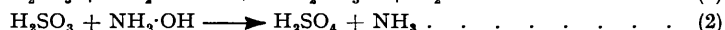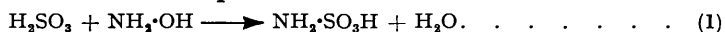**796.** *The Reaction between Hydroxylamine and Sodium Sulphite in Solution in Dilute Acid.*

By D. S. BRACKMAN and W. C. E. HIGGINSON.

The kinetics of the reaction between hydroxylamine and sodium sulphite, and the properties of sulphamic acid and ammonia formed have been studied in the pH range 1—7. The mechanism of the reaction is discussed.

IN dilute acid solution hydroxylamine and sulphurous acid react directly to give sulphamic acid and small amounts of ammonia and sulphuric acid :

$$H_2SO_3 + NH_2 \cdot OH \longrightarrow NH_2 \cdot SO_3H + H_2O. \quad \quad \ldots \ldots \quad (1)$$

$$H_2SO_3 + NH_2 \cdot OH \longrightarrow H_2SO_4 + NH_3. \quad \quad \ldots \ldots \quad (2)$$

Sisler and Audrieth (*J. Amer. Chem. Soc.*, 1939, **61**, 3389) showed that in strongly acid or strongly alkaline solution no reaction occurs, and proposed a reaction mechanism for the formation of sulphamic acid involving reaction between sulphur dioxide and hydroxylamine molecules. Reaction between other species present in solution could lead to similar observations, and these authors did not examine the effect of changes of acidity upon the formation of ammonia by reaction (2). We have determined the proportion of ammonia formed to hydroxylamine consumed at different values of pH, and the dependence of the rate of disappearance of sulphite upon pH. This enables more reliable conclusions to be drawn about the reaction mechanism.

Hydroxylamine hydrochloride and excess of sodium sulphite were allowed to react in the pH range 1·5—7·05. The sulphite, ammonia, and sulphamic acid concentrations were determined at the end of the reaction, and in some cases before reaction was complete. An accurate suitable method of estimating hydroxylamine was not available; however, when reaction was complete the consumption of sulphite was within $\pm 1\%$ of the hydroxylamine used, and in all cases the sum of sulphamic acid and ammonia concentrations was within $\pm 2\%$ of the sulphite consumption. We conclude that throughout the ratio of the sulphite and hydroxylamine consumptions is unity. In the annexed Table the proportion of ammonia formed to sulphite and hydroxylamine consumed is shown for several pH values. In these experiments the initial total sulphite concentration was between 0·05 and 0·20M, and the initial total hydroxylamine concentration was approximately half that of the sulphite. The temperature was 25°. (Here and subsequently " total hydroxylamine " refers to the sum of $NH_2 \cdot OH$ and $NH_2 \cdot OH \cdot H^+$ concentrations, and total sulphite to the sum of SO_3^-, HSO_3^-, H_2SO_3, and dissolved SO_2 concentrations.)

pH	1·5	1·5	1·5	1·5	1·5	3·5	4·7	4·7	4·7	4·7	6·0	6·0	6·0	6·0	7·05
% reaction	29	45	67	91	100	100	45	71	90	100	29	51	96	100	80
$\Delta[NH_3]/\Delta[NH_2 \cdot OH]$, %	9·0	9·5	9·1	9·2	9·3	8·5	9·7	9·6	9·5	9·5	12·1	15·1	12·0	12·0	8·8

These results show that throughout a given experiment the proportion of ammonia formed is constant, and that this proportion varies little with pH over the range studied. The rates of formation of sulphamic acid and of ammonia and sulphuric acid thus depend in the same way upon pH and reactant concentrations, *i.e.*, the transition complexes of reactions (1) and (2) are kinetically indistinguishable. In finding the form of this dependence by kinetic experiments it was therefore sufficient to determine the concentration of sulphite only.

The rate of disappearance of sulphite was determined in experiments in the pH range 1·0—6·8. The initial sulphite concentration varied from 0·046 to 0·070M, and the initial hydroxylamine concentration from 0·021 to 0·042M. The reaction was studied to *ca.* 85% consumption of the hydroxylamine, sulphite always being in excess. The equivalence of sulphite and hydroxylamine being assumed, good second-order rate plots were obtained. A plot of the second-order rate constants, k, on an arbitrary scale, against pH is shown in the Figure, where $k = \{d[\text{total sulphite}]/dt\}/[\text{total sulphite}][\text{total hydroxylamine}]$. The full curve A is a plot of the product, on an arbitrary scale, of the fractions of total sulphite and total hydroxylamine present as HSO_3^- and $NH_2 \cdot OH, H^+$ in solutions of the pH indicated. Curve B is a similar plot of the product of the fractions present as HSO_3^- and $NH_2 \cdot OH$. In evaluating these products, values of the first and the second dissociation constant of sulphurous acid, K_{s1} and K_{s2}, have been taken as $1·72 \times 10^{-2}$ and
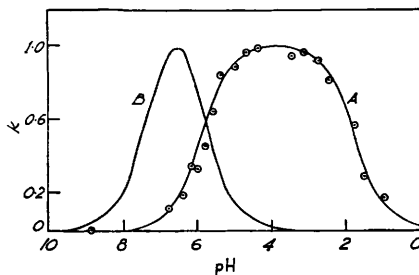
$6·24 \times 10^{-8}$ mole l.$^{-1}$, respectively (Tartar and Garretson, *J. Amer. Chem. Soc.*, 1941, **63**, 808), and the acid dissociation constant of the hydroxylammonium ion, K_N, as $1·04 \times 10^{-6}$ mole l.$^{-1}$ (Hagisawa, *Bull. Inst. Phys. Chem. Res., Tokyo*, 1941, **20**, 251). These are thermodynamic dissociation constants, and it is therefore an approximation to use them in the above manner.

The Figure shows that the observed variation of the rate constants with pH follows curve A fairly closely, and that within experimental error there is no contribution from curve B. We cannot, however, conclude that reaction occurs between $NH_2 \cdot OH, H^+$ and HSO_3^-, since plots of the functions

$$\frac{[H_2SO_3][NH_2 \cdot OH]}{[\text{total sulphite}][\text{total hydroxylamine}]} \quad \text{and} \quad \frac{[SO_2][NH_2 \cdot OH]}{[\text{total sulphite}][\text{total hydroxylamine}]}$$

against pH give precisely the same form of curve. Thus it is impossible to maintain that reaction occurs between any one of these pairs of molecules or ions, and though the transition complex can formally be represented as containing SO_2, $NH_2 \cdot OH$, and an unspecifiable number of water molecules, the atomic arrangement within this complex is also uncertain. The detailed mechanism of the reaction cannot therefore be decided by kinetic experiments, as implied by Sisler and Audrieth (*loc. cit.*). Our work does however enable us to reject the alternative reaction path involving the formation of a negatively charged transition complex containing $NH_2 \cdot OH$ and HSO_3^- which would also lead to a maximum rate in weakly acid solution (curve B).

At ionic strength 0·5 and 25° the second-order velocity constant,

$$k = 2·09 \times 10^{-3}[H^+]^2/([H^+] + K_{s1})([H^+] + K_{s2})([H^+] + K_N)$$

mole^{-1} l. min.$^{-1}$, and k attains the maximum value of 0·120 mole^{-1} l. min.$^{-1}$ at pH 3·9.

EXPERIMENTAL

" AnalaR " or recrystallised reagents were used. Hydroxylamine hydrochloride stock solution was standardised against potassium bromate (Kurtenacker and Wagner, *Z. anorg. Chem.*, 1922, **120**, 261). The stock sodium sulphite solution contained *ca.* 0·008 mole of disodium ethylenediaminetetra-acetate per mole of sulphite and was standardised against iodine. Such a solution, even in contact with air, is relatively stable, probably because traces of free copper ions are removed by the complexing agent, and the copper-catalysed aerial oxidation to sulphate (Titoff, *Z. physikal. Chem.*, 1903, **45**, 641) is thereby prevented. As an added precaution the stock solution was kept under nitrogen, and most experiments were done under nitrogen.

Except for experiments at pH 1—2, reaction mixtures were buffered with phosphate ($HPO_4^-/H_2PO_4^-$), acetate, formate, or chloroacetate mixtures as appropriate. Concentrations of reactants were so chosen that in most cases the change in pH during an experiment was not more than 0·05. At pH 1—2 hydrochloric acid and sodium chloride were used; here somewhat larger changes in pH occurred, and an average value was taken. In all experiments the initial ionic strength was 0·5.

Total sulphite was found by adding the sample to a small excess of iodine in sufficient 3N-sulphuric acid to make the final solution approximately N with respect to sulphuric acid. Excess of iodine was determined by slow titration with standard sodium thiosulphate solution. Under these conditions hydroxylamine is not affected by iodine. Ammonia was determined by the Kjeldahl method; before the solution was made alkaline, hydroxylamine and sulphite were removed by potassium permanganate oxidation in acid solution. Sulphamic acid was determined by titration against sodium nitrite in acid solution (Bowler and Arnold, *Analyt. Chem.*, 1947, **19**, 336) after the hydroxylamine and sulphite had been removed.

The Reaction Catalysed by Transition-metal Ions.—Raschig (" Schwefel- und Stickstoff-studien," Verlag Chemie, Berlin, 1924, p. 225) found that at pH 6—7·5 more hydroxylamine than sulphite was consumed, and nitrogen was evolved. At pH 7·2 with approx. 0·1M-sulphite and -hydroxylamine, and with 10^{-4}M-iron(III) or -copper(II) ion we found that a gas was evolved and that the consumption ratio of hydroxylamine to sulphite was approx. 1·85 : 1. The hydroxylamine concentration in these experiments was determined by titration with iodine at pH *ca.* 4·7 (acetate buffer), after sulphite had been estimated as above. This method is approximate, but the hydroxylamine concentration could be determined with an accuracy of ±5% (cf. Bray, Simpson, and MacKenzie, *J. Amer. Chem. Soc.*, 1919, **41**, 1363). Using unpurified reagents without deliberate addition of transition-metal ions we observed a very slow evolution of gas at pH 7·2, and we think it possible that Raschig's results were obtained owing to trace impurities of this kind. In our main experiments the ethylenediaminetetra-acetate introduced with the sulphite solution was probably effective in suppressing this reaction.

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