

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.]

## The Reactions of Hydroxylamine-O-sulfonic Acids with Water and with Hydriodic Acid

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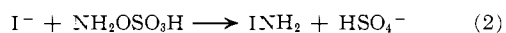
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At low acidities, the reduction of hydroxylamine-O-sulfonic acids with iodide is first order in substrate, first order in iodide ion, and independent of acidity. The rate-determining step is interpreted to be a nucleophilic displacement by iodide ion on the nitrogen atom to give an iodoamine, followed by rapid reduction by more iodide to form iodine and ammonia. Alkyl groups on the nitrogen greatly retard the reaction. Hydrolysis to hydroxylamine and sulfate is first order in substrate and roughly first order in acidity. Alkyl groups on the nitrogen have little effect on the rate, suggesting that attack by water, which may be the rate-determining step or may follow it, occurs at sulfur rather than nitrogen. This implication is supported by the fact that solvolysis of N-methylhydroxylamine-O-sulfonic acid in anhydrous methanolic hydrogen chloride gives N-methylhydroxylamine and methyl hydrogen sulfate rather than a methoxyamine and sulfuric acid. The activation energy for hydrolysis is nearly 50% higher than for the reaction with iodide. Amine oxide-O-sulfonates are reduced by iodide and are hydrolyzed much faster than the hydroxylamine-O-sulfonic acids.

Although hydroxylamine is thermodynamically a moderately strong oxidizing agent ( $E_0 = 1.35$  v.) as well as a reducing agent, the kinetic behavior of hydroxylamine and most of its derivatives is almost exclusively as a reducing agent. Certain derivatives stand in marked contrast to the foregoing generalization in that they liberate iodine from acidic iodide solutions,<sup>2</sup> as in the case of hydroxylamine-O-sulfonic acid, rapidly and quantitatively at 0°. The present research was begun in order to find the reason for this difference in behavior.



All of the hydroxylamine derivatives that oxidize iodide to iodine can be considered as O-acylhydroxylamines, although not all O-acylhydroxylamines do this. Examples are hydroxylamine-O-sulfonic acid,<sup>2a</sup> benzoyloxyamine,<sup>3</sup> and O,N-diacetylhydroxylamine. It has also been qualitatively observed that these hydroxylamines are rather selective about what they will oxidize, oxidation potentials not playing a dominant role. These facts suggested to us the working hypothesis that reduction by iodide is actually a displacement reaction on the nitrogen atom, producing an iodoamine, which would be expected to react with more iodide to form iodine and ammonia (or amine). The first of these steps (eq. 2) might take place by bimolecular



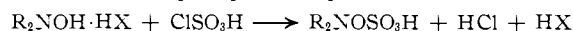
nucleophilic displacement, by unimolecular ionization into  $\text{NH}_2^+$  and  $\text{HSO}_4^-$ , or by 1,1-elimination to produce  $\text{NH}$ , which could subsequently combine with hydrogen iodide.

The foregoing questions were investigated from two standpoints: the order of the rate dependence on the reactants, and the effect of alkyl substitution at the nitrogen atom on the relative rates of reaction of different hydroxylamine-O-sulfonic acids.

### Results

Hydroxylamine-O-sulfonic acid has been known since 1914, when it was prepared by the action of chlorosulfonic acid on hydroxylamine salts,<sup>2</sup> but substituted derivatives other than fixed zwitterions appear not to have been reported before. We prepared a variety of them by the same reaction, as summarized in Table I. Similar to the parent compound, the alkyl deriva-

tives were found to be very hygroscopic and had to be stored over phosphorus pentoxide. Purification



presented a problem, for the acids were soluble only in water or alcohols, with which they react at a significant rate. Recrystallization from cold absolute alcohol was sometimes successful, but always entailed heavy loss. It was usually more satisfactory to treat the initially prepared acids with fresh chlorosulfonic acid, for the only significant contaminants appeared to be unreacted hydroxylamine salts. When free of such impurity, the acids did not immediately reduce Fehling solution or Tollens reagent.

*p*-Sulfobenzylhydroxylamine-O-sulfonic acid was obtained as the sole product from the attempted preparation of benzylhydroxylamine-O-sulfonic acid. The position taken by the sulfo group on the ring was confirmed by the nuclear magnetic resonance spectrum, in which the aromatic hydrogens appeared as a symmetrical quadruplet of the  $A_2B_2$  type. The required hydroxylamines were prepared by published means, except for *t*-butylhydroxylamine, which was conveniently prepared by reduction of 2-nitroisobutane with aluminum amalgam.

TABLE I  
HYDROXYLAMINE-O-SULFONIC ACIDS,  $\text{RR}'\text{NOSO}_3\text{H}$

R	R'	M.p., °C.	Hydroxyl-amine salt used	Yield, %
CH <sub>3</sub>	H	171-174 dec.	HCl	91 <sup>a</sup>
CH <sub>3</sub>	CH <sub>3</sub>	142 dec.	HCl	93 <sup>b</sup>
(CH <sub>3</sub> ) <sub>2</sub> CH	H	145-148 dec.	(COOH) <sub>2</sub>	90 <sup>c</sup>
(CH <sub>3</sub> ) <sub>3</sub> C	H	156-159 dec.	(COOH) <sub>2</sub>	Good <sup>d</sup>
(CH <sub>2</sub> ) <sub>6</sub>		135-137 dec.	(COOH) <sub>2</sub>	92 <sup>e</sup>
<i>p</i> -HO <sub>3</sub> S-	H	162-164 dec.	HCl	61 <sup>f</sup>
C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>				

<sup>a</sup> *Anal.* Calcd. for CH<sub>3</sub>NO<sub>3</sub>S: C, 9.45; H, 3.96; N, 11.02; neut. equiv., 127. Found: C, 9.76; H, 4.15; N, 11.16; neut. equiv., 125. <sup>b</sup> *Anal.* Calcd. for C<sub>2</sub>H<sub>7</sub>NO<sub>3</sub>S: C, 17.02; H, 5.00; N, 9.93; neut. equiv., 141. Found: C, 16.92; H, 5.06; N, 9.77; neut. equiv., 155. <sup>c</sup> *Anal.* Calcd. for C<sub>3</sub>H<sub>9</sub>NO<sub>3</sub>S: C, 23.21; H, 5.85; neut. equiv., 155. Found: C, 22.71; H, 6.01; neut. equiv., 154.2. <sup>d</sup> *Anal.* Calcd. for C<sub>4</sub>H<sub>11</sub>NO<sub>3</sub>S: C, 28.41; H, 6.56; neut. equiv., 169.1. Found: C, 27.92; H, 6.49; neut. equiv., 165.8. <sup>e</sup> *Anal.* Calcd. for C<sub>6</sub>H<sub>13</sub>NO<sub>3</sub>S: C, 33.14; H, 6.12; neut. equiv., 181.2. Found: C, 32.75; H, 6.27; neut. equiv., 181.4. <sup>f</sup> *Anal.* Calcd. for C<sub>7</sub>H<sub>9</sub>NO<sub>3</sub>S<sub>2</sub>: C, 29.68; H, 3.21. Found: C, 29.34; H, 3.41.

The rate of the reaction of hydroxylamine-O-sulfonic acid with potassium iodide in dilute hydrochloric acid was followed by measuring the appearance of iodine spectroscopically. The points obtained obeyed second-order kinetics according to the rate law  $d(\text{I}_2)/dt = k(\text{NH}_2\text{OSO}_3\text{H})(\text{I}^-)$ . In 0.1 *N* hydriodic acid,  $k$  remained constant between 22.3 and 22.7 l. mole<sup>-1</sup>

(1) From the doctoral dissertations of H. R. L. and R. L. B.

(2) (a) F. Sommer, O. F. Schultz, and M. Nassau, *Z. anorg. allgem. Chem.*, **147**, 142 (1925); (b) F. Sommer and H. G. Templin, *Ber.*, **47**, 1221 (1914); (c) G. Zinner, *Arch. Pharm.*, **292**, 1 (1959); *Chem. Ber.*, **91**, 302 (1958); *Angew. Chem.*, **72**, 76 (1960).

(3) (a) L. A. Carpino, C. A. Giza, and B. A. Carpino, *J. Am. Chem. Soc.*, **81**, 955 (1959); (b) W. P. Jencks, *ibid.*, **80**, 4581 (1958).

hr.<sup>-1</sup> at 1.2°. Acid accelerated the reaction up to a concentration of about 1 *M*, beyond which it had little effect (see Table II). Different samples of hydroxylamine-O-sulfonic acid were used, varying in iodometric titer from 88 to 98.8% purity. The same values, within experimental error, were obtained from all samples. The expected impurity, hydroxylamine sulfate, was shown not to affect the measurements.

TABLE II

RATE CONSTANTS FOR THE REACTION OF NH<sub>2</sub>OSO<sub>3</sub>H WITH HI AT 1.2 ± 0.3°

[HCl], moles/l.	[I <sup>-</sup> ], moles/l.	<i>k</i> , l. mole <sup>-1</sup> hr. <sup>-1</sup>	<i>k</i> /γHI l. mole <sup>-1</sup> hr. <sup>-1</sup>
0.100	0.100	22.3	27.3
.120	.120	22.5	27.7
.300	.100	36.9	48.6
.500	.100	36.1	47.4
1.000	.100	36.7	44.4
2.000	.100	47.0	43.2

The foregoing rate constants are, of course, subject to considerable uncertainty arising from the use of relatively concentrated solutions for practical reasons. Some of the variation can be smoothed out by using the activity coefficient of hydriodic acid<sup>4</sup> at the respective acid concentration used as an approximate correction for the change of activity of iodide.

In contrast to the parent compound, the substituted hydroxylamine-O-sulfonic acids were found to react with iodide far short of quantitatively. Hydrolysis was found to be the competing reaction, and the relative extent of reduction and hydrolysis was a function of both temperature and the acidity of the medium. Since concomitant hydrolysis was unavoidable, the rate of the reduction reaction could not be determined without first knowing the hydrolysis rate constants for similar conditions. These were accordingly determined.

Since both reduction and hydrolysis of the substituted hydroxylamine-O-sulfonic acids were slow, their rates were measured at 30° instead of the 1.2° used for the parent compound. The rates of hydrolysis were followed by measuring the appearance of hydroxylamine salt by titration with standard iodine solution of aliquots neutralized with bicarbonate. Under these conditions, the hydroxylamines are oxidized quantitatively to nitroso or oxime derivatives,<sup>5</sup> and the O-sulfonic acids were found to be inert. The rates were first order in [R<sub>2</sub>NOSO<sub>3</sub>H] at constant acidity, and were approximately proportional to the acidity function *h*<sub>0</sub>, as reported by Candlin and Wilkins<sup>6</sup> for the unsubstituted compound. In three examples, the presence of 1 *M* sodium perchlorate did not significantly affect the rates. The results are collected in Table III.

N-Methylhydroxylamine-O-sulfonic acid was examined at 40° as well, in order to estimate the magnitude of the activation energy. The value calculated, 22.6 kcal./mole, agrees closely with that obtained by Candlin and Wilkins<sup>6</sup> for the unsubstituted compound (22.8 kcal./mole). N-*p*-Sulfobenzylhydroxylamine-O-sulfonic acid, however, gave a value of only 12 kcal./mole.

(4) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press, Inc., New York, N. Y., 1953.

(5) (a) O. L. Brady and R. F. Goldstein, *J. Chem. Soc.*, 2407 (1926); (b) O. L. Brady and M. D. Porter, *ibid.*, 1604 (1931); (c) R. T. Sheen, H. C. Kohler, W. H. Betz, and L. D. Betz, *Ind. Eng. Chem.*, **8**, 127 (1936).

(6) (a) J. P. Candlin and R. G. Wilkins, paper presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961; (b) *cf.* also H. E. Harnsberger and J. P. Moroney, paper presented at the 121st National Meeting of the American Chemical Society, Buffalo, N. Y., March, 1952.

TABLE III  
HYDROLYSIS OF HYDROXYLAMINE-O-SULFONIC ACIDS,  
RR'NOSO<sub>3</sub>H, AT 30°

R	R'	Concn. HCl, moles/l.	<i>k</i> ' <sup>d</sup> , hr. <sup>-1</sup>	<i>k</i> '/ <i>h</i> <sub>0</sub> <sup>e</sup> , l. mole <sup>-1</sup> hr. <sup>-1</sup>
H	H	0.500	0.038	0.0602
		0.500 <sup>a</sup>	.0379	.0602
		1.00	.0736	.0464
		1.445	.116	.0411
		1.01	.0597	.0368
CH <sub>3</sub>	H	0.500	.028	.0440
		0.485 <sup>a</sup>	.026	.0422
		1.01	.0597	.0368
		1.493	.0944	.0324
		0.500 <sup>b</sup>	.0917	.0324
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	H	.491	.0207	.0336
		.491 <sup>a</sup>	.0201	.0326
		.997	.0457	.0289
		1.493	.0849	.0290
		2.45	.243	.0339
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	0.500	.015	.0238
		.496 <sup>a</sup>	.014	.0222
		.996	.0337	.0212
		1.493	.0588	.0202
		2.45	.160	.0223
CH <sub>3</sub>	CH <sub>3</sub>	0.503	.0282	.0452
		0.991	.0676	.0430
		1.497	.124	.0422
		2.45	.330	.0460
		0.500	.030	.0476
(CH <sub>2</sub> ) <sub>6</sub>	H	0.996	.0866	.0547
		1.493	.157	.0538
		2.530	.401	.0528
		0.485	.022	.0359
		.291 <sup>c</sup>	.0079	.0198
<i>p</i> -HO <sub>3</sub> SC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	H	.497 <sup>c</sup>	.0133	.0181
		.500 <sup>c</sup>	.0138	.0186
		1.000 <sup>c</sup>	.0213	.0117
		2.084 <sup>c</sup>	.0334	.0047
		0.497 <sup>b,c</sup>		

<sup>a</sup> Solution contained 1 *M* sodium perchlorate. <sup>b</sup> At 40.0°. <sup>c</sup> Sulfuric acid, moles per liter. <sup>d</sup> *k*' = first-order rate constant. <sup>e</sup> Values for *h*<sub>0</sub> were obtained by interpolation from the data of M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957); the contribution of the sulfonic acid was ignored for this purpose, and the values, determined at 25°, were not corrected for the change to 30°.

The reductions with iodide were followed titrimetrically, for they were much slower than with the parent compound. The liberated iodine was in all cases first titrated in aliquots of the acidic reaction medium; thereafter, two situations were encountered, differing according to whether hydrolysis or reduction was faster. When hydrolysis was faster, the reaction mixture at any given time contained a hydroxylamine in greater equivalent amount than the iodine liberated. The addition of excess sodium bicarbonate solution to a fresh aliquot allowed these two species to react with each other, leaving an excess of the hydroxylamine, which was then titrated with standard iodine solution. When reduction was faster, the amount of iodine liberated was more than enough to oxidize the hydroxylamine after buffering with sodium bicarbonate, and the excess iodine was titrated with standard sodium thiosulfate.

The mole ratio of iodine to hydroxylamine present at any given time represents the ratio of the reduction and hydrolysis rates (and pseudo-first-order rate constants) under the prevailing conditions as long as the two rate laws are of the same order. The presence of both acid and iodide in large excess approximated pseudo-first-order conditions for both reactions. The results are summarized in Table IV; the values for the

rate constants for reduction were obtained by multiplying the rate constant ratios by the hydrolysis rate constant interpolated for the prevailing conditions from the previously determined values. The unknown effect on the hydrolysis rate of the considerable concentration of iodide present could not, of course, be brought into the calculations. The absence of an effect by added sodium perchlorate suggests that the iodide would not exert a primary salt effect; on the other hand, the difference in hydrolysis rate constants determined in hydrochloric and sulfuric acids for *p*-sulfobenzylhydroxylamine-O-sulfonic acid (Table III) suggests that a specific ion effect may be appreciable.<sup>5b</sup> Comparison of the results at 30 and 40° shows that temperature affects the rate of hydrolysis faster than that of reduction; the very approximate values of 13 kcal./mole may be estimated for the energy of activation of N-methylhydroxylamine-O-sulfonic acid, and 9 kcal./mole for the *p*-sulfobenzyl compound.

TABLE IV  
THE REDUCTION OF HYDROXYLAMINE-O-SULFONIC ACIDS,  
RR'NOSO<sub>3</sub>H, BY IODIDE AT 30°

R	R'	HCl				
		concn., moles/l.	$k'_R/k'_H$	[I <sup>-</sup> ], moles/l.	$k'_R/[I^-]$	$k'_R/[I^-]_0$
CH <sub>3</sub>	H	0.560	1.18	1.00	0.033	0.0456
		.572	1.04	1.00	.033	.0439
		.720	1.01	1.00	.0414	.0410
		.727	0.783	1.00	.037	.0361
		1.169	.421	1.00	.0304	.0193
		1.190	.425	1.00	.0306	.0148
		1.200	.477	1.00	.0346	.0115
		2.05	.26	1.00	.0429	.00837
		2.96	.103	1.00	.0319	.00334
		0.727 <sup>a</sup>	.525 <sup>a</sup>	1.00	.075 <sup>c</sup>	
		<i>i</i> -C <sub>6</sub> H <sub>5</sub>	H	0.635	.140	4.00
1.555	.182			4.00	.00438	.00140
2.380	.552			4.00	.032	.00468
<i>t</i> -C <sub>6</sub> H <sub>5</sub>	H	0.635	V. small	4.00		
		1.453	0.171	4.00	0.00239	0.000848
		2.083	0.410	4.00	0.0123	0.00235
CH <sub>3</sub>	CH <sub>3</sub>	0.613	V. small	4.00		
		1.433	0.124	4.00	0.0036	0.00131
		2.162	0.417	4.00	0.028	0.00635
(CH <sub>3</sub> ) <sub>3</sub>		0.615	V. small	4.00		
		1.572	0.199	4.00	0.0089	0.00279
		2.148	.442	4.00	.035	.00622
<i>p</i> -HO <sub>3</sub> SC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	H	0.485	.464	1.00	.0102	.0165
		.272 <sup>b</sup>	.814	1.00	.0062	.0162
		.486 <sup>b</sup>	.52	1.00	.0068	.0096
		1.015 <sup>b</sup>	.504	1.00	.0108	.0060
		1.995 <sup>b</sup>	.529	1.00	.0175	.0026
		0.486 <sup>a,b</sup>	.426	1.00	.0111	

<sup>a</sup> At 40.0°. <sup>b</sup> Sulfuric acid, moles per liter. <sup>c</sup> Estimated by correcting the interpolated value of  $k'_H$  at 30° for the effect of the temperature change and multiplying the resulting figure by  $k'_R/k'_H$ : (0.0917/0.028) × 0.0438 × 0.525 = 0.0753.

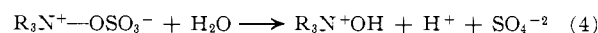
Amine oxide-sulfur trioxide addition products have the structure of the zwitterion form of hydroxylamine-O-sulfonic acids. Although earlier reports state that such compounds do not oxidize iodide,<sup>7</sup> we found that they can, indeed, be made to do so in an acid solution in the presence of a high concentration of iodide. The determinations of the ratios of the rate constants for the reduction and the hydrolysis reactions were made in the usual way, except that the extent of hydrolysis could not be determined directly, owing to the inertness of amine oxides (the hydrolysis products) toward iodine. As a result, the ratios could only be determined from reactions that had been allowed to run to completion; the extent of hydrolysis was determined by difference from the original number of moles of sample and the equivalents of iodine produced. All results are collected in Table V. For the same reason, the hydrolysis rates could not be measured separately by the same

means used for the other hydroxylamine-O-sulfonic acids. Of the many methods considered, the choice was dictated by the qualitative observation that hydrolysis was extremely rapid.

TABLE V  
REDUCTION AND HYDROLYSIS OF AMINE N-OXIDE-O-SULFONATES

Amine N-oxide-O-sulfonate	[HCl], moles/l.	$k'_R/k'_H$ at 30°
Pyridine	$1.00 \times 10^{-4}$	$7.3 \times 10^{-3}$
	$1.00 \times 10^{-3}$	$8.7 \times 10^{-3}$
	0.682	V. small
	1.576	0.15
	1.621	.11
	2.226	.488
2,6-Lutidine	$1.00 \times 10^{-4}$	$2 \times 10^{-3}$
	$1.00 \times 10^{-3}$	$4.8 \times 10^{-3}$
	0.095	$4.2 \times 10^{-3}$
	.500	$2.5 \times 10^{-3}$
	.920	0.026
	1.330	.039
Trimethylamine	1.820	.113
	2.235	.478
	$1.00 \times 10^{-4}$	.0127
	$1.00 \times 10^{-3}$	.0167
	0.095	.0054
	.480	.0067
	.920	.0127
	1.416	.0135
	1.922	.071
	2.425	.44

A conductometric method was chosen, based on the fact that hydrolysis converts a nonconducting zwitterion into a salt (amine oxide bisulfate). Even this method



was not sufficiently rapid to give reliable measurements and, in addition, it has the serious limitation that high concentrations of other electrolytes, particularly acids, render the method insensitive, and meaningful measurements could only be made at very low acidities. In  $10^{-3}$  and  $10^{-4}$  M HCl, hydrolysis appeared to be a second-order, base-catalyzed process. Hydrolysis was sensibly complete in 2 min. at 25° in the case of trimethylamine N-oxide-O-sulfonate, in 8 min. with pyridine N-oxide-O-sulfonate, and 15 min. with 2,6-lutidine-N-oxide-O-sulfonate, but only with the last substance did the measurements permit a rate constant to be estimated. Values ranging between  $1.2 \times 10^{10}$  and  $2.0 \times 10^{10}$  l. mole<sup>-1</sup> min.<sup>-1</sup> were obtained; the pyridine and trimethylamine analogs can be estimated to have constants approximately five and ten times the lutidine value, respectively. The comparison with the ordinary hydroxylamine-O-sulfonic acids is more readily seen from the fact that they required about 3 days for complete hydrolysis, instead of 15 min. or less.

For comparison purposes, an attempt was made to measure the rate of reduction of methylchloramine by iodide under the conditions used with the sulfonic acids. The reaction was too rapid for measurement by the titrimetric method, being complete in less than 1 min., and is evidently several orders of magnitude faster than with methylhydroxylamine-O-sulfonic acid. The transient appearance of a red solid in the reaction mixture suggested the intermediate formation of methyliodamine.

Alcoholysis of N-methylhydroxylamine-O-sulfonic acid was accomplished by preparing solutions of it in magnesium-dried methanol containing about 8% of dry hydrogen chloride, and allowing them to stand until reaction was complete (1.5 to 6 days). Titration with standard iodine solution, which will react with

N-methylhydroxylamine but not with O,N-dimethylhydroxylamine, showed the formation of 92 to 98% of the former compound.

### Discussion

The results reported here may be regarded as only a first approximation to a study of the kinetics of the reactions concerned, for secondary effects have had to be largely neglected, and experimental factors have limited the measurements that could be made. Nevertheless, they are sufficient to allow certain significant inferences to be made regarding the gross mechanism of the reactions.

The very different rates of hydrolysis and reduction by iodide, as well as the rate law  $d[I_2]/dt = k[I^-][NH_2OSO_3H]$  for the reduction of hydroxylamine-O-sulfonic acid, are consistent with a rate-determining displacement on the nitrogen by iodide, but not consistent with ionization to  $NH_2^+$  or elimination to form  $NH$  as the rate-determining step. Furthermore, the elimination of sulfuric acid to produce  $NH$  would be opposed by increasing acidity of the medium; in the presence of strong bases, of course, it may become an important reaction.<sup>8</sup> There is ample precedent for displacement reactions occurring with hydroxylamine-O-sulfonic acid, but those so far reported, such as the reaction with amines to produce hydrazines,<sup>9</sup> the reaction with thiosulfate to produce sulfhydrylamine,<sup>10</sup> and the reaction with phenoxides to produce aryloxyanines,<sup>11</sup> all require basic solutions, in which there is the ambiguity that elimination to form  $NH$  as the reactive intermediate may be anticipated.

The existence of a bimolecular displacement reaction on the nitrogen of hydroxylamine-O-sulfonic acid would have two predictable consequences: first, since  $HSO_4^-$  is a better leaving group than  $SO_4^{2-}$ , molecular  $NH_2OSO_3H$  should react faster than the anion  $NH_2OSO_3^-$ ; second, alkyl substituents on the nitrogen atom should retard the reaction to a pronounced degree. The first consequence implies that at low acidities, where there is an appreciable concentration of the anion, the rate will be pH dependent, but will become independent of acidity as the substrate becomes essentially all converted to the molecular form. This is borne out by the results shown in Table II. A value of 1.5 for  $pK_a$  for hydroxylamine-O-sulfonic acid has been estimated,<sup>6</sup> according to which the substance can indeed be calculated to be essentially entirely in the molecular form at the acidities where leveling off was observed.

There is the unanswered question of whether molecular hydroxylamine-O-sulfonic acid in aqueous solution exists principally in the form  $NH_2OSO_3H$ , or the zwitterion form,  $H_3N^+OSO_3^-$ , for whose existence in the solid phase there is supporting evidence.<sup>7,12</sup> Both forms are, of course, presumably present to at least some extent. The zwitterion form might also be expected to react with iodide more rapidly than would the anion, for although the leaving group would be  $SO_4^{2-}$  rather than  $HSO_4^-$ , the site of attack would be a center of greater positive charge density, which should promote attack by anions such as iodide. Although the question must remain unanswered at this time, we favor the overwhelming predominance of the  $NH_2OSO_3H$  form,

because of the great difference in rate of reaction between hydroxylamine-O-sulfonic acid and its mono- and dialkyl derivatives on the one hand, and the fixed zwitterions, the amine oxide-O-sulfonates, on the other. It is recognized, however, that alkyl substitution, by increasing the basicity of the nitrogen, might increase the relative importance of the zwitterion form.

The effect of alkyl substitution can be seen qualitatively to agree with the requirements of a rate-determining displacement on nitrogen—all substitution retards reduction, and the bulkiest substituents retard it the most. Zinner<sup>2c</sup> has reported a similar qualitative effect, in that O-acetylhydroxylamine oxidizes iodide, but its N,N-dialkyl derivatives do not. A quantitative comparison can be only approximate, however, because of the errors introduced by having to correct for the concomitant hydrolysis. Furthermore, the results suggest that the reduction reaction becomes pH dependent for some of the substituted compounds, although it is not so for the parent compound and its methyl derivative in the range studied (cf. the values of  $k'_R/[I^-]$  and  $k'/[I^-]h_0$  in Table IV).

The most accurate comparison can be made between hydroxylamine-O-sulfonic acid and its methyl derivative. The difference in reaction rate toward iodide, and thus presumably the difference in displacement rates at the nitrogen, is approximately  $10^4$  after correction to the same temperature. Since  $NH_2X$  and  $CH_3NHX$  are isoelectronic with  $CH_3X$  and  $CH_3CH_2X$ , this difference can be compared with the difference in displacement by iodide on methyl and ethyl chlorides (est. 5–20-fold)<sup>13</sup> and on methyl and ethyl bromides (155-fold).<sup>14</sup> Even making an improbably large allowance for experimental error and for the fact that displacement of halide is being compared with displacement of bisulfate, the conclusion seems inescapable that nucleophilic displacement on nitrogen is far more sensitive to the influence of alkyl substitution than is displacement on carbon. This is most easily understood by inferring that the transition state for substitution on nitrogen must be more crowded, tighter. Such an inference is reasonable on two counts: the N–C bond distance, 1.47 Å., is shorter than the C–C distance (1.54 Å.),<sup>15</sup> so that an alkyl substituent would be closer to the site of displacement in the nitrogen case; and reduced nitrogen shows itself to be less ready to exist as a cation,  $R_2N^+$ , than its carbon isostere,  $R_2CH^+$  (compare the very different qualities of reaction of  $R_2NCl$  and  $R_2CHCl$ ), thus requiring a closer approach of the displacing nucleophile before the leaving group can be released.

A similarly steep decrease in rate of displacement appears to be shown by the derivatives with larger substituents, although the results are not without ambiguity stemming from the influence of acidity. Since a very high concentration (4 M) of sodium iodide was necessary in order to make the very sluggish reduction reactions competitive with hydrolysis, the concomitant hydrolysis reaction was not taking place under conditions strictly comparable with those under which its rate was measured in the independent, separate experiments (Table III). The inorganic salt would have two predictable consequences: the acidity,  $h_0$ , of the medium would be increased,<sup>16</sup> and the activity of water would be decreased. These would have opposite effects, the first increasing the rate of hydroly-

(8) R. Appel and O. Büchner, *Angew. Chem.*, **74**, 430 (1962).

(9) (a) A. Meuwesen and R. Gösl, *Chem. Ber.*, **92**, 2521 (1959); (b) H. H. Sisler, R. A. Bafford, G. M. Omietanski, B. Rudner, and R. J. Drago, *J. Org. Chem.*, **24**, 859 (1959).

(10) A. Meuwesen and R. Gösl, *Angew. Chem.*, **71**, 736 (1959).

(11) C. L. Bumgardner and R. L. Lilly, *Chem. Ind. (London)*, 559 (1962).

(12) R. N. Keller and P. A. S. Smith, *J. Am. Chem. Soc.*, **66**, 1112 (1944).

(13) J. B. Conant and R. E. Hussey, *ibid.*, **47**, 476 (1925).

(14) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 323.

(15) "Tables of Interatomic Distances and Configuration in Molecules and Ions," L. E. Sutton, Ed., The Chemical Society, London, 1958.

(16) J. E. Leffer and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 276.

sis, the second perhaps decreasing it (*cf.* the discussion of hydrolysis ahead). Neither effect can at this time be evaluated quantitatively, but it does not seem qualitatively unreasonable to assume that the effects would be of approximately equal magnitude, and thus cancel each other. The absence of a significant effect of added sodium perchlorate on the rates of hydrolysis lends support to this assumption, which was used in calculating the values of  $k'_R$  shown in Table IV.

Since increasing acidity promotes reduction over hydrolysis under conditions where acid has been found to accelerate hydrolysis (Table III), one must conclude that the compounds in question are being converted in kinetically significant amounts into some considerably more reactive species. Acid *per se* cannot be expected

to influence the equilibrium  $R_2NOSO_3H \rightleftharpoons R_2NH-O^+SO_3^-$ , but it may do so indirectly by a differential effect on the activity coefficients of these tautomers. Such an effect on a tautomeric equilibrium has indeed been observed in other cases, for example, with *p*-aminoazobenzene cations.<sup>17</sup> The more reactive species

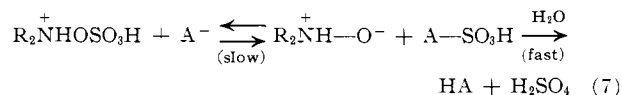
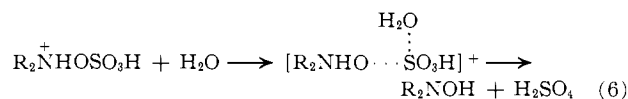
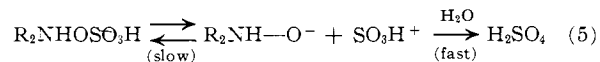
may instead be the cation,  $R_2NHOSO_3H^+$ . Since such an effect is not observed in the same range of acidity for the parent compound and its methyl derivative, one must conclude that the activities of their tautomers are less sensitive to the composition of the medium, that these two compounds are less basic than the other derivatives, or that the contribution of the protonated species is not as easily detected against the background of the already rapid reactions of the neutral molecules. The latter argument implies a compressed scale of reactivity of the cations compared to the neutral molecules. The high rate of reduction of the fixed zwitterions and its acceleration with increasing acidity (Table V) provides evidence that the protonated

forms  $R_2NHOSO_3H^+$  would, indeed, be more reactive. A comparison of the ratios of reduction to hydrolysis of the several fixed zwitterions, which differ considerably in steric environment about their nitrogen atoms, is not inconsistent with such a compressed scale of reactivity.

A compressed scale might indeed be expected if the attraction of opposite ionic charges is the dominant influence in the rate-determining step of reduction of these compounds. Attack by anions on the tertiary amino group of  $R_2N-OSO_3H$  would be considerably interfered with by the repulsion of the unshared electron pair. Conversion to the ammonio group in  $R_2NHOSO_3H^+$  would replace this by the repulsion of a hydrogen atom (little change in bond angles would be anticipated).<sup>18</sup> However, the concomitant positive charge should enormously accelerate the reaction by lowering the energy of activation; if the lowering is proportional rather than simply additive, that is, if the ratios of the activation energies for the differently substituted substrates remain the same, a compression of the scale of reactivity would result.<sup>19</sup>

The hydrolysis reactions obey a rate law of the form  $d(R_2NOH)/dt = k(R_2NOSO_3H)/h_0$  (see Table III, values of  $k'/h_0$ ). A noticeable downward drift of  $k$  at higher acidities may perhaps be attributed to the

decreasing activity of water. The acceleration of hydrolysis by acid does not level off at pH levels where the substrates would be substantially completely converted to the molecular acid; hydrolysis therefore does not depend primarily on the species  $R_2NOSO_3H$  or  $R_2NHOSO_3^-$ , but on a more highly protonated species, probably  $R_2NHOSO_3H^+$ . At this stage, hydrolysis could then proceed in three ways: by unimolecular cleavage followed by rapid reaction with water (eq. 5); by direct nucleophilic attack of a water molecule (eq. 6); or by attack of an anion, such as  $Cl^-$  or  $HSO_4^-$ , giving  $ClSO_3H$  or  $HO_3SOSO_3H$ , both of which react rapidly with water (eq. 7). The first



of these ways is analogous to the path deduced by Candlin and Wilkins<sup>20</sup> for the hydrolysis of sulfamic acid.

The question of whether it is the N-O or the S-O bond that is cleaved in the hydrolysis has already been answered for the parent compound by <sup>18</sup>O isotope experiments reported by Candlin and Wilkins.<sup>6</sup> In basic solution, where OH<sup>-</sup> is the attacking agent, N-O bond cleavage occurs, but in acid solution, the S-O bond is cleaved instead. There is no reason to doubt that the substituted hydroxylamine-O-sulfonic acids also undergo S-O bond cleavage in hydrolysis in acid solution. The relative rates of hydrolysis strongly support this assumption. In contrast to the reduction reaction, hydrolysis shows little sensitivity to the presence of substituents; all of the second-order rate constants fall within the same order of magnitude. Nucleophilic attack by water (or anions) on the nitrogen atom would be subject to the pronounced retardation by the presence of substituents observed in the reaction with iodide, but nucleophilic attack on the sulfur atom, two atoms removed from the site of alkyl substitution, should be little affected. Unimolecular cleavage should be similarly insensitive to the presence of substituents.

The distinction among the reasonable paths for hydrolysis requires knowing whether water is involved in the rate-determining step. The measurements are not extensive enough to permit Bunnett's *w*-value equation<sup>21</sup> to be applied with precision, but the results do lead to large positive *w*-values ( $\sim 15$  in the case of *p*-sulfobenzylhydroxylamine-O-sulfonic acid), usually associated with proton transfer in the rate-determining step. On the other hand, it is easier to explain the difference in bond cleavage between basic and acidic hydrolysis on the basis of unimolecular cleavage in acid solution prior to attack by water. Otherwise, one must assume that the nucleophiles OH<sup>-</sup> and I<sup>-</sup> on the one hand and H<sub>2</sub>O on the other have a qualitatively entirely different preference for their site of attack,

(17) Yu. L. Kaminskii and I. Y. Bernshtein, in "Korreljatsionnie Uravneniya v Organicheskoj Khimii," V. Palm, Ed., Tartu University, Tartu, 1962, p. 338.

(18) The C-N-C bond angle in trimethylamine has recently been determined as  $108^\circ 40' \pm 1^\circ$ , which is within experimental error of the tetrahedral angle,  $109^\circ 28'$ , to be expected of tetracoordinate nitrogen in ammonium ions: D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **28**, 572 (1958).

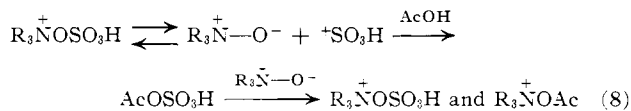
(19) This argument is closely related to that used by A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 2888 (1957), in connection with a rather different type of system.

(20) J. P. Candlin and R. G. Wilkins, *J. Chem. Soc.*, 4236 (1960).

(21) J. F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4956, 4968 (1961).

apart from differences in mechanism.<sup>22</sup> Iodide and hydroxide ions ( $n = 5.04$  and  $4.20$ , respectively)<sup>23</sup> are much stronger nucleophiles than water and chloride ion ( $n = 0.00$  and  $3.04$ , respectively),<sup>23</sup> and would presumably be able to take part in displacement reactions at the nitrogen atom at rates competitive with unimolecular cleavage; poor nucleophiles would be unable to do this. That chloride ion by itself does not engage in nucleophilic attack on the nitrogen atom to a significant extent is shown by the fact that hydrolysis in hydrochloric acid solution gives essentially quantitative yields of hydroxylamine salts; involvement of chloride would produce chloramine, and from it, chlorine or hypochlorous acid and ammonium salts.

An experiment carried out in the near absence of water, in glacial acetic acid, with 2,6-lutidine N-oxide-O-sulfonate, gave a very much higher ratio of reduction to hydrolysis ( $k_R/k_H = 3.08$ ). At first consideration this would seem to support the contention that water is involved in the rate-determining step for hydrolysis. However, unimolecular solvolysis in such a medium should give rise to acetyl bisulfate, a powerful acylating agent that would be expected to regenerate the O-acyl hydroxylamine structure as its principal reaction (eq. 8), thereby also promoting reduction by iodide over hydrolysis.



### Experimental<sup>24</sup>

**Hydroxylamines.**—N-Methylhydroxylamine<sup>25</sup> and N,N-dimethylhydroxylamine<sup>26</sup> were prepared by well known methods. N-Isopropylhydroxylamine was prepared by the reduction of 2-nitropropane by dropping its ethereal solution onto wet aluminum amalgam under ether at such a rate as to maintain refluxing. The product was obtained crystalline in 55% yield by concentration of the dried ether phase, and had m.p.  $85-86^\circ$  after one recrystallization from ether. It was converted to the oxalate, m.p.  $157^\circ$  (reported<sup>27</sup> m.p.  $159-160^\circ$ ), for use. *t*-Butylhydroxylamine was prepared similarly from 2-nitroisobutane in 61% yield. As it rapidly became blue on exposure to air, owing to oxidation to 2-nitroisobutane, it was converted to the oxalate by treatment with ethereal oxalic acid. Recrystallization from hot water gave colorless needles, m.p.  $200-202^\circ$ .

*Anal.* Calcd. for  $C_{10}H_{24}N_2O_6$ : C, 44.76; H, 9.02. Found: C, 44.55; H, 8.94.

N-Benzylhydroxylamine<sup>28</sup> was prepared by the hydrolysis of benzaldehyde N-benzylnitron obtained by the oxidation of N,N-dibenzylhydroxylamine.

**Hydroxylamine-O-sulfonic Acids.**—All compounds of this type were prepared in the same manner, essentially the procedure originally reported for the parent compound.<sup>2a</sup> A hydroxylamine salt (hydrochloride, sulfate, or oxalate) was mixed with approximately four times its weight of chlorosulfonic acid in an erlenmeyer flask of at least five times the volume of the reactants. A vigorous reaction always ensued, with evolution of hydrogen chloride and the formation of a clear sirup (sometimes a paste). The mixtures were then warmed to about  $75^\circ$  for about 5 min., and then allowed to cool in a desiccator. Chilled, dry ether was then added in excess, and the resulting suspension was filtered rapidly through a large, coarse, sintered glass funnel and the solid washed with fresh ether. Treatment with chlorosulfonic acid and ether was then repeated once, followed by thorough washing

with dry ether. The solid preparations thus obtained were analyzed after drying *in vacuo* over phosphorus pentoxide, either without further purification or after recrystallization from cold methanol, and their neutral equivalents were determined by titration to a phenolphthalein end point. The results are recorded in Table I.

**Amine Oxide-O-sulfonates.**—These substances were prepared in good yields by a slight modification of the method of Baumgarten and Erbe,<sup>7</sup> using chlorosulfonic acid on the hydrochlorides of the amine oxides. It was found more convenient to remove excess chlorosulfonic acid from the products by triturating with several portions of dry ether on a sintered glass funnel. Pyridine N-oxide-O-sulfonate had m.p.  $178-180^\circ$  (reported<sup>7</sup> m.p.  $179-180^\circ$ ). 2,6-Lutidine N-oxide-O-sulfonate, a white solid, had m.p.  $160-163^\circ$  after preliminary sintering.

*Anal.* Calcd. for  $C_7H_9O_4NS$ : C, 41.37; H, 4.46;  $SO_4^{-2}$ , 15.77; neut. equiv., 101.6. Found: C, 39.58; 39.46; H, 4.29, 4.33; gravimetric sulfate, 15.10; neut. equiv., 102.6.

Trimethylamine N-oxide-O-sulfonate was obtained as a white, hygroscopic solid, m.p.  $125-130^\circ$ , that smoked on exposure to moist air. A satisfactory purification procedure could not be devised, and the preparations were obviously seriously contaminated.

*Anal.* Calcd. for  $C_3H_9O_4NS$ : C, 23.22; H, 5.74. Found: C, 20.09, 19.77; H, 4.82, 5.04.

These compounds were too reactive toward water to allow purification by recrystallization; owing to their extremely hygroscopic character, they must be stored over phosphorus pentoxide.

**Volumetric Determination of Hydroxylamines.**—The hydroxylamine salts used in the preparations and those produced by hydrolysis in the kinetic experiments were assayed by iodometric titration in neutral solution (sodium bicarbonate) as described by Brady and Goldstein.<sup>2a</sup> Their procedure was modified by running standard iodine solution into the hydroxylamine solution until a slight excess was present, and then back-titrating with a standard solution of N-methylhydroxylamine hydrochloride. No reaction occurred in acid solution; a control experiment in 0.1 M HCl was allowed to run overnight, and was found to have consumed no detectable quantity of iodine. In addition to N-methylhydroxylamine hydrochloride, whose titration was described by Brady and Goldstein, N,N-dimethylhydroxylamine hydrochloride and the oxalates of N-isopropylhydroxylamine, N-*t*-butylhydroxylamine, and N-hydroxypiperidine were examined. They assayed 99.1, 98.4, 99.3, and 99.5% respectively.

**Reaction of Methylchloramine with Iodine.**—Methylchloramine<sup>29</sup> (0.352 g.) was added to 50 ml. of a solution 0.500 M in HCl and 1.00 M in KI at  $30^\circ$ . The solution turned yellow immediately, and a rouge-red solid then formed momentarily and vanished in a few seconds, after which the brown color of iodine appeared rapidly. The reaction was too fast to follow titrimetrically, and was complete in less than 5 min., as evidenced by unchanging titer of aliquots and unchanging color density.

**Alcoholysis of N-Methylhydroxylamine-O-sulfonic Acid.**—A solution of 4 g. of dry hydrogen chloride in 50 g. of magnesium-dried methanol was prepared, and 1.338 g. of N-methylhydroxylamine-O-sulfonic acid was dissolved in it. After 36 hr., during which the stoppered flask was stored in a desiccator at room temperature, the mixture was diluted with water, concentrated to remove alcohol, and an aliquot titrated against standard iodine solution. The assay was 98.4% of the original hydroxylamine content as  $CH_3NHOH$ ;  $CH_3NHOCH_3$  is reported<sup>30</sup> to be non-reducing, and  $NH_2OCH_3$  was found to react with iodine at a rate negligibly slow in comparison to the time required in the titrations.

**Hydrolysis Reactions.**—Solutions were prepared of weighed quantities of hydroxylamine-O-sulfonic acid or its substituted derivatives in 50 ml. of hydrochloric acid of appropriate standard concentration previously adjusted to a temperature of  $30^\circ$ , and kept in a thermostated bath at  $30 \pm 0.1^\circ$ . Aliquots (5 ml.) were withdrawn at measured time intervals. In the case of the unsubstituted compound, these were added to potassium iodide solution, and the iodine that was liberated from the unhydrolyzed substrate was titrated with standard thiosulfate solution after sufficient time (*ca.* 1 hr.) for complete reaction. In the case of the substituted compounds, which do not oxidize iodide quantitatively, the aliquots were added to ice-cold, saturated sodium bicarbonate solution, a measured excess of standard iodine solution was added, and the excess was quickly back-titrated. A representative set of data is shown in Table VI. The rate constants for pseudo-first-order reaction given in Table III are the averages of those calculated from the integrated first-order rate equation,  $k' = 2.303/t \times \log a/(a-x)$ , for each point determined for each run. The pseudo-first-order treatment is justified by the fact that the contribution to the acidity by the substrates,  $R_2NOSO_3H$ , would be practically equivalent to that

(22) There is precedent for differing selectivity among nucleophiles, which may be correlated at least in part with differences in nucleophilicity. The case of  $SN_2$  vs.  $SN_2'$  attack on allylic systems is well documented (*cf.* R. H. De Wolfe and W. G. Young, *Chem. Rev.*, **56**, 781 (1956)). The different behavior of unsymmetrical aziridinium ions in alcoholysis in the presence and in the absence of alkoxides (which has been ascribed to a mechanistic difference,  $SN_1$  vs.  $SN_2$ ) provides another example (N. J. Leonard, K. Jann, J. Y. Paukstelis, and C. K. Steinhardt, *J. Org. Chem.*, **28**, 1499 (1963)).

(23) C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953).

(24) Melting points are uncorrected. Analyses by Spang Microanalytical Laboratory, Ann Arbor, Mich.

(25) L. Semper and L. Lichtenstadt, *Ber.*, **51**, 933 (1918).

(26) H. Hepworth, *J. Chem. Soc.*, **119**, 254 (1921).

(27) A. U. Ryer and G. B. L. Smith, *J. Am. Chem. Soc.*, **73**, 5677 (1951).

(28) L. W. Jones and C. N. Sneed, *ibid.*, **39**, 674 (1917).

(29) G. H. Coleman, *ibid.*, **55**, 3001 (1933).

(30) L. W. Jones, *Am. Chem. J.*, **20**, 43 (1898).

by the products,  $R_2\text{NHOH}^+\text{HSO}_4^-$  (this small contribution was not reckoned into the values of  $k'/h_0$  given in Table III, however). The maximum deviation from the average value of  $k$  within a run and among duplicate runs was never more than 5.0% and in most cases about half that.

TABLE VI

HYDROLYSIS OF N-METHYLHYDROXYLAMINE-O-SULFONIC ACID<sup>a</sup>  
IN 0.50 M HCl AT 30.00 ± 0.02°

Time, hr.	Vol. of 0.0275 N KI <sub>3</sub> , ml.	X <sup>b</sup>	k', hr. <sup>-1</sup>
0	1.25	...	...
5	3.55	2.30	0.0285
10	5.45	4.20	.0278
20	8.60	7.35	.0276
30	11.05	9.80	.0277
45	13.40	12.15	.0269
120	18.55	17.30 <sup>c</sup>	

<sup>a</sup> 0.3242 g. <sup>b</sup> Vol. of 0.0275 N KI<sub>3</sub> equivalent to N-methylhydroxylamine produced <sup>c</sup> Taken as the value of  $a$  in the expression  $k' = \frac{2.303}{t} \log \frac{a}{a-x}$

**Reactions with Iodide.**—The substituted hydroxylamine-O-sulfonic acids were added in weighed quantities to 50 ml. of deoxygenated solutions, previously adjusted to a temperature of 30°, containing hydrochloric acid and potassium iodide in known concentration, and the resulting mixtures were pipetted in separate 10.0-ml. aliquots to each of four flasks. The air in the flasks was displaced by nitrogen; the flasks were tightly stoppered and kept in a thermostated bath at 30 ± 0.02°. Four flasks of acid and iodide solution for use as blanks were prepared similarly. At recorded time intervals a flask was opened and its content divided in two by removing 5.0 ml. with a pipet. One part was diluted with 50 ml. of water and the iodine titrated with standard thiosulfate solution; one of the blanks was handled similarly. To the other part was added a mixture of 100 ml. of saturated sodium bicarbonate solution and about 30 g. of ice. This treatment usually caused the iodine to be completely consumed by the hydroxylamine, the excess of which was then titrated with standard iodine solution. A representative set of observations is shown in Table VII; the collected results are shown in Table IV. The experiments for each set of conditions were run between one and five times, depending on the quantity of material available. The maximum deviation from the average value of  $k_R/k_H$  within one run varied between 2.8 and 7.0%.

TABLE VII

REACTION OF N-METHYLHYDROXYLAMINE-O-SULFONIC ACID<sup>a</sup>  
WITH 1.00 M POTASSIUM IODIDE AT 30.00 ± 0.02° IN 0.727 M  
HCl  
(10.00 ml. of KI<sub>3</sub> solution equivalent to 11.30 ml. of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>  
solution)

Time, hr.	—Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , ml.—		KI <sub>3</sub> , ml.	$k_R/k_H$
	Blank	Sample		
0			0.95	
2	0.10	3.50	1.60	0.804
4	.35	6.25	2.10	.781
6	.60	8.55	2.40	.780
10	.85	11.95	3.05	.774

<sup>a</sup> 0.6251 g.

The reaction of unsubstituted hydroxylamine-O-sulfonic acid with iodide was carried out in a Beckman Model DU spectrophotometer in a jacketed cell around which ice water was circulated. The cell temperature during runs was 1.2 ± 0.2°. A solution of known concentration of hydrochloric acid and potassium iodide was brought to temperature, and 3.3 ml. of it was added to a cell containing a weighed quantity of solid hydroxylamine-O-sulfonic acid, also cooled to 1.2°. The mixture was quickly stirred with a cold, dry, glass rod, and the cell was placed in the instrument along with a similarly prepared blank. The transmission at 6000 Å. was recorded at measured time intervals, and the concentration of I<sub>3</sub><sup>-</sup> determined from a standard transmission curve determined under the same conditions. A representative set of data is shown in Table VIII. Rate constants were determined from the slope of a plot of  $\log(a-x)/(b-y)$  against time, which gave a straight line, or by calculation from the integrated rate equation,  $k = 2.303/t(a-b) \log b(a-x)/a(b-x)$ . In calculating  $x$  and  $y$ , which are the amounts of reacted iodide and sulfonic acid, respectively, the stoichiometry of eq. 9 was assumed. The results are summarized in Table II, in



which the average values of  $k$  are given. The maximum deviation from the average for four runs was 1.3% (or 0.005 l. mole<sup>-1</sup> min.<sup>-1</sup>). The temperature control in the spectrophotometric experiments was considerably less precise than in the others, it should be noted.

TABLE VIII

REACTION OF HYDROXYLAMINE-O-SULFONIC ACID<sup>a</sup> WITH 0.10 M  
POTASSIUM IODIDE IN 0.10 M HCl AT 1.2 ± 0.2°

Time, min.	Transmission, %	[I <sub>3</sub> <sup>-</sup> ], M × 10 <sup>2</sup>	$\log \frac{a-x}{b-y}$	$k$ , l. mole <sup>-1</sup> hr. <sup>-1</sup>
5	75	0.35	0.8726	23.1
10	61	.60	0.9361	21.8
15	52.8	.795	1.0037	22.5
20	47.5	.94	1.0708	22.3
30	41	1.14	1.2055	22.2
40	37	1.27	1.3445	22.5
50	34.5	1.36	1.4940	22.8
60	33.2	1.41	1.6150	22.5
90	30.6	1.50	2.0414	

<sup>a</sup> 5.85 mg. in 3.30 ml. of solution.

**Reactions of Amine Oxide-O-sulfonates.**—Accurately weighed samples (about 0.5 g.) of the amine oxide-O-sulfonate were dissolved in 50 ml. of a solution containing known concentrations of hydrochloric acid and potassium iodide, previously adjusted to a temperature of 30°. At recorded intervals, 10.0-ml. aliquots were withdrawn and titrated for the iodine produced. A blank was treated similarly. The reaction was assumed to be complete when the corrected titer remained constant. The values of  $k_R/k_H$  were determined from the amount of iodine produced and the amount of substrate taken, under the assumption that both reduction and hydrolysis would be pseudo-first order. While this assumption is probably valid for the higher acidities, it is almost certainly incorrect for the experiments run at [HCl] = 10<sup>-3</sup> and 10<sup>-4</sup> M. The results are collected in Table V.

An attempt to follow the kinetics of hydrolysis of the amine oxide-O-sulfonates was made by means of a Wheatstone bridge conductivity apparatus with a Wagner ground and an aural balance signal. In use, a sample sufficient to make a 10<sup>-3</sup> M solution was added to 100 ml. of standard hydrochloric acid in a conductivity cell in a constant-temperature bath, and measurements of cell resistance made at recorded intervals. Even with the slowest substrate, 2,6-lutidine N-oxide-O-sulfonate, the reaction rate was too fast for following without a relatively large error in either time or resistance measurement. The presence of ionic impurities in the substrates was a further source of error, for the resistance at  $t = 0$  could never be properly determined. Nevertheless, roughly reproducible results were obtained in terms of the time required for the conductance to reach a constant value, which was 2 min. for trimethylamine N-oxide-O-sulfonate, 8 min. for pyridine N-oxide-O-sulfonate, and 15 min. for 2,6-lutidine N-oxide-O-sulfonate in 10<sup>-3</sup> M hydrochloric acid. For the last compound, rate constants were determined graphically by assuming the rate law  $-d[\text{R}_3\text{NOSO}_3]/dt = k[\text{R}_3\text{NOSO}_3][\text{OH}^-]$ , expressing the concentration variables in terms of [H<sup>+</sup>], and solving the integrated equation for  $kt$ . Plots of  $t$  against  $-\ln \frac{a_0 + b_0 - [\text{H}^+]}{a_0 + b_0 - [\text{H}^+]}$  were roughly linear with erratic rather than systematic deviations, with a slope equal to  $kK_w$ . In determining the proportionality between instrument reading (ohms) and [H<sup>+</sup>], account was taken of the facts that the conductivity at  $t = 0$  was due to H<sup>+</sup> and Cl<sup>-</sup> (from the standard HCl) plus any contribution from ionic impurities, and at  $t = \infty$  was due to H<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and R<sub>3</sub>NOH<sup>+</sup>. The molar conductivities of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>/2 are known to be about 0.2Λ<sub>H+</sub>, and that of R<sub>3</sub>NOH<sup>+</sup> was assumed to be similar. Therefore, the proportionality factor,  $p$ , required in  $L_{\text{H}^+} = pL_{\text{Cl}^-}$  must vary from 1/1.2 at  $t = 0$  to 1/1.4 (10<sup>-4</sup> M HCl) or 1/1.56 (10<sup>-3</sup> M HCl) at  $t = \infty$ . The proportionality factor was therefore adjusted for each point in proportion to the extent of reaction. The values of  $k$  thus obtained were not different within experimental error for reactions in 10<sup>-3</sup> or 10<sup>-4</sup> M HCl, and had the following values in different experiments: in 10<sup>-3</sup> M HCl, 7.8 × 10<sup>11</sup>, 8.1 × 10<sup>11</sup>, 8.4 × 10<sup>11</sup>; in 10<sup>-4</sup> M HCl, 7.2 × 10<sup>11</sup>, 10.2 × 10<sup>11</sup>, 12 × 10<sup>11</sup> l. mole<sup>-1</sup> hr.<sup>-1</sup>.

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