mmole) was dissolved in aqueous perchloric acid (250 c.c.) containing sodium perchlorate at the required temperature. At various times a portion of the solution was removed and cooled quickly, an aliquot part (20·0 c.c.) partially neutralised with aqueous ammonia (to pH 3—5), and 0·06M-ammonium sulphate was added (5·00 c.c.). The precipitate obtained by adding 0·06M-lead nitrate (5·0 c.c.) was

Kinetics of hydrolysis of sulphamic acid.

Run no.	Added $[HClO_4]$ [M]	μ [M]	10^4k (min.$^{-1}$)
At 80·0°			
1[a]	0·097	0·136	9·8
2[a]	1·04	1·08	19·4
3[b]	1·04	1·08	19·2
4[c]	1·04	1·08	20·1
5	1·04	1·08	20·7
6[c]	3·25	3·29	22·3
At 95·0°			
7	—	1·03	<0·025
8	0·00155	1·03	0·83
9	0·0032	1·03	1·5
10	0·0047	1·03	2·5
11	0·0068	1·03	3·5
12	0·0103	0·0103	13·8
13	0·0103	1·03	5·3
14	0·0206	1·03	10·8
15	0·0308	1·03	18·5
16	0·0514	1·03	28·8
17	0·1030	1·03	41·6
At 95·0° (*contd.*)			
18	0·2575	1·03	74·9
19	0·514	1·03	89·8
20	1·030	1·03	108·4
21	1·030	2·06	115·2
22	2·06	2·06	132·5
23	5·76	5·76	108·0
24	0·0099	0·0147	16·6
25	0·0103	0·0150	18·6
26[d]	0·0099	0·0147	30·8
27[d]	0·0103	0·0150	32·9
28	2·55	2·55	144·5
29[e]	2·57	2·57	136·8
30[f]	2·57	2·57	135·8
31[c]	0·103	0·96	49·4
32[c]	0·103	0·96[g]	44·4

[a] Dithizone estimation. [b] EDTA estimation. [c] NO_2^-–Ce(IV) estimation. [d] 99·8% D_2O. [e] 99·8% D_2O containing $DClO_4$. [f] As *e* but also using $ND_2{\cdot}SO_3D$. [g] Including 0·03M-$BaCl_2$.

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[8] Archer, *Analyst*, 1957, **82**, 208; White, *Mikrochim. Acta*, 1959, 254.

[9] Bond, *Chem. and Ind.*, 1955, 941.

[10] Whitman, *Analyt. Chem.*, 1957, **29**, 1684.

[11] Libby, *Analyt. Chem.*, 1947, **19**, **2**.

filtered off, washed with water, alcohol, and ether, matted (~60 mg. cm.$^{-2}$) on thick aluminium discs,[12] and radio-assayed by a Geiger–Müller tube and the usual electronic equipment. The " infinite " sample of sulphate was obtained from the reaction mixture after 6—7 half-lives, but the same result was obtained by the more convenient procedure of adding excess of NO_2^- in about 0·1M-perchloric acid, sulphate then being quantitatively formed. The results are shown in the Table. The pseudo-first-order rate constants k refer to the relation: rate = k[sulphamate + sulphamic acid]. All measurements were in perchlorate medium except run 32. In the majority of the runs by the radiochemical method, 5 × 10^{-5}M-$NH_2\cdot{}^{35}SO_3H$ was used, except for the D_2O and comparative H_2O experiments (runs 24—30) where 5 × 10^{-3}M-concentrations were used to conserve deuterium oxide. The chemical assay runs used 0·04M-sulphamic acid (0·01M in runs 31 and 32). Runs 31 and 32 showed that homogeneous precipitation of barium sulphate used in gravimetric determination of barium is not accelerated by barium ions.

DISCUSSION

The experiments at 80° establish that the radiochemical method of estimation of total sulphate (sulphate and bisulphate) produced in the reaction gives similar results to chemical analysis for either total sulphate or sulphamate. They also indicate, as expected, that no sulphur exchange occurred between $NH_2\cdot SO_3H$ and SO_4^{2-} during the hydrolysis. The majority of the experiments were conducted at 95° to give reasonable rates for measurement. Those for 10^{-3}M to 6M-perchloric acid are given by runs 8—23, and the first-order rate constants, k, are shown in Fig. 1 as a function of pH. Obviously it was not possible to extrapolate the rates at higher acid concentrations to zero ionic strength (as did Maron and Berens [1] in their low-acidity work), and runs 8—20 were carried out at constant ionic strength (1·0M) so as to minimise activity coefficients effects. Runs 22—23 were at " natural " ionic strength, when the rate was insensitive to ionic strength. At low acidity, k is of first order in hydrogen-ion concentration, confirming Maron and Berens's results. Run 24 gives a value for second-order rate constant of 0·112 mole l.$^{-1}$ min.$^{-1}$. We have interpolated to 95° Maron and Berens's value for k at a similar ionic strength and obtain a value 0·098 mole l.$^{-1}$ min.$^{-1}$ in fair agreement. The discrepancy may arise from the fact that the latter authors (*a*) took a value for $K^\circ_{HSO_4^-}$ (0·012) not now

FIG. 1. *Variation with* pH *of first-order rate constant for hydrolysis of sulphamate ion.*

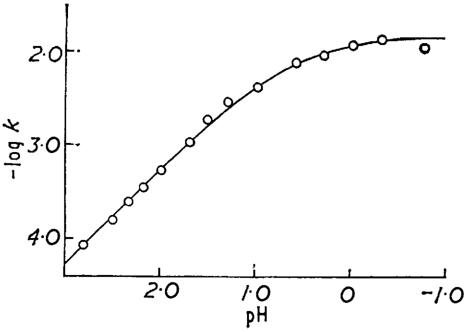
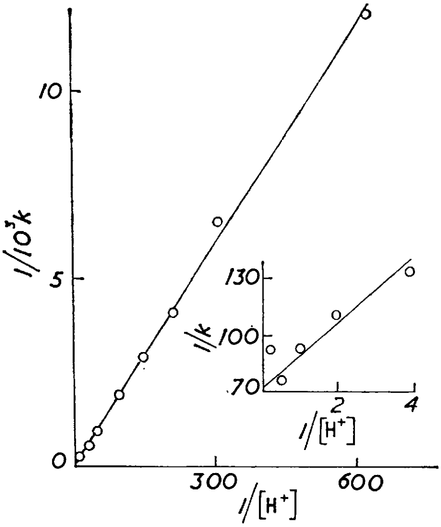


FIG. 2. *Plot of reciprocal of first-order rate constant against reciprocal hydrogen-ion concentration.*



considered correct and (*b*) were not able to allow in their treatment for incomplete ionisation of sulphamic acid at the concentrations which they employed. At higher acidities ($>0{\cdot}1$M), k becomes less dependent on pH and reaches a limiting value at about 2M-perchloric acid. These results are in agreement with the pre-equilibrium mechanism where at higher acidity the sulphamate is converted largely into the acid form:

$$H_2N{\cdot}SO_3^- + H^+ \rightleftharpoons H_2N{\cdot}SO_3H \qquad \text{Equilibrium (constant } 1/K\text{)}$$

$$H_2N{\cdot}SO_3H + H_2O \longrightarrow NH_4^+ + HSO_4^- \qquad \text{Slow, } k_2$$

A value for the ionisation constant for sulphamic acid (K) can be obtained from the kinetic results, for:

$$\begin{aligned} d[SO_4^{2-} + HSO_4^-]/dt = -d[NH_2{\cdot}SO_3^- + NH_2{\cdot}SO_3H]/dt &= k_2[NH_2{\cdot}SO_3H] \\ &= k[NH_2{\cdot}SO_3^- + NH_2{\cdot}SO_3H] \end{aligned}$$

Therefore

$$k = k_2[H^+]/(K + [H^+]) \qquad (1)$$

$$1/k = K/k_2[H^+] + 1/k_2 \qquad (2)$$

From the linear plot of $1/k$ against $1/[H^+]$ (Fig. 2), k_2 and K can be calculated. The values (139×10^{-4} min.$^{-1}$ and $0{\cdot}266$ at $95{\cdot}0°$) have been substituted in (1) in order to calculate the theoretical curve which is shown in Fig. 1.

The thermodynamic ionisation constant of sulphamic acid has been determined by E.M.F.[2] and conductance[3] measurements. A relationship, $-\log K = (3792{\cdot}8/T) - 24{\cdot}122 + 0{\cdot}041544T$, has been deduced from the measurements between 10° and 50°,[2] leading to a *probable* value for pK of 1·45 at 95°. It is difficult to assess the magnitude of the effect of a 1·0M-ionic strength on this value, but from the modified Debye–Hückel relationship ($A = 0{\cdot}597$ at 95°)

$$pK_{\mu=1} \approx pK_{\mu=0} - 2A\mu^{\frac{1}{2}}/(1 + \mu^{\frac{1}{2}}) \approx 0{\cdot}85$$

This value is reasonable in view also of some data on the effect of sodium chloride concentration on the ionisation constant,[2] and its agreement with the kinetic value (0·6), in view of the extrapolations involved, strongly supports the suggested mechanism.

The results in deuterium oxide can also be rationalised.[13] In the limiting region (runs 28—30), when we are considering simply the hydrolysis of sulphamic acid, $k^{D_2O}/k^{H_2O} = k_2^{D_2O}/k_2^{H_2O} = 0{\cdot}95$, a not unexpected isotope effect. In dilute acid, on the other hand (runs 24—27), the reaction is faster in deuterium oxide ($k^{D_2O}/k^{H_2O} = 1{\cdot}80$) and this also is expected for a reaction involving a rapid pre-equilibrium proton transfer.[4b] The observed ratio is, however, somewhat lower than is usually encountered for such a reaction. However, the reactions were studied at 95°, the temperature (29°) of the maximum pK value for sulphamic acid has been exceeded, and the dissociation constant of the deutero-acid in D_2O ($K_{ND_2{\cdot}SO_3D}$) will be closer to (although smaller in value than) that of the proto-acid in H_2O ($K_{NH_2{\cdot}SO_3H}$) than is the case at lower temperatures.[14] Since at a constant low acidity:

$$\frac{k^{D_2O}}{k^{H_2O}} = \frac{k_2^{D_2O}}{k_2^{H_2O}} \cdot \frac{K_{NH_2{\cdot}SO_3H}}{K_{ND_2{\cdot}SO_3D}} \approx \frac{K_{NH_2{\cdot}SO_3H}}{K_{ND_2{\cdot}SO_3D}}$$

the higher temperature will itself lower the k^{D_2O}/k^{H_2O} ratio from that encountered at lower temperature.

The energies and entropies of activation determined by Maron and Berens (30·5 kcal./mole and 9·7 e.u.), as was pointed out by them, include the energy and entropy of formation of sulphamic acid. These latter values can be estimated from the data of

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[12] Popplewell and Wilkins, *J.*, 1955, 4098.

[13] For discussion of relative rates of acid-catalysed reaction in D_2O and H_2O, see Long and Bigeleisen, *Trans. Faraday Soc.*, 1959, **55**, 2077.

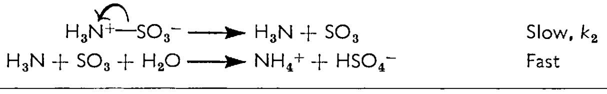
[14] Gurney, "Ionic Processes in Solution," McGraw-Hill, New York, 1953, pp. 150—155.

King and King[2] as +0·9 kcal./mole and +9 e.u., and this will mean values for the energy and entropy of activation of hydrolysis of sulphamic acid (the slow step) of 29·6 kcal./mole and 0·7 e.u. respectively. Our values for the rate constant in high acid concentration at 80·0° and 95·0° yield kinetic parameters of 29·7 kcal./mole and 3·2 e.u. respectively, in satisfactory agreement. Maron and Berens commented that their observed energy and entropy of reaction were unusually high because these included the thermodynamic terms for the pre-equilibrium. It is seen now that the slow hydrolysis step is still accompanied by a large energy of activation, and Maron and Berens's reasons for the complex mechanism they correctly postulated are less convincing.

In this paper, sulphamic acid in solution has been formulated, purely for convenience, as the neutral species. The evidence from *X*-ray[15] and infrared[16] studies for the zwitterionic structure, $NH_3^+SO_3^-$, in solid sulphamic acid appears overwhelming. The species in solution is less certain, but from dielectric-constant measurements in certain organic solvents[17] and from Raman spectra in aqueous solution,[16] the zwitterion is believed to be present here also. The low value for the entropy of ionisation of sulphamic acid in water supports this idea, since usually negative entropy changes of some 20 entropy units are observed for ionisation of a number of uncharged acids.[18] There will be less change of solvation when a zwitterion rather than an uncharged acid ionises.

Siebert[16] has suggested, from spectral analysis, that the S–N bond is weaker in the acid than in sulphamate ion, and that this is an explanation for the easier hydrolysis of the acid than of the ion. In fact the longer S–N bond distance in sulphamic acid[15] (1·74 Å) than in potassium sulphamate[19] (1·60 Å) supports this contention. That there is a relation between the S–N bond distance and hydrolytic stability has been noted by Jeffrey and Jones,[20] since an S–N distance in potassium iminodisulphonate of 1·66 Å is observed and this hydrolyses more rapidly in acid solution than does the sulphamate.[21] Here too a base–acid pre-equilibrium is probably involved, and it is reasonable to suppose that the S–N distance in the (unobtainable) iminodisulphonic acid is longer than that in sulphamic acid.

It is uncertain whether, in the slow step, water is actively involved in the transition state (*i.e.*, *A*-2 reaction[22]) or whether a kinetic intermediate is formed which subsequently reacts rapidly with water (*A*-1 reaction). Pritchard and Long[23] contended that values for k^{D_2O}/k^{H_2O} in the range 1·9—2·6 are often found for *A*-1 reactions, and that with these reactions the difference in $k_2^{D_2O}$ and $k_2^{H_2O}$ will be small, as we have found. For reasons we have already considered, our value for k^{D_2O}/k^{H_2O} (1·80) would be raised at the lower temperatures with which Pritchard and Long's semi-empirical correlation is concerned. In addition, with similar classes of compounds, an *A*-1 mechanism is generally associated with more positive entropy of activation (5—10 e.u.) than with an *A*-2 mechanism (—20 to —25 e.u.).[24] Although these relations refer to the hydrolysis of neutral molecules, and we are here concerned with the sulphamate ion, an *A*-1 mechanism appears favoured then, in which case the hydrolysis of sulphamic acid may involve:



$$H_3N^+\text{—}SO_3^- \longrightarrow H_3N + SO_3 \qquad \text{Slow, } k_2$$

$$H_3N + SO_3 + H_2O \longrightarrow NH_4^+ + HSO_4^- \qquad \text{Fast}$$

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[15] Kanda and King, *J. Amer. Chem. Soc.*, 1951, **73**, 2315; Osaki, Tadokoro, and Nitta, *Bull. Chem. Soc. Japan*, 1955, **28**, 524.

[16] *E.g.*, Siebert, *Z. anorg. Chem.*, 1957, **292**, 167.

[17] Hovermale and Sears, *J. Phys. Chem.*, 1956, **60**, 1579.

[18] Frost and Pearson, " Kinetics and Mechanism," Wiley, New York, 1953, p. 123; Harned and Owen, " The Physical Chemistry of Electrolytic Solutions," Rheinhold, New York, 1950, p. 514.

[19] Jeffrey and Stadler, *J.*, 1951, 1467.

[20] Jeffrey and Jones, *Acta Cryst.*, 1956, **9**, 283.

[21] Doyle and Davidson, *J. Amer. Chem. Soc.*, 1949, **71**, 3491.

[22] Long and Paul, *Chem. Rev.*, 1957, **57**, 935.

[23] Pritchard and Long, *J. Amer. Chem. Soc.*, 1956, **78**, 6008.

[24] Long, Pritchard, and Stafford, *J. Amer. Chem. Soc.*, 1957, **79**, 2362.

The kinetics observed can also be explained by slow protonolysis of sulphamate ion:

$$H_2N{\cdot}SO_3^- + H_3O^+ \longrightarrow NH_4^+ + HSO_4^-$$

The limiting rate is reached when the (low) sulphamate concentration decreases proportionately as the hydrogen-ion concentration increases. In addition, the differentiation of the two mechanisms from rate behaviour in deuterium oxide has been questioned recently.[25] It does, however, seem unreasonable that hydrolysis should proceed preferentially through the anion, when the shorter N–S bond distance in the latter is borne in mind, and for at least this reason we favour the pre-equilibrium mechanism.

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[25] Gold, *Trans. Faraday Soc.*, 1960, **56**, 255.