

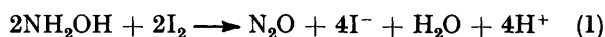
## Kinetics and Mechanism of the Oxidation of Hydroxylamine by Iodine

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The rate law for the iodine oxidation of hydroxylamine in acidic aqueous solution has been determined and a plausible mechanism is suggested. The reactivity of unprotonated hydroxylamine is much higher than that of the protonated form. The reaction is autoinhibitory: the rate is inversely proportional to the first and second power of the iodide concentration due to two pre-equilibria.

We discovered recently that the oxidation of hydroxylamine by iodate or periodate ion is an oligo-oscillatory reaction: the concentration of iodide may show three extrema during the reaction; iodine is also formed. Since no information on the kinetics and mechanism of the reaction between iodine and hydroxylamine was available we decided to undertake this study.

In weakly alkaline medium the reaction takes place smoothly and rapidly according to the stoichiometry (1). According to Bartousek<sup>1</sup> this reaction can be



applied to the iodometric determination of hydroxylamine provided the pH of the solution is adjusted by the addition of solid magnesium oxide. We found this method to be reliable. However, in acidic media the reaction is rather slow and the stoichiometry depends on the pH and the ratio of hydroxylamine to iodine.

### EXPERIMENTAL

All chemicals were of analytical grade and used without further purification. The solutions were prepared using doubly distilled water. Iodine was dissolved in acetic acid.

**Analytical Procedures.**—Hydroxylamine was determined iodometrically using starch as indicator and solid magnesium oxide to adjust the pH. The iodide-ion concentration was monitored using a Radelkis OP-I 7112D iodide-selective electrode, with a saturated calomel electrode as reference and a Radiometer PHM64 pH meter. We found that this electrode could not distinguish between  $\text{I}^-$  and  $\text{I}_3^-$ . The sum of the concentrations of  $\text{I}_2$  and  $\text{I}_3^-$  was spectrophotometrically determined at the isosbestic point (468 nm;  $\epsilon = 740 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) using a Beckman Acta III spectrophotometer. Nitrous acid was also determined spectrophotometrically using the Griess-Ilosvay reaction. Two reagent solutions were prepared: A, sulphanilic acid (0.5 g) dissolved in 30% acetic acid (150  $\text{cm}^3$ ); B,  $\alpha$ -naphthylamine (0.1 g) dissolved in hot water (20  $\text{cm}^3$ ) and poured into 30% acetic acid (180  $\text{cm}^3$ ). Immediately prior to measurement, equal volumes of A and B were mixed. Samples (0.1  $\text{cm}^3$ ) of the reaction mixtures were removed and added to a mixture of the reagents (10  $\text{cm}^3$ ). The absorbance was determined after 20 min. A calibration curve was obtained by an analogous procedure using sodium nitrite solution of known concentration. The gaseous products were analysed by an ATOMKI NZ-850 quadrupole mass spectrometer.

**Kinetic Experiments.**—All solutions were deoxygenated by bubbling argon through them. The pH was adjusted using acetic and monochloroacetic acids. The reaction

mixtures were thermostatted at  $25 \pm 0.2$  °C. Reaction was initiated by injecting a small volume of iodine dissolved in glacial acetic acid into the deoxygenated reaction mixture in the cell.

**Calculation.**—The system of differential equations was solved numerically by a fourth-order Runge-Kutta method using a Hewlett-Packard 9810 calculator.

### RESULTS AND DISCUSSION

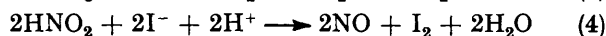
**Stoichiometry.**—The ratios of the amount of reacted iodine to hydroxylamine and of the initial concentrations at pH 2.53 are given in Table 1. It appears that in the

TABLE 1

Ratios of the amounts of reacted iodine and hydroxylamine and of initial concentrations of the reactants. pH = 2.53,  $[\text{I}_2]_0 = 9.0 \times 10^{-4} \text{ mol dm}^{-3}$

$[\text{I}_2]_0/[\text{NH}_2\text{OH}^+]_0$	$[\text{I}_2]/[\text{NH}_2\text{OH}^+]$
4.5	1.62
3.0	1.53
2.2	1.45
1.8	1.25
1.5	1.19
1.3	1.11
1.1	1.03
1.0	0.97
0.8	1.01
0.5	1.05

case of excess of iodine there is a deviation from the stoichiometry (1). The dependence of the stoichiometry of the oxidation of hydroxylamine on the excess of oxidant is a general observation and was also noted when cerium(IV),<sup>2</sup> hexacyanoferrate(III),<sup>3</sup> chromium(VI),<sup>4</sup> and cobalt(III)<sup>5</sup> were used as oxidants. In the present case it is due to the sequence of reactions (2)–(4). The



contributions of the various reactions to the consumption of hydroxylamine and iodine are determined by the kinetics of the reaction. According to the mass spectrometric analysis of the gaseous products in the case where hydroxylamine is in excess, mainly  $\text{N}_2\text{O}$  is formed besides NO, while no trace of  $\text{N}_2$  could be detected. If iodine is in excess, only trace amounts of  $\text{N}_2\text{O}$  are found and slow evolution of NO is observed.

**Kinetics.**—As can be seen from Figure 1 the rate of reaction decreases sharply with increasing ionic strength

at low salt concentrations but is practically independent of the ionic strength in the range  $I = 0.2$ – $1.0$  mol  $\text{dm}^{-3}$ . In all kinetically evaluated experiments the ionic strength was within this range and in most of the experiments was  $0.2$  mol  $\text{dm}^{-3}$ .

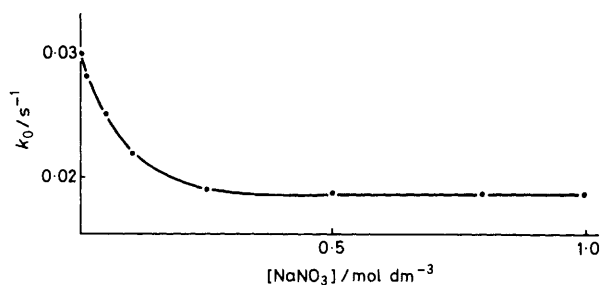


FIGURE 1 Dependence of the pseudo-first-order rate constant on ionic strength.  $[\text{I}_2]_0 = 5.0 \times 10^{-4}$ ,  $[\text{NH}_3\text{OH}^+]_0 = 1.0 \times 10^{-3}$ , and  $[\text{H}^+] = 4.17 \times 10^{-3}$  mol  $\text{dm}^{-3}$

In a 1 mol  $\text{dm}^{-3}$  acetic acid solution ( $[\text{H}^+] = 4.17 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ) the initial rate is proportional to the concentrations of both iodine and hydroxylamine. The dependence of the pseudo-first-order rate constant on hydroxylamine concentration is illustrated in Figure 2.

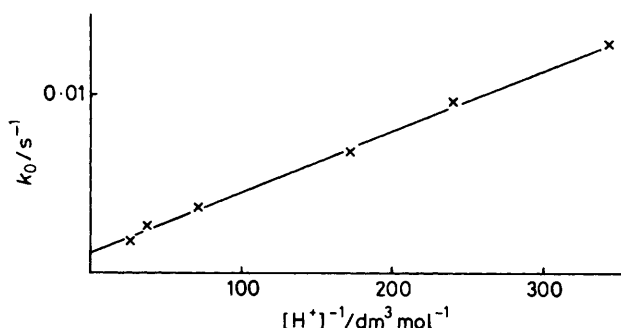


FIGURE 2 The pseudo-first-order rate constant as a function of reciprocal hydrogen-ion concentration.  $[\text{I}_2]_0 = [\text{NH}_3\text{OH}^+]_0 = 5.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$

The reaction is autoinhibitory, *i.e.* iodide ion, one of the products of the reaction, decreases the rate. Autoinhibition is a rather unusual kinetic phenomenon. In principle, autoinhibition is to be expected in all oxidations by iodine due to the difference in the rate of reactions involving iodine and tri-iodide ion respectively. However, in most cases the difference is insufficient to cause autoinhibition to become manifest. As is apparent from Figure 3, in this particular reaction iodide ion has a large inhibitory effect and the initial rate is not simply inversely proportional to the iodide concentration.

$$\frac{1}{[\text{I}_2]_0} \frac{d[\text{I}_2]_0}{dt} = k_0 = \left( k_2 + \frac{k_2'}{[\text{H}^+]} \right) \frac{[\text{NH}_3\text{OH}^+]_0}{1 + K[\text{I}^-]_0 + Q[\text{I}^-]_0^2} \quad (5)$$

as follows:  $k_2 = 2.34$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>;  $k_2' = 6.67 \times 10^{-2}$  s<sup>-1</sup>;  $K = 785$  dm<sup>3</sup> mol<sup>-1</sup>; and  $Q = 4.94 \times 10^4$  dm<sup>6</sup> mol<sup>-2</sup>. Agreement between the experimentally

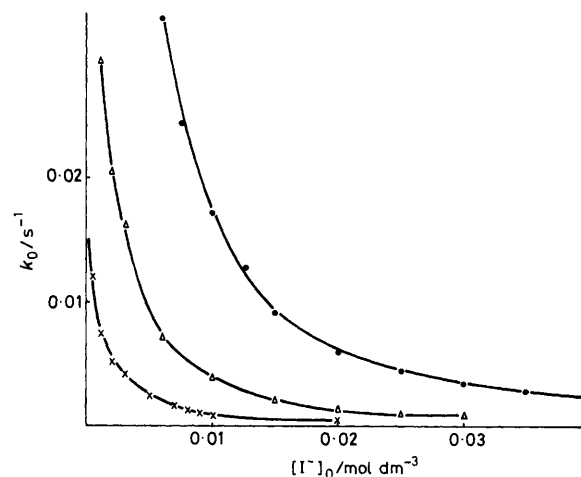


FIGURE 3 The effect of iodide-ion concentration on the pseudo-first-order rate constant.  $[\text{I}_2]_0 = 5.0 \times 10^{-4}$ ,  $[\text{H}^+] = 4.17 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ;  $[\text{NH}_3\text{OH}^+]_0 = 5.0 \times 10^{-4}$  (●),  $2.0 \times 10^{-3}$  (△), and  $1.0 \times 10^{-2}$  mol  $\text{dm}^{-3}$  (×)

determined and the calculated constants is reasonably good as can be judged from a comparison of the data from several randomly selected experiments (Table 2).

Although equation (5) satisfactorily describes the concentration dependence of the initial rate, it fails to

TABLE 2

Measured and calculated values of first-order rate constants at  $[\text{I}_2]_0 = 5.0 \times 10^{-4}$ ,  $I = 0.2$  mol  $\text{dm}^{-3}$ , and  $25^\circ\text{C}$

Initial concentrations/mol $\text{dm}^{-3}$			$10^3 k_0/\text{s}^{-1}$	
$10^4$ $[\text{NH}_3\text{OH}^+]_0$	$10^3$ $[\text{I}^-]_0$	$10^3$ $[\text{H}^+]$	Measured	Calculated
5	1.0	4.17	4.88	4.99
5	2.5	4.17	3.10	2.80
5	3.0	4.17	2.58	2.41
5	4.0	4.17	1.86	1.86
5	10.0	4.17	0.69	0.67
5	20.0	4.17	0.26	0.25
5	20.0	4.17	0.30	0.25
50	3.0	4.17	24.4	24.1
50	4.0	4.17	18.8	18.6
50	5.0	4.17	15.50	14.9
50	6.0	4.17	13.1	12.3
50	8.0	4.17	9.20	8.80
50	10.0	4.17	7.60	6.70
50	20.0	4.17	2.49	2.51
100	2.0	4.17	52.2	66.2
100	4.0	4.17	32.8	37.1
100	6.0	4.17	22.2	24.5
100	7.0	4.17	20.1	20.5
100	8.0	4.17	17.1	17.5
100	9.0	4.17	14.9	15.2
100	10.0	4.17	13.4	13.3
100	20.0	4.17	4.98	5.03
100	40.0	4.17	1.92	1.65
7.5	10.0	4.17	1.02	0.99
10	10.0	4.17	1.57	1.33
25	10.0	4.17	3.40	3.33
5	0	2.95	12.4	12.5
5	0	4.17	9.32	9.15
5	0	5.88	6.42	6.35
5	0	14.12	3.48	3.53
5	0	28.84	2.48	2.32
5	0	39.81	1.72	2.00

give an account, when combined with reaction (2), of the change of concentration with time. The deviations between the experimentally determined and calculated concentrations of iodine, hydroxylamine, and nitrous acid increase with increasing extent of reaction. Evidently, the rate of reactions (3) and (4) should also be considered. These two reactions can be studied independently and some data are available. Hughes and Stedman<sup>6</sup> studied the reaction between nitrous acid and hydroxylamine. Using their rate equation, (6), and the

$$v_3 = k_3[\text{HNO}_2][\text{NH}_3\text{OH}^+][\text{H}^+] \quad (6)$$

activation energy determined by them, the rate constant at 25 °C is  $k_3 = 2.5 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ . The rate law for the reaction between nitrous acid and iodide<sup>7</sup> is given by equation (7) where  $k_4 = 3.7 \times 10^3 \text{ dm}^9 \text{ mol}^{-3} \text{ s}^{-1}$  and

$$v_4 = k_4[\text{HNO}_2][\text{H}^+][\text{I}^-]^2 + k_4'[\text{HNO}_2]^2[\text{H}^+]^2[\text{I}^-]^2 \quad (7)$$

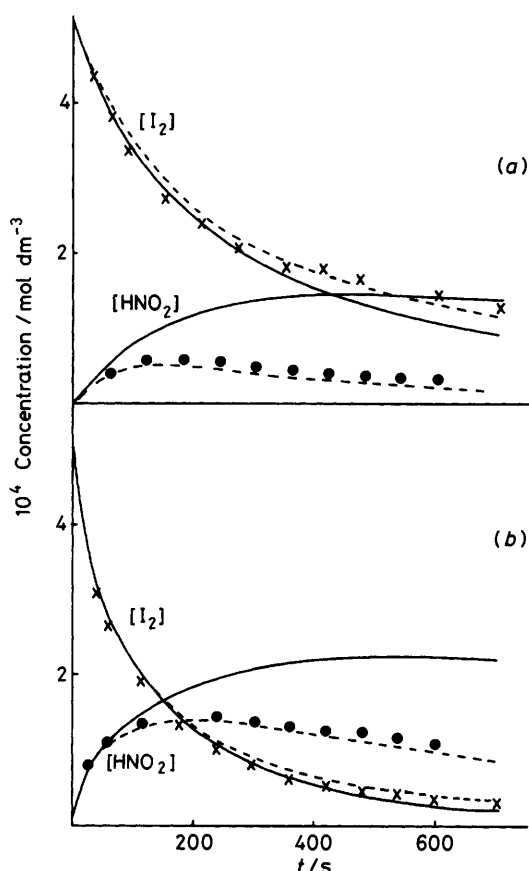


FIGURE 4 Kinetic curves of the iodine-hydroxylamine reaction. The points indicate experimentally measured values whereas the continuous line indicates the calculated values using the following set of constants:  $k_3 = 2.34 \text{ dm}^6 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $k_3' = 6.67 \times 10^{-2} \text{ s}^{-1}$ ,  $K = 785 \text{ dm}^3 \text{ mol}^{-1}$ ,  $Q = 4.94 \times 10^4 \text{ dm}^6 \text{ mol}^{-2}$ ,  $k_3 = 2.5 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ ,  $k_4 = 3.7 \times 10^3 \text{ dm}^9 \text{ mol}^{-3} \text{ s}^{-1}$ , and  $k_4' = 3.7 \times 10^{10} \text{ dm}^{15} \text{ mol}^{-5} \text{ s}^{-1}$ . Dashed lines represent the curves calculated using the same constants but also considering the second term of rate equation (6') ( $k_3' = 1 \times 10^4 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ ).  $[\text{I}_2]_0 = [\text{NH}_3\text{OH}^+]_0 = 5.0 \times 10^{-4}$ ,  $[\text{H}^+] = 2.9 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{I}^-]_0 = 2.0 \times 10^{-3}$  (a), 0 mol  $\text{dm}^{-3}$  (b)

$k_4' = 3.7 \times 10^{10} \text{ dm}^{15} \text{ mol}^{-5} \text{ s}^{-1}$ . Using these rate constants, good agreement was found between the experimental and calculated iodine concentrations, whereas the deviations between the found and calculated concentrations of nitrous acid monotonously increase with time (Figure 4).

According to the investigations of Hughes and Stedman,<sup>6</sup> bromide and thiocyanate ions catalyse reaction (3) and it is thus reasonable to assume that iodide is an even more active catalyst of this reaction. That is, the rate equation (6) should be extended to give (6'). It is

$$v_3 = k_3[\text{HNO}_2][\text{NH}_3\text{OH}^+][\text{H}^+] + k_3'[\text{NH}_3\text{OH}^+][\text{HNO}_2][\text{I}^-] \quad (6')$$

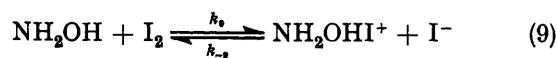
apparent from the curves of Figure 4 that using  $k_3' = 1 \times 10^4 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$  gives a fairly good agreement between the calculated and found concentrations of nitrous acid throughout the reaction.\*

**Mechanism.**—The dependence of the initial rate on hydrogen-ion concentration indicates that the reaction takes place along two pathways involving either unprotonated or protonated hydroxylamine. Although it follows from the protonation constant of hydroxylamine<sup>8</sup> ( $K_p = 1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1}$ ) that at the pH of our reaction mixture (pH 1.3–3.0)  $\text{NH}_3\text{OH}^+$  is the dominant species, the contribution of the route involving  $\text{NH}_2\text{OH}$  is greater.

To explain the dependence of rate on iodide-ion concentration it is not enough to consider the triiodide ion equilibrium (8),  $K_8 = 725 \text{ dm}^3 \text{ mol}^{-1}$  at 25 °C



and to assume a much reduced reactivity of  $\text{I}_3^-$  relative to that of  $\text{I}_2$ . A similar dependence of rate on the concentration of iodide was recently observed in the reaction of hydrazine with iodine. King *et al.*<sup>9</sup> assumed that in the iodine oxidation of hydrazine there was an iodide-producing pre-equilibrium. Analogously, reactions (9)–(13) are taken into account. Applying the steady-



state treatment to the  $\text{NH}_2\text{OHI}^+$  and  $\text{NH}_3\text{OHI}^{2+}$  intermediates and considering that the free iodide concentration is practically equal to the initial total iodide concentration, equation (14) is obtained for the dependence of apparent rate constant on the concentration of iodide and hydrogen ions where  $K_p$  is the protonation constant of hydroxylamine. From a comparison of

\* The authors are grateful to one of the referees for his helpful suggestion to take the catalytic effect of iodide ion into account.

$$k_0 = k_{12} \left( \frac{[\text{NH}_3\text{OH}^+]_0}{\{(k_{-12}/k_{13}) + K_8\}[\text{I}^-]_0 + (k_{-12}K_8/k_{13})[\text{I}^-]_0^2 + 1} \right) + \left( \frac{k_9}{[\text{H}^+]K_p} \right) \left( \frac{[\text{NH}_3\text{OH}^+]_0}{\{k_{-9}/k_{10} + K_8\}[\text{I}^-]_0 + (k_{-9}K_8/k_{10})[\text{I}^-]_0^2 + 1} \right) \quad (14)$$

equations (5) and (14), it follows that  $k_{-9}/k_{10}$  does not differ much from  $k_{-12}/k_{13}$ , and the experimentally obtained values are as follows:  $k_2 = k_{12}$ ;  $k_2' = k_9/K_p$ ;  $K = k_{-12}/k_{13} + K_8$ ; and  $Q = K_8k_{-12}/k_{13}$ . Since  $K = 785 \text{ dm}^3 \text{ mol}^{-1}$  and  $Q = 4.94 \times 10^4 \text{ dm}^6 \text{ mol}^{-2}$ , a value for  $K_8$  of  $716 \text{ dm}^3 \text{ mol}^{-1}$  is obtained which agrees well with the independently obtained equilibrium constant. It appears that the oxidation of unprotonated hydroxylamine is much faster ( $k_9 = 6.67 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) than that of the protonated species ( $k_{12} = 2.34 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ). Although it is unlikely that there are four orders of magnitude difference between the rates of the reactions involving iodine and tri-iodide ion, the experiments do not allow us to determine the reactivity of the latter.

[1/1112 Received, 14th July, 1981]

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