

Sulfur-Nitrogen Compounds. III. The Acid Hydrolysis of Hydroxylamine N,N-Disulfonate and Hydroxylamine N- and O-Monosulfonates¹

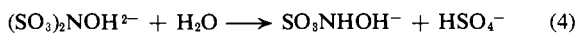
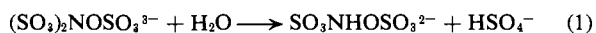
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The kinetics of acid hydrolysis of hydroxylamine O-monosulfonate (reaction 3) can be explained in terms of reactions involving hydrolysis of $\text{NH}_2\text{OSO}_3^-$ and acid-catalyzed hydrolysis of $\text{NH}_3^+\text{OSO}_3^-$. Above 0.1 M acid, the rate of hydrolysis (R) of the acid form ($pK = 1.5$) in perchloric, hydrochloric, and sulfuric acids obeys the expression $R = k_2 h_0 [\text{NH}_3^+\text{OSO}_3^-]$ for H_0 values from +1 to -6.3. From measurements at 0.5 M $[\text{H}^+]$, $k_2 = 10^{11.2} \exp(-22,100/RT) \text{ M}^{-1} \text{ sec}^{-1}$. Experiments in H_2^{18}O show O-S bond cleavage occurs in acid hydrolysis but N-O breakage results in alkaline medium. In the hydrolysis of hydroxylamine N,N-disulfonate (reaction 4), $R = k_2 [\text{H}^+][(\text{SO}_3)_2\text{NOH}^{2-}]$ from 10^{-5} to 0.5 M $[\text{H}^+]$, $k_2 = 10^{13.8} \exp(-21,200/RT) \text{ M}^{-1} \text{ sec}^{-1}$ at $I = 0.5 \text{ M}$. At higher acidities the correlation of rate with h_0 is good, resembling the results for hydroxylamine tri- and N,O-disulfonates. Hydrolysis of hydroxylamine N-monosulfonate (reaction 5), however, parallels C_H - rather than h_0 ; $R = 10^{10.5} \exp(-22,800/RT)[\text{H}^+][\text{SO}_3\text{NHOH}^-]$ in $\text{M}^{-1} \text{ sec}^{-1}$. The effects of ionic strength and deuterium oxide on the rates of these reactions were investigated and the mechanism of hydrolysis of the five hydroxylamine sulfonates discussed and compared.

Introduction

In the previous paper,³ we examined the hydrolysis of hydroxylamine trisulfonate and hydroxylamine N,O-disulfonate ions in perchloric acid (eq. 1 and 2). The present paper reports fully on the acid hydrolysis of hydroxylamine O-monosulfonate (eq. 3) and in somewhat less detail that of hydroxylamine N,N-disulfonate (eq. 4) and hydroxylamine N-monosulfonate (eq. 5).



The question of N-O or O-S bond cleavage arises only in (3) and this has been resolved by carrying out the hydrolysis in ^{18}O -enriched water and assaying the isotopic composition of the sulfate produced using an infrared method. In all studies, primarily four effects

on the rates of hydrolysis have been examined: viz., acidity, ionic strength, temperature, and deuterium oxide as solvent.

Experimental

Materials. Hydroxylamine-O-sulfonic acid was prepared by a slight modification of the original method of Sommer and co-workers.^{4,5} Redistilled chlorosulfonic acid (160 cc.) was poured carefully on powdered, dried hydroxylammonium chloride (35 g.) in a flask with a P_2O_5 guard-tube. The mixture was heated, with frequent swirling, on a steam bath for about 1 hr., and then poured slowly with stirring into dried ether (1 l.); the deposited white solid was filtered quickly and washed with dry ether. The product was purified by dissolving in dried methanol (300 cc.) and precipitating with chloroform (1 l.), finally washing with dry ether and storing in a vacuum desiccator over P_2O_5 ; yield 98%, containing about 0.5% sulfate and negligible chloride ions; purity 98.5–99%, from I_2 equivalent.

$\text{NH}_2\text{O}^{35}\text{SO}_3\text{H}$ was prepared by heating $\text{NH}_3\text{OH}^+\text{Cl}^-$ (0.2 g.) with fuming sulfuric acid (0.4 cc. containing 30% free SO_3 and 5 mc. of $\text{Na}_2^{35}\text{SO}_4$) on a steam bath for about 1 hr., using a P_2O_5 guard-tube. The product was washed with dry ether and stored in a vacuum desiccator over P_2O_5 . It contained about 2% sulfate impurity.

Potassium hydroxylamine N-monosulfonate was prepared⁶ and analyzed for hydroxylamine and sulfate after hydrolysis by heating with acid in a sealed tube for several hours.

Anal. Calcd. for $\text{H}_2\text{KNO}_4\text{S}$: N, 9.2; S, 21.7. Found: N, 8.7; S, 20.4.

Potassium hydroxylamine N,N-[^{35}S]disulfonate was prepared from $^{35}\text{SO}_2$ as described previously.³ All other chemicals were reagent grade.

Kinetic Procedure. The methods used for following the rate of production of sulfate and the assay of hydroxylamine-O-sulfonic acid have been described previously.^{3,7} In the "chemical" methods of analysis, 40 mM solutions were usually employed, whereas with the radiochemical method usually 10^{-4} M , but occasionally even as low as 10^{-6} M in compound, solutions were hydrolyzed. The hydrolysis of hydroxylamine N-monosulfonate was followed by the sulfate released, estimated by the dithizone or by the ethylenediaminetetraacetate method, for runs in high ionic strength. The former method was slightly modified

(1) Presented in part at the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961.

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Table I. Kinetics of Hydrolysis of Hydroxylaminesulfonates

Method ^a	Temp., °C.	Added acid, M	<i>I</i> , M ^b	- <i>H</i> ₀	10 ⁶ <i>k</i> _{obsd} , sec. ⁻¹	Temp., °C.	Added [HClO ₄], M	<i>I</i> , M	10 ⁶ <i>k</i> ₁ , sec. ⁻¹	10 ⁴ <i>k</i> ₁ /[H ⁺], M ⁻¹ sec. ⁻¹
(a) Hydroxylamine O-Sulfonate						(b) Hydroxylamine N,N-Disulfonate				
Effect of HClO ₄						Effect of Acid				
R	45.0	0.00064	1.00	-3.2	0.88	25.0	pH 6.4 ^d	0.50	0.005	133
R	45.0	0.0155	1.00	-1.8	1.5	25.0	10 ^{-5.0}	0.50	0.037	37
D	45.0	0.0151		-1.8	1.4	25.0	10 ^{-4.0}	0.50	0.37	37
I	45.0	0.0204	1.00	-1.7	1.5	25.0	0.0010	0.50	3.7	37
I	45.0	0.0513	1.00	-1.3	3.2	25.0	0.010	0.50	36	36
D	45.0	0.0708	1.00	-1.15	4.2	25.0	0.10	0.50	358	36
I	45.0	0.102	1.00	-1.0	5.7	25.0	0.50	0.50	1767	35
D	45.0	0.205		-0.69	12	0.1	1.00	6.0	345	3.5
D	45.0	0.507		-0.30	35	0.1	6.00	6.0	2.2 × 10 ⁴	37
R, D, I	45.0	1.00		0.06	82-93					
D	45.0	1.52		0.45	118	25.0	10 ⁻⁶ -0.50	0.50	...	37
D	45.0	2.40		0.86	310	25.0	0.00050	0.008	11	222
D	45.0	3.05		1.16	522					
I	25.0	1.01		0.23	8.5	0.8	0.10	0.50	15	1.5
D	25.0	2.52		1.00	32	8.3	0.10	0.50	46	4.6
D	25.0	3.03		1.23	55	17.2	0.10	0.50	158	15.8
I	25.0	6.00		2.82	1317	25.0	0.10	0.50	358	35.8
I	25.0	0.30	6.00	-0.85	2.3					
I	25.0	1.00	6.00	1.46	10.5	25.0	0.10	0.50	380	38.0
I	25.0	3.00	6.00	2.13	73	25.0	0.10	0.50	1152	115.2 ^e
Effect of HCl						(c) Hydroxylamine N-Monosulfonate				
I	45.0	1.03		-0.13	110					
I	45.0	3.08		0.95	600					
I	45.0	4.10		1.39	1107					
Effect of H ₂ SO ₄						Effect of Acid				
I	45.0	0.26		-0.34	20	75.0	pH 6.4 ^d	0.50	0.67 ^e	...
I	45.0	0.52		0.00	43	75.0	0.0006	0.50	2.0 ^f	...
I	45.0	1.30		0.31	167	75.0	0.025	0.50	7.0	2.8
I	45.0	2.08		0.74	375	75.0	0.050	0.50	16	3.2
I	0.1	5.10		2.35	32	75.0	0.10	0.50	27	2.7
I	0.1	6.97		3.55	265	75.0	0.10	0.50	32 ^f	3.2
I	0.1	9.54		4.85	2317	75.0	0.20	0.50	54	2.7
I	0.1	12.5		6.3	5 × 10 ⁴	45.0	0.40	0.50	117	2.9
I	0.1	17.2	~9	<i>t</i> _{1/2} < 2 sec.		45.0	0.50	0.54	3.0	0.06
I	65.0	0.045	0.05		17	45.0	1.00	1.04	6.8	0.07
I	65.0	0.045	0.15		17	45.0	3.00 ^g	3.04	9.2	0.03
I	65.0	0.045	0.55		16.5	45.0	6.30 ^g	6.34	25	0.03
I	65.0	0.045	1.05		17					
Effect of Ionic Strength						Effect of Ionic Strength				
I	65.0	0.045	1.05		17	85.0	0.050	0.06	66	13.3
Effect of Temperature						Effect of Temperature				
D	25.0	0.51			3.3	85.0	0.050	0.16	61	12.2
D	35.0	0.51			12	85.0	0.050	0.31	54	10.8
D	45.0	0.51			35	85.0	0.050	0.56	47	9.3
Effect of D ₂ O						Effect of Temperature				
D	45.0	0.46			30	45.0	1.00	1.04	7.2	0.072
D	45.0	0.46			15 ^c	55.0	1.00	1.04	20.2	0.20
D	45.0	0.46				65.1	1.00	1.04	60.8	0.61
Effect of Buffer (Cl ₂ CHCOOH = Cl ₂ CHCOONa)						Effect of D ₂ O				
		Added buffer				65.1	0.46	0.50	35	0.77
I	45.0		1.0		2.7	65.1	0.46 ^c	0.50	100	2.17
I	45.0		0.1		3.0					
I	45.0		0.5		3.8					
I	45.0		1.0		5.0					

^a R designates radiochemical; D, dithizone; and I, iodometric analytical method. ^b *I* is "natural" ionic strength except where stated. ^c 96% D₂O. ^d 2,6-Lutidine-2,6-lutidine perchlorate buffer. ^e First-order production of sulfate. ^f Radiochemical estimation. ^g Hydrochloric acid.

since Pb[(SO₃)₂NOH] was insoluble in acetone-water mixture. A 2-propanol-water (50:50 v./v.) titration medium was used instead. Two radiochemical runs were carried out with hydroxylamine N-monosulfonate; (³⁵SO₃)₂NOH²⁻ was hydrolyzed to (³⁵SO₃)NHOH⁻ (and H³⁵SO₄⁻) at 25° and then the temperature raised to 75° to complete the second stage, followed kinetically by the rate of further production of H³⁵SO₄⁻. The hydrolysis of hydroxylamine N,N-disulfonate ion was

studied only by the radiochemical technique. All methods were used for the investigation of NH₂OSO₃⁻. Results for the different methods were in satisfactory agreement. Kinetic data are given in Table I.

Ionization Constant for Hydroxylamine O-Sulfonate Ion. This was measured at 45° in 1.0 M sodium perchlorate, the conditions for the majority of the kinetic experiments. The pH of solutions containing known amounts of the solid acid and sodium hydroxide was

measured with a glass electrode, and application of the Henderson equation gave the pK for hydroxylamine-O-sulfonic acid. The value (1.48) was the mean for several determinations with varying ratios of acid and base.

Hydrolysis of Hydroxylamine O-Sulfonate Ion in ^{18}O -Enriched Aqueous Hydrochloric Acid. Hydroxylamine-O-sulfonic acid (5.6 mg.) was heated in water (100 μ l., containing 13.9% $H_2^{18}O$) and concentrated hydrochloric acid (5 μ l.) for 8 min. in a test tube in boiling water. The nonimmersed part of the tube was air cooled to prevent excess evaporation. After cooling, the hydrolyzed material was diluted with water (1 cc.) and the sulfate precipitated with 0.5 M barium chloride solution (1 cc.). The barium sulfate was washed with 1 M hydrochloric acid (two 2-cc. portions), water (five 2-cc. portions), and ethanol (four 2-cc. portions) and finally dried overnight in a vacuum desiccator over P_2O_5 . Measurement of the infrared peak heights at 984 (due to $BaS^{18}O_4$) and 961 cm^{-1} (due to $BaSO_3^{18}O$) enables the determination of $SO_3^{18}O^{2-}$ in the liberated sulfate.⁸ The experimental value (14.0%) agrees well with that calculated for 100% O-S breakage (13.2%).

Alkaline hydrolysis was similarly investigated, heating for 5 min. the sulfonic acid (5.6 mg.), water (100 μ l., containing 13.9% $H^{18}O$), and sodium hydroxide (6 mg.). The liberated sulfate was isolated as the barium salt, after the addition of 1 M hydrochloric acid (1 cc.). In this case (and in a repeat experiment) there was no peak at 961 cm^{-1} indicating complete N-O bond cleavage.

Results and Discussion

Hydroxylamine O-Sulfonate Ion. This is the only member of the series which is an oxidizing agent and which can be isolated as the free acid,^{4,5,9} a white hygroscopic solid, stable in a vacuum desiccator over P_2O_5 but decomposing rapidly on exposure to the atmosphere.

In the weakly acid region ($pH > 2$), where the anionic form $NH_2OSO_3^-$ predominates, stoichiometric amounts of hydroxylamine according to (3) are not produced. For example, only 83% of that expected is obtained at pH 2. This is in general agreement with the findings of Matsuguma and Audrieth,¹⁰ who investigated the hydrolytic and disproportionation decomposition of hydroxylamine-O-sulfonic acid in aqueous acid solution. In addition we have observed that the usual first-order kinetic plots at constant pH for hydrolysis are markedly curved in this acid region although the rate of production of sulfate ion varies little with acid concentration from pH 2.3 to 6.6. Only one result of these experiments is included in Table I.

In the pH region 1.0–2.0, substantial amounts of both anionic and acid¹¹ forms are present in solution,

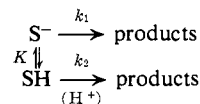
(8) B. Spencer, *Biochem. J.*, **73**, 442 (1959).

(9) A good account of the hydroxylamine sulfonates is contained in D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, p. 90.

(10) H. J. Matsuguma and L. F. Audrieth, *J. Inorg. Nucl. Chem.*, **12**, 186 (1959).

(11) The acid in solution will be written in the zwitterionic form, $NH_2^+O-SO_3^-$, although a small amount of nonzwitterionic species, NH_2OSO_3H , may also be present. For chemical and infrared evidence for zwitterion in the solid, see U. Wannagat and R. Pfeiffersneider,

since pK for ionization has been determined as 1.5 ± 0.1 (at 45° in 1.0 M $HClO_4$). The kinetic data in this region can be explained in terms of two concurrent reactions, one involving hydrolysis of the anion (S^-) and the other acid-catalyzed hydrolysis of the acid (SH).



d/dt (products) = $k_1[S^-] + k_2[SH][H^+] = k_{\text{obsd}}[S^- + SH]$, whence $k_{\text{obsd}} = (k_1K + k_2[H^+])/(K + [H^+])$.

The solid line in Figure 1 represents this relation between the pseudo-first-order rate constant k_{obsd} and $[H^+]$. It was constructed knowing $K = 3.3 \times 10^{-2}$, $k_1 = 8.8 \times 10^{-7} \text{ sec}^{-1}$ (from limiting rate at $pH \sim 3$), and $k_2 = 8.0 \times 10^{-5} M^{-1} \text{ sec}^{-1}$ (i.e., the value of k_{obsd} at $[HClO_4] = 1.0 M$). The experimental points are in satisfactory agreement with the theoretical curve. The mechanism resembles that proposed by Harnsberger and Maroney,¹² who, however, report a minimum rate at pH 0.5, which we have failed to observe. The full experimental details of this work have never been published, but it appears that buffers were employed, the constituents of which (acetate, phthalate) we have observed accelerate markedly the rate of hydrolysis of the sulfonate ion, thus probably altering the shape of Figure 1. The qualitative results of Specht, Browne, and Sherk,¹³ who found the rate of hydrolysis to be faster in 0.16 M than in 0.014 M hydrochloric acid, are in agreement with our findings. No variation of behavior was observed with different samples of hydroxylamine-O-sulfonic acid or with traces of copper ion present.¹⁰

The region above 0.1 M acid was studied most thoroughly since only the acid form predominates here and, in addition, hydrolyzes quantitatively according to (3). The rate of hydrolysis (R) in perchloric, hydrochloric, and sulfuric acids obeys the expression $R = k_2 h_0 [NH_3^+OSO_3^-]$ over an extremely wide range of H_0 values from +1 to -6.3. This is shown in Figure 2 which has lines drawn of unity slope. From measurements at 0.5 M $[H^+]$ and varying temperatures, $k_2 = 10^{11.2} \exp(-22,100/RT) M^{-1} \text{ sec}^{-1}$. At acidities higher than 12.5 M H_2SO_4 , the rate was too rapid to measure and in 103% H_2SO_4 hydrolysis was incomplete. This latter is understandable in view of the preparation of hydroxylamine-O-sulfonic acid from hydroxylamine salts and sulfur trioxide adducts. The hydrolysis appears to be generally acid catalyzed from the data in dichloroacetate-dichloroacetic acid buffers, although at the high concentrations of hydronium ions used it is difficult to add a comparable concentration of another acid without introducing complicating medium changes. The correlation with h_0 and the much slower rate of hydrolysis in deuterium oxide imply that a slow protonolysis mechanism might apply.

Z. anorg. allgem. Chem., **297**, 151 (1958), and for proton magnetic resonance studies of the solid and in dimethylformamide solution, see R. E. Richards and R. W. Yorke, *J. Chem. Soc.*, 2821 (1959).

(12) H. E. Harnsberger and J. P. Maroney, paper presented at 121st National Meeting of the American Chemical Society, Buffalo, N. Y., March 1952.

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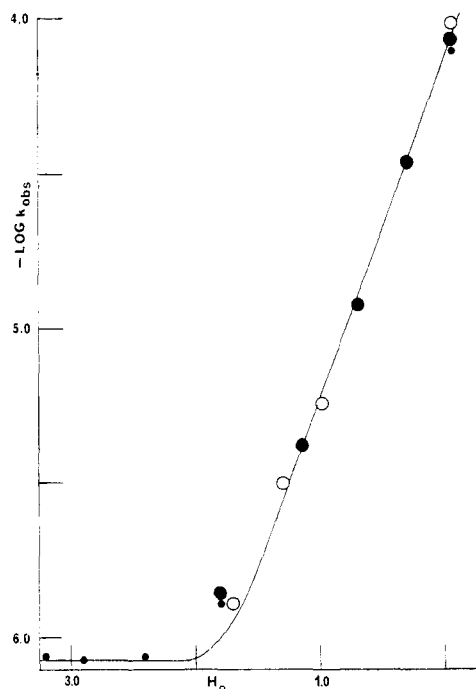
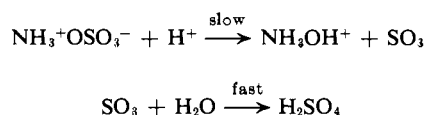
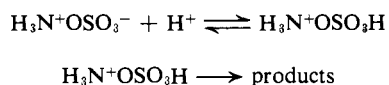


Figure 1. Plot of $-(\log k_{\text{obsd}})$ against H_0 for hydrolysis of hydroxylamine-O-monosulfonic acid and ion: small full circle, radiochemical; large full circle, dithizone; large circle, iodide; temperature 45° .



The present state of theory of the mechanisms of acid-catalyzed reactions is, however, confused. It is therefore not possible to rule out an alternative path for the hydrolysis in which a pre-equilibrium step is followed by a rate-determining slow step. The latter is probably a unimolecular decomposition (A1) since correlation with h_0 rather than C_{H^+} is observed.¹⁴



A similar mechanism, involving reaction of the conjugate acid, has also been suggested (as one possibility) from recent studies of the hydrolysis of hydroxylamine-O-sulfonic acid and derivatives.¹⁵ This work was more concerned with the effects of substitution within the sulfonate on rate and involved no detailed study of the acid hydrolysis of the parent compound.

Finally, the experiments in H_2^{18}O show unambiguously that O-S bond cleavage occurs during the hydrolysis in acid medium. In alkaline solution, on the other hand, only N-O bond fission occurs and in these conditions the amination reagent may therefore be NH_2^+ (or NH).

Hydroxylamine *N,N*-Disulfonate Ion. This ion is moderately stable in neutral solution but hydrolysis is fairly rapid in acid or alkaline solution. Since stage 4

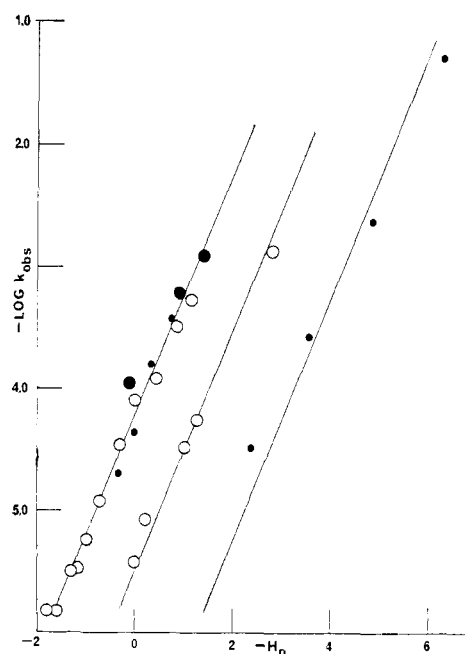


Figure 2. Plot of $-(\log k_{\text{obsd}})$ against $-H_0$ for hydrolysis of hydroxylamine-O-monosulfonic acid: small full circle, H_2SO_4 ; large full circle, HCl ; large circle, HClO_4 ; temperature 45 , 25 , and 0° from left to right.

is much faster than stage 5, the subsequent hydrolysis of N-monosulfonate does not have to be considered. Wagner¹⁶ made a single measurement of the rate of hydrolysis (as he did of several hydroxylamine and amine sulfonates) and found it to be proportional to the concentrations of the disulfonate and hydrogen ions. Naiditch and Yost¹⁷ investigated the hydrolysis by measuring the rate of production of $[\text{H}^+]$ arising from dissociation of the product bisulfate ion. Only a limited range of acidity could thus be studied by this method. Using the radiochemical method, however, small concentrations of compounds could be used in the present study (10^{-4} – 10^{-5} M), thus causing negligible changes of pH during the reaction and obviating the necessity of buffers. A wide range of acid concentrations were used.

From 10^{-3} – 0.5 M perchloric acid, the rate (R) is accurately represented by $R = k_2[\text{disulfonate}][\text{H}^+]$, $k_2 = 10^{13.8} \exp(-21,200/RT) \text{ M}^{-1} \text{ sec}^{-1}$ at $I = 0.5$ M. We thus confirm the second-order hydrolysis, but whereas the Naiditch and Yost results indicate that water reaction should become important at pH values 4 and higher, we do not observe any such limiting rate for the k_{obsd} -pH plot, and there are only slight indications of the water reaction at a pH as low as 6. In addition, our energy of activation is markedly higher (21.9 vs. 17.6 kcal. mole⁻¹). A plot of $\log k_2$ against $1.018 \cdot I^{1/2}/(1 + I^{1/2})$ gives a good line, slope -2.0 with $k_2 (I \rightarrow 0) = 0.025 \text{ M}^{-1} \text{ sec}^{-1}$ at 25° . The corresponding plot from the Naiditch and Yost data is curved although $k_2 (I \rightarrow 0) \sim 0.024 \text{ M}^{-1} \text{ sec}^{-1}$ is in good agreement with our value. Our results do not vary when higher concentrations of substrate are employed ($\sim 10^{-2}$ M), similar to those used by Yost and Naiditch, and we

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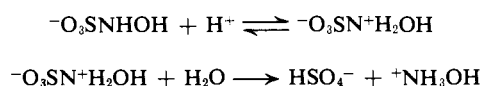
(16) M. Wagner, *Z. physik. Chem.*, **19**, 668 (1896).

(17) S. Naiditch and D. M. Yost, *J. Am. Chem. Soc.*, **63**, 2123 (1941).

can only conclude that our results differ because of their decidedly more complicated and less accurate method of following the rate.

The results in strong acid are similar to those obtained for tri- and N,O-disulfonates.⁴ The correlation of rate with h_0 is good, the value for $\Delta \log k_1/\Delta(-H_0)$ being 0.83. The ratio k_{D_2O}/k_{H_2O} is high (3.1) and an A1 mechanism for hydrolysis is suggested, similar to that for the sulfonates previously studied.

Hydroxylamine N-Monosulfonate. A study of the hydrolysis at pH values less than 2 was not attempted since the stoichiometry of reaction 5, like reaction 3, was not maintained, the yield of hydroxylamine decreasing from $\geq 95\%$ at pH 1 and 84% at pH 2 to only 6% at pH 3.5. The product formed at the expense of hydroxylamine was probably hyponitrite,¹⁸ although this was not investigated. There is a distinctly better correlation of rate constant k_1 with C_{H^+} than with h_0 for this compound. The rate constant increases 30-fold in changing from 0.5 to 6.0 M HClO₄, a change similar to that observed, for example, in the hydrolysis of ethyl acetate¹⁹ (25-fold over the same acidity range) and for which an A2 mechanism is firmly established. We thus believe that hydrolysis of the N-monosulfonate involves nucleophilic attack by the water on the conjugate acid.



From measurement at 1.0 M HClO₄, $k_2 = 10^{10.5} \exp(-22,800/RT) M^{-1} \text{sec}^{-1}$. A plot of $\log k_2$ against $2 \times 0.581 I^{1/2}/(1 + I^{1/2})$ gives a slope of -0.75 , somewhat lower than that expected theoretically for a $-1, +1$ reaction, and leads to a value $k_2 (I \rightarrow 0) = 1.75 \times 10^{-3} M^{-1} \text{sec}^{-1}$ at 85°. The ratio k_{D_2O}/k_{H_2O} (2.86) suggests a pre-equilibrium, although the value is rather high for an A2 mechanism,²⁰ although the ratios obtained for the other sulfonates also appear to be larger than those usually encountered.

Summary

This paper completes the study of the hydrolysis of the hydroxylamine sulfonates in acid medium. The results are collected in Table II. Rate constants and entropies of activation at 25° were not always obtained with the same conditions, but the effect of ionic strength

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Table II. Kinetic Data for the Acid Hydrolysis of Hydroxylamine Sulfonates at 25°

Ion	$10^6 k_2$, M^{-1} sec^{-1}	E_{act} , kcal. mole ⁻¹	ΔS^* , e.u.
(SO ₃) ₂ NOSO ₃ ³⁻	2070 ^a	23.7	+11
(SO ₃)NHOSO ₃ ²⁻	0.32 ^b	29.2	+15
NH ₃ ⁻ OSO ₃ ⁻	0.67 ^c	22.1	-9
(SO ₃) ₂ NOH ²⁻	370 ^c	21.2	+4
(SO ₃)NHOH ⁻	0.065 ^d	22.8	-12

Ionic strengths: ^a Zero. ^b 0.1 M. ^c 0.5 M. ^d 1.0 M.

was relatively unimportant so that comparisons of values were still valid. Some of the common features already have been discussed.³ The results refer in all cases (except for the O-sulfonate) to N-S bond breakage. All hydrolyses are first order in sulfonate and first order in [H⁺] at acidities ≤ 0.5 M. At higher acidities, however, except for the N-sulfonate, the rates deviate markedly from proportionality with the stoichiometric concentration of hydrogen ion, and a correlation with H_0 is more satisfactory. A complete relation with H_0 would not be expected for the tri- and disulfonates, since we are not dealing here with neutral species to which the H_0 scale refers, but the correlation with the zwitterion O-sulfonate could be expected and is indeed observed. The effect of ionic strength on the rate of these reactions can be well predicted, perhaps surprisingly, from the charge of the ions involved. This has been observed also with the amine sulfonates.²¹ As with the amine sulfonates also, the rates of hydrolysis steadily decrease as sulfate groups are removed.^{7,21} This arises mainly from a decreasing entropy of activation, which might be expected from the decreasing charge of ions involved. It is impossible to be dogmatic about the mechanism of acid hydrolysis, but a common mechanism is favored, involving an A1 reaction of the conjugate acid, except perhaps for the N-monosulfonate where an A2 mechanism may take place, the change favored by the reduced steric hindrance to water attack with the latter compound.²² For the tri- and disulfonates, no limiting rate (to pH 3-5) was observed, whereas with the monosulfonates the water reaction is important at pH below 2 or so, although the stoichiometries of (3) and (5) are not maintained in this region.

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