325. *The Hydroxylamine–Sulphur Dioxide Reaction*

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The reaction of sulphur dioxide and hydroxylamine may yield either sulphamic acid or ammonium bisulphate. Rate studies have been carried out from 1·0 to 45·0° and the activation parameters evaluated. The entropy of activation for the formation of ammonium bisulphate is very unfavourable and a possible model for the transition complex is suggested.

Hydroxylamine and sulphur dioxide react in aqueous solution to form sulphamic acid together with traces of ammonium and bisulphate ions:

$$H_2SO_3 + NH_2{\cdot}OH \longrightarrow NH_2{\cdot}SO_3H + H_2O \qquad (1)$$

$$H_2SO_3 + NH_2{\cdot}OH \longrightarrow NH_4{\cdot}HSO_4 \qquad (2)$$

The rate depends on the pH of the solution: it tends to zero in either strong acid or alkali [1] and at 25° reaches a maximum at pH 4. The kinetics fit the rate law

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

and the percentage of ammonia formed appears to be independent of pH, so that the transition complexes of the two reactions are kinetically indistinguishable [2] and have the composition $(SO_2,NH_2{\cdot}OH,x\ H_2O)$. This Paper reports a study of the reaction as a function of temperature.

Since the total sulphite concentration is given by the sum of $[SO_2{\cdot}H_2O]$, $[HSO_3^-]$, and $[SO_3^{2-}]$, and the total hydroxylamine concentration by the sum $[NH_3OH] + [NH_2OH]$, the rate law can be rewritten as

$$-\mathrm{d}[\text{total sulphite}]\mathrm{d}t = k_{\text{obs.}}[SO_2,H_2O][NH_2{\cdot}OH](1 + K_1[H^+]^{-1} + K_2K_2[H^+]^{-2})(1 + [H^+]K_{\mathrm{n}}^{-1})$$

where K_1, K_2, and K_{n} are, respectively, the first and second dissociation constants for sulphurous acid and the acid dissociation constant for hydroxylamine. The values of K_2 and K_n are small compared with K_1, so that at pH 4 the rate law can be simplified to

$$-\mathrm{d}[\text{total sulphite}]/\mathrm{d}t = k_{\text{obs.}}\,K_1K_n^{-1}\,[SO_2,H_2O][NH_2{\cdot}OH].$$

Table 1 lists the values found for the rate constant $k_{\text{obs.}}$ over the range studied. The value of K_1 decreases with increasing temperature while that of K_n increases, so that the ratio $K_1K_n^{-1}$ is largest at 1·0°:

Temp.	1·0°	10·5°	20·0°	25·0°	30·0°	35·0°	45·0°
$10^{-3}K_1K_n^{-1}$	64·7	39·0	22·7	16·4	11·7	9·10	4·57

The percentage of ammonia found in the products was independent of the extent of reaction and decreased from 40% at 1·0° to 20% at 10·5°, 9% at 25·0°, and 3% at 45·0°.

Temp.	[Total sulphite]$_{\text{init.}}$ (M)	$k_{\text{obs.}}$ (M^{-1} min.$^{-1}$)
1·0°	0·194	0·0075
10·5	,,	0·0193
20·0	,,	0·059$_5$
20·0	0·076	0·060
25·0	0·194	0·114
30·0°	0·097	0·208
30·0	0·194	0·206
35·0	,,	0·374
45·0	,,	1·34
45·0	0·097	1·38

As the two transition complexes are described by the same empirical formula, the rate law can be written in the general form

$$-\mathrm{d}\,[\text{total sulphite}]/\mathrm{d}t = (k_1 + k_2)\,[SO_2,H_2O][NH_2OH],$$

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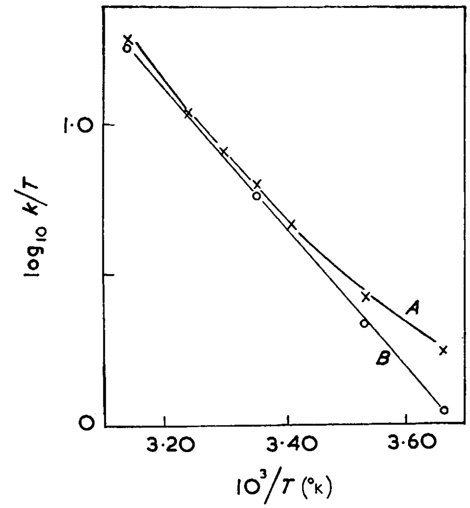
[1] H. H. Sisler and L. F. Audrieth, *J. Amer. Chem. Soc.*, 1939, **61**, 3389.

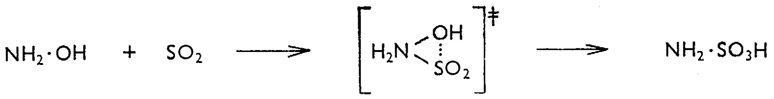
[2] D. S. Brackman and W. C. E. Higginson, *J.*, 1953, 3896.

the sum of k_1 and k_2 will be given by $k_{\text{obs.}}K_1K_n^{-1}$ and the ratio k_1/k_2 by the corresponding ratio of the products, $[NH_2SO_3H]/[NH_3]$. The Figure shows a logarithmic plot of $k_{\text{obs.}}K_1K_n^{-1}$ as a function of the absolute temperature and a similar plot of $k_{\text{obs.}}K_1K_n^{-1}[NH_2SO_3H]/([NH_2SO_3H] + [BH_3])$. The activation parameters obtained from the Figure for the sulphamic acid formation are $\Delta H^{\ddagger} = 10{\cdot}9$ kcal. mole^{-1} and $\Delta S^{\ddagger} = -16$ e.u. A plot of the rate constants of the ammonia reaction gives $\Delta H^{\ddagger} = 1$ kcal. mole^{-1} and $\Delta S^{\ddagger} = -56$ e.u.

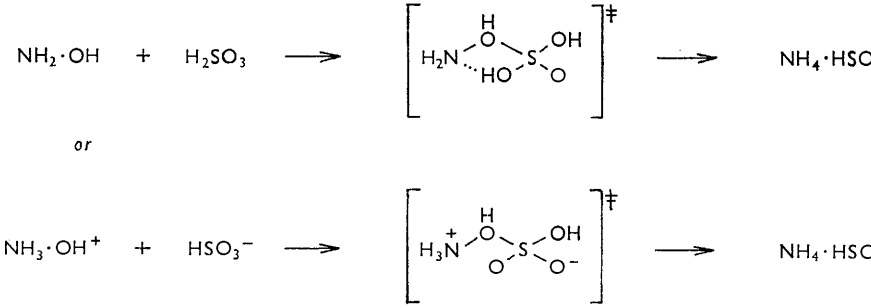


(*A*) $k = k_{\text{obs.}}K_1K_n^{-1}$. (*B*) $k = k_1$, the specific rate for the formation of sulphamic acid alone.

Formation of the sulphamic acid involves attack by the sulphur dioxide on the hydroxylamine nitrogen:



whereas formation of ammonium bisulphate requires attack at the hydroxylamine oxygen:



An examination of models shows that the simultaneous formation of ammonia and sulphuric acid (or ammonium ion and bisulphate ion) impose severe steric conditions on the activated complex, and this is reflected in the negative entropy of activation which is much more unfavourable than might be predicted on the basis of any charge separation.

EXPERIMENTAL

Materials.—The purest grades available of sodium sulphite and hydroxylamine (" Certified reagent ") were used without further purification. Stock solutions of these chemicals in distilled water were prepared and the molarities checked as described previously.[2] Enough sodium ethylenediaminetetra-acetate was added to the sulphite solution to give a concentration of 0·008 moles for each mole of sulphite. Free hydroxylamine was prepared by the action of sodium propoxide in propanol on the hydrochloride. The base was stored at −78° until required.

Kinetic Measurements.—Glass-stoppered flasks containing the solutions of sulphite, hydroxylamine hydrochloride, and a sodium acetate–acetic acid buffer were equilibrated in a water bath constant to $\pm 0{\cdot}05°$. Equal volumes (100 ml.) of the reactant solutions were added to 200 ml. of the buffer, and concentrations were such that the ionic strength of the reactant solution was 0·5, pH 4·1 and [total sulphite]/[total hydroxylamine] at zero time 2·00. The reaction was followed by removing 25 ml. aliquot portions, quenching in a solution of potassium tri-iodide in 1N-sulphuric acid, and determining the concentrations of sulphite, sulphamic acid, and ammonia as described previously.[2] Reactions were followed to at least 95% completion.

Determination of Acid Dissociation Constants.—A solution of sodium sulphite was titrated with sulphuric acid and a solution of hydroxylamine hydrochloride with standard sodium hydroxide at each of the temperatures 4·0, 20·0, and 45·0°. Enough sodium perchlorate was added to make the ionic strength of each solution 0·5 when $[SO_2{\cdot}H_2O] = [HSO_3^-]$ or $[NH_3OH^+] = [NH_2OH]$. The dissociation constants for the other temperatures were obtained from equations derived from the experimental values. For sulphurous acid, pK_1 is given[3] at T°K by

$$\mathrm{p}K_1 = 3021/T + 0{\cdot}0402T - 20{\cdot}487$$

and for hydroxylamine,

$$\mathrm{p}K_n = 1517/T - 0{\cdot}0038T + 1{\cdot}893$$

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[3] R. A. Robinson and H. S. Harned, *Trans. Faraday Soc.*, 1940, **36**, 973.