Stoicheiometric and Nitrogen-15 Labelling Studies on the Hyponitrous Acid–Nitrous Acid Reaction

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The stoicheiometry of the hyponitrous acid–nitrous acid reaction has been determined over a wide acidity range, up to 8.5 mol dm^{-3} $HClO_4$. For approximately 1 : 1 reaction conditions, the major reaction pathway gives N_2 and HNO_3 as products, together with the production of N_2O (by self decomposition of hyponitrous acid) and NO (by self decomposition of nitrous acid). In addition, ^{15}NO produced by self decomposition of $H^{15}NO_2$ reacts with $H_2{}^{14}N_2O_2$ to give some ^{14}NO and N_2O of mixed isotopic composition. Reactions under other conditions gave products that may be accounted for by varying contributions from these reactions.

The reaction between nitrous acid and hyponitrous acid has previously been studied under limited conditions. Hughes and Stedman[1] have shown that at least two pathways are present for the reaction in perchloric acid solutions in the acidity range 0.02—0.5 mol dm^{-3}. One involves the production of N_2 and nitrate [equation (1)], while superimposed upon this is a second reaction which was described as a 'nitrous acid-catalysed decomposition of hyponitrous acid to N_2O' [equation (2)]. The second pathway becomes more important at high concentrations of hyponitrous acid, and at increased acidity. The self decomposition of hyponitrous acid occurs only to a negligible extent under these conditions.[2,3]

$$HNO_2 + H_2N_2O_2 \longrightarrow N_2 + NO_3^- + H_2O + H^+ \quad (1)$$

$$H_2N_2O_2 \xrightarrow{HNO_2} N_2O + H_2O \quad (2)$$

The interpretation previously offered in earlier work on the reaction between hyponitrous acid and nitrous acid needs to be slightly modified. It is extremely difficult to obtain carbonate-free sodium hyponitrite, and so the absorption coefficient of 3 980 dm^3 mol^{-1} cm^{-1} at $\lambda_{max.}$ = 248 nm reported by Addison *et al.*[4] is low. A revised value of 6 920 dm^3 mol^{-1} cm^{-1} is now available.[5] The results given in ref. 1 thus have to be recalculated, although the overall pattern of the results is not changed by the use of the revised absorption coefficient. The recalculated results show that, with excess nitrous acid, the value of the ratio $\Delta[H_2N_2O_2]/\Delta[HNO_2]$ is less than unity at low $[H_2N_2O_2]$ due to self decomposition of nitrous acid. As $[H_2N_2O_2]$ is increased so the ratio increases to include values significantly greater than unity.

The rate law established for reaction (1) is given in equation (3). For several reasons this was not interpreted in terms of a conventional nitrosation mechanism, but rather in terms of a nucleophilic attack, either by HNO_2 on $H_2N_2O_2$, or by NO_2^- on $H_3N_2O_2^+$.

$$\text{Rate} = k_2[HNO_2][H_2N_2O_2] \quad (3)$$

Buchholz and Powell[6] observed the presence of the hyponitrous acid–nitrous acid reaction during their investigation of the decomposition of hyponitrous acid. They showed that nitrous acid is formed by disproportionation of hyponitrous acid, and then reacts with hyponitrous acid *via* a free-radical chain reaction, which is suppressed by added ethanol.

The reaction has also been studied in acetate buffers,[7,8] but its complexity did not allow a full interpretation of the kinetic data.

More recently Wimbledon[9] has studied the kinetics of the reaction over the perchloric acid concentration range 0.1 to 11.6 mol dm^{-3}, as described in the following paper.[10] He also measured the stoicheiometry of the reaction at several acidities, and showed that $\Delta[HNO_3]/\Delta[HNO_2] \approx 1.2$. Correction of his data using the revised absorption coefficient for hyponitrite gives similar results to those of ref. 1, *i.e.* that the ratio $\Delta[H_2N_2O_2]/\Delta[HNO_2]$ increases from values less than one at high $[HNO_2]$ and low $[H^+]$, to values substantially greater than unity at high acidity (>7 mol dm^{-3}) and high $[H_2N_2O_2]$.

Wimbledon observed that NO cannot be detected in reactions carried out at high acidity or with excess $H_2N_2O_2$, and concluded that any NO formed by disproportionation of HNO_2 is consumed by reaction with $H_2N_2O_2$. He then bubbled NO into a reaction solution having $H_2N_2O_2$ in excess. The normally observed[9] induction period for the onset of the catalysed decomposition of $H_2N_2O_2$ was eliminated, and the rate of the subsequent reaction was greater than normal. Wimbledon suggested that NO was responsible for the catalysed decomposition of $H_2N_2O_2$.

We have now carried out a much more detailed analysis of the stoicheiometry under a wide range of conditions up to 8.5 mol dm^{-3} perchloric acid solution. In one series of experiments, the gaseous products of the reaction were analysed and the origin of the nitrogen atoms in these products established by isotopic labelling. In a second series of experiments the consumption of nitrous acid and hyponitrous acid and the production of nitrate were determined by u.v. and colorimetric techniques. These results are described in this paper, while the following paper gives details of the kinetic studies.

Experimental

All chemicals were of AnalaR or AristaR quality. Nitrogen-15 labelled sodium nitrite at 33% enrichment was purchased from Stohler. Solutions of perchloric acid were prepared by dilution from 72% perchloric acid and standardised against sodium hydroxide solution prepared from Volucon ampoules.

Sodium hyponitrite was prepared by the reduction of sodium

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nitrite with sodium amalgam,[4] the reaction being carried out under an N_2 atmosphere to avoid the formation of sodium carbonate. (It appears that early work on sodium hyponitrite has been undertaken with grossly impure samples.) The absorption coefficient[4] usually quoted at 248 nm ($\lambda_{max.}$) for $Na_2N_2O_2$, of 3 980 dm^3 mol^{-1} cm^{-1}, has been redetermined as 6 550 ± 200[11] and 6 920 ± 140 dm^3 mol^{-1} cm^{-1}.[5] The latter value has been used in this work.

Nitrate was determined by the absorption at 300 nm, where ε = 7.0 dm^3 mol^{-1} cm^{-1}. This value varies as [$HClO_4$] is increased, and so the absorption coefficient and $\lambda_{max.}$ for nitrate were checked at each acidity used. In a few cases, nitrate was measured by reduction to ammonia with Devarda's alloy, and distillation of the ammonia into excess of dilute standard hydrochloric acid solution, followed by back titration. The two methods always agreed well. Nitrite was determined by a colorimetric method, involving the diazotisation of sulphanilic acid and coupling to β-naphthol to give an azo dye with ε = 23 500 dm^3 mol^{-1} cm^{-1} at 485 nm.

In experiments where gaseous products were to be isolated, reactions were carried out in a two-legged reaction vessel attached to the vacuum line. A solution of sodium nitrite and sodium hyponitrite in 0.1 mol dm^{-3} sodium hydroxide solution was placed in one leg and the appropriate concentration of perchloric acid in the other. The total volume of reaction solution was 4 cm^3. Solutions were degassed by freezing in liquid nitrogen, evacuating, and thawing, three times. For gas chromatographic analysis, CF_4 at a known partial pressure was introduced into the flask prior to the start of the reaction after temperature equilibration had been reached. Reactions were left overnight and the gaseous products collected in a sample bulb after passage through a helical trap at 195 K to remove water vapour. The gases were then analysed by gas chromatography as described earlier.[12,13]

Tracer experiments were carried out in a manner similar to that described above. Upon conclusion of each reaction, all gaseous products were passed through a helical trap held at 77 K, condensing all components but N_2 which was then collected by Toepler pump for mass spectrometry. The temperature of the trap was then raised to 195 K, holding H_2O while NO and N_2O were collected by distillation. Separation of NO and N_2O was carried out by repeated trap-to-trap distillation between 77 and 113 K. Final traces of NO remaining in N_2O samples were removed by pumping at 77 K. These samples were then collected over Ascarite, to remove any trace of CO_2 prior to mass spectrometry.

Removal of N_2O traces from NO samples was not satisfactorily accomplished, so that mass spectrometry of NO for reaction conditions in which it was a minor product could not be carried out. Under conditions of its substantial abundance as product, samples were held at 77 K, holding back N_2O while NO was introduced into the mass spectrometer under its own vapour pressure at that temperature. Mass spectrometry was carried out employing an AEI MS-30 instrument, with gas inlet at the reference side (Stony Brook Mass Spectrometry Facility).

Results

The products of the hyponitrous acid–nitrous acid reaction are nitrate, dinitrogen, dinitrogen monoxide, and nitrogen monoxide, with relative yields depending upon the acidity and upon the concentrations of reactants.

Table 1. The gaseous products at approximately 1:1 stoicheiometry

[H^+]/ mol dm^{-3}	10^5[HNO_2]/ mol	10^5[$H_2N_2O_2$]/ mol	$10^5 n_{N_2}$/ mol	$10^5 n_{NO}$/ mol	$10^5 n_{N_2O}$/ mol
1.97	4.17	3.29	2.82	1.06	0.42
1.97	4.36	3.47	3.49	0.60	0.38
2.81	4.03	3.54	3.01	0.60	0.49
3.05	4.24	3.25	2.22	1.02	0.53
3.05	4.24	3.36	1.78	0.78	0.44
3.90	3.95	2.74	2.45	1.12	0.76
3.90	3.95	2.83	2.07	0.99	0.84
5.07	4.36	3.54	2.18	1.05	1.10
5.66	3.91	2.69	1.62	1.75	1.21
6.94	4.42	3.22	1.28	1.61	0.95
6.94	4.42	3.28	1.20	1.66	1.09
7.65	4.36	3.44	1.19	1.47	1.82
7.65	4.36	3.39	1.51	1.32	1.69

Table 2. Production of nitrate at approximately 1:1 stoicheiometry

[H^+]/ mol dm^{-3}	$10^3\Delta$-[HNO_2]/ mol dm^{-3}	$10^3\Delta$-[$H_2N_2O_2$]/ mol dm^{-3}	$10^3\Delta$-[HNO_3]/ mol dm^{-3}	$\frac{n_{HNO_3}}{n_{\text{Total N}}}$
1.07	9.70	10.2	12.4	0.41
2.06	9.59	10.2	12.6	0.42
2.06	9.82	10.0	13.8	0.46
3.04	9.55	10.2	12.3	0.41
4.08	9.54	10.2	12.1	0.40
6.18	9.63	10.2	12.1	0.40
6.62	9.64	10.2	13.0	0.43
7.62	9.97	10.0	14.1	0.47
8.00	9.47	10.2	13.0	0.43
8.00	9.78	10.0	15.8	0.53
8.64	9.55	10.0	16.0	0.55
9.09	8.23	10.0	14.6	0.52
9.63	7.30	10.0	13.5	0.49

Reaction Stoicheiometry.—Experiments were carried out at approximate stoicheiometries 2:1, 1:1, and 1:2. Hyponitrite concentrations in experiments for the determination of gaseous products were calculated from the weight of $Na_2N_2O_2$ used, the purity of the sample having been checked by u.v. spectroscopy using ε_{248} = 6 920 dm^3 mol^{-1} cm^{-1}, while in other experiments hyponitrite concentration was determined by direct u.v. absorption measurement of the solution.

Data on the production of gases and nitrate at a reaction stoicheiometry [$H_2N_2O_2$]:[HNO_2] ≈ 0.8:1 over the [$HClO_4$] range 1.07—9.63 mol dm^{-3} are shown in Tables 1 and 2 respectively, and graphically in Figure 1. Extrapolation to low acidity indicates that the products are almost entirely N_2 and nitrate. The yield of nitrate remains constant with increase in acidity until about 6 mol dm^{-3} $HClO_4$, and then rises slightly. The production of nitrate as determined directly is somewhat higher than the nitrogen left unaccounted for by the sum of the gaseous products. These measurements were carried out in independent experiments, but may reflect accumulative errors in the latter measurements. Increasing acidity is seen (Figure 1) to result in a steady decrease in N_2 formation along with increased production of N_2O. The amount of NO formed, expressed as n_{NO}/n_{NT} (where n_{NT} represents total moles of nitrogen atoms in the reactants), lies between 5 and 20% and appears to rise to a maximum at about 6 mol dm^{-3} H^+. The decrease in production of NO at high acidities may result from the increasing conversion of nitrous acid to NO^+ with resulting stabilisation with respect to disproportionation. The ratio $\Delta[H_2N_2O_2]/\Delta[HNO_2]$ increases to 1.37 at high acidity, showing the presence of an additional pathway for decomposition of hyponitrous acid.

Data for the reaction with approximately two-fold excess of nitrous acid (Tables 3 and 4: Figure 2) show enhanced production of NO and nitrate compared to that found at 1:1 stoicheiometry. This may result from additional decomposition

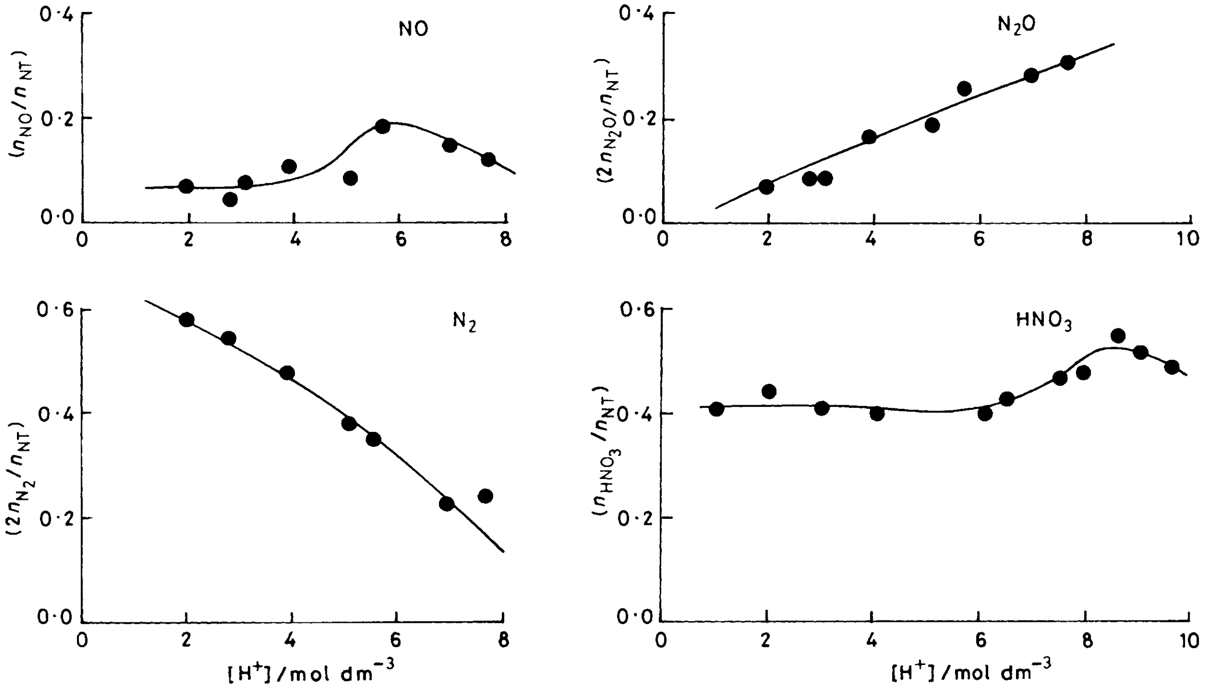

Figure 1. The effect of acidity on the stoicheiometry of product formation for the hyponitrous acid–nitrous acid reaction at 1:1 reaction stoicheiometry. The amount of product is expressed by the ratio of moles of nitrogen atoms in the product to the total number of moles of nitrogen atoms in the reactants (n_{NT})

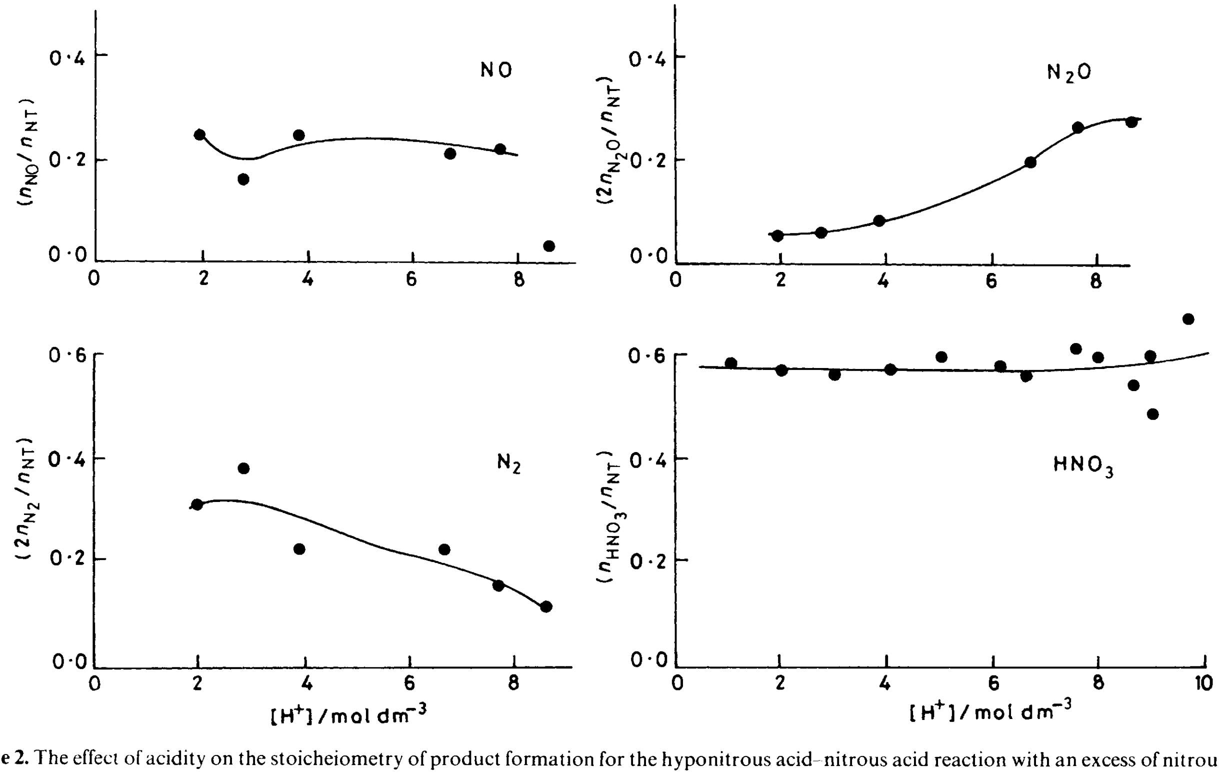

Figure 2. The effect of acidity on the stoicheiometry of product formation for the hyponitrous acid–nitrous acid reaction with an excess of nitrous acid. The amount of product is expressed by the ratio of moles of nitrogen atoms in the product to the total number of moles of nitrogen atoms in the reactants (n_{NT})

of nitrous acid to give NO and nitrate. It is noteworthy that there is a marked fall in the formation of NO between 7.65 and 8.54 mol dm^{-3} HClO$_4$ (from 25 to 3%) without an equivalent fall in the yield of nitrate. This suggests that NO has been consumed by reaction with hyponitrous acid. The constancy of [NO$_3^-$] production argues against the possibility that less NO has been formed. In general, for this reaction stoicheiometry, increase in acidity is associated with decrease in production of N$_2$ and increase in production of N$_2$O.

The results for hyponitrous acid in approximately two-fold

Table 3. The gaseous products with excess nitrous acid

$[H^+]$/ mol dm^{-3}	$10^5[HNO_2]$/ mol	$10^5[H_2N_2O_2]$/ mol	$10^5n_{N_2}$/ mol	10^5n_{NO}/ mol	$10^5n_{N_2O}$/ mol
1.97	9.00	2.96	2.52	3.92	0.37
1.97	9.00	3.06	2.15	3.57	0.41
2.81	7.72	3.69	2.91	2.42	0.48
3.90	10.0	2.90	1.65	3.78	0.61
3.90	10.0	2.81	1.86	4.07	0.64
6.74	7.59	3.08	1.49	2.94	1.31
7.65	7.59	2.99	1.04	3.00	1.77
8.54	7.59	3.33	0.92	0.32	2.04
8.54	7.59	3.41	0.74	0.44	2.08
8.54	8.13	3.59	0.70	0.42	1.80

Table 4. Production of nitrate with excess nitrous acid

$[H^+]$/ mol dm^{-3}	$10^3\Delta$-$[HNO_2]$/ mol dm^{-3}	$10^3\Delta$-$[H_2N_2O_2]$/ mol dm^{-3}	$10^3\Delta$-$[HNO_3]$/ mol dm^{-3}	$\frac{n_{HNO_3}}{n_{Total\ N}}$
1.07	18.5	10.1	22.6	0.58
2.06	18.4	10.1	21.2	0.55
2.06	19.0	9.13	22.2	0.59
3.04	18.5	10.1	21.8	0.56
4.08	18.7	10.1	22.4	0.57
5.10	18.9	10.1	22.5	0.57
5.10	19.3	9.13	23.4	0.62
6.18	18.9	10.1	22.7	0.58
6.62	18.4	10.1	21.8	0.56
7.62	19.3	9.13	23.1	0.61
8.00	18.4	10.1	22.0	0.57
8.00	19.5	9.13	23.5	0.62
8.64	19.8	9.13	20.6	0.54
9.09	16.4	10.1	22.0	0.60
9.09	19.5	9.13	18.6	0.49
9.63	17.7	9.13	24.0	0.67

excess over nitrous acid are given in Tables 5 and 6 and Figure 3. The production of NO is very small, but that of nitrate is similar to that found for the reaction with the 1:1 stoicheiometry, suggesting that NO has been formed and then consumed. The behaviour with respect to production of N_2 and N_2O is similar to that observed under other conditions.

Studies with $H^{15}NO_2$.—Table 7 contains the results of experiments using ^{15}N-labelled nitrite at 33% abundance. These were carried out for the three stoicheiometries described above. For all conditions, the N_2 produced did not contain ^{15}N above natural abundance showing that the N_2 is derived entirely from hyponitrite nitrogen atoms. Interestingly, the data for NO and N_2O show that both these products are derived from both reactants. It is an oversimplification, therefore, to attribute the production of NO and N_2O to self decomposition of HNO_2 and $H_2N_2O_2$ respectively. While only limited data are available for NO, it is quite clear that some NO is derived from hyponitrous nitrogen atoms to an extent that increases with acidity and with $[H_2N_2O_2]$ (Table 8). This suggests that the HNO_2-catalysed decomposition of $H_2N_2O_2$ may give NO derived from hyponitrite. This view is supported by the high value (67%) observed for NO derived from $H_2N_2O_2$ at 8.54 mol dm^{-3} $HClO_4$ and excess of $H_2N_2O_2$, conditions in which the HNO_2-catalysed reaction is favoured.

The isotopic data for N_2O show that there is negligible production of the doubly labelled product and substantial amounts of the singly labelled species. The fragmentation pattern suggests that this is $N^{15}NO$. The data at 1:1 reaction stoicheiometry and for the case with excess of nitrous acid show that about two thirds of the N_2O contains a nitrogen atom derived from nitrous acid, although this value drops at the highest acidities studied. In reactions with excess of hyponitrous acid, and at 2.81 mol dm^{-3} $HClO_4$ only about 22% of the N_2O contains a nitrogen atom from nitrous acid, but the value increases steadily as the acidity is raised, becoming 49% at 8.54 mol dm^{-3} $HClO_4$.

Table 5. The gaseous products with excess hyponitrous acid

$[H^+]$/ mol dm^{-3}	$10^5[HNO_2]$/ mol	$10^5[H_2N_2O_2]$/ mol	$10^5n_{N_2}$/ mol	10^5n_{NO}/ mol	$10^5n_{N_2O}$/ mol
1.97	3.83	6.94	4.56	0.48	3.44
2.81	4.08	6.11	4.03	0.32	2.17
3.90	4.37	7.03	4.14	0.48	2.61
3.90	4.37	7.16	4.33	0.41	2.51
5.66	3.82	7.08	3.53	0.49	3.03
6.74	3.76	6.40	2.89	0.89	2.80
8.54	4.02	6.74	1.51	0.25	3.61
8.54	4.02	6.76	1.47	0.20	3.72
8.54	4.08	7.10	1.74	0.21	3.64

Table 6. Production of nitrate with excess hyponitrous acid

$[H^+]$/ mol dm^{-3}	$10^3\Delta$-$[HNO_2]$/ mol dm^{-3}	$10^3\Delta$-$[H_2N_2O_2]$/ mol dm^{-3}	$10^3\Delta$-$[HNO_3]$/ mol dm^{-3}	$\frac{n_{HNO_3}}{n_{Total\ N}}$
1.07	9.84	12.9	20.8	0.41
2.06	9.84	13.3	21.6	0.41
3.04	9.84	14.3	23.4	0.39
4.08	9.84	15.0	25.0	0.37
5.10	9.84	16.1	27.7	0.34
6.18	9.84	17.4	30.9	0.31
6.62	9.84	17.8	30.4	0.33
7.62	9.77	19.9	31.8	0.36
8.00	9.54	17.8	29.6	0.34
8.00	9.56	19.9	31.8	0.36
8.64	8.85	19.9	31.3	0.35
9.09	7.95	17.8	28.9	0.33
9.09	7.83	19.9	31.1	0.35
9.63	8.99	19.9	31.5	0.35

Discussion

The results described in this paper have demonstrated great complexity on the part of the reaction between nitrous acid and hyponitrous acid. However, it is clear that several parallel reactions are taking place, including the reaction to give N_2 and nitrate [equation (1)], the normal self decompositions of hyponitrous[14] and nitrous acids [equations (4) and (5)], and

$$H_2N_2O_2 \longrightarrow N_2O + H_2O \qquad (4)$$

$$3\,HNO_2 \longrightarrow 2\,NO + HNO_3 + H_2O \qquad (5)$$

the HNO_2-catalysed decomposition of $H_2N_2O_2$ [equation (2)]. The data obtained with ^{15}N-labelled HNO_2 indicate the relative importance of these reactions.

The stoicheiometric data for the approximately 1:1 reaction at 3.90 mol dm^{-3} $HClO_4$ are summarised in Table 1 and equation (6). The NO and N_2O products both contain ^{14}N and ^{15}N species as detailed in the Results section. The isotopic composition of the HNO_3 was not determined but must be ^{15}N. The yield of nitrate in equation (6) is that calculated as necessary to give a correct nitrogen balance, but does also give the correct redox balance. The concentration of nitrate found in parallel experiments is a little higher than this, as noted earlier. If it is assumed that $^{14}N_2$, ^{15}NO, and $^{14}N_2O$ are formed by the

Table 7. Mass spectroscopic data on the hyponitrous acid–nitrous acid reaction

$[H^+]$ (mol dm^{-3})	$10^2[HNO_2]$ (mol dm^{-3})	$10^2[H_2N_2O_2]$ (mol dm^{-3})	Dinitrogen (%)				Dinitrogen monoxide (%)				Nitrogen monoxide (%)		
			^{15}N	$^{15}N_2$	$^{14}N^{15}N$	$^{14}N_2$	^{15}N	$^{15}N_2O$	$^{14}N^{15}NO$	$^{14}N_2O$	^{15}N	^{15}NO	^{14}NO
(*a*) 1 : 1 Stoicheiometry													
1.97	0.99	0.93	0.36	0	0.73	99.8	11.5	0.29	22.3	77.4			
2.81	1.06	1.05	0.46	0	0.92	99.1	11.6	0.15	22.8	77.0	23.5	23.5	76.5
3.90	1.06	1.05	0.56	0	1.12	98.9	12.5	0.34	24.3	75.4			
5.07	1.05	0.99	0.77	0	1.54	98.5	12.3	0.30	24.1	75.6			
5.66	1.10	1.01	1.26	0.34	1.84	97.8	11.7	0.23	22.9	76.9	22.8	22.8	77.2
6.74	1.16	0.98	1.18	0	2.35	97.6	3.61	0	17.2	82.8			
8.54	1.10	0.99	0.88	0	1.76	98.4	9.62	0.12	19.0	80.9			
(*b*) Excess HNO_2													
2.81	2.03	1.12	0.46	0	0.92	99.1	11.0	0.50	21.1	78.4	28.3	28.3	71.7
5.66	2.03	1.12	1.56	0	3.12	96.9	13.0	0.45	25.1	74.5	25.1	25.1	74.9
8.54	0.99	0.50	1.44	0.45	1.97	97.6	11.0	0.15	21.6	78.2			
8.54			1.01	0	2.02	98.0	11.0	0.13	21.8	78.0			
(*c*) Excess $H_2N_2O_2$													
2.81	1.00	2.02	0.29	0	0.58	99.4	5.83	0.16	7.33	92.5			
5.66	1.00	2.02	0.54	0	1.08	98.1	6.69	0.02	13.3	86.6	17.6	17.6	82.4
8.54	1.02	1.99	0.88	0	1.76	98.2	8.26	0.06	16.4	83.5	11.0	11.0	89.0

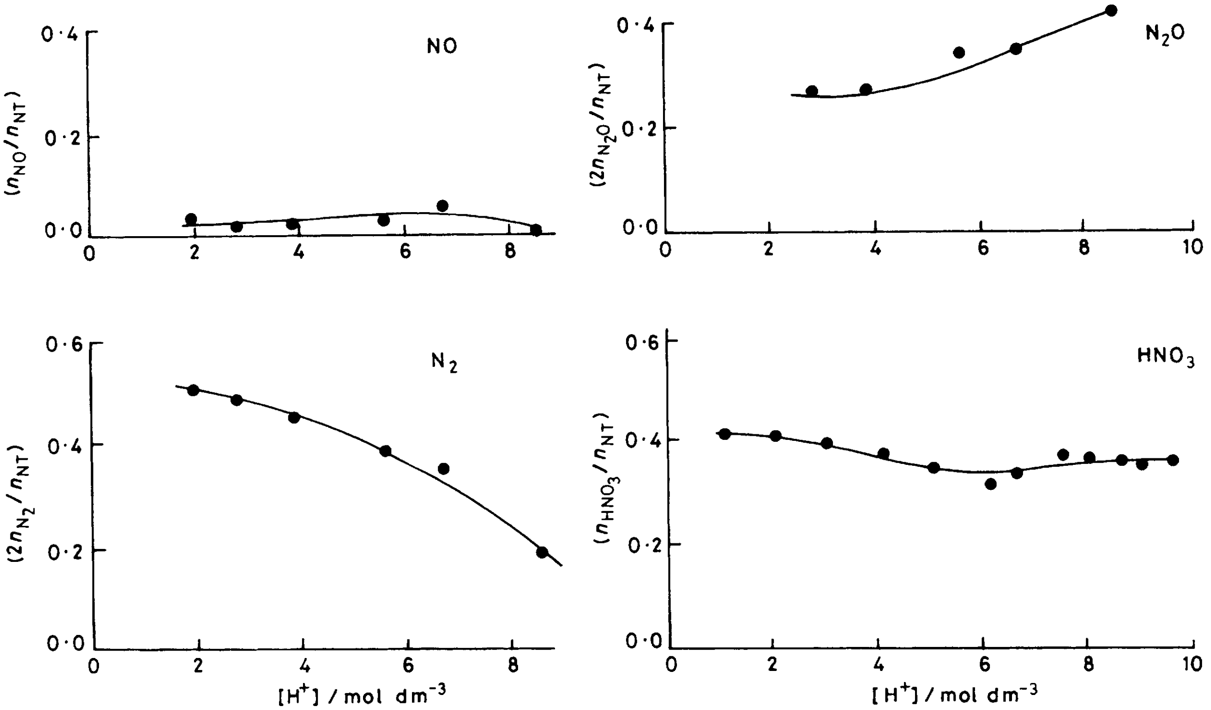

Figure 3. The effect of acidity on the stoicheiometry of product formation for the hyponitrous acid–nitrous acid reaction with an excess of hyponitrous acid. The amount of product is expressed by the ratio of moles of nitrogen atoms in the product to the total number of moles of nitrogen atoms in the reactants (n_{NT})

reactions described in equations (1) (Table 1), (5) (Tables 1 and 8), and (4) (Tables 1 and 7), then equations (7)—(9) may be written to account for the formation of specific products in equation (6). The difference between the sum of these three component reactions and the measured stoicheiometry shown in equation (6) represents an additional stoicheiometry not yet accounted for and described in equation (10).

$$3.95\ H^{15}NO_2 + 2.83\ H_2{}^{14}N_2O_2 \longrightarrow 2.07\ {}^{14}N_2 + 0.99\ NO + 0.84\ N_2O + 2.80\ H^{15}NO_3 \quad (6)$$

$$2.07\ H^{15}NO_2 + 2.07\ H_2{}^{14}N_2O_2 \longrightarrow 2.07\ {}^{14}N_2 + 2.07\ H^{15}NO_3 + 2.07\ H_2O \quad (7)$$

$$1.05\ H^{15}NO_2 \longrightarrow 0.7\ {}^{15}NO + 0.35\ H^{15}NO_3 \quad (8)$$

$$0.21\ H_2{}^{14}N_2O_2 \longrightarrow 0.21\ {}^{14}N_2O + 0.21\ H_2O \quad (9)$$

$$0.83\ H^{15}NO_2 + 0.55\ H_2{}^{14}N_2O_2 \longrightarrow 0.29\ {}^{14}NO + 0.63\ {}^{14}N^{15}NO + 0.38\ H^{15}NO_3 \quad (10)$$

Table 8. Origin of NO product in the HNO_2–$H_2N_2O_2$ reaction

$[H^+]$/mol dm^{-3}	$[HNO_2]:[H_2N_2O_2]$ (approx.)	% NO from HNO_2	% NO from $H_2N_2O_2$
2.81	1:1	72	28
5.66	1:1	68	32
2.81	2:1	85	15
5.66	2:1	75	25
5.66	1:2	53	47
8.54	1:2	33	67

Alternatively, it may be assumed that the nitrous acid in equation (10) has undergone self decomposition [by equation (11)] and that the products of self decomposition of $H^{15}NO_2$ should be considered as participating in equation (10). The combination of equations (10) and (11) thus gives an alternative, previously unknown reaction between ^{15}NO and $H_2N_2O_2$ to give ^{14}NO and $^{14}N^{15}NO$ among the products [equation (12)].

$$0.83\ H^{15}NO_2 \longrightarrow 0.55\ {}^{15}NO + 0.28\ H^{15}NO_3 \quad (11)$$

$$0.55\ {}^{15}NO + 0.55\ H_2{}^{14}N_2O_2 \longrightarrow 0.29\ {}^{14}NO + 0.63\ {}^{14}N^{15}NO + 0.1\ H^{15}NO_3 \quad (12)$$

Following up on the results described above, we examined the NO–$H_2N_2O_2$ system directly and have confirmed that a reaction does occur.[15] The course of the reaction depends upon the presence or absence of ethanol, and in the non-ethanol (non-chain-inhibited) case with ^{15}NO as reactant ^{14}NO, $^{14}N_2O$, $^{14}N^{15}NO$, and $^{15}N_2O$ were observed among the products. Also in this case, substantial production of $^{14}N_2$ was observed, and the production of NO_3^- inferred. The NO–$H_2N_2O_2$ reaction has been interpreted as resulting from hydrogen-atom abstraction to NO, forming HNO and the radical species $^{\bullet}ONNOH$, with the latter either decomposing to yield N_2O and OH radical, or reacting with OH to yield NO.

Because of the great complexity of this reaction system, a more detailed assessment of the stoicheiometry and isotopic data is not justified. The existence of the NO–$H_2N_2O_2$ reaction may well complicate the analysis further by allowing additional pathways for isotopic exchange. However, it is now clear that the overall reaction stoicheiometry and the isotopic distribution among gas products can be accounted for in terms of the reactions between HNO_2 and $H_2N_2O_2$, self decomposition of HNO_2, self and catalysed decomposition of $H_2N_2O_2$, and the newly identified NO–$H_2N_2O_2$ reaction [see equations (7), (8), (9), and (12)].

The variation of stoicheiometry with acidity shows that the N_2-producing reaction becomes less significant, while the production of N_2O by self and catalysed decomposition of $H_2N_2O_2$ becomes more so, with increasing H^+ concentration. Experiments with $H_2N_2O_2$ in excess over HNO_2 show decreased NO production, while experiments with HNO_2 in excess show greater NO. The production of N_2O appears to be less $[H^+]$ dependent with $H_2N_2O_2$ than with HNO_2 in excess. More detailed mechanistic considerations are reserved for the following paper.

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