707. *Sulphur–Nitrogen Compounds. Part II.*[1] *The Hydrolysis of Hydroxylaminetrisulphonate and Hydroxylamine-*NO*-disulphonate Ions in Perchloric Acid.*

By J. P. CANDLIN and R. G. WILKINS.

By using $[(SO_3)_2NO(^{35}SO_3)]^{3-}$ and $[^{35}SO_3{\cdot}NH{\cdot}O{\cdot}SO_3]^{2-}$, hydroxylamine trisulphonate ion has been shown to be hydrolysed exclusively to hydroxylamine-*NO*-disulphonate ion, which is then hydrolysed at a much slower rate to hydroxylamine-*O*-sulphonate (rather than to the *N*-sulphonate). The rates (R) of hydrolysis of the tri- and di-sulphonate ions (S) are given by the expression $R = k_2[\mathrm{S}][\mathrm{H}^+]$ from pH ~3 to 0·5M-perchloric acid but thereafter the rates increase more rapidly than C_{H^+}. The values of k_2 (extrapolated to zero ionic strength) are $10^{15\cdot7}\exp(-23{,}700/\boldsymbol{R}T)$ and $10^{16\cdot5}\exp(-29{,}200/\boldsymbol{R}T)$ l. mole^{-1} sec.$^{-1}$ for the trisulphonate and *NO*-disulphonate respectively. A simple mechanism is proposed for the hydrolysis of the two compounds. The dependence of the rates on the ionic strength and on D_2O/H_2O content is examined.

FREMY[2] first prepared potassium hydroxylaminetrisulphonate but it was not until many years later that Haga[3] correctly formulated it as a triacylated hydroxylamine. The anion is hydrolysed in acid in three stages:

$$(SO_3)_2N{\cdot}O{\cdot}SO_3^{3-} + H_2O \longrightarrow SO_3{\cdot}NH{\cdot}O{\cdot}SO_3^{2-} + HSO_4^- \quad . \; . \; . \; . \; . \quad (1)$$

$$SO_3{\cdot}NH{\cdot}O{\cdot}SO_3^{2-} + H_2O \longrightarrow NH_2{\cdot}O{\cdot}SO_3^- + HSO_4^- \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$NH_2{\cdot}O{\cdot}SO_3^- + H_2O \longrightarrow NH_2{\cdot}OH + HSO_4^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

The first of these stages appears to be the fastest since hydroxylamine-*NO*-disulphonate ion was first prepared by Haga[4] and independently by Raschig[5] by the hydrolysis of potassium hydroxylaminetrisulphonate. It is stable enough for the salts to be recrystallised from dilute acid solution. It is hydrolysed, however, slowly in acid solution leading eventually to hydroxylamine and hydrogen sulphate. Raschig[5] found evidence for the intermediate formation in solution of an oxidising agent which he considered to be the, then unknown, hydroxylamine-*O*-sulphonate ion. Only some early qualitative kinetic studies in acid solution have been previously reported.[6]

In this paper we report the kinetics of hydrolysis of trisulphonate ion (1) and of hydroxylamine-*NO*-disulphonate ion (2), and a later paper will examine stage (3) which, it transpires, is the most complicated of the three. All these reactions are acid-catalysed. They produce, commonly, hydrogen sulphate (or sulphate) and the rates can be conveniently followed by analysing for this ion chemically or (to increase the range of observations) radiochemically.[1]

Stage (1) can be easily isolated kinetically from the subsequent stages but, because the rates of steps (2) and (3) are similar, the investigation of the kinetics of stage (2) from the rate of sulphate production would be complicated by the early incursion of stage (3). This difficulty was avoided by studying the hydrolysis of a dilute solution (~10^{-4}M) of $K_2[^{35}SO_3{\cdot}NH{\cdot}O{\cdot}SO_3]$. $[^{35}S]$Sulphate is produced during stage (2) and is diluted with a large constant excess of inactive sulphate, so that the varying but very small amount of inactive sulphate produced by stage (3) is not important. The rate of increase of specific activity of sulphate thus measures directly the progress of the hydrolysis of only the hydroxylamine-*NO*-disulphonate ion. In all studies four effects primarily have been

---

[1] Part I, Candlin and Wilkins, *J.*, 1960, 4236.
[2] Fremy, *Ann. Chim. Phys.*, 1845, **15**, 408.
[3] Haga, *J.*, 1904, **85**, 78.
[4] Haga, *J.*, 1906, **89**, 240.
[5] Raschig, *Ber.*, 1906, **39**, 245.
[6] Wagner, *Z. phys. Chem.*, 1896, **19**, 668.

examined, *viz.*, acidity, ionic strength, temperature, and the effect of replacing water by deuterium oxide.

EXPERIMENTAL

Materials.—$K_3[(SO_3)_2N{\cdot}O{\cdot}SO_3],1\frac{1}{2}H_2O$ was prepared by a modification of Fremy's original method.[2] Potassium hydroxylamine-*NN*-disulphonate [7] (50 g.), potassium hydroxide (5 g.), and lead dioxide (100 g.) were boiled in water (750 c.c.) until the supernatant liquor became colourless (approx. 15 min.). The mixture was cooled and filtered and lead salts in the filtrate were removed as a basic carbonate after precipitation with carbon dioxide at pH $\geqslant$ 9. The filtrate was evaporated to about 150 c.c. under reduced pressure at *ca.* 40° and, on cooling, the trisulphonate crystallised (65 g., 90%). The material was recrystallised from slightly alkaline solution. It was washed with cold water, methanol, and ether and stored in a vacuum-desiccator over KOH. It was sulphate-free. It was analysed after hydrolysis to hydroxylamine and sulphate by 0·5M-perchloric acid at 140° for several hours (Found: N, 3·2; S, 22·9. Calc. for $K_3NO_{10}S_3,1\frac{1}{2}H_2O$: N, 3·4; S, 23·2%).

Potassium hydroxylamine[$^{35}S_3$]trisulphonate was obtained similarly from potassium hydroxylamine-*NN*-[$^{35}S_2$]disulphonate (4 g.). The latter was prepared from [^{35}S]sulphur dioxide generated by electrical ignition of a mixture of dried sodium [^{35}S]sulphate (200 mg.) and red phosphorus (400 mg.) in dried oxygen.[8] The radioactive sulphur dioxide, followed by inactive sulphur dioxide to flush out the ignition apparatus, was passed into a mixture of potassium nitrite and hydrogen carbonate until the [^{35}S]disulphonate was precipitated.[7]

For preparation of $K_3[(SO_3)_2N{\cdot}O{\cdot}{}^{35}SO_3],1\frac{1}{2}H_2O$, [^{35}S]sulphur dioxide from dried sodium [^{35}S]sulphate (200 mg.) and red phosphorus (400 mg.) was absorbed in 10% potassium hydroxide solution. The ignition apparatus was then flushed with dried nitrogen which was also passed through the potassium hydroxide. Potassium nitrosyl disulphonate [9] (4 g.) was added and a few minutes afterwards potassium metabisulphite (3·3 g.) in water (20 c.c.), the solution being alkaline at this stage. Concentrated barium acetate solution was added to the colourless solution until precipitation of barium sulphate was complete, and carbon dioxide passed into the alkaline filtrate. After removal of barium carbonate, the filtrate was evaporated under reduced pressure to about 15 c.c. and cooled, and the material separating filtered off and washed as before (yield 2 g.). This compound, when hydrolysed completely in acid, gave barium sulphate (1760 counts/min. with standard conditions, " infinitely " thick, 0·8 sq. cm. " mat "). When hydrolysed to the first stage it gave inactive barium sulphate (4 counts/min.) and a filtrate containing the *NO*-disulphonate, which when decomposed gave barium sulphate (2620 counts/min.). The trisulphonate exchange rate with sulphate or sulphite ions was very slow, amounting to about 10% in 24 hr. at 25°, of which at least 8% was due to coprecipitation of barium trisulphonate with barium sulphate or sulphite, addition of barium ions being the separation procedure used. It was found later that there was negligible coprecipitation when lead ions were used as precipitant.

$K_3[({}^{35}SO_3)_2N{\cdot}O{\cdot}SO_3],1\frac{1}{2}H_2O$ was prepared from $NO({}^{35}SO_3K)_2$ and inactive potassium metabisulphite by the method described above. Potassium nitrosyl [^{35}S]disulphonate was prepared on a small scale from [^{35}S]sulphur dioxide [8] by the method of Harvey and Hollingshead.[9] Hydrolysis of the labelled hydroxylaminetrisulphonate (2 g. in 50 c.c. of 0·1M-hydrochloric acid) led directly to the desired $K_2[{}^{35}SO_3{\cdot}NH{\cdot}O{\cdot}SO_3]$. The solution was left overnight and made alkaline with potassium hydroxide, and barium hydroxide added until all sulphate was precipitated. The barium sulphate was removed and carbon dioxide passed into the filtrate to precipitate the excess of barium hydroxide. The filtrate was then evaporated to about 10 c.c. under reduced pressure at *ca.* 40°, ethanol (10 c.c.) added, and the solution cooled. The precipitated potassium hydroxylamine-*NO*-[^{35}S]disulphonate was washed with a small amount of ice-water, alcohol, and ether and stored in a vacuum-desiccator over KOH. The inactive compound was prepared similarly and recrystallised from mildly alkaline solution. It was analysed after hydrolysis to hydroxylamine and sulphate (Found: N, 4·7; S, 23·5. Calc. for $HK_2NO_7S_2$: N, 5·1; S, 23·8%).

Kinetic Procedure.—The methods used for following the rate of production of sulphate were

---

[7] Palmer, " Experimental Inorganic Chemistry," Cambridge, 1954, p. 279.

[8] Johnson and Huston, *J. Amer. Chem. Soc.*, 1950, **72**, 1841.

[9] Harvey and Hollingshead, *Chem. and Ind.*, 1953, 244.

described in Part I. Direct estimation with lead nitrate, with dithizone as indicator and 10^{-2}M-trisulphonate, gave excellent first-order kinetic plots and was used to examine the effects of ionic strength, temperature, and deuterium oxide on the rate. For the experiments in low ionic strength, only the radiochemical method could be used, employing 1—6 × 10^{-4}M-$K_3[(^{35}SO_3)_2N{\cdot}O{\cdot}{}^{35}SO_3]$ from several freshly prepared stock 3 × 10^{-3}M-solutions kept at 0°. The small amount of chemical sulphate produced containing $^{35}SO_4^{2-}$ was diluted with a large excess of sulphate and precipitated and radioassayed as lead sulphate.[1] The material was easier to filter off and wash when precipitated at pH ~3. Both the radiochemical and the ethylenediaminetetra-acetate method were used for the experiments in high acidity, the former giving the better results. Runs 25—29 were carried out in a total volume of 2·5—5·0 c.c. to conserve deuterium oxide and the H_2O–D_2O mixtures were made up accurately by volume since the molar and the partial molar volumes of the two solvents are very similar. The buffer solutions were made up from standard solutions of formic acid and sodium formate (prepared from "AnalaR" formic acid and sodium carbonate) and the pH (3·5) measured with a Pye pH meter.

Apart from the initial rate (followed to the extent of 7% total reaction) and total sulphate

Kinetics of hydrolysis of hydroxylaminesulphonates.

(a) *Hydroxylaminetrisulphonate*

Run no.	Temp.	Added $[HClO_4]$ (M)	I (M)	10^4k_1 (min.$^{-1}$)	$10^2k_1/[H^+]$ (l. mole^{-1} min.$^{-1}$)
		Effect of acid			
1	25·0°	pH ~9	0·06	⩽2% reaction in 41 days	
2 [a]	0·1	0·00060	0·56	0·0086 [b]	0·15 [b]
3	0·1	0·025	0·56	0·419	0·17
4	0·1	0·050	0·56	0·852	0·17
5	0·1	0·100	0·56	1·71	0·17
6	0·1	0·300	0·56	6·87	0·23
7 [c]	0·1	0·100	3·06	0·933	0·09
8 [c]	0·1	0·500	3·06	4·63	0·09
9 [c]	0·1	1·00	3·06	10·7	0·11
10 [c]	0·1	2·00	3·06	22·3	0·11
11 [c]	0·1	3·00	3·06	62·0	0·21
12 [a]	0·1	0·500	6·00	3·36	0·07
13 [a]	0·1	6·00	6·00	1060	1·8
		Effect of ionic strength			
14 [a]	25·0	0·00050	0·0011	5·34	107
15	25·0	0·050	0·110	110	22·0
16	25·0	0·050	0·160	86·0	17·2
17	25·0	0·050	0·210	68·7	13·7
18	25·0	0·050	0·310	51·7	10·3
19	25·0	0·050	0·410	42·6	8·5
20	25·0	0·050	0·610	31·3	6·3
		Effect of temperature			
21	5·15	0·100	0·160	11·0	1·10
22	10·60	0·100	0·160	24·8	2·48
23	15·55	0·100	0·160	51·4	5·14
24	20·40	0·100	0·160	103	10·3
		Effect of H_2O/D_2O			
25	25·0	0·096	0·160	193	20·2
26 [d]	25·0	0·096	0·160	241	25·1
27 [e]	25·0	0·096	0·160	334	34·8
28 [f]	25·0	0·096	0·160	431	44·9
29 [g]	25·0	0·096	0·160	600	62·5 (66·7) [h]
		Effect of buffer			
		$[H{\cdot}CO_2H]$ = $[H{\cdot}CO_2Na]$ (M)			
30	45·0	0·025	0·56	2·53	78
31 [a]	45·0	0·075	0·56	2·52	78
32 [a]	45·0	0·150	0·56	2·44	74

(b) *Hydroxylamine*-NO-*disulphonate*

Run no.	Temp.	Added $[HClO_4]$ (M)	I (M)	10^4k_1 (min.$^{-1}$)	$10^2k_1/[H^+]$ (l. mole^{-1} min.$^{-1}$)
		Effect of acid			
33	75·0°	pH ~9·5		~8% reaction in 20 days	
34	65·0	0·0013	0·50	0·567	4·35
35	65·0	0·025	0·50	9·49	3·8
36	65·0	0·050	0·50	20·3	4·1
37	65·0	0·100	0·50	37·1	3·7
38	65·0	0·200	0·50	81·0	4·05
39 [i]	65·0	0·200	0·50	85·1	4·3
40	65·0	0·400	0·50	173	4·3
41	40·0	1·00	1·00	14·9	0·15
42	40·0	1·00	6·00	14·8	0·15
43	40·0	6·00	6·00	1250	2·1
		Effect of ionic strength			
44	75·0	0·025	0·025	108	43·2
45	75·0	0·025	0·075	70·3	28·1
46	75·0	0·025	0·225	44·0	17·6
47	75·0	0·025	0·325	37·8	15·1
48	75·0	0·025	0·525	31·2	12·5
		Effect of temperature			
49	60·05	0·100	0·100	34·9	3·5
50	65·28	0·100	0·100	68·9	6·9
51	70·28	0·100	0·100	132	13·3
52	75·23	0·100	0·100	236	23·6
		Effect of D_2O			
53	65·0	0·100	0·100	71·7	7·2
54 [g]	65·0	0·100	0·100	187	18·7

[a] Radiochemical estimation. [b] Estimated from run at 25·0° and $E_{act.}$ [c] EDTA estimation. [d] 24% D_2O. [e] 48% D_2O. [f] 72% D_2O. [g] 96% D_2O. [h] Extrapolated value for 100% D_2O. [i] From initial rate (dithizone method).

runs (dithizone method), only the radiochemical method was used for the *NO*-disulphonate study, employing 5×10^{-4}M- to 5×10^{-3}M-active compound. Hydroxylamine-*O*-sulphonic acid was estimated in a solution (150 c.c.) containing *ca.* 0·25M-sulphuric acid, sodium hydrogen carbonate (0·25 g.), potassium iodide (0·5 g.), and a chip of solid carbon dioxide. The stoppered solution was set aside for about 3 hr. in the dark, and the liberated iodine then estimated with standard thiosulphate solution.

The ionic strength was adjusted with recrystallised sodium perchlorate. For runs between 0° and room temperature, the thermostat was placed in a refrigerated room. The results are given in the Table. Values of H_0 are taken from Long and Paul's review.[10] The addition of either 0·2M- or 0·4M-potassium tri- or di-sulphonate or potassium chloride did not affect the pH of an 0·1M-hydrochloric acid solution, thus indicating that the tri- and di-sulphonate ions remained unprotonated at these acidities.

RESULTS

A point is reached and retained for some time in the hydrolysis of the trisulphonate when the amount of sulphate produced (estimated chemically or radiochemically) is one-third of the final amount obtained on ultimate hydrolysis to hydroxylamine. This proves that the first stage is much faster than the subsequent hydrolysis of the disulphonate. It remains then to show that the nitrogen-bound, rather than the oxygen-bound, sulphonate is broken exclusively in the hydrolysis of the trisulphonate. This is accomplished by studying the products of the first stage of the hydrolysis of $K_3[(SO_3)_2N\cdot O\cdot {}^{35}SO_3]$. The sulphate is inactive and the specific activity of the hydroxylaminedisulphonate 50% higher than that of the original compound, both estimated as sulphate. These experiments confirm the validity of equation (1).

FIG. 1. *Effect of ionic strength on the second-order rate constant for hydrolysis of hydroxylamine-trisulphonate.*

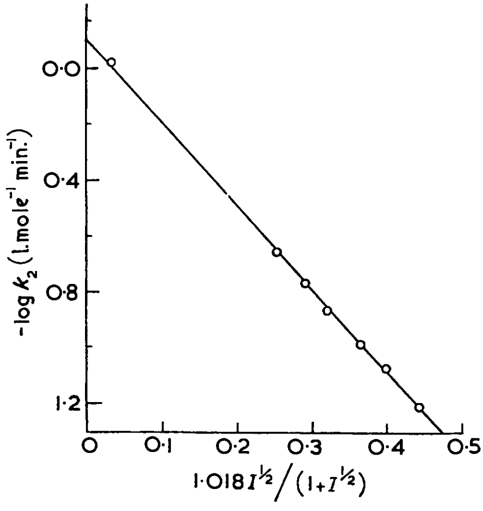
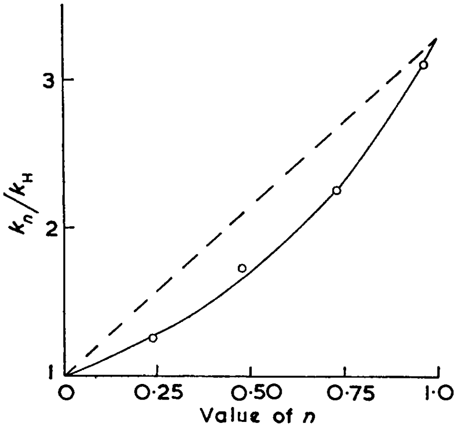


FIG. 2. *Effect of deuterium oxide on the rate of hydrolysis of hydroxylaminetrisulphonate.*



The hydrolysis of hydroxylamine-*NO*-disulphonate leads also exclusively to N–S bond rupture, forming hydroxylamine-*O*-sulphonate with negligible production of hydroxylamine-*N*-sulphonate $[SO_3\cdot NH\cdot OH]^-$. This was clear when the initial (and overall) rate of production of ${}^{35}SO_4{}^{2-}$ from $[{}^{35}SO_3\cdot NH\cdot O\cdot SO_3]^{2-}$ was found to be equal to the *initial* rate of production of sulphate (runs 38 and 39). Only a very small amount of sulphate from stage (3) accumulates in the early part of stage (2). Since sulphate results from both N–S and O–S (or N–O) bond rupture, whereas radioactive sulphate is produced only from N–S breakage, the latter must account for $\geqslant 95\%$ of cleavage acts.

The trisulphonate ion is not hydrolysed significantly, nor is there a perceptible change in the pH of the solution, in 41 days at pH 9 (run 1). However, the disulphonate ion is hydrolysed

---

[10] Long and Paul, *Chem. Rev.*, 1957, **57**, 1.

very slowly in weakly alkaline solution (run 33), with slight attendant rise in acidity, and more rapidly in strongly alkaline solution.[11] From approximately 10^{-3}M- to 0·5M-perchloric acid, the rate (R) of hydrolysis of both compounds [S] can be expressed adequately by $R = k_2[\mathrm{S}][\mathrm{H}^+]$. This is indicated by the reasonable constancy for $k_1/[\mathrm{H}^+]$ $(=k_2)$ (runs 2—6, 7, 8; 34—40), k_1 being the pseudo-first-order rate constant for hydrolysis at constant acidity, independent of a variation of the concentration of the sulphonate (run 2, 3×10^{-4}M; runs 3—6, 10^{-2}M; run 50, 5×10^{-4}M; run 53, 5×10^{-3}M).

Simple pH experiments show that up to (at least) 0·5M-acid, the tri- and di-sulphonate ions remain substantially unprotonated and this is also indicated by the effect of ionic strength on the rate (runs 14—20 and 44—48). The values of $\log_{10} k_2$ against $1{\cdot}018\, I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ for the trisulphonate deviate little from a line of slope $-2{\cdot}9$ (Fig. 1), as might be expected for a reaction between trinegative and monopositive ions. The validity of this expression (at this admittedly high ionic strength) for this compound is substantiated by the radiochemical measurement which could be carried out at low ionic strength (Fig. 1). If the fuller expression

$$\log k_2 = \log k_2{}^{\circ} + \frac{3 \times 1{\cdot}018 I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + BI$$

is employed, a reasonable value for B of 0·074 is obtained. A similar plot for the disulphonate ion of $\log k_2$ against $1{\cdot}134 I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ is also linear with slope of $-1{\cdot}87$.

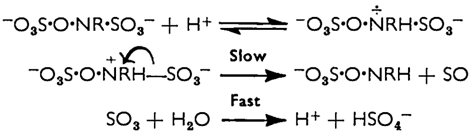
From Fig. 1 and from the above extended relationship, for the trisulphonate ion, $k_2(I \longrightarrow 0)$ at 25° is 0·0207 l. mole^{-1} $\mathrm{sec.}^{-1}$. By using the experimentally determined value for the energy of activation of 23·7 kcal. mole^{-1} (runs 16, 21—24; also runs 4 and 20) and the relationship[12] $k_2(I \longrightarrow 0) = (\boldsymbol{e k T/h}) \exp(\Delta S^*/\boldsymbol{R}) \exp(-E_{\mathrm{act}}/\boldsymbol{RT})$, $\Delta S^* = +11{\cdot}2$ e.u. Similarly, for hydroxylamine-*NO*-disulphonate ion, $k_2(I \longrightarrow 0)$ at 75·0° is 0·013 l. mole^{-1} $\mathrm{sec.}^{-1}$. With the energy of activation of 29·2 kcal. mole^{-1} (runs 49—52 or 35 and 48), this leads to a value for $\Delta S^* = +14{\cdot}9$ e.u. The positive values for the entropies of activation are expected for reactions between oppositely charged ions.

The effect of D_2O/H_2O composition on the rate of hydrolysis of hydroxylaminetrisulphonate is shown in Fig. 2, n signifying the atom fraction of deuterium in the solvent. The solid curve indicates that expected theoretically on the basis of a value of either 8·2[13] or 11·0[14] for the equilibrium constant for the reaction $2D_3O^+ + 3H_2O \rightleftharpoons 2H_3O^+ + 3D_2O$.

Above about 1·0M-perchloric acid, the values for $k_1/[\mathrm{H}^+]$ increase quite markedly for both compounds. This suggests that the rates of hydrolyses parallel Hammett's acidity function h_0 rather than C_{H^+}. However, the values of $\Delta \log k_1/\Delta(-H_0)$ deviate from the expected ratio of unity, being 0·61 in the case of the trisulphonate (runs 6 and 13) and 0·71 for the disulphonate (runs 41 and 43). At a constant ionic strength of 6·0M these values both increase to 1·45 (runs 12 and 13; 42 and 43).

DISCUSSION

The following mechanism is proposed for the hydrolysis of hydroxylamine-trisulphonate ($\mathrm{R} = \mathrm{SO_3}^-$) and -*NO*-disulphonate (R = H) ions:



$$^-O_3S{\cdot}O{\cdot}NR{\cdot}SO_3{}^- + H^+ \rightleftharpoons {}^-O_3S{\cdot}O{\cdot}\overset{+}{N}RH{\cdot}SO_3{}^-$$

$$^-O_3S{\cdot}O{\cdot}\overset{+}{N}RH\text{—}SO_3{}^- \xrightarrow{\text{Slow}} {}^-O_3S{\cdot}O{\cdot}NRH + SO_3$$

$$SO_3 + H_2O \xrightarrow{\text{Fast}} H^+ + HSO_4{}^-$$

It is difficult to distinguish between the suggested mechanism involving a pre-equilibrium followed by a slow reaction ($\mathrm{S} + \mathrm{H}^+ \rightleftharpoons \mathrm{SH}^+$; $\mathrm{SH}^+ \longrightarrow$ Products) and an alternative slow protonolysis ($\mathrm{S} + \mathrm{H}^+ \longrightarrow$ Products).[15] A dependence of the rate on h_0 can be

---

[11] Nast, Nyul, and Grziwok, *Z. anorg. Chem.*, 1952, **267**, 304.

[12] Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, 1941, p. 417.

[13] Swain, Bader, and Thornton, *Tetrahedron*, 1960, **10**, 200.

[14] Purlee, *J. Amer. Chem. Soc.*, 1959, **81**, 263.

[15] See (*a*) Melander and Myhre, *Arkiv Kemi*, 1959, **13**, 507, and (*b*) Gold, *Trans. Faraday Soc.*, 1960, **56**, 255, for recent discussions of this point.

explained on the basis of either mechanism.[15a,16] A much faster hydrolysis of both compounds in deuterium oxide is observed, $k_2^{\mathrm{D_2O}}/k_2^{\mathrm{H_2O}}$ being 3·3 and 2·6 for the tri- and di-sulphonate respectively. Such behaviour has been used extensively to support a pre-equilibrium mechanism, because of the formation of larger concentrations of the conjugate acid in the deuterated solvent.[17] Further, a curve for the dependence of the rate on the D_2O/H_2O composition can be derived theoretically (Butler–Gross) and the agreement with experimental data for the trisulphonate (see Fig. 2) lends further support to the pre-equilibrium step. However, recently, even this criterion has been challenged,[15b] and although a slow protonolysis might be expected to lead to $k^{\mathrm{D_2O}}/k^{\mathrm{H_2O}}$ values less than one,[18] [*] the distinction based solely on consideration of kinetic data is somewhat unsatisfactory.

For the trisulphonate ion, the second-order rate constant in formate buffers varies little with buffer concentration (runs 30—32) and is similar to the value expected in perchloric acid (0·82 l. mole^{-1} min.$^{-1}$ from runs 3—5 and energy of activation). There is thus little evidence for general acid-catalysis of these compounds and it is certainly much easier to understand specific acid catalysis in terms only of a pre-equilibrium, while reactions which proceed *via* a slow proton-transfer would be expected to be generally acid-catalysed.[20] It is interesting that the hydrolysis of amine-trisulphonate [21] and -disulphonate [22] ions also appears to be specifically catalysed by hydronium ions.

The position of the proton in the conjugate acid is uncertain; placing it on a sulphonate group (other than the one being removed) or the nitrogen atom gives the same result. However, most electrostatic effect will be obtained if it is placed on the nitrogen atom, by attracting the N—S bonding electrons despite the presence of positive charge on the sulphur atom.[23] This electron-attracting nature of the sulphonate group at short distances [23] will also mean that smaller amounts of the conjugate acid will be formed in the pre-equilibrium step with increasing numbers of sulphonate groups in the compound.[†] The faster rate of hydrolysis of hydroxylamine trisulphonate must indicate, then, that the rate constant for the slow step must be larger for the tri- than the di-sulphonate. This may perhaps be due to steric factors. With the aminesulphonates too, the presence of sulphonate groups facilitates acid hydrolysis, the sequence being $N(SO_3)_3^{3-} > NH(SO_3)_2^{2-} > NH_2SO_3^-$.[21,22,1]

It has been suggested (Hammett–Zucker hypothesis) that in acid-catalysed reactions, a value of *about* unity for the ratio $\Delta \log k_1/\Delta(-H_0)$ implies a transition state involving only the conjugate acid of the substrate with no intervention of a solvent molecule (designated A-1).[16] The idea has been applied particularly to neutral molecules, although the small amount of work that has been carried out appears to show that H_- and H_+ functions are very much like H_0 (for example,[25] the hydrolyses of aromatic sulphonic acids follow H_0). We are dealing with negative ions and values for H_{2-} and H_{3-}, appropriate for our case, are unknown. Neither are we necessarily justified in, for example, assuming the constancy of $(f_{\mathrm{BH^+}}/f_{\mathrm{B}})(f_{\mathrm{S^{3-}}}/f_{\ddagger^{2-}})$ which would be the basis for the application of the

---

[*] Schubert and Myhre [19] have shown that in the reaction $\mathrm{S + HA} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{SH^+ + A^-} \xrightarrow{k_2}$ products (where S = 2,4,6-tri-isopropylbenzaldehyde) k_1 is the rate-determining step above 85% H_2SO_4 and $k^{\mathrm{D_2SO_4}}/k^{\mathrm{H_2SO_4}} \sim 0{\cdot}2$.

[†] In acidities of 0·1M, hydroxylamine-*O*-sulphonate and sulphamate ions are almost completely protonated.[1, 24]

[16] Long and Paul, *Chem. Rev.*, 1957, **57**, 935.
[17] Wiberg, *Chem. Rev.*, 1955, **55**, 713.
[18] Long and Bigeleisen, *Trans. Faraday Soc.*, 1959, **55**, 2077.
[19] Schubert and Myhre, *J. Amer. Chem. Soc.*, 1958, **80**, 1755.
[20] *E.g.*, Kresge and Chiang, *J. Amer. Chem. Soc.*, 1959, **81**, 5509.
[21] Seel, Degener, and Kehrer, *Z. anorg. Chem.*, 1957, **290**, 103.
[22] Doyle and Davidson, *J. Amer. Chem. Soc.*, 1949, **71**, 3491.
[23] Bell, " The Proton in Chemistry," Methuen, London, 1959, p. 99.
[24] Harnsberger and Maroney, 121st Meeting Amer. Chem. Soc., Buffalo, 1952.
[25] Gold and Satchell, *J.*, 1956, 1635.

Hammett–Zucker hypothesis, where B = neutral indicator, S^{3-} = trisulphonate, and $\ddagger^{2-}$ = transition state. It is, therefore, perhaps not surprising that the hydrolysis does not produce the theoretical value of +1 for $\Delta \log k_1/\Delta(-H_0)$. In addition, there is the unsatisfactory feature that the rates remain approximately constant (runs 6 and 12; 41 and 42) when the ionic strength is increased to 6·0M, whereas the h_0 value increases 15—20 fold.[10] However, we can tentatively suggest that the second step in the hydrolysis is A–1, and consider further evidence for the nature of this slow step.

Aminetrisulphonate ion, $N(SO_3)_3{}^{3-}$, acts as a sulphonating agent in forming dithionate ions with sulphite.[21] The yield is admittedly small (6%) but this may be due to the acidity of the solution since Baumgarten [26] observed no formation of dithionate ion from hydrogen sulphite and pyrosulphate, or the pyridine–sulphur trioxide adduct, whereas the yield from sulphite and pyrosulphate increases markedly in M-sodium hydroxide.[27] There is thus some evidence that aminetrisulphonate ion does produce some SO_3 on hydrolysis and by analogy the two hydroxylaminesulphonates might be expected to act similarly, since in all cases an N–S bond is cleaved. They would not, however, be expected to produce any dithionate with sulphite since they hydrolyse only in the acid region where the latter exists as hydrogen sulphite (p*K* = 7·2).

The hydrolyses of the tri- and *NO*-di-sulphonates have certain common features with those of the hydroxylamine-*NN*-disulphonate: [28,29]

$$(SO_3)_2N{\cdot}OH^{2-} + H_2O \longrightarrow SO_3{\cdot}NH{\cdot}OH^- + HSO_4{}^-$$

All exist as unprotonated species in the acid range studied, and here the hydrolysisis of second-order—first-order in each reactant. In the absence of acid they are hydrolysed extremely slowly, *i.e.*, $k_w \ll k_2$ in the general expression $R = k_2[\text{sulphonate}][H^+] + k_w[\text{sulphonate}][H_2O]$.* They are hydrolysed about three times faster in deuterium oxide than in water and this supports a common mechanism involving the pre-formation of the conjugate acid (see also ref. 28), which is then slowly hydrolysed either without (A–1) or with (A–2) participation of solvent molecule. There is some preference for the former in view of the fact that the rates above about 0·5M-perchloric acid follow h_0 more closely than C_{H^+}. The much slower hydrolysis of the *NO*-disulphonate arises mainly from an energy of activation very much higher (29·2 kcal./mole) than for the trisulphonate (23·7 kcal./mole) or the *NN*-disulphonate [29] (21·2 kcal./mole). This behaviour is paralleled by that of the corresponding aminesulphonates (containing one and two N–S bonds) where we are also concerned with nitrogen–sulphonate bond cleavage. Thus the sulphamate ion, $NH_2{\cdot}SO_3{}^-$ (E_{act} = 30·5 kcal./mole) [1,30] is hydrolysed much more slowly than the iminodisulphonate ion, $NH(SO_3)_2{}^{2-}$ (E_{act} = 23·5 kcal./mole).[22] All three hydroxylaminesulphonates have positive entropies of activation, from 5 to 15 e.u. If the pre-equilibrium mechanism is correct, the quoted kinetic parameters will incorporate the thermodynamic data for the pre-equilibrium step but, judged from the behaviour of sulphamate ion, this will not be a large contribution.[1]

Our analytical method for studying the hydrolysis of *NO*-disulphonate avoided the problem of the hydrolysis of the monosulphonate. It is nevertheless worth considering the complete hydrolysis of hydroxylamine-*NO*-disulphonate (A, below) which represents at constant acidity two successive first-order reactions:

$$\begin{aligned} A &\longrightarrow B + SO_4{}^{2-}\ (k_1) \\ B &\longrightarrow C + SO_4{}^{2-}\ (k_2) \end{aligned}$$

---

* Our observation [29] that the hydrolysis of hydroxylamine-*NN*-disulphonate is not significantly water-catalysed is in direct contrast to that reported by Naiditch and Yost.[28]

[26] Baumgarten, *J.*, 1936, 1569.

[27] Aten, Louwrier, Coppens, Kok, Roos, Kriek, Hillege, Vollbracht, and Hartog, *J. Inorg. Nuclear Chem.*, 1956, **3**, 296.

[28] Naiditch and Yost, *J. Amer. Chem. Soc.*, 1941, **63**, 2123.

[29] Candlin and Wilkins, unpublished experiments.

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

When k_1 and k_2 are comparable, then a significant quantity of the intermediate B, hydroxylamine-*O*-sulphonate ion, will accumulate and then disappear during the reaction. Since we have studied separately the hydrolysis of B,[29] we now have the data to calculate the amounts of this intermediate and of *total* sulphate produced during the reaction:[31]

$$[B] = \frac{[A]_0 k_1}{(k_2 - k_1)} (e^{-k_1 t} - e^{-k_2 t})$$

$$[SO_4^{2-}] = 2[C] + [B] = 2[A]_0 - 2[A]_0 e^{-k_1 t} - [B]$$

Since hydroxylamine-*O*-sulphonate [but not A or C (hydroxylamine)] oxidises iodide to iodine in acid solution it is possible to estimate its concentration during the hydrolysis. The result is shown in Fig. 3 for one set of conditions, namely, 10^{-2}M-compound hydrolysing in 0·2M-perchloric acid at 65°, k_1 and k_2 being $8·0 \times 10^{-3}$ (runs 34—40) and $5·9 \times 10^{-3}$ min.$^{-1}$ respectively. The agreement between the experimental results and the theoretical curves is very satisfactory and indicates that at least with these conditions stage (2) occurs to the exclusion of any by-reactions. This is significant since it has been shown that, in the hydrolysis of the *O*- and *N*-monosulphonates,[29,32] hydroxylamine is not formed quantitatively in lower acid concentrations. The Figure also shows the validity of the method of initial rates, the early production of sulphate reflecting the loss of the disulphonate because of the induction period in the production of hydroxylamine (and further sulphate). Since the effect of temperature and acidity is markedly different for hydroxylamine-*NO*-di- and -*O*-mono-sulphonate, k_1 and k_2 may differ appreciably for conditions other than the experiment above and intermediate the may well be very much less stable. Haga[4] could find no evidence for the formation of hydroxylamine-*O*-monosulphonate when he studied the hydrolysis of hydroxylamine-*NO*-disulphonate, but, apart from his erroneous assumption that it would be a reducing agent, in his experiments at *ca.* 15° much less monosulphonate would accumulate during hydrolysis (second-order rate constants = $2·0 \times 10^{-5}$ and $9·0 \times 10^{-5}$ l. mole^{-1} min.$^{-1}$ respectively). Raschig,[5] on the other hand, treated the warm mixture of hydroxylamine-*NO*-disulphonate and hydrochloric

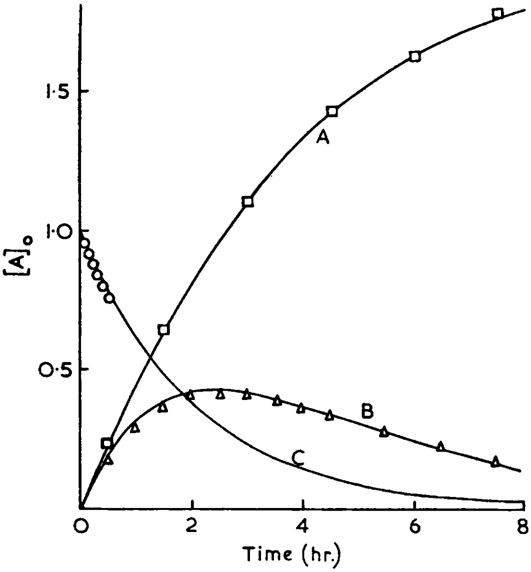


FIG. 3. *Composition, with time, of a solution originally containing* 10^{-2}M-*hydroxylamine-NO-disulphonate in* 0·2M-*perchloric acid at* 65°.

A, *Total sulphate.*
B, *Hydroxylamine-O-sulphonate.*
C, *Hydroxylamine-NO-disulphonate.*

---

[31] Frost and Pearson, " Kinetics and Mechanism," Wiley, New York, 1953, p. 153.
[32] Matsuguma and Audrieth, *J. Inorg. Nuclear Chem.*, 1959, **12**, 186.

acid with iodide so that the *O*-sulphonate would react as it was formed, and its detection thus presented no problems.

We are grateful for the award of a Leverhulme Research Scholarship (to J. P. C.), and to the Referees for valuable comments.

THE UNIVERSITY, SHEFFIELD. [*Received, February 27th,* 1961.]