974. *The Hydroxylamine–Sulphur Dioxide Reaction. Part II*[1]

By R. T. M. Fraser

Oxygen tracer studies and rate measurements in methanol show that the reaction of sulphur dioxide with *N*-methylhydroxylamine proceeds *via* three paths. Two of the activated complexes have the same composition, but yield different products: in one case, water and *N*-methylsulphamic acid; in the other, methylammonium hydrogen sulphate. The kinetics can be described satisfactorily by the rate equation

$$-\mathrm{d}[SO_2]/\mathrm{d}t = \{k_1[SO_2] + (k_2 + k_3)[H_2SO_3]\}[CH_3NHOH].$$

O-Methylhydroxylamine does not react in the same way.

Hydroxylamine and sulphur dioxide react in aqueous solution to form sulphamic acid and ammonium hydrogen sulphate, according to the equations

$$H_2SO_3 + NH_2OH \longrightarrow NH_2SO_3H + H_2O$$

$$H_2SO_3 + NH_2OH \longrightarrow NH_4HSO_4$$

The observed kinetics fit the rate law

$$-\mathrm{d}[\text{total sulphite}]\mathrm{d}t = k_{\text{obs}}\,[\text{total sulphite}]\,[\text{total hydroxylamine}],$$

where k_{obs} depends on the acidity of the solutions, and reaches a maximum at pH 4. There the rate law becomes [2,3]

$$-\mathrm{d}[\text{total sulphite}]/\mathrm{d}t = k_{\text{obs}}\,K_1K_n^{-1}[SO_2,H_2O][NH_2OH]$$

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[1] Part I, R. T. M. Fraser, *J.*, 1965, 1747.

[2] H. H. Sisler and L. F. Audrieth, *J. Amer. Chem. Soc.*, 1939, **61**, 3389.

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(where K_1 is the first dissociation constant of sulphurous acid and K_n is the acid dissociation constant of hydroxylamine). Since the percentage of ammonia formed is independent of both the extent of reaction and the solution pH, the transition complexes of the two reactions are kinetically indistinguishable,[3] and have the composition (SO_2,NH_2OH,$x H_2O$). Since sulphamic acid can be formed from dry sulphur dioxide and hydroxylamine in the gas phase, it was suggested [1] that the value of x is unity for the ammonium hydrogen sulphate formation, but zero for the sulphamic acid. To obtain further information on this point, and to determine in more detail the configurations of the transition complexes, a study has been made of the reaction of sulphur dioxide with *O*- and *N*-methylhydroxylamines in water, with *N*-methyl[^{18}O]hydroxylamine in water, and with *N*-methylhydroxylamine in methanol.

TABLE 1

Effect of pH on the observed second-order rate constant

Total ionic strength = 0·5M

[Total SO_3^{2-}]$_{init}$ (M)	[Total CH_3NHOH]$_{init}$ (M); 25°	pH	k (mole^{-1} min.$^{-1}$)	[Total SO_3^{2-}]$_{init}$ (M)	[Total CH_3NHOH]$_{init}$ (M); 35°	pH	k (mole^{-1} min.$^{-1}$)
0·060	0·090	2·0	0·100	0·080	0·040	3·1	0·349
0·090	0·045	2·3	0·100	,,	,,	4·0	0·322
0·060	0·060	3·1	0·113	0·040	0·080	5·1	0·247
0·080	0·040	4·0	0·113	,,	,,	6·3	0·035
0·040	0·080	5·1	0·068				
,,	,,	6·3	0·032				

Table 1 lists the values found for the rate constant k_{obs} in the reduction of aqueous *N*-methylhydroxylamine over the pH range studied. The rate behaviour is similar to that found in the hydroxylamine reduction: the reaction is second order, and the observed rate constant reaches a maximum value between pH 3 and 4. At pH 3, the rate law can be expressed [1,3]

$$-d[\text{total sulphite}]/dt = k_{obs}\,(K_1 + 10^{-3\cdot0})K_n^{-1}\,[SO_2,H_2O][CH_3NHOH],$$

and, as before,[1] the value of K_n decreases with temperature while that of K_1 increases so that $(K_1 + 10^{-3\cdot0})K_n^{-1}$ is largest at 0°:

Temp.	0°	15·0°	25·0°	35·0°	45·0°
pK_n	6·13	5·89	5·80	5·70	5·59
$10^{-3}(K_1 + 10^{-3\cdot0})K_n^{-1}$	39·9	20·5	15·2	10·5	6·61
k_{obs} (mole^{-1} min.$^{-1}$)	0·007	0·040	0·113	0·349	1·13
[CH_3NHSO_3H]/[CH_3NH_2]	0·67	2·7	$3{\cdot}4_5$	4·9	$7{\cdot}4_5$

The rate law can also be expressed as

$$-d[\text{total sulphite}]/dt = (k_{\text{sulph.}} + k_{\text{amm.}})[SO_2,H_2O][CH_3NHOH],$$

where the ratio of the two rate constants ($k_{\text{sulph.}}/k_{\text{amm.}}$) is equal to the ratio of the corresponding products, [CH_3NHSO_3H]/[CH_3NH_2]. Plots of $\log_{10}k_{\text{sulph.}}/T$ and $\log_{10}k_{\text{amm.}}/T$ in turn against $10^3/T$ yield enthalpies of activation of 13·3 and 3·7 kcal. mol.$^{-1}$ and entropies of activation of −9 and −42 e.u., respectively.

Previously it was suggested [1] that sulphamic acid was formed through attack by sulphur dioxide on the hydroxylamine nitrogen, while ammonium hydrogen sulphate resulted from attack on the oxygen. This implies that the [sulphamic acid]/[ammonium bisulphate] ratio should be affected by steric hindrance in the hydroxylamine; methyl substitution on the nitrogen should lead to a decrease, while substitution on the oxygen should lead to an increase in the ratio, but such is not the case. A decrease is found in the reduction of *N*-methylhydroxylamine, but the reaction of *O*-methylhydroxylamine yields (at least within the accuracy of the experimental measurements) ammonia only. Further, this ammonia is formed very slowly (the specific rate at 35° is less than 0·002 mole^{-1} min.$^{-1}$) in contrast to the rate of formation from the *N*-methyl isomer. The hydrogen on the hydroxylamine oxygen thus plays an important part in the reaction, and to investigate this further the reduction of *N*-methyl[^{18}O]hydroxylamine in water has been studied. Table 2 lists the percentages of ^{18}O found in the two products. On the basis of the quantities of sodium nitrite and [^{18}O]H_2O originally taken, the *N*-methylhydroxylamine could have contained at most 26·6% ^{18}O.

TABLE 2

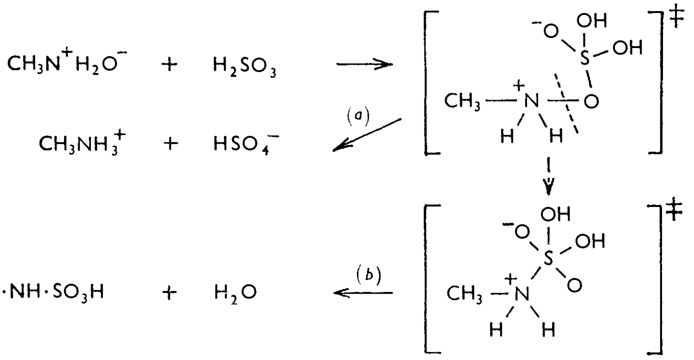
Oxygen-18 content of products from the sulphite reduction of *N*-methyl[^{18}O]hydroxylamine

	[^{18}O] (%)			[^{18}O] (%)	
Source	(*a*)	(*b*)	Source	(*a*)	(*b*)
Acid sulphate	27	27	Sulphamate	17	21
	27	28		16	19
		24		19	
				23	
Average	27	26 ± 2		19 ± 3	20 ± 1

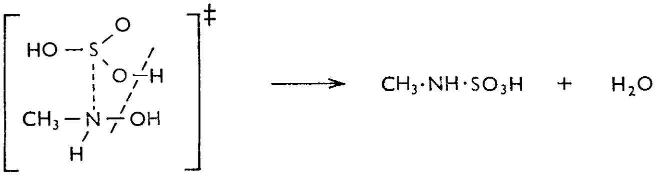
(*a*) Instrument used, Perkin-Elmer Infracord. (*b*) Instrument used, Perkin-Elmer 21 spectrophotometer.

The results show conclusively that the methylammonium hydrogen sulphate contains as much oxygen-18 as the hydroxylamine from which it was formed, but that the methylsulphamic acid contains only ¾ as much. This in turn means that the two transition complexes involved have the same composition and are formed from *N*-methylhydroxylamine as its zwitterion:

$$CH_3NHOH \rightleftharpoons CH_3N^+H_2O^-$$



Both paths involve the formation of a sulphur–oxygen bond and fission of the bond between nitrogen and oxygen. In addition, a sulphur–nitrogen bond is formed in the transition complex leading to the sulphamic acid, and this results in the formation of a group containing a five-covalent sulphur atom. Normal covalency is restored by the random elimination of the elements of water (path *b*). Proton transfer and sulphur attack on oxygen are both necessary steps for, while a possible mechanism might include attack by



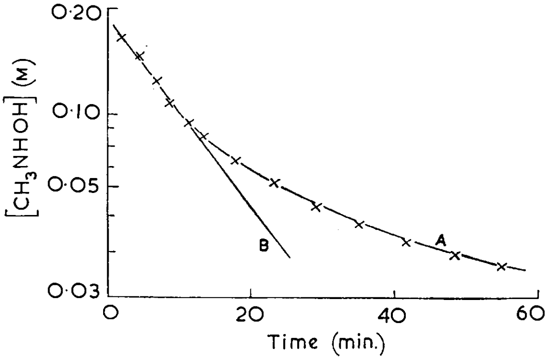
sulphur directly on nitrogen, followed by fission of the nitrogen–oxygen bond, such a step would be just as available to the *O*-methyl isomer as to *N*-methylhydroxylamine and would lead to the formation of a sulphamic acid containing no oxygen-18.

Because sulphamic acid can be formed in the absence of water,[1] some rate studies have been carried out in methanol to assess the relative importance of the water-independent path. Table 3 lists the values of the ratio $[CH_3NHSO_3H]/[CH_3NH_2]$ found at the completion of the reduction. Even at the highest concentrations of water studied, the amine comprises only 12% of the products; the predominant path is still formation of the sulphamic acid. If sulphur dioxide is present in large excess, it seems reasonable to make the approximation that $[SO_2] = [SO_2]_{total} - [H_2O]$ and also $[H_2O,SO_2] = [H_2O]$, where $[H_2O]$ is the total concentration of water in the methanol. Then the rate of sulphur dioxide consumption should be given by

TABLE 3

Effect of water concentration on the formation of methylamine in methanol at 22°

$[SO_2]$ (M)	0·102	0·102	0·102	0·204	0·980	0·980	0·980
$[CH_3NHOH]$ (M)	0·057	0·057	0·057	0·0372	0·177	0·177	0·177
$[H_2O]$ (M)	0·040	0·330	0·600	0·096	0·040	0·150	0·370
$[CH_3NHSO_3H]/[CH_3NH_2]$	9·2	8·3	7·2	8·8	9·2	7·5	7·2



Variation of $[CH_3NHOH]$ with time in methanol at 22°: (A) $[CH_3NHOH]_0 = 0{\cdot}177$M, $[SO_2]_0 = 0{\cdot}980$M, $[H_2O]_0 = 0{\cdot}040$M; (B) first-order plot with rate constant $k = 0{\cdot}064$ mole^{-1} min.$^{-1}$

$$-d[SO_2]/dt = \{k_1[SO_2] + (k_2 + k_3)[H_2O,SO_2]\}[CH_3NHOH]$$

and the product relation by

$$d[CH_3NHSO_3H]/d[CH_3NH_2] = k_1[SO_2]/k_3[H_2O,SO_2] + k_2/k_3,$$

where k_1 and k_2 are rate constants for methylsulphamic acid formation and k_2 and k_3 relate to paths involving water. Since water is consumed only in the production of methylammonium hydrogen sulphate, the second expression can be integrated to give

$$[CH_3NHSO_3H] = (-k_1/k_3)[SO_2]\log_e([H_2O]_0 - [CH_3NH_2]) + (k_2/k_3)[CH_3NH_2] + \text{constant}.$$

Initially, $[CH_3NH_2] = [CH_3NHSO_3H] = 0$, so that the constant of integration can be eliminated and

$$\frac{[CH_3NHSO_3H]}{[CH_3NH_2]} = \frac{k_1}{k_3}\cdot\frac{[SO_2]}{[CH_3NH_2]}\log_e\left(\frac{[H_2O]_0}{[H_2O]_0 - [CH_3NH_2]}\right) + \frac{k_2}{k_3}$$
$$= k_1x/k_3 + k_2/k_3.$$

A least-squares fit to values of $[CH_3NHSO_3H] : [CH_3NH_2]$ and x obtained from the results in Table 3 gives a straight line of slope 0·076 ($=k_1/k_3$) and intercept 6·75 ($=k_2/k_3$). The rate of disappearance of water is much slower than the overall rate of reaction, so that the reduction will follow pseudo first-order kinetics initially, before the concentrations of the products become significant; the Figure shows a typical rate plot. The values for each of the rate constants can be obtained from k_{init}:

$$k_{\text{init}} = k_1[SO_2] + (k_2 + k_3)[H_2O].$$

At 22°, $k_1 = 0{\cdot}012$, $k_2 = 1{\cdot}1$, and $k_3 = 0{\cdot}16$ mole^{-1} min.$^{-1}$.

Whilst it is not possible to compare directly the results obtained in methanol containing less than 1% water with those obtained in water as solvent, it does seem clear that the water-independent path will make only a very small contribution to the kinetics in water; most of the reaction will proceed through two activated complexes (with identical compositions), one leading to the sulphamic acid and one to the ammonium salt.

EXPERIMENTAL

Materials.—The purest grades available of sodium sulphite, sulphur dioxide, and *N*-methyl- and *O*-methyl-hydroxylamine hydrochlorides were used without further purification. The stock solution of sodium sulphite was prepared as described previously.[3] Solutions of the hydroxylamine hydrochlorides were made up by weight as required.

The methanol used in the kinetic studies was reagent grade anhydrous (0·055% water) solvent. The stock solution (2—4M) of sulphur dioxide was obtained by passing the dry gas directly into the solvent. Solutions of the free base *N*-methylhydroxylamine were prepared by adding sodium methoxide to the hydrochloride, and filtering off the precipitated sodium chloride.

Preparation of N-*methyl*[^{18}O]*hydroxylamine.*—Sodium nitrite (4·5 g.) was mixed to a paste with [^{18}O]-enriched water (66·8 atom-% ^{18}O; 1·5 g.) the pH adjusted to 4·5 with a few drops of acetic acid, and the mixture set aside at room temperature for 5 days. The oxygen exchange was followed by observing the changes in the infrared spectrum of the nitrite at 787 cm.$^{-1}$. Silver nitrite was prepared by the method of Anbar [4] and used to convert methyl iodide into [^{18}O]nitromethane.[5] The nitromethane was converted into *N*-methyl-[^{18}O]hydroxylamine by reduction with zinc dust,[6] and this was stored as the hydrochloride.

Isotopic Analyses.—The percentages of oxygen-18 associated with sulphur in the products were determined from the infrared absorption spectra of barium sulphate samples in Nujol, by using the method of Spencer.[7] Hydrogen [^{18}O]sulphate was converted directly into barium sulphate by addition of barium chloride to the reaction mixture. Since barium sulphamate is considerably more soluble than the sulphate, the precipitates obtained were almost pure sulphate. The solutions were filtered, and the residues divided into two parts. One part was washed with cold water, ethanol, and ether, and dried at 70°: the other was mixed with a few ml. of water, one or two drops of concentrated hydrochloric acid were added, and the mixture was heated to 80°. The solution was filtered while hot, and the precipitate washed and dried.

The solution containing the excess of barium chloride and the sulphamic acid was made acid with hydrochloric acid and heated to 90°. The slow hydrolysis of the sulphamic acid gave a continous precipitation of barium sulphate, and this was filtered off at 5-min. intervals. Experiments performed with barium sulphate and water containing oxygen-18 showed that oxygen exchange between the precipitate and the solvent was negligible under the conditions of the hydrolysis.

Kinetic Measurements.—The rates of reaction in water were followed as previously described.[3] Solutions for rate-studies in methanol were prepared by mixing equal volumes (10 ml.) of *N*-methylhydroxylamine (0·05—0·20M) and sulphur dioxide (0·03—1·0M) together with 5 ml. of methanol containing water (0—1·0M). All water concentrations were corrected for the water present in the " anhydrous " solvent (0·055%, 0·024M).

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