The Kinetics and Mechanism of the Hyponitrous Acid–Nitrous Acid Reaction at 0 °C

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The kinetics of the reaction between hyponitrous acid and nitrous acid have been examined, mainly at 0 °C, over the acidity range 0.01 to 11.6 mol dm^{-3} perchloric acid. Values of $k_{obs.}$, the measured first-order rate constant, increase dramatically with $[HClO_4]$ from about 4 mol dm^{-3} $HClO_4$ and then decrease again as $[HClO_4]$ increases beyond about 7 mol dm^{-3}. The maximum value of $k_{obs.}$ at 0 °C occurs just above 7 mol dm^{-3} perchloric acid and is greater than 2.5×10^{-2} s^{-1} at 0.005 mol dm^{-3} nitrous acid. The reaction may be described by the two-term rate law: rate = $\{k_2' + k_3^{**}(K/(K + h_r))h_0a_w\}[HNO_2][H_2N_2O_2]$, where $k_2' = 4.62 \times 10^{-2}$ dm^3 mol^{-1} s^{-1} and $k_3^{**} = 5.41 \times 10^{-3}$ dm^6 mol^{-2} s^{-1} at 0 °C, and acidity functions, $H_R = -\log_{10}h_R$ and $H_0 = -\log_{10}h_0$. The fall in rate at high acidity is attributed to the conversion of nitrous acid to the nitrosonium ion, suggesting that molecular nitrous acid is a kinetically active species. Added bromide ion at 5.56 mol dm^{-3} perchloric acid results in lowered rates due to the conversion of nitrous acid to nitrosyl bromide.

In the preceding paper,[1] it was shown that the stoicheiometry of the nitrous acid–hyponitrous acid reaction could be understood in terms of the four reactions shown in equations (1)—(4).

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

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

$$3\,HNO_2 \longrightarrow 2\,NO + HNO_3 + H_2O \qquad (3)$$

$$H_2N_2O_2 \xrightarrow{HNO_2,\,NO} \text{Products}\ (N_2O, NO, HNO_3) \qquad (4)$$

Reactions (2) and (3) are self decompositions of hyponitrous acid and nitrous acid respectively, while reaction (4) requires NO, the product of disproportionation of nitrous acid, and leads to isotopic exchange.[2] Reaction (4) is of particular importance in accounting for the catalysed decomposition of hyponitrous acid, which takes place alongside reaction (1). The relative contributions of these reactions depends upon the experimental conditions. Reaction (1) is dominant at 1:1 stoicheiometry and low acidity, while reaction (4) becomes more important at high $[H_2N_2O_2]$ and/or $[H^+]$. High levels of nitrous acid will also favour reaction (4) *via* reaction (3).

The use of nitrogen-15 labelled nitrous acid has shown[1] that the N_2 produced in reaction (1) is derived only from the hyponitrous acid, while N_2O and NO are derived from both reactants.

Some kinetic studies of the hyponitrous acid–nitrous acid reaction have been reported.[3–5] Equation (5) represents the rate law established over a limited acidity range,[3] and shows the reaction to be independent of acidity up to 0.5 mol dm^{-3} $HClO_4$. The rate law may be rewritten as equation (6), which is the familar rate law found for nitrosations involving the rate-determining attack of NO^+ on the substrate. However, for several reasons, this mechanism was rejected for the hyponitrous acid–nitrous acid reaction,[3] and the suggestion made that reaction occurred between the undissociated acids or between nitrite ion and the conjugate acid of hyponitrous acid. Added bromide failed to catalyse the reaction, confirming it to be unlike normal nitrosation reactions. This paper reports kinetic studies carried out over the acidity range 0.01 to 11.6 mol dm^{-3} $HClO_4$.

$$\text{Rate} = k_2[HNO_2][H_2N_2O_2] \qquad (5)$$

$$\text{Rate} = k_3[H^+][HNO_2][HN_2O_2^-] \qquad (6)$$

Experimental

Sodium hyponitrite was prepared by the reduction of sodium nitrite with sodium amalgam,[6] as described in the previous paper. The absence of nitrite in the product was confirmed by the use of a standard colorimetric method involving sulphanilic acid and β-naphthol. The product appeared to be contaminated with carbonate, as shown by the measured absorption coefficient at 248 nm. The purity of the compound was calculated using the recently corrected value of the absorption coefficient[7,8] (6 920 dm^3 mol^{-1} cm^{-1}). All kinetic studies were carried out under pseudo first-order conditions, with a large excess of nitrous acid over hyponitrous acid, so the presence of carbonate impurity had no effect on rate constants. Rate constants were independent of the batch of hyponitrite used. All other chemicals were the best grade available.

Kinetic runs were started by the addition of a suitable volume of sodium nitrite solution to a thermostatted, deoxygenated solution of all the other components of the reaction mixture, using an ice-jacketed pipette for runs at 0 °C. The sodium hyponitrite had been added as the solid to the reaction solution. The reaction was followed by withdrawing aliquots at known times and running into volumes of ice-cold sodium hydroxide solution, of concentration appropriate to give an alkaline final solution. Absorbances at 248 and 352 nm were measured. From the absorbance due to nitrite at 352 nm, the contribution of nitrite to the absorbance at 248 nm could be calculated. Subtraction from the measured absorbance at 248 nm gave the absorbance due to hyponitrite, A_H.

Results

The reaction was studied at acidities from 0.01 to 11.6 mol dm^{-3} $HClO_4$, with an excess of nitrous acid over hyponitrous acid, at

0 °C. Excellent plots of $\log(A_H)$ against time were obtained under all conditions, showing the reaction to be first order in $[H_2N_2O_2]$. The reaction is also first order in nitrous acid concentration, as shown by the constancy of values of $k_2 = k_{obs.}/[HNO_2]$, where $k_{obs.}$ is the measured first-order rate constant [equations (7) and (8)]. At low acidity the reaction is independent of $[HClO_4]$, confirming the conclusions previously reported. Data are given in Table 1.

$$\text{Rate} = k_{obs.}[H_2N_2O_2] \tag{7}$$

$$= k_2[HNO_2][H_2N_2O_2] \tag{8}$$

Values of $k_{obs.}$ at constant $[HNO_2]$ increase slightly with increase of acidity up to about 3—4 mol dm^{-3} $HClO_4$, but show a dramatic increase as $[HClO_4]$ is increased to about 7 mol dm^{-3}. Values of $k_{obs.}$ then decrease as $[HClO_4]$ is increased further. The data in the Figure show that maximum values of $k_{obs.}$ occur at about 7.2 mol dm^{-3} $HClO_4$. Values of $k_{obs.}$ at various $[HClO_4]$ are given in Table 2, together with values of the second-order rate constant $k_2 = k_{obs.}/[HNO_2]$. The second-order rate constant for the acid-catalysed reaction is given by $k_2'' = k_2 - k_2'$, where k_2' is the second-order constant for the acid-independent pathway (4.62 × 10^{-2} dm^3 mol^{-1} s^{-1}).[3]

Table 1. Dependence of rate on nitrite at 0 °C and $[H_2N_2O_2] = 0.001$ mol dm^{-3}

$[HClO_4]$/ mol dm^{-3}	$[HNO_2]$/mol dm^{-3}	$10^4k_{obs.}/s^{-1}$	$10^2k_{obs.}/[HNO_2]$ (dm^3 mol^{-1} s^{-1})
1.36	0.005	3.08	6.16
1.36	0.010	6.65	6.65
1.36	0.020	13.0	6.50
1.36	0.040	26.4	6.60
8.04	0.002	27.1	136
8.04	0.005	67.0	134
8.04	0.010	152	152
8.04	0.020	335	167
0.01 *	0.005	2.45	4.90
0.01 *	0.010	4.93	4.93
0.01 *	0.015	7.30	4.87
0.01 *	0.020	8.55	4.28

* Runs carried out with 0.25 mol dm^{-3} added bromide, which appears to exert a slight catalytic effect at low acidity.

Values of a third-order rate constant k_3 have also been calculated, where $k_3 = k_2''/h_0$. This assumes that the protonation of a reactant (probably $H_2N_2O_2$) follows the acidity function H_0, where $H_o = -\log_{10}h_o$.[9] The justification for this assumption is not immediately apparent, but H_0 is the best established of the wide variety of acidity functions available, while, as will be seen later, the use of H_0 does give constant overall rate coefficients.

At concentrations of $HClO_4$ up to about 3.5 mol dm^{-3}, values of k_3 are fairly constant, but fall away at higher acidities. In an attempt to explain this decrease in k_3, account was taken of the activity of water [10] (a_w), which decreases under these conditions.

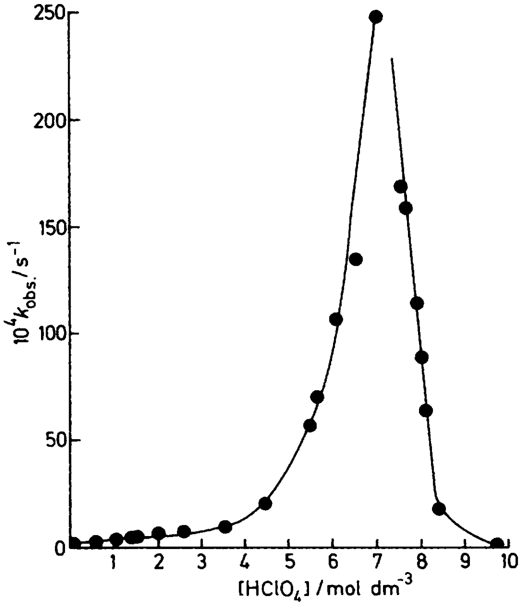


Figure. Variation of $k_{obs.}$ with acidity at 0 °C and $[HNO_2] = 0.0050$ mol dm^{-3}

Table 2. Dependence of rate on acidity at 0 °C, $[HNO_2] = 0.005$ mol dm^{-3}, $[H_2N_2O_2] = 0.001$ mol dm^{-3}

$[HClO_4]$/mol dm^{-3}	$10^4k_{obs.}/s^{-1}$	10^2k_2/dm^3 mol^{-1} s^{-1}	$10^2k_2''$/dm^3 mol^{-1} s^{-1}	10^3k_3/dm^6 mol^{-2} s^{-1}	$10^3k_3^*$/dm^6 mol^{-2} s^{-1}	$10^3k_3^{**}$/dm^6 mol^{-2} s^{-1}
1.06	2.82	5.64	1.02	4.35	4.54	4.54
1.36	3.08	6.16	1.54	4.65	4.95	4.95
1.43	3.20	6.40	1.78	4.79	5.11	5.11
2.04	4.26	8.52	3.90	5.38	5.98	5.98
2.61	5.55	11.1	6.48	4.91	5.72	5.72
3.56	10.2	20.4	15.8	4.43	5.70	5.70
4.58	20.2	40.4	35.8	2.98	4.47	4.47
5.56	56.7	113	109	2.61	4.91	4.95
5.75	70.3	140	136	2.53	5.09	5.16
6.09	106	212	207	2.32	5.15	5.32
6.51	136	272	269	1.68	4.30	4.73
7.00	247	494	489	1.48	4.66	6.70
7.51	170	340	335	0.422	1.67	5.96
7.60	159	318	313	0.328	1.36	6.52
7.70	116	232	227	0.217	0.940	5.82
7.90	89.6	179.2	175	0.105	0.470	5.10
8.05	63.3	126.6	122	0.058	0.305	5.45
8.53	19.7	39.4	34.8	0.006		
9.75	7.33	14.7	10.1			
11.6	5.05	11.1	5.5			

$k_2 = k_{obs.}/[HNO_2]$; $k_2' = 4.62 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}; $k_2'' = k_2 - k_2'$; $k_3 = k_2''/h_0$; $k_3^* = k_3/a_w$; $k_3^{**} = k_3/\{[HNO_2]/[HNO_2 \cdot NO^+]\}$.

Table 3. Effect of added bromide on the $H_2N_2O_2$–HNO_2 reaction at 0 °C*

$[HClO_4] = 5.56$ mol dm^{-3} ($I = 5.60$ mol dm^{-3})

$10^2[Br^-]$/mol dm^{-3}	$10^4k_{obs.}$/s^{-1}	10^3K_{NOBr}/dm^6 mol^{-2}
0	47.5	
0.25	39.8	4.0
0.50	36.9	2.6
0.75	26.8	5.3
1.00	18.2	8.6
2.00	9.23	9.6
5.00	4.88	7.2

$[HClO_4] = 0.1$ mol dm^{-3} ($I = 0.5$ mol dm^{-3})

$[Br^-]$/mol dm^{-3}	$10^4k_{obs.}$/s^{-1}	$10^4(k_{obs.} - k_0)/[Br^-]$ (dm^3 mol^{-1} s^{-1})
0	2.02	
0.1	2.39	3.70
0.25	2.45	1.72
0.32	2.60	1.81
0.37	2.63	1.65

* $[HNO_2] = 0.005$ mol dm^{-3}; $[H_2N_2O_2] = 0.001$ mol dm^{-3}. Each rate constant is the mean of several values.

Table 2 lists values of $k_3^* = k_3/a_w$, which are fairly constant up to about 7 mol dm^{-3} $HClO_4$, but then rapidly decrease in value as $[HClO_4]$ is increased. Clearly, some other factor must also be responsible for the decrease of k_3^* at very high acidities. At these high acidities, molecular nitrous acid is progressively converted to the nitrosonium ion, NO^+. The equilibrium constant for this process is known.[11] If it is assumed that only molecular nitrous acid is kinetically active towards hyponitrous acid (and that NO^+ is inactive), then the reaction rate will decrease at very high acidity in proportion to the extent of conversion of nitrous acid to the nitrosonium ion. Accordingly, a further third-order rate constant (k_3^{**}) was calculated, in which allowance was made for the fraction of nitrous acid present as the molecular species at each acidity. This calculation involved the use of the literature value for the equilibrium constant (K) and the acidity function H_R, where $H_R = -\log_{10}h_R$, which describes the acidity dependence of the HNO_2–NO^+ equilibrium.[11] Values of k_3^{**} are satisfactorily constant over the entire acidity range studied, 1—8 mol dm^{-3} $HClO_4$. This is particularly noteworthy in view of the dramatic dependence of $k_{obs.}$ on $[HClO_4]$. Thus, the acid-catalysed reaction may be described by rate law (9) and the overall reaction by rate law (10). These results confirm that the reaction of nitrous acid and hyponitrous acid is not a conventional nitrosation as NO^+, the most reactive nitrosating agent, is inactive in this reaction.

$$\text{Rate} = k_3^{**}h_0a_w(K/(K + h_R))[HNO_2][H_2N_2O_2] \quad (9)$$

$$\text{Rate} = \{k_2' + k_3^{**}h_0a_w(K/(K + h_R))\}[HNO_2][H_2N_2O_2] \quad (10)$$

Effect of Added Bromide.—Some kinetic runs were carried out with added bromide, to check if conversion of HNO_2 to NOBr would result in decreased rates of reaction. The results in Table 3 show that, at 0.1 mol dm^{-3} $HClO_4$, bromide may exert a slight catalytic effect, but at 5.56 mol dm^{-3} $HClO_4$ there is inhibition of reaction. Addition of 0.05 mol dm^{-3} bromide causes a decrease in $k_{obs.}$ from 47.5×10^{-4} to 4.88×10^{-4} s^{-1}.

The results in Table 3 may be used to calculate an equilibrium constant for the formation of NOBr on the assumption that decrease in $k_{obs.}$ provides a measure of the extent of conversion of HNO_2 to NOBr. Values of K_{NOBr} are listed in Table 3. The data obtained at high $[Br^-]$ are more reliable, and give a value for K_{NOBr} (at 0 °C and 5.6 mol dm^{-3} ionic strength) of *ca.* 0.9×10^{-2} dm^6 mol^{-2}. This compares with a literature value[12] of 2.2×10^{-2} dm^6 mol^{-2} measured at 0 °C and 0.1 mol dm^{-3} ionic strength. These two values are in satisfactory agreement and support strongly the view that molecular nitrous acid is the kinetically active species in the acid-catalysed reaction between HNO_2 and $H_2N_2O_2$.

Table 4. Temperature dependence of the $H_2N_2O_2$–HNO_2 reaction*

$[HClO_4] = 8.53$ mol dm^{-3}

T/K	273.2	278.2	280.6	283.2
$10^4k_{obs.}$/s^{-1}	19.7	34.5	45.3	58.0

$[HClO_4] = 4.58$ mol dm^{-3}

T/K	273.2	277.9	280.3	283.2
$10^4k_{obs.}$/s^{-1}	20.0	33.5	43.4	58.4

* $[HNO_2] = 0.005$ mol dm^{-3}; $[H_2N_2O_2] = 0.001$ mol dm^{-3}.

Temperature Dependence.—The reaction was studied over a temperature range at 4.58 and 8.53 mol dm^{-3} perchloric acid. Results are shown in Table 4. Values of $\Delta H^\ddagger$ were found to be 68 ± 3 and 71 ± 3 kJ mol^{-1} and those of $\Delta S^\ddagger$ to be -46 ± 7 and -35 ± 5 J K^{-1} mol^{-1} respectively. These parameters are, of course, composite quantities.

Discussion

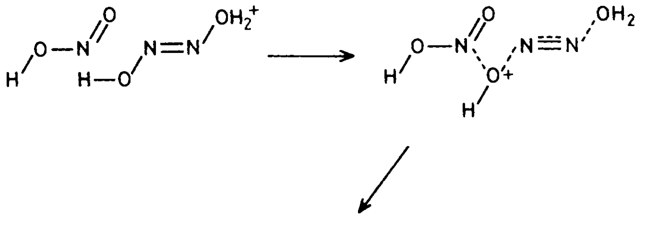
The study of the kinetics of this reaction has been carried out by following the disappearance of hyponitrous acid in the presence of excess of nitrous acid. It is appropriate, therefore, to consider first the fate of the hyponitrous acid. The work on the stoicheiometry described in the previous paper shows that there is a major pathway accounting for some 72% of the decomposition of hyponitrite that leads to the production of dinitrogen and nitrate [equation (1)], a minor pathway involving a reaction with nitrogen monoxide accounting for about 20% of reaction (11), and the self decomposition pathway which amounts to some 7—8% of the reaction [equation (2)]. Our kinetic data reflect mainly reaction (1) and a minor contribution from reaction (11).

$$^{15}NO + H_2N_2O_2 \longrightarrow 0.53\ NO + 1.14\ N^{15}NO + 0.18\ H^{15}NO_3 \quad (11)$$

The kinetics fit a two-term rate law involving an acid-independent term, and another component that shows strong acid catalysis up to about 7 mol dm^{-3} $HClO_4$, followed by rapid fall off in rate at higher acidities.

The first term, characterised by k_2', has been discussed in an earlier paper[3] in which it was concluded that reaction did not involve an electrophilic nitrosation of the hyponitrite anion as the rate of reaction was orders of magnitude greater than the encounter rate. Nothing in our present work leads us to modify this view.

For the acid-catalysed reaction, the most striking feature is the dramatic fall off in rate above 7 mol dm^{-3} $HClO_4$. This is the range of acidity where molecular nitrous acid is converted to the nitrosonium ion. Now, NO^+ is the most reactive electrophilic nitrosating agent possible, and the fact that the rate decreases as NO^+ is formed is direct evidence that hyponitrous acid is not susceptible to electrophilic nitrosation, and that molecular nitrous acid is the reactive species. The acid catalysis, represented by the h_0a_w term, cannot be due to protonation of nitrous acid and so must refer to protonation of hyponitrous acid. It is not known which acidity function of the many available describes the protonation of $H_2N_2O_2$, and it must be assumed that h_0a_w approximates to an acidity function that does this. It would be somewhere between H_0 and H_A. We attach no mechanistic significance to the a_w term. The isotopic data imply a product distribution for the acid-catalysed reaction identical with that for the uncatalysed reaction, and the simplest explanation involves attack of nitrous acid on an oxygen atom of hyponitrous acid, with oxygen-atom transfer taking place in a subsequent step [equation (12)]. This results in the dinitrogen being formed entirely from hyponitrite N atoms in accord with the isotopic data.



$$HNO_3 + N_2 + H_3O^+ \quad (12)$$

Buchholz and Powell[4] have suggested the radical scheme shown in equations (13)—(16) which could occur in parallel to the reaction shown in equation (12).

$$HNO_2 + HONNOH \longrightarrow N_2 + NO_2 + {}^{\bullet}OH + H_2O \quad (13)$$

$$NO_2 + {}^{\bullet}OH \longrightarrow HNO_3 \quad (14)$$

$$HNO_2 + {}^{\bullet}OH \longrightarrow H_2O + NO_2 \quad (15)$$

$$HONNOH + NO_2 \longrightarrow HNO_3 + N_2 + OH \quad (16)$$

The reaction leading to the HNO_2–NO-catalysed decomposition of hyponitrous acid is a complex one. It constitutes about 20% of the consumption of hyponitrite and hence is capable of disturbing the kinetics of the overall loss of hyponitrous acid. The third pathway constitutes only some 7—8% of the reaction, and so its influence would probably not be readily detectable in the overall kinetics. The presence of the NO-catalysed reaction does not perturb the kinetics of the acid-catalysed reaction with nitrous acid and so it must also be first order in hyponitrite and be subject to similar acid catalysis, again probably involving a protonated hyponitrous acid molecule. As noted, the NO involved in this reaction is assumed to be formed from nitrous acid by self decomposition. Any lag in the onset of this reaction may thus be eliminated by passing NO into the reaction solution. It should be noted that the excellent quality of the kinetic data, which show no signs of deviation from a first-order dependence upon $[HNO_2]$ and $[H_2N_2O_2]$ is a little surprising. The disproportionation reaction of nitrous acid is not usually thought to provide a reliable and steady concentration of dissolved nitrogen monoxide. If equilibrium (3) is established then the concentration of NO should vary in proportion to $[HNO_2]^{1.5}/[NO_3^-]^{0.5}$, and nitrite might act as an inhibitor. Such an effect was not observed. These observations suggest that consideration should also be given to the possibility that nitrous acid has a direct catalytic role rather than acting as a source of NO. Reaction (17) is one such possibility.

$$H^+ + HNO_2 + H_2N_2O_2 \longrightarrow 2\,NO + NOH + H_3O^+ \quad (17)$$

However the suggestion that NO has a catalytic role in the decomposition of hyponitrous acid in the presence of nitrous acid is strongly supported by the observation of direct reaction between NO and hyponitrous acid.[2] Reaction of ^{15}NO with hyponitrous acid in 5.0 mol dm^{-3} perchloric acid in the absence of ethanol gives $^{15}N_2O$ (17.2% of total N_2O), $^{14}N^{15}NO$ (45.5%), and $^{14}N_2O$ (37.3%), while in the presence of ethanol the products are $^{15}N_2O$ (15%) and $^{14}N_2O$ (82%). In contrast, the N_2O produced in the $(NO–HNO_2)–H_2N_2O_2$ reaction comprises only 1% $^{15}N_2O$ and substantial amounts of $^{14}N^{15}NO$. The latter reaction system is complicated by the presence, and possible involvement, of large amounts of nitrous acid. For experiments with a 1:1 stoicheiometry of nitrous acid and hyponitrous acid and for those with an excess of nitrous acid, about two thirds of the N_2O produced contains a nitrogen atom derived from nitrous acid. With excess of hyponitrous acid at 2.81 mol dm^{-3}, some 22% of the N_2O has a nitrogen atom from nitrous acid, but this increases to 49% at 8.54 mol dm^{-3} perchloric acid. The isotopic data thus emphasise the production of $^{14}N^{15}NO$ derived from both nitrous acid and hyponitrous acid nitrogen atoms, similar to the results found for the non-chain inhibited $(NO + H_2N_2O_2)$ reaction.

The data from the present work will not be so clear cut as some ^{14}NO will be formed from the $(^{15}NO + H_2N_2O_2)$ reaction. As discussed earlier, the kinetic data suggest that the hyponitrous acid is protonated, presumably at an oxygen atom. Attack of the NO will then probably be directed towards a nitrogen atom, so accounting for the appearance of a new reaction pathway under more acidic conditions, or will involve hydrogen atom abstraction. Alternative schemes are considered below, and could occur in parallel.

$$\begin{gathered}
{}^{*}NO + H_2\overset{+}{O}NNOH \longrightarrow \begin{matrix} {}^{*}NO \\ | \\ H_2\overset{+}{O}NNOH \end{matrix} \longrightarrow N^{*}NO + H^+ + HNO + {}^{\bullet}OH \\
2\,HNO \longrightarrow NNO + H_2O \\
{}^{\bullet}OH + H_2\overset{+}{O}NNOH \longrightarrow H_2O + H_2\overset{+}{O}NNO^{\bullet} \\
H_2\overset{+}{O}NNO^{\bullet} \longrightarrow H^+ + {}^{\bullet}OH + NNO
\end{gathered}$$

Scheme A.

This scheme gives $^{14}N^{15}NO$ and $^{14}N_2O$ products, but appears to depend upon $[^{15}NO]$, suggesting that the reaction should be erratic in character if the NO is produced by the normal self decomposition of nitrous acid. Possibly some later step in the scheme is rate determining.

$$\begin{gathered}
{}^{*}NO + H_2\overset{+}{O}NNOH \longrightarrow H^{*}NO + {}^{\bullet}ONNOH + H^+ \\
{}^{\bullet}ONNOH \longrightarrow N_2O + {}^{\bullet}OH \\
2\,H^{*}NO \longrightarrow {}^{15}N_2O + H_2O \\
{}^{\bullet}OH + {}^{\bullet}ONNOH \longrightarrow 2\,NO + H_2O \\
{}^{\bullet}OH + HONNOH \longrightarrow ONNOH + H_2O \\
{}^{*}NO + {}^{\bullet}OH \longrightarrow H^{*}NO_2 \\
NO + {}^{\bullet}ONNOH \longrightarrow NO_2 + N_2 + {}^{\bullet}OH \\
2\,NO_2 + H_2O \longrightarrow HNO_2 + H^+ + NO_3^-
\end{gathered}$$

Scheme B.

This scheme leads to a range of products and could account for the longstanding results of Partington and Shah[13] on the decomposition of hyponitrous acid in concentrated mineral acids at high temperatures. Under these conditions decomposition occurred to give erratic and unusual stoicheiometries. Contamination of their sample with nitrite could have led to the presence of the NO-catalysed decomposition reaction.

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