Kinetics, Mechanism, and Stoicheiometry of the Oxidation of Hydroxylamine by Nitric Acid

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Hydroxylamine is oxidised by nitric acid to form dinitrogen monoxide and nitrous acid, the proportions varying with reaction conditions. The yield $[HNO_2]_\infty/[NH_3OH^+]_0$ is a maximum at *ca.* 4—5 mol dm^{-3} HNO_3, and is also a function of the hydroxylamine concentration. In 5 mol dm^{-3} HNO_3 the limiting yield is *ca.* 0.85 at very low initial hydroxylamine concentrations, but decreases towards zero at higher values of $[NH_3OH^+]_0$. Reaction is only observed at sufficiently high nitric acid concentrations; at 25 °C the cut-off point is *ca.* 2.5 mol dm^{-3} HNO_3. The reaction is characterised by an induction period, followed by a rapid autocatalytic process. Addition of nitrite eliminates the induction period, while addition of nitrite scavengers completely prevents any reaction. Nitrous acid is an essential catalyst for the reaction, and the initial rate of reaction obeys the equation $d[HNO_2]/dt = V_0 = k[HNO_2][NH_3OH^+]$. Isotopic experiments, using ^{15}N-enriched hydroxylamine show that virtually all of the N_2O arises from reaction between HNO_2 and hydroxylamine. The mechanism suggested involves oxidation of unprotonated hydroxylamine by N_2O_4 to form the nitroxyl diradical HNO; this is then further oxidised to HNO_2, which reacts with hydroxylamine to form N_2O.

THE kinetics and mechanism of the reaction between nitrous acid and hydroxylamine have been investigated in considerable detail,[1,2] but very little is known about the oxidation of NH_2OH by nitric acid. Qualitative observations in the literature are held [3a] to support a stoicheiometry (1). There are no kinetic studies. Aqueous solutions of hydroxylammonium nitrate are stable at room temperature, but when they are heated with excess of nitric acid reaction (1) occurs. From qualitative observations of the way in which the solution foamed as dinitrogen monoxide was evolved, it appeared that reaction occurred rather suddenly and rapidly. Brown fumes were observed to be evolved from the boiling solution, presumably nitrogen dioxide, and from this it is clear that equation (1) does not give a completely satisfactory description of the stoicheiometry.

$$4[NH_3OH]^+ + 2\,HNO_3 \longrightarrow 3N_2O + 4[H_3O]^+ + 3H_2O \quad (1)$$

The present paper describes an investigation of this interesting system. The chemistry of hydroxylamine in nitric acid is of potential technological interest, since it has been proposed as a reagent for the reduction of plutonium(IV) to plutonium(III).[3b]

EXPERIMENTAL

Materials.—Most experiments were carried out with solutions of hydroxylammonium nitrate, prepared from hydroxylamine hydrochloride by an anion-exchange method. These solutions proved reasonably satisfactory, but occasionally problems could arise when on standing the solution developed a yellow colour. Kinetic measurements made with these solutions gave results that were not in agreement with our other work, so such yellow solutions were always discarded. Some experiments were carried out with solutions of hydroxylamine sulphate.

Analytical Methods.—Nitrous acid was determined by direct u.v. spectrophotometry, using the peaks at 385 and 370 nm, and analysing by a standard colorimetric procedure. Solutions of hydroxylamine salts were analysed by the standard bromate method,[4] or by titration with standard alkali. Mass-spectrometric analysis of the evolved gas was made on an M.S.9 instrument.

Kinetic Measurements.—Most runs were followed by direct spectrophotometry at 370 nm in a Unicam SP 700 recording instrument, using a thermostatted cell holder. Measurements of the kinetics of reaction between nitrous acid and hydroxylamine were made with a Canterbury SF-3A stopped-flow apparatus.

Isotopic Measurements.—A sample of hydroxylamine hydrochloride, enriched to 97% with nitrogen-15 was obtained from Prochem/B.O.C. Ltd. and used without further purification. Samples of dinitrogen monoxide produced by reaction with isotopically normal nitric acid were separated from traces of nitrogen monoxide by freezing to −130 °C and pumping, and were stored over NaOH. We are indebted to Mr. Clipsham of A.E.R.E., Harwell, for isotopic analyses.

Pressure-rise Measurements.—These were made with a Bell and Howell pressure transducer (4-366-0001-01MO). Since the only gas evolved was dinitrogen monoxide, the apparatus was calibrated by use of the reaction between nitrous acid and hydroxylamine [equation (2)]. The reaction vessel was immersed in a thermostat, and the solution was stirred magnetically. When reaction was sufficiently slow the system gave good kinetic results, with rate constants in agreement with values obtained by other methods. However, when reaction was rapid, going to completion in 20—30 s, then the stirring used was not sufficiently vigorous to maintain satisfactory equilibrium between the liquid and vapour phase.

Temperature Measurements.—As is explained below, the reaction is exothermic, and the reaction solution heats up during the course of the oxidation of hydroxylamine. We have measured the temperature change with a small bead thermistor which is protected by a very thin outer layer of inert material (Mullard VA-3010). Although we have used this in media containing up to 7.8 mol dm^{-3} nitric acid, and at temperatures up to 70 °C, we have not had any problems with corrosion and the characteristics of the bead have remained constant. It responds rapidly to changes in the temperature of its surroundings, within 0.1 s. Thus the thermistor can be used to follow the progress of reaction by measuring the temperature rise.

RESULTS

In our initial experiments we attempted to follow the reaction by a conventional sampling technique, analysing

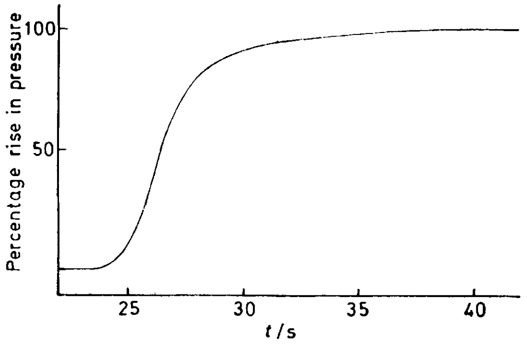

FIGURE 1 Pressure rise as a function of time for the oxidation of 0.4 mol dm^{-3} hydroxylamine by 6.1 mol dm^{-3} HNO_3, initially at 25 °C

for hydroxylamine by the standard bromate method of analysis. The results were confusing, since we usually found either no reaction or complete reaction, and variations in hydroxylamine concentration, nitric acid concentration. and temperature produced no improvement. Attempts to analyse for hydroxylamine by accurate pH titrations gave essentially the same results, and we could not find a consistent pattern of behaviour. At low nitric acid concentrations, <2 mol dm^{-3}, at 25 °C, reaction did not occur, but at higher acidities repeated experiments under apparently identical conditions would sometimes yield different results, 0 or 100% completion of reaction. The problem was solved by working in a closed system and continuously monitoring the pressure by means of a pressure transducer. The resulting curves showed an induction period, followed by a rapid autocatalytic reaction which was usually complete in 20—30 s after the start of the reaction. A typical trace is shown in Figure 1. The length of the induction period was not very reproducible, and probably depended on the presence of traces of nitrous acid in the nitric acid (see below). An increase in temperature generally produced a decrease in the induction period, but we did not find a consistent dependence on nitric acid concentration. This variability, together with the fact that once reaction started it went to completion in less than 30 s, led us to abandon attempts to follow reaction by sampling methods and concentrate upon continuous monitoring techniques.

Stoicheiometry.—Analysis of the gas evolved by mass spectrometry confirmed that it was dinitrogen monoxide; there did not appear to be any other components. Measurements of the pressure of gas liberated indicated that at high concentrations of hydroxylamine, *ca.* 0.1 mol dm^{-3}, *ca.* 96% of the pressure rise expected on the basis of equation (1) was observed. Acid–base titrations also confirmed this stoicheiometry. Dinitrogen monoxide was, however, not the only product. The u.v. spectrum of the 'infinity' solution showed the characteristic peaks of nitrous acid, and this was confirmed by colorimetric analysis. The fact that nitrous acid is a product could account for the fact that brown fumes were observed when hydroxylammonium nitrate was decomposed by boiling nitric acid. Measurements of the yield of nitrous acid, $[HNO_2]_\infty/[NH_3OH^+]_0$, showed that this varied with nitric acid concentration, and also with the initial concentration of hydroxylamine. Typical results are shown in Figure 2, from which it can be seen that the maximum yield is obtained at *ca.* 4—5 mol dm^{-3} HNO_3. Measurements carried out at a given nitric acid concentration showed that the yield increased with decrease in $[NH_3OH^+]_0$, and experiments at 5 mol dm^{-3} gave a limiting yield of nitrous acid of 0.84 at low hydroxylamine concentrations. It is difficult to measure the yield of dinitrogen monoxide at these very low concentrations, and the most that we have been able to do is to measure the amount of N_2O formed at various values of $[NH_3OH^+]_0$, and extrapolate the results to $[NH_3OH^+]_0 = 0$. This gives a yield $[N_2O]_\infty/[NH_3OH^+]_0 = 0.55$. The only other common nitrogen compound that might be a product and be stable under our conditions is the ammonium ion. We have analysed for this species in our infinity solutions, but have not detected any traces of it. The easiest species to analyse is nitrous acid, so we have expressed the stoicheiometry in terms of the amount of nitrous acid formed. Taking z to be 0.84, then the yield of dinitrogen monoxide is

$$[NH_3OH]^+ + 0.5\,(1 + z)[NO_3]^- \longrightarrow 0.25\,(3 - z)\,N_2O + z HNO_2 + 0.5\,(1 - z)H^+ + 0.25\,(7 - z)\,H_2O \quad (2)$$

0.54, in good agreement with the observed value. The fact that the yield of HNO_2 is a function of $[NH_3OH^+]_0$ suggested that the stoicheiometry might well vary during the course of an individual run. Unfortunately, pressure measurements are not a reliable measure of the progress of reaction, as has already been explained, and so we have not obtained direct evidence on this point.

Isotopic Measurements.—A limited number of experiments have been carried out on the decomposition of ^{15}N-labelled hydroxylamine in isotopically normal nitric acid, examining the evolved dinitrogen monoxide mass spectrometrically. The results are summarised in Table 1. The most striking features of note are the facts that the peak at $m/e = 45$ is much more intense than the peaks at $m/e = 44$ and 46, and that the peaks at $m/e = 30$ and 31 are normally of equal intensity. In order to check on the reliability of

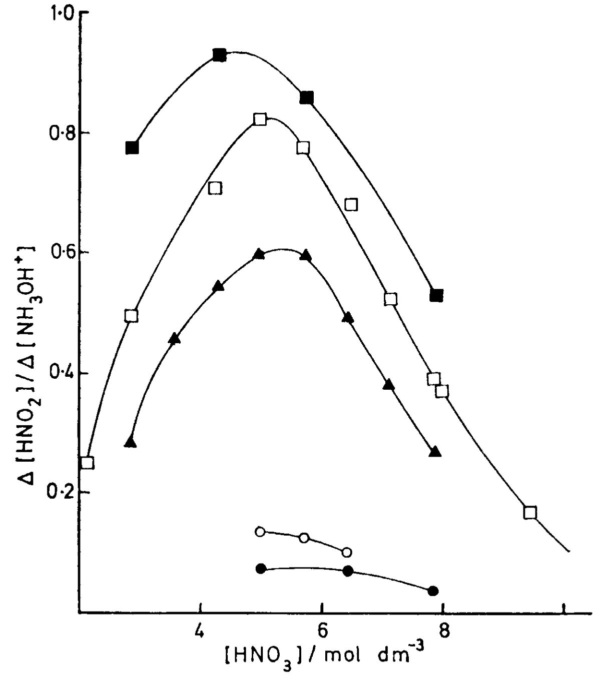

FIGURE 2 Yield of nitrous acid as a function of the concentrations of nitric acid and hydroxylamine at 25 °C. $[NH_3OH^+]_0$/mol dm^{-3} = 0.002 (■), 0.005 (□), 0.01 (▲), 0.1 (○), or 0.2 (●)

TABLE 1

Mass spectrometric measurements on dinitrogen monoxide

Expt. no.	$[HNO_3]$	$[^*NH_3OH^+]$	Relative ion currents at given m/e values				
	mol dm^{-3}		46	45	44	31	30
1E	5.0	0.056 5	5.12	100	3.74	10.2	12.4
1H	5.0	0.013 3	0.35	100	3.6	11	12
1F	5.0	0.001 4	1.44	100	4.33	11.8	12.4
2M	5.0	0.203	22.1	100	3.86	18.4	17.3
2S	5.0	0.001 1	0.85	100	5.43	14.9	17.0
2V	3.4	0.052 3	20.2	100	3.30	19.1	17.0
2W	7.0	0.051 7	1.68	100	3.79	12.6	17.9
1A [a]	$Na[NO_2] + [NH_3OH]^+$		0.23	0.82	100	0.10	23
1B [a]	$Na[NO_2] + [^*NH_3OH]^+$		0.42	100	3.34	10	10
1K [b]	$HNO_2 + [^*NH_3OH]^+$		0.55	100	3.3	11	11

[a] pH 7. [b] 1 mol dm^{-3} $HClO_4$.

our method, we have also examined the N_2O evolved in the reaction between enriched hydroxylamine and isotopically normal nitrous acid (*a*) at pH 7 and (*b*) in excess of perchloric acid. The system at pH 7 was originally investigated by Friedman and Bothner-By,[1] and our results agree with theirs in showing the presence of a symmetrical intermediate, with the nitrogen-15 tracer equally distributed between the two nitrogens of the dinitrogen monoxide. The peaks at $m/e = 30$ and 31 are presumably due to $[NO]^+$ derived from N_2O under electron impact. Our results appear to be self-consistent and reliable. The general conclusion that can be drawn is that the isotopic composition of the N_2O obtained from the oxidation by HNO_3 is similar to that obtained by the hydroxylamine–nitrous acid reaction.

Kinetics.—Attempts to follow the kinetics of reaction by gas evolution were unsuccessful because with the equipment and methods that we were using the rate of pressure build-up was at least partly mass-transfer controlled. Thus our pressure–time curves have provided only qualitative kinetic information. Examination of the rate of pressure build-up in the hydroxylamine–nitrous acid reaction (for which the kinetics have been studied spectrophotometrically) enables us to conclude that in the nitric acid–hydroxylamine reaction the induction period and the autocatalytic characters are real chemical effects, and are not artefacts due to mass-transfer phenomena.

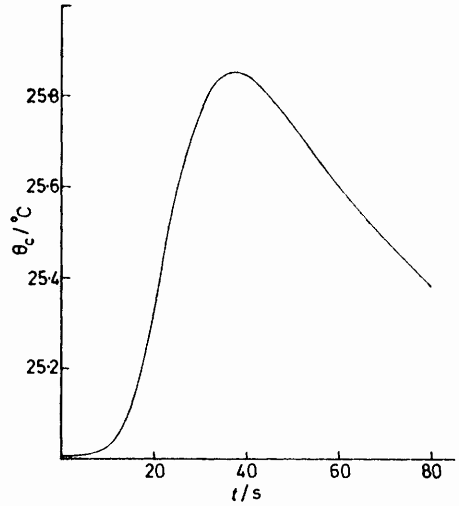

FIGURE 3 Rise of temperature with time during the oxidation of 0.025 mol dm^{-3} hydroxylamine by 4.0 mol dm^{-3} HNO_3

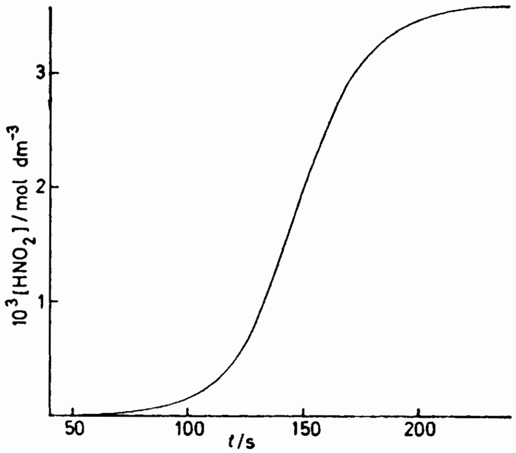

FIGURE 4 Increase of nitrous acid concentration with time in the oxidation of 0.005 mol dm^{-3} hydroxylamine by 5.0 mol dm^{-3} HNO_3 at 25 °C

One effect of the very rapid reaction between nitric acid and hydroxylamine is that it is difficult to carry out experiments under isothermal conditions. The reaction is markedly exothermic. For the decomposition of 0.1 mol dm^{-3} hydroxylammonium ion in 5 mol dm^{-3} HNO_3 in a Dewar vessel the temperature rises by *ca.* 4.5 °C for reactants initially at room temperature. This corresponds to a value of ΔH of *ca.* 210 kJ [per mol of hydroxylamine for the stoicheiometry (1)]. From the known heats of formation of the reactants and products one would expect that in infinite dilution ΔH would be 207 kJ mol^{-1}. Since this heat is liberated over a very short period of time, the rate of conduction of heat from the reaction vessel to the thermostat is not great enough to maintain temperature equilibrium, and the reaction mixture rapidly warms up. This must make some contribution, albeit only a minor one, to the autocatalytic nature of the reaction. This effect makes the interpretation of reaction-time curves complicated when the initial concentration of hydroxylamine is high, and in the present paper we restrict discussion to more dilute solutions, less than 0.01 mol dm^{-3} hydroxylamine, for which temperature rises of less than *ca.* 0.5 °C are observed. We have attempted to use this phenomenon to follow the progress of reaction, rather as in the thermal-maximum method.[5]

We have carried out two types of experiment. In the first hydroxylamine reacts with nitric acid solution in a Dewar vessel. There is a short induction period. The temperature then rises rapidly, finally levelling off giving a sigmoidal curve. The other type of experiment involves a normal reaction vessel immersed in a thermostat, with both the contents of the reaction vessel and the thermostat well stirred. Under these conditions a plot of temperature against time has a maximum, and a typical graph is shown in Figure 3. From the final section of the curve it is possible to obtain the cooling constant from a plot of log ΔT against time, and then by graphical integration to correct for heat losses to the thermostat, and plot heat liberated as a function of time.

Most of our experiments have been carried out by monitoring the increase in nitrous acid concentration by direct u.v. spectrophotometry. These runs showed the same characteristics as those followed by pressure and temperature measurements, an induction period followed by an autocatalytic increase in nitrous acid concentration, which

TABLE 2

Kinetic data on the formation of nitrous acid in the oxidation of hydroxylamine by nitric acid at 25 °C

$[HNO_3]$/mol dm^{-3}	$[NH_3OH^+]$/mol dm^{-3}	10^2k_1/s^{-1}	k_2/dm^3 mol^{-1} s^{-1}	$[HNO_3]$/mol dm^{-3}	$[NH_3OH^+]$/mol dm^{-3}	10^2k_1/s^{-1}	k_2/dm^3 mol^{-1} s^{-1}
2.86	0.01	8.6	8.6	5.71	0.01	11.0	11.0
2.86	0.005	10.2	20.4	5.71	0.005	5.4	10.8
2.86	0.003 75	6.8	18.1	5.71	0.003 75	3.6	9.6
2.86	0.002	3.8	19.0	5.71	0.002	2.5	12.5
3.57	0.01	16.1	16.1	6.43	0.01	8.4	8.4
3.57	0.005	9.8	19.7	6.43	0.005	4.84	9.7
4.28	0.01	16.3	16.3	7.14	0.01	8.1	8.1
4.28	0.005	8.3	16.6	7.14	0.005	4.42	8.8
4.28	0.003 75	5.2	14	7.14	0.005	4.10	8.2
4.28	0.002	3.4	17	7.86	0.01	7.9	7.9
5.0	0.01	12.5	12.5	7.86	0.005	3.2	6.4
5.0	0.005	7.2	14.4	7.86	0.0375	2.75	7.3
				7.86	0.002	1.2	6.0

finally levelled off. A typical run is shown in Figure 4. In none of our experiments did we observe a maximum in the absorbance due to the nitrous acid, followed by a decrease (other than the slight decay on standing due to the instability of HNO_2). Addition of sodium nitrite to the initial reaction solution removed the induction period and increased the rate of reaction. Addition of nitrite scavengers such as sulphamic acid and hydrazine stopped the reaction altogether. Runs carried out at concentrations where the normal yield of nitrous acid was very low, and the main product was dinitrogen monoxide, showed no pressure rise in the presence of added nitrite scavengers. It is thus clear that nitrous acid is an essential catalyst for reaction to take place. Plots of log $[HNO_2]$ against time were linear in the early stages of reaction, and provided pseudo-first-order rate constants k_1. These were independent of the initial nitrite concentration over a ten-fold range, and proved to be proportional to $[NH_3OH^+]_0$ for low hydroxylamine concentrations. Values of $k_2 = k_1/[NH_3OH^+]_0$ are included in Table 2, and are shown graphically in Figure 5. Inspection of this Figure shows that there is a very sharp fall-off in the rate of reaction at low nitric acid concentrations. We have very few data for this region, so the line is indicated by a dashed curve. It appears that as the hydroxylamine concentration increases the fall-off occurs at somewhat higher nitric acid concentrations. Further work on this aspect of the problem is in progress. The activation energy for reaction of 0.05 mol dm^{-3} hydroxylamine in 5 mol dm^{-3} HNO_3 was measured by the temperature-rise method over the range 16—35 °C, and a value of 107 kJ mol^{-1} was obtained. We also confirmed that dissolved oxygen had no effect upon our rates.

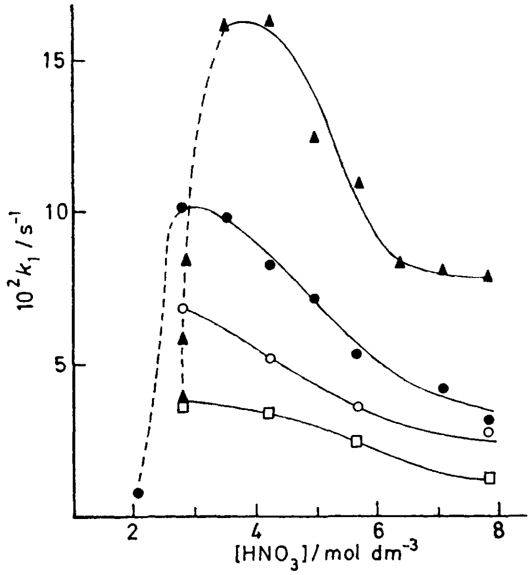

FIGURE 5 Variation of rate of nitrous acid formation in the oxidation of hydroxylamine by nitric acid at 25 °C. $[NH_3OH^+]$/mol dm^{-3} = 0.01 (▲), 0.005 (●), 0.003 75 (○), or 0.002 (□)

Kinetics of the Nitrous Acid–Hydroxylamine Reaction.—Previous work on this reaction in perchloric acid had been carried out at 0 °C, and there were no values for the activation energy in the range of acid concentration of interest. A few experiments were carried out at 25 °C, using solutions containing a large excess of hydroxylamine over nitrite, and reaction was followed by the disappearance of the characteristic peak of nitrous acid at 370 nm. Individual runs gave good pseudo-first-order kinetics with respect to nitrite concentration (k_a). Second-order constants, $k_a/[NH_3OH^+]$, were 19.9, 24.2, 17.6, and 13.1 dm^3 mol^{-1} s^{-1} for 2, 3, 4, and 6 mol dm^{-3} $HClO_4$ respectively. Activation energies calculated from experiments carried out at 0—25 °C were 64.8 and 64.6 kJ mol^{-1} at 4 and 6 mol dm^{-3} $HClO_4$. The variation of rate with concentration of perchloric acid is very similar to that observed at 0 °C.

DISCUSSION

The most interesting feature of this system is that at $>$ *ca.* 2.8 mol dm^{-3} HNO_3 the nitrous acid-catalysed reaction between hydroxylamine and nitric acid actually *generates* nitrous acid. Normally, nitrous acid and hydroxylamine react in acidic media as shown in equation (3), and nitrous acid is consumed.

$$[NH_3OH]^+ + HNO_2 \longrightarrow N_2O + H_2O + [H_3O]^+ \quad (3)$$

The reaction obeys simple second-order kinetics, and at $>$*ca.* 2 mol dm^{-3} mineral acid k_3 decreases slowly with increase of acidity. This has the same kinetic form (4)

$$-d[HNO_2]/dt = k_3[NH_3OH^+][HNO_2] \quad (4)$$

as is observed for the generation of nitrous acid in the present system. We do not, of course, have values for k_3 in HNO_3, but it is reasonable to assume that they will be similar to the values obtained for other mineral acids at the same acidity. We have chosen to use our data obtained for $HClO_4$ at 25 °C to *estimate* values of k_3 for HNO_3, assuming that k_3 will have similar values in solutions of the same H_0 value. These are shown as k_3* in Table 3. It can be seen that they are of the same

TABLE 3

Kinetic data on the oxidation of hydroxylamine by nitric acid at 25 °C

$[HNO_3]$/mol dm^{-3}	2.86	3.57	4.28	5.0	5.71	6.43	7.14	7.86
k_2/dm^3 mol^{-1} s^{-1}	19.1	17.9	16.0	13.5	11.0	9.05	8.37	6.9
k_3^*/dm^3 mol^{-1} s^{-1}	25.3	23.6	20.6	17.9	16.8	16.0	15.3	14.7
k_3/dm^3 mol^{-1} s^{-1}	19.7	14.0	11.1	9.04	8.25	7.86	9.32	10.4
k_4/dm^3 mol^{-1} s^{-1}	38.8	31.9	27.0	22.5	19.3	16.9	17.7	17.3

order of magnitude as k_2, and since the kinetic forms are the same we can write an overall equation (5), where k_4 is the rate constant for the autocatalytic generation of

$$d[HNO_2]/dt = k_2[HNO_2][NH_3OH^+] = (k_4 - k_3)[HNO_2][NH_3OH^+] \quad (5)$$

nitrous acid. All of the values k_2, k_3, and k_4 are functions of nitric acid concentration. We need to be able to assign a value to either k_4 or k_3, the others being obtainable by substitution from the experimentally measured k_2 values. It seems undesirable to use our estimated k_3* values, since the error in these values is uncertain, and we prefer instead to use stoicheiometric data.

The general pattern of reaction in which hydroxylamine is oxidised is clear from the large numbers of studies that have been carried out. The two intermediates commonly postulated are $NH_2O^{\bullet}(-1e)$ HNO $(-2e)$ or species related to these by tautomeric equilibria. These are held to yield dinitrogen and dinitrogen monoxide by dimerisation reactions [equations (6) and (7)]. With some reagents further oxidation to compounds in a higher oxidation state occurs. We have found no evidence for dinitrogen, and so we now consider the fate of the nitroxyl. It could dimerise to form N_2O, or it might be further oxidised to HNO_2 or NO [equations (8) and (9)]. If reaction (9) occurred, then this would lead to the formation of nitrous acid by the sequence in equations (10)—(12).

$$2\,NH_2O^{\bullet} \longrightarrow N_2 + 2\,H_2O \quad (6)$$

$$2\,HNO \longrightarrow N_2O + H_2O \quad (7)$$

$$H_2O + HNO \xrightarrow{-2e} HNO_2 + 2H^+ \quad (8)$$

$$HNO \xrightarrow{-1e} NO + H^+ \quad (9)$$

$$N_2O_4 \rightleftharpoons 2NO_2^{\bullet} \quad (10)$$

$$NO^{\bullet} + NO_2^{\bullet} \rightleftharpoons N_2O_3 \quad (11)$$

$$H_2O + N_2O_3 \rightleftharpoons 2HNO_2 \quad (12)$$

Now dinitrogen monoxide is definitely a product of the reaction, even at low hydroxylamine concentrations, and this must be formed either by the dimerisation reaction (7) or by the reaction of nitrous acid with hydroxylamine (3). Here the isotopic results are very helpful. Since the hydroxylamine is 97% labelled with nitrogen-15, the nitroxyl should also be labelled, and dimerisation should produce doubly labelled N_2O. Inspection of Table 1 shows that the peak at $m/e = 46$ is very small. One possible explanation is that there is some exchange reaction whereby nitroxyl exchanges nitrogen atoms with nitric and nitrous acids. However, if this were so, one would expect to obtain unlabelled dinitrogen monoxide. Further inspection of Table 1 shows that the peak at $m/e = 44$ is also very small. In fact the isotopic distribution is very similar to that observed for the direct reaction between isotopically normal HNO_2 and ^{15}N-labelled hydroxylamine. We suggest therefore that the nitroxyl radicals are further oxidised to nitrous acid, and that HNO_2 reacts with hydroxylamine to produce N_2O. This is consistent also with the equal size of the peaks at $m/e = 30$ and 31 observed for dinitrogen monoxide produced by oxidation of hydroxylamine by nitric acid, and formed by reaction (3).

This still leaves a problem because reaction (8) should produce labelled nitrous acid, which on reacting with labelled hydroxylamine will produce doubly labelled dinitrogen monoxide. However, there should be a relatively rapid exchange of nitrogen between HNO_2 and HNO_3 *via* the formation and hydrolysis of N_2O_4. From the known rate of this reaction we calculate that $t_{\frac{1}{2}}$ for exchange should be *ca.* 0.4 s for 4.25 mol dm^{-3} HNO_3 at 25 °C. This figure is based on measurements of the rate of oxygen-18 exchange between nitric acid and water, catalysed by nitrous acid.[6] We thus expect the isotopic composition of the HNO_2 to be close to normal and this is consistent with the isotopic composition of the N_2O as being made up of mainly $m/e = 45$. We do not at this stage discuss the minor variations in the sizes of the peaks at $m/e = 44$ and 46.

If hydroxylamine is oxidised to nitrous acid, then there must be an equivalent reduction of nitric acid, and the stoicheiometry can be written as (13). The rate

$$[NH_3OH]^+ + 2\,HNO_3 \longrightarrow 3\,HNO_2 + [H_3O]^+ \quad (13)$$

equations for hydroxylamine consumption and nitrite formation become (5) and (14), and the final yield of

$$-d[NH_3OH^+]/dt = [(k_4/3) + k_3][NH_3OH^+][HNO_2] \quad (14)$$

nitrous acid is given by (15). From our yields of HNO_2 we can now calculate values of k_3, and these are

$$[HNO_2]/[NH_3OH^+]_0 = (k_4 - k_3)/(0.333\,k_4 + k_3) \quad (15)$$

given in Table 3. It can be seen that the values are reasonably close to our 'estimated' values, k_3*, and that over most of the range they show the same trend, a decrease with increased acidity. The values at the higher nitric acid concentration show a small increase.

Now the present reaction is only observed in nitric acid solution, and the formation of nitrous acid must involve reduction of HNO_3. A good many reactions of this type are known, and the active species is almost invariably dinitrogen tetraoxide or nitrogen dioxide. Reactions involving the former have rates that are usually first order with respect to nitrite concentration, while reactions involving the second are often half order with respect to nitrite concentration. Examples of autocatalytic nitrous acid-catalysed oxidation by HNO_3 that involve N_2O_4 are those involving plutonium(III)[7] and thiocyanic acid[8] as substrates. We therefore postulate reaction between dinitrogen tetraoxide and either hydroxylamine or the hydroxylammonium ion. Now the proportion of nitrite present as N_2O_4 increases rapidly with increase in nitric acid concentration, as has been shown spectrophotometrically by Longstaff and Singer,[9] and if k_4 is to decrease slightly with increased $[HNO_3]$ then the concentration of the active hydroxylamine species must decrease sharply, *i.e.* the active species must be the free base. Our overall mechanism can thus be written as in equations (16)—(18), (12), and (3). Over the range studied we suggest

$$H^+ + HNO_2 + [NO_3]^- \underset{k_6}{\overset{k_5}{\rightleftharpoons}} N_2O_4 + H_2O \quad (16)$$

$$NH_2OH + N_2O_4 \xrightarrow{k_7} HNO + N_2O_3 + H_2O \quad (17)$$

$$HNO + N_2O_4 \longrightarrow HNO_2 + N_2O_3 \quad (18)$$

$$N_2O_3 + H_2O \rightleftharpoons 2\ HNO_2 \quad (12)$$

$$HNO_2 + [NH_3OH]^+ \xrightarrow{k_3} N_2O + H_2O + [H_3O]^+ \quad (3)$$

that (17) is the rate-determining step, with (16) as a rapid pre-equilibrium, and (12) and (18) also as rapid reactions. The final rate equation is (19), where K_a is the ionisation constant of the hydroxylammonium ion.

$$\mathrm{d}[HNO_2]/\mathrm{d}t = 3\ k_5k_7[H^+][HNO_2][NO_3^-][NH_3OH^+](k_6K_a[H^+] + k_7[NH_3OH^+])^{-1} - k_3[HNO_2][NH_3OH^+] \quad (19)$$

Two checks on this mechanism can be carried out. It has been assumed that dinitrogen tetraoxide is in equilibrium with nitric and nitrous acids, *i.e.* the rate of its formation and hydrolysis is much faster than the rate of reaction with hydroxylamine. Bunton *et al.*[6] measured the nitrous acid-catalysed exchange of oxygen between nitric acid and water, using oxygen-18 as a tracer. At the lowest HNO_3 concentration, 4.25 mol dm^{-3}, the exchange rate was first order with respect to nitrous acid concentration, and we have argued that this is due to the formation and hydrolysis of N_2O_4. The activation energy for the formation is known[8] to be 71.9 kJ mol^{-1}. From this we calculated the rate of formation and hydrolysis of N_2O_4 in 4.25 mol dm^{-3} HNO_3 containing 0.005 mol dm^{-3} HNO_2 at 25 °C to be 2.28 mol dm^{-3} s^{-1}, which compares with the highest rate of nitrite generation observed at 4.28 mol dm^{-3} HNO_3 of 0.145 mol dm^{-3} s^{-1}. The second check is to see whether the value of the rate of reaction is consistent with the expected encounter rate. At 6.2 mol dm^{-3} HNO_3 Longstaff and Singer[9] have suggested that $[N_2O_4]$/[nitrite] lies between 0.01 and 0.05. Taking 0.03 as a mean, and interpolating a value for k_3 of 17 dm^3 mol^{-1} s^{-1}, h_0 as 67.6, and K_a for the hydroxylammonium ion as 1.26×10^{-6} mol dm^{-3}, then we obtain expression (20).

$$\text{Rate} = 17[\text{nitrite}][NH_3OH^+] = 17 \times 67.6/(60 \times 0.03 \times 1.26 \times 10^{-6})\,[N_2O_4][NH_2OH] = 3.0 \times 10^{10}[N_2O_4][NH_2OH]\ \text{mol dm}^{-3}\ \text{s}^{-1} \quad (20)$$

There are clearly uncertainties associated with this calculation, not the least being the assumption that the protonation of hydroxylamine follows the H_0 acidity function. It appears that the mechanism does meet these two tests. Equation (17) represents a complex change, and it may be that there are several rapid reactions following the encounter between dinitrogen tetraoxide and hydroxylamine that together produce the proposed reaction.

We must also consider why the autocatalytic reaction is only observed at sufficiently high nitric acid concentrations. We have postulated that the active oxidising agent is N_2O_4, and this is formed relatively slowly in dilute HNO_3 because the nitrate ion is a weak nucleophile. This can provide a rate-limiting process for the autocatalytic reaction. Values of the rate constant are known for zero ionic strength, and an estimate of the rate constant at higher nitric acid concentrations can be made by use of the activity-coefficient data of Davis and De Bruin,[10] provided we assume the activity coefficient of the activated complex, which having no overall charge may be taken as unity. We can also calculate the expected rate of nitrous acid generation using equation (19) and, allowing for changes in activity coefficients, the degree of dissociation of nitric acid, *etc.* To allow for changes in the protonation of hydroxylamine we have assumed that this can be described by the Hammett acidity function. We have made our comparisons just below the point at which the autocatalytic reaction is observed, 2.86 mol dm^{-3} HNO_3, and at a hydroxylammonium ion concentration of 0.005 mol dm^{-3} and nitrous acid concentration of 0.001 mol dm^{-3}. The rates are set out below. It would be unwise to lay much stress on these values, because of the uncertainties involved in correcting for changes in activity coefficients; however, it does appear that the decrease in the rate of the autocatalytic reaction occurs when the rate of dinitrogen tetraoxide formation falls below the expected rate of the autocatalytic reaction.

$[HNO_3]$/mol dm^{-3}	2.86	2.5	2.0
10^4 Rate of N_2O_4 formation/mol dm^{-3} s^{-1}	2.5	1.5	0.96
10^4 Rate of nitrite formation/mol dm^{-3} s^{-1}	1.9	1.5	1.2

Finally we consider the isotopic measurements made on the nitrous acid–hydroxylamine reaction, as they bear upon a point where there is a conflict of evidence in the literature. Friedman and Bothner-By[1] examined the reaction between $[NH_3OH]Cl$ and $Na[\overset{*}{N}O_2]$, and found that at pH 7 a symmetrical intermediate was involved (equal amounts of $\overset{*}{N}NO$ and $N\overset{*}{N}O$) but at pH 1 an unsymmetrical species was involved (34% $\overset{*}{N}NO$ and

$66\%\ N\overset{\bullet}{N}O$). Hughes *et al.*[11] examined the same system using oxygen-18 as a tracer; they agreed that a symmetrical intermediate was involved at low acidities, but found it was observed up to *ca.* 4 mol dm^{-3} perchloric or sulphuric acid. An unsymmetrical species was only observed in the region 5—8 mol dm^{-3} mineral acid. The conflict is of some significance so far as the mechanistic interpretation of results is concerned, because there is a marked difference in mechanism for reaction at pH 7 and at pH 1. (The former involves *N*-nitrosation of NH_2OH, the latter *O*-nitrosation of $[NH_3OH]^+$.) The present results, which in general give equal-intensity peaks at $m/e = 30$ and 31, indicate that the tracer is equally distributed between the two nitrogens of N_2O, and hence that a symmetrical species is involved up to *ca.* 5 mol dm^{-3} HNO_3. We discussed the differences between the two sets of results in a previous paper,[11] and have nothing new to add to that discussion.

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