799. *The Mechanism of the Oxidation of Nitrous Acid by Hyponitrous Acid. Part I.*

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Hyponitrous acid reacts with nitrous in aqueous perchloric acid to form nitrogen and nitric acid. The rate equation is $v = k_2[HNO_2][H_2N_2O_2]$. The rate constant and the entropy of activation are much greater than expected for a nucleophilic substitution by the hydrogen hyponitrite ion at the nitrous acidium ion to form nitrosyl hydrogen. hyponitrite. As the rate of such reactions are thought to be collision-controlled, this otherwise very plausible mechanism is rejected. It is suggested that reaction occurs by a nucleophilic attack either by nitrous acid on hyponitrous acid or by the nitrite ion on the conjugate acid of hyponitrous acid. Some results on the temperature variation of the rate of some reactions of nitrous acid are reported.

During an investigation of the mechanism of the reaction between nitrous acid and hydroxylamine, it was necessary to study the properties of one of the postulated intermediates, hyponitrous acid. We found that the acid was stable in an excess of dilute perchloric acid at 0°, but that in the presence of nitrous acid it acted as an oxidising agent. Divers[1] has reported the existence of such a reaction, and Latimer and Zimmerman[2] have postulated its existence to explain certain observations on the stability of hyponitrous acid, but there do not seem to be any detailed studies of its stoicheiometry or mechanism. Addison *et al.*[3] found that liquid dinitrogen tetroxide and solid sodium hyponitrite give a solid compound $Na_2N_2O_3$ which is rapidly hydrolysed by water. They established the stoicheiometry of these reactions but were not concerned with the mechanisms. We report here a study of the stoicheiometry, kinetics, and mechanism of the oxidation of aqueous nitrous acid by hyponitrous acid. The rate equation and the nature of the products suggested a mechanism involving nucleophilic substitution of the hydrogen hyponitrite ion at the nitrous acidium ion, but the rate was about four hundred times greater than the apparent limiting rate for such substitutions. This unusual result led us to examine the reaction in detail.

Results

We find that there are at least two mechanisms by which reaction occurs in aqueous solutions containing both nitrous and hyponitrous acid, with different stoicheiometries and different rate laws, observed in different concentration ranges. At low hyponitrous acid concentrations only one mechanism contributes significantly to the rate, and so it can be studied in isolation. At high hyponitrous acid concentrations the second mechanism becomes important.

Stoicheiometry.—Typical results for a range of concentrations of the two acids in an excess of perchloric acid at 0° are given in Table 1. They show that when the hyponitrous

Table 1.

Stoicheiometry of nitrous acid–hyponitrous acid reaction at 0°. (Concentrations are in mole $l.^{-1}$.)

$[H^+]$	0·060	0·10	0·17	0·10	0·39	0·39	0·39
$10^3[HNO_2]$	3·0	5·0	1·3	5·0	5·0	5·0	5·0
$10^3[H_2N_2O_2]$	1·3	1·0	1·06	15·0	15·0	23·0	53·0
$\Delta[H_2N_2O_2]/\Delta[HNO_2]$	1·0	1·05	1·0	1·4	1·5	2·0	2·1
$[H^+]$	0·017	0·053	0·32	0·10	0·39	0·39	
$10^3[HNO_2]$	20·0	10·0	10·0	5·0	5·0	5·0	
$10^3[H_2N_2O_2]$	20·0	10·0	10·0	15·0	23·0	55·0	
$\Delta[H_2N_2O_2]/\Delta[HNO_2]$	0·85	1·1	1·0	1·0	1·0	1·1	

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[1] Divers, *J.*, 1899, 77.

[2] Latimer and Zimmerman, *J. Amer. Chem. Soc.*, 1939, **61**, 1551.

[3] Addison, Gamlen, and Thompson, *J.*, 1952, 338.

acid concentration is $<10^{-3}$M, nitrous acid and hyponitrous acid react in a 1 : 1 ratio. When it is higher the ratio rises as high as 2, owing to incursion of a second mechanism. The ratio $\Delta[HNO_3]/\Delta[HNO_2]$ remains 1 under all conditions. The measurements of this second ratio were carried out at rather higher concentrations than those for the first. This was because the nitrate concentration was determined spectrophotometrically from the peak at 3020 Å, whose extinction coefficient is only 7, so that an appreciable concentration was necessary for sufficient accuracy. In concentrated solutions a colourless, odourless gas was evolved. The composition of the gaseous products was examined for a number of initial hyponitrous acid concentrations. With 0·002M-hyponitrous acid only about 10% of the gas was condensed by liquid air, with 0·007M-hyponitrous acid about 20%, and with 0·02M-acid about 50%. Mass-spectrometric analysis showed a peak at mass number 28 at low hyponitrous acid concentration, and at higher concentrations an additional peak at mass number 44. We conclude that at low hyponitrous acid concentrations the main product is nitrogen, while at high concentrations nitrous oxide is also produced. We have evidence that the gaseous products contain some nitric oxide, but this may be formed by the decomposition of nitrous acid. Attempts to obtain a quantitative analysis of the mixture of nitrogen, nitric oxide, and nitrous oxide by mass-spectrometry were unsuccessful. The reaction is thus:

$$HNO_2 + H_2N_2O_2 \longrightarrow HNO_3 + N_2 + H_2O \qquad (1)$$

It appears that at high hyponitrous acid concentrations there is a catalysed reaction,

$$H_2N_2O_2 \longrightarrow N_2O + H_2O \qquad (2)$$

In addition to the spectrophotometric evidence, we have confirmed the stoicheiometry of reaction (1) by titrimetric methods.

Kinetics.—The kinetics were followed spectrophotometrically with an excess of perchloric acid at 0° (see Table 2). In the presence of a large excess of nitrous acid the reaction was first-order in hyponitrous acid in all runs. The concentration of nitrous acid was varied, and a further check was made by carrying out runs with a large excess of hyponitrous acid, and following the disappearance of nitrous acid colorimetrically: in every case the kinetics were of first order with respect to nitrous acid. The effect of varying the acidity, and the ionic strength, was investigated in separate sets of experiments. From 0·099 to 0·522M, changes in acidity and ionic strength had almost no effect on the rate. Thus the rate equation is

$$v = k_2[HNO_2][H_2N_2O_2] \qquad (3)$$

The very small salt effect is as expected for a rate equation involving only neutral molecules.

TABLE 2.

Rate constants for the nitrous acid–hyponitrous acid reaction at 0°.

(k_1 in sec.$^{-1}$; k_2 in l. mole^{-1} sec.$^{-1}$; concns. in mole l.$^{-1}$.)

$[H^+]$	$10^3[H_2N_2O_2]$	$10^3[HNO_2]$	10^4k_1	10^2k_2
	With an excess of nitrous acid			
0·099	1·0	5·0	2·24	4·48
0·099	0·1	10·0	4·72	4·72
0·187	1·0	5·0	2·38	4·76
0·243	1·0	5·0	2·25	4·50
0·522	1·0	5·0	2·53	5·10
0·086 *	1·0	5·0	8·96	17·9
0·086 *	1·0	10·0	18·2	18·1
0·080 †	1·0	5·0	24·2	48·4
0·080 †	1·0	10·0	45·1	45·1

$[H^+]$	$10^3[H_2N_2O_2]$	$10^3[HNO_2]$	10^1k_1	10^2k_2
	With an excess of hyponitrous acid			
0·100	6·92	0·16	1·93	2·79
0·100	3·64	0·16	1·10	3·01
0·100	1·66	0·16	0·58	3·52

Ionic strength effect ‡

$[H^+] = 0·243$. $[HNO_2] = 5·10^{-3}$.

$[H_2N_2O_2] = 10^{-3}$.

Ionic strength	0·25	1·37	2·26	3·00
10^2k_2	4·50	5·30	6·32	6·68

* Temp. = 15°. † Temp. = 25°. ‡ Added $NaClO_4$.

Reaction at High Hyponitrous Acid Concentrations.—The additional mechanism observed as the hyponitrous acid concentrations increases is observed in the kinetics, the values of $v/[HNO_2][H_2N_2O_2]$ decreasing, as shown in the second part of Table 2. This change in kinetic form is associated with a simultaneous change in stoicheiometry, illustrated by the increase in the values of $\Delta[H_2N_2O_2]/\Delta[HNO_2]$ in Table 1 and by the appearance of nitrous oxide as product. The present results, however, do not suffice to establish the detailed mechanism.

Variation of Rate with Temperature.—The rate measurements were extended to other temperatures, with the following results. 10^2k_2 (mean) = 4·60 (0°), 18·0 (15°), 47·3 (25°), and 106·6 (35°). One of the likely mechanisms for the reaction is nucleophilic substitution by the hydrogen hyponitrite ion at the nitrous acidium ion. To check this it was necessary to compare the above results with the way that the rate of known substitutions at the nitrous acidium ion varied with temperature. Very little has been published on this subject; [4] some information is available for substitution by the nitrite and the iodide ion. To obtain more we extended earlier studies [5] on the mechanism of the azide–nitrite reaction from 0° to 25°. We find that the relative rates of substitution of azide, bromide, and thiocyanate ions are independent of temperature. Schmid *et al.*[6] have published results on the temperature variation for substitution by the nitrite ion, and Challis *et al.*[7] did the same for the iodide ion. The rates can be expressed in the form $k_3 = kT/h \exp(\Delta S^{\ddagger}/\boldsymbol{R}) \exp(\Delta H^{\ddagger}/\boldsymbol{R}T)$, and the values of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are summarised in Table 3. As these results have been obtained by three different groups of workers, at different times, in different laboratories, by different methods, it would be unwise to attach much significance to small differences in $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$. The outstanding feature is the marked difference in the $\Delta S^{\ddagger}$ value for the hydrogen hyponitrite ion compared with the other ions.

TABLE 3.

Temperature-variation of the rate of substitution at the nitrous acidium ion.

X^-	$HN_2O_2^-$	N_3^-	NO_2^-	NCS^-	Br^-	I^-
$\Delta S^{\ddagger}$ (cal. mole^{-1} degree^{-1}) ...	17·1	2·1	5·3	1·1	0·7	5·1
$\Delta H^{\ddagger}$ (kcal. mole^{-1})	14·2	12·3	13·2	12·3	12·3	13·4

DISCUSSION

We consider first the reactions observed by Addison *et al.*[3] The rate equation (3) can be interpreted as an electrophilic nitrosation of the hydrogen hyponitrite ion by the nitrous acidium ion. As dinitrogen tetroxide is known as a nitrosating agent it is necessary to see if the reactions observed by them can explain our results. They found that the stoicheiometry was approximately:

$$Na_2N_2O_2 + N_2O_4 \longrightarrow Na_2N_2O_3 + N_2O_3 \qquad (4)$$

$$2Na_2N_2O_3 + H_2O \longrightarrow 1{\cdot}1NaNO_2 + 1{\cdot}88NaOH + 0{\cdot}94N_2O + 0{\cdot}26Na_2N_2O_2 + 0{\cdot}52NaNO_3 \qquad (5)$$

This is patently different from the action observed by us at low hyponitrous acid concentrations.

Rate equation (3) can be rewritten in two equivalent forms:

$$v = k_6[H^+][HNO_2][HN_2O_2^-] \qquad (6)$$

$$v = k_7[H^+][H_2N_2O_2][NO_2^-] \qquad (7)$$

If we assume an equilibrium between nitrous and hyponitrous acid and their conjugate bases, then $k_2 = k_6K_1 = k_7K_3$, where K_1 is the first dissociation constant of hyponitrous acid, and K_3 the dissociation constant of nitrous acid. The most attractive of these three rate equations is (6), because it is similar to the general rate equation $v = k_3{}^X[H^+][HNO_2][X^-]$ for nucleophilic substitution by a variety of anions X^- at the nitrous acidium ion to form NOX.[4] In the present case the mechanism would be:

$$H^+ + HNO_2 \rightleftharpoons H_2NO_2^+ \quad \text{Fast} \qquad (8)$$

$$HO{\cdot}N{:}N{\cdot}O^- + H_2NO_2^+ \longrightarrow HO{\cdot}N{:}N{\cdot}O{\cdot}NO + H_2O \quad \text{Slow} \qquad (9)$$

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[4] Ridd, *Quart. Rev.*, 1961, **15**, 418.
[5] Stedman, *J.*, 1959, 2949.
[6] Schmid and Woppman, *Monatsh.*, 1959, **90**, 903.
[7] Challis, Larworthy, and Ridd, *J.*, 1962, 5203.

Nitrosyl hydrogen hyponitrite could break down either by a nucleophilic attack by water (10) or by an ionisation mechanism (11):

$$HO\cdot N{:}N\cdot O\cdot NO + H_2O \longrightarrow HO^- + N_2 + H_2NO_3^+ \qquad (10)$$

$$HO\cdot N{:}N\cdot O\cdot NO \longrightarrow HO^- + N_2 + NO_2^+ \qquad (11)$$

Reaction (10) seems more likely. From results in the range 15—35°, it can be estimated that K_1 is $3{\cdot}4 \times 10^{-8}$ at 0°. Hence k_6 is $1{\cdot}36 \times 10^6$ l.^{2} mole^{-2} sec.$^{-1}$. This value is very much higher than the corresponding rate constants for other substitutions at the nitrous acidium ion,[4] *e.g.*, $CH_3{\cdot}CO_2^-$ *ca.* 3000, N_3^- 2340, NO_2^- 1890, I^- 1370, SCN^- 1460, Br^- 1170, Cl^- 975 l.^{2} mole^{-2} sec.$^{-1}$. These reagents vary in basicity by about 12 pK units from chloride to acetate, and yet the reactivity varies by a factor of only three. The hydrogen hyponitrite ion is only two pK units more basic than the acetate or azide ion, and yet it appears to be about 400 times more reactive. Ridd [4] suggested that these substitutions at the nitrous acidium ion are collision-controlled and that this satisfactorily accounts for the small spread in reactivity. It is important to establish whether the present reaction between nitrous and hyponitrous acid proceeds by path (9). If it does, then the fact that k_6 is so much greater than the other values of k_3^X would disprove the suggestion of a collision-controlled reaction.

The $\Delta S^\ddagger$ and $\Delta H^\ddagger$ values in Table 3 show that the apparently high reactivity of the hydrogen hyponitrite ion is due to the large $\Delta S^\ddagger$ value, and that $\Delta H^\ddagger$ is actually slightly greater than for other anions. This could be explained by supposing that in the transition state the hydroxyl ion shown as being formed in (10) and (11) has largely separated from the $^-N{:}N\cdot O\cdot NO$ fragment. We do not think this explanation satisfactory; it seems much more likely that reaction occurs mainly by another path, and that the transition state has a markedly different structure from that for substitutions at the nitrous acidium ion. This does not exclude the possibility that a small amount of reaction occurs by paths (8) and (9); indeed it would be surprising if it did not, but this represents only a small fraction of the total rate. We have not considered the possibility that nitrous acid itself acts as an electrophilic nitrosating agent. It would be expected to be a very weak nitrosating agent and no examples of its functioning in this manner in aqueous solution are known. It would presumably do so with a very reactive substrate, but there is no sign that hyponitrous acid is so reactive.

The two mechanisms that we have rejected are electrophilic nitrosations, and involve oxygen–nitrogen bond fission in the nitrous acid molecule, $^-HO\vdots NO^+$, the nitrate produced containing one oxygen from the nitrous acid, one from the hyponitrous acid, and one from the water. We suggest that the correct mechanism does not involve any nitrogen–oxygen bond fission in the nitrous acid, $HO\cdot NO + {}^+HO\vdots N{:}N\cdot OH^-$. The nitrous acid or nitrite ion would function as a nucleophilic reagent, attacking the oxygen of hyponitrous acid. The nitrate formed would contain two oxygen atoms from the nitrous acid and one from the hyponitrous acid. Reaction could occur between two neutral molecules (3), or between a nitrite ion and protonated hyponitrous acid (7). These differ only in the position assigned to the proton, and it seems pointless to attempt to distinguish between them. The transition state would have a different structure from that expected for a substitution at the nitrous acidium ion. For substitution by the nitrite ion at protonated hyponitrous acid it might resemble $^{\frac{1}{2}-}O_2N\cdots OH_2^+\cdots N\overset{\cdots}{=}N\cdots OH^{\frac{1}{2}-}$. As hyponitrous acid has the bent *trans*-structure, while the product is nitrogen, it seems likely that the O–N–N angle is closer to 180° in the transition state. In principle it should be possible to distinguish between the two modes of bond fission by labelling the nitrous acid with oxygen-18, but oxygen exchange between nitrous acid and water is rapid and would compete with the chemical reaction with hyponitrous acid. In perchloric acid at 0° the rate of oxygen exchange between nitrous acid and water is about $250[H^+][HNO_2]$ mole l.$^{-1}$ sec.$^{-1}$. The rate of reaction between hyponitrous acid and water is $0{\cdot}046[HNO_2][H_2N_2O_2]$ mole l.$^{-1}$ sec.$^{-1}$. If the reaction were carried out at pH 5, the hyponitrous acid concentration would have to be about M for the rate of the chemical reaction to be much faster than the rate of oxygen exchange, and at these concentrations catalysed decomposition of hyponitrous acid (2) would be very important. If the pH is raised much above 5, the spontaneous decomposition of hyponitrous acid [8] would become significant. It does not seem to be easy to use oxygen-18 as a tracer to distinguish between these two modes of bond fission.

In an attempt to obtain further evidence, the effect of added bromide and thiocyanate ions on the rate of reaction has been investigated. These ions frequently catalyse electrophilic nitrosations by forming nitrosyl bromide and nitrosyl thiocyanate, which act as nitrosating agents. At low concentrations (10^{-3}M) of these ions—sufficient to accelerate strongly the diazotisation of many aromatic amines—there is little effect on the rate. At higher concentrations of bromide ion a side-reaction occurs in which it appears that bromide is oxidised to bromine. The stoicheiometry and mechanism of this reaction have not been worked out. These observations suggest that the nitrous acid species involved in the reaction with hyponitrous acid does not function as an electrophilic reagent.

EXPERIMENTAL

Materials.—Sodium hyponitrite was prepared by the method of Addison *et al.*[3] From the ultraviolet spectra of solutions in sodium hydroxide it was estimated to be more than 99% pure. All other materials were of " AnalaR " grade and were used without further purification.

Kinetics.—The reaction was followed by conventional methods. Samples of the reaction mixture were removed at suitable times and added to an excess of alkali. The concentration of nitrite was determined spectrophotometrically from the intensity of the peak at 3520 Å. The concentration of hyponitrite was obtained by measuring the optical density at 2480 Å and subtracting a correction due to absorption by the nitrite ion. With a large excess of hyponitrite over nitrite the disappearance of nitrous acid was followed colorimetrically.

Products.—The concentrations of nitrous and hyponitrous acid were measured as described above. The concentration of nitrate was determined from the light absorption at 3020 Å, after correction for any overlapping absorption due to nitrous acid or hyponitrous acid.[3]

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[8] Hughes and Stedman, *J.*, 1963, 1239.