

# Nitrogen-15 Tracer Evidence Discounting the Occurrence of a Cyclic Azide Intermediate in the Reaction between Nitrous Acid and Hydrazine

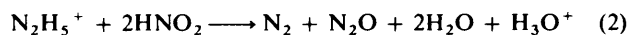
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Analysis by  $^{15}\text{N}$  NMR spectroscopy of a sample of hydrazoic acid isolated from a reaction mixture of labelled hydrazine and nitrous acid has shown that there is no rearrangement of tracer, and that the earlier suggestion of a cyclic azide intermediate must be discarded. Mass-spectrometric analyses of the evolved dinitrogen and dinitrogen monoxide showed that there are probably three distinct pathways by which reaction proceeds, one *via* the formation of hydrazoic acid, one *via* the dinitrosated species ONNHNHNO and a third route which leads to an excess of doubly labelled  $\text{N}_2$  which may involve  $\text{HN}=\text{N}-\text{N}(\text{NO})\text{OH}$ .

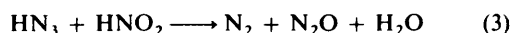
The reaction between nitrous acid and excess of hydrazine at acidities greater than *ca.*  $0.5 \text{ mol dm}^{-3}$  is known<sup>1</sup> to obey equation (1), while when nitrous acid is in sufficient excess (at



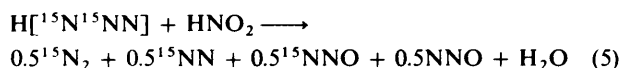
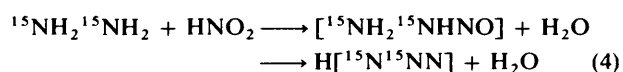
least two-fold) the stoichiometry is<sup>2</sup> (2). As hydrazoic acid is



known<sup>3</sup> to react readily with nitrous acid as shown in equation (3) it originally seemed likely that reaction (2) was simply due to



(1) followed by (3). An  $^{15}\text{N}$  labelling study of the reaction showed<sup>2</sup> that the situation was considerably more complicated than this. Reaction (1) involves a rate-determining N-nitrosation process and hence the expected distribution of tracer is shown in (4) and (5), the pattern for (5) having previously been



established by Clusius and Effenberger<sup>4</sup> as consistent with the breakdown of nitrosyl azide, NNNNO. However, the pattern of tracer distribution was much closer to  $0.33^{15}\text{N}_2$ ,  $0.67^{15}\text{NN}$ ,  $0.67^{15}\text{NNO}$  and  $0.33\% \text{ NNO}$ . We previously interpreted<sup>2</sup> this as showing that there was a cyclic form of azide as a transient intermediate, although it was recognised that this was likely to be a high-energy species. Recent calculations<sup>5</sup> found that the triplet ground state of cyclic  $\text{N}_3^-$  is about  $180 \text{ kJ mol}^{-1}$  higher in energy than the singlet ground state of linear  $\text{N}_3^-$ . Another explanation of the tracer results, parallel reaction paths (1) + (3), and a mechanism involving a doubly nitrosated species ONNHNHNO was also recognised<sup>2</sup> as a possibility. Bonner and co-workers<sup>6</sup> followed these observations up by examining the reaction of hydrazine with  $^{15}\text{N}$ -labelled nitrous acid. Their mass-spectrometric analyses were almost certainly superior in quality to the original measurements. They also found that the results did not fit equations (4) + (5), and suggested that there

was a variation in the pattern of tracer distribution with reaction conditions. Although some of their experiments were close to the one-third/two-thirds distribution, they felt marginally that their results did not favour a cyclic azide species. Now hydrazine is commonly used as a nitrite scavenger, particularly in nitric acid solution, and it seemed desirable to resolve these uncertainties by repeating and extending the work, using improved techniques.

## Experimental

**Materials.**—97.5 atom%  $^{15}\text{N}$  hydrazinium hydrogensulfate was obtained from Amersham International. Other materials were AnalaR chemicals.

**Analysis for Isotopically Labelled Azide.**—The reaction between labelled hydrazine and isotopically normal nitrous acid was carried out in a Dreschel bottle, and the solution was sparged with a stream of  $\text{N}_2$ . The gas stream, containing volatile hydrazoic acid, was then passed through a second Dreschel bottle containing NaOD in  $\text{D}_2\text{O}$ , and the azide was absorbed as sodium azide. After neutralisation and evaporation to concentrate the solution, it was sent to the PCMU at Harwell for  $^{15}\text{N}$  NMR analysis.

**Mass-spectrometric Analyses for  $\text{N}_2$  and  $\text{N}_2\text{O}$ .**—Our original tracer work<sup>2</sup> suffered from certain limitations, and the samples were undoubtedly contaminated due to leakage of air. The samples were in tubes fitted with taps, they had to be transported 150 miles for analysis, and in some cases had to wait weeks before a mass spectrometer was available. It was felt desirable to repeat some of the work with a modified technique to avoid these problems, and to use the PCMU service at Harwell to improve the quality of the mass-spectrometric analyses. Reaction was carried out in two-legged vessels, with solutions of  $^{15}\text{N}_2\text{H}_5^+$  and perchloric acid in one leg and  $\text{NaNO}_2$  in the other. The vessel was evacuated, and the solutions degassed by repeated freeze–evacuate–thaw cycles. After mixing the reactants the product gases were collected in evacuated glass tubes sealed to a glass break-seal. The side arm of the tube was sealed with a blow-torch and the samples sent to the PCMU at Harwell for mass-spectrometric analysis. The mass spectra confirmed that there were no problems with leakage using this procedure. During the analysis the tube was cooled in liquid argon to freeze out the NO and  $\text{N}_2\text{O}$ , and the

**Table 1** Mass-spectrometric analyses for dinitrogen and dinitrogen monoxide

	[HNO <sub>2</sub> ] <sub>0</sub>	[ <sup>15</sup> N <sub>2</sub> H <sub>5</sub> <sup>+</sup> ] <sub>0</sub>	[H <sup>+</sup> ]	N <sub>2</sub>	<sup>15</sup> NN	<sup>15</sup> N <sub>2</sub>	NNO	<sup>15</sup> NNO
	mol dm <sup>-3</sup>							
				%				
M1	0.05	0.02	1.0	3.1	54.7	40.2	46.3	53.2
M2	0.05	0.02	1.0	3.6	53.1	43.2	38.8	60.7
M3	0.05	0.02	1.0	1.1	56.3	42.5	40.5	59.0
M4	0.10	0.02	1.0	2.8	41.8	55.3	43.0	56.6
M5	0.10	0.02	1.0	2.2	42.8	54.9	49.0	50.2
M6	0.04	0.04	1.0	0.7	68.6	30.6	26.2	73.2
M7	0.05	0.02	2.0	4.5	51.4	44.1	41.3	58.3
M8	0.05	0.02	3.0	3.5	48.7	47.8	43.3	56.2
M9	0.05	0.02	4.0	4.5	51.9	43.6	42.7	56.8
M10	0.05	0.02	pH 3.7	4.8	32.7	62.5	8.2	91.3
M11	0.04	0.04	1.0	0.1	71.0	28.9	27.4	72.1
M12	0.02	0.04	1.0	0.0	75.0	25.0	25.7	72.7

**Table 2** Effect of the nitrous acid:hydrazine ratio on the tracer distribution for reaction in 1 mol dm<sup>-3</sup> H<sup>+</sup>

	[HNO <sub>2</sub> ]/[ <sup>15</sup> N <sub>2</sub> H <sub>5</sub> <sup>+</sup> ]	<sup>15</sup> NN	<sup>15</sup> N <sub>2</sub>	NNO	<sup>15</sup> NNO
		%			
M4,M5	5.0	42.3	55.1	46.0	53.4
M1,M2,M3	2.5	54.7	42.6	41.9	57.6
M6,M11	1.0	69.8	29.8	26.8	72.7
M12	0.5	75.0	25.0	25.7	73.7

isotopic composition of the N<sub>2</sub> was determined. The N<sub>2</sub> was pumped off and a pentane-liquid nitrogen slush was used to vaporise the NO for analysis. The NO was then removed by pumping, and the temperature raised so that the N<sub>2</sub>O vaporised for analysis. Measurements at *m/z* 32 revealed very small peaks for O<sub>2</sub> in some samples, indicating a very slight contamination. From the known peak-height ratio of O<sub>2</sub>:N<sub>2</sub> a small correction was subtracted from the peak at *m/z* 28 for N<sub>2</sub>. The distribution of tracer in N<sub>2</sub>O was determined by the standard method of measuring the amount of <sup>15</sup>NO<sup>+</sup> and <sup>14</sup>NO<sup>+</sup> formed under electron impact in the mass spectrometer, allowing for the known rearrangement <sup>15</sup>NNO → <sup>15</sup>NO<sup>+</sup>.

## Results

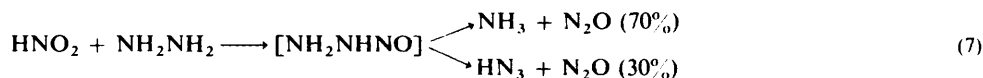
In view of the previous suggestion that a cyclic azide species might be involved, it seemed important to isolate some hydrazoic acid from the reaction mixture and determine the distribution of <sup>15</sup>N tracer between the terminal and central atoms. If cyclic azide is involved, then apart from complications due to kinetic isotope effects, the decomposition of doubly labelled cyclic N<sub>3</sub><sup>-</sup> to the much more stable linear species would give rise to 0.67 [<sup>15</sup>N<sup>15</sup>NN]<sup>-</sup> and 0.33 [<sup>15</sup>NN<sup>15</sup>N]<sup>-</sup>. The first of these should give rise to an <sup>15</sup>N NMR spectrum of two doublets corresponding to the terminal and central nitrogen atoms. The latter would give rise to a singlet whose chemical shift would place it in the middle of the doublet due to the terminal nitrogen atom. Thus, the combined spectrum would have the appearance of a 1:2:1 triplet and a doublet. The observed spectrum showed a doublet, *J* = 11 Hz, at δ -280 (relative to NO<sub>3</sub><sup>-</sup>). This corresponds to the known spectrum of a terminal <sup>15</sup>N split by an <sup>15</sup>N in the central position of an azide ion. This shows the presence of an <sup>15</sup>N<sup>15</sup>NN unit, and the absence of any detectable amount of <sup>15</sup>NN<sup>15</sup>N. The absence of the second doublet, due to the central nitrogen, was due to relaxation-time problems. This was established by evaporating the sodium azide aqueous solution to dryness, dissolving in

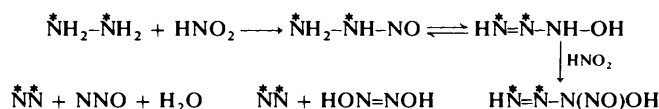
(CD<sub>3</sub>)<sub>2</sub>SO and adding [Cr(acac)<sub>3</sub>] (acac = acetylacetonate) as a relaxation agent. The <sup>15</sup>N NMR spectrum now showed two doublets at δ -280 and -130, each with *J* = 11 Hz in agreement with literature data.<sup>7</sup> To complete the evidence we treated two samples of the isolated NaN<sub>3</sub> with excess of HNO<sub>2</sub>, collected the evolved gas and analysed mass spectrometrically in an MS9 instrument which is designed for studies of organic mass spectra and not well suited to isotope ratio determinations. These analyses gave ratios of peak intensities for *m/z* 44 and 45 of 0.9 and 1.0:1 respectively, as expected for <sup>15</sup>N<sup>15</sup>NN. This evidence shows unambiguously that the azide formed has the tracer distribution expected for reaction (4) and eliminates the original suggestion of a transient cyclic azide.

This result still left unresolved the problem of the tracer distribution in the evolved N<sub>2</sub> and N<sub>2</sub>O, and we therefore repeated the mass-spectrometric studies. The results for N<sub>2</sub> and N<sub>2</sub>O are summarised in Tables 1 and 2. Analyses for NO were isotopically normal. Since we felt it essential to establish the self-consistency of our work, M1, M2 and M3 are repeat experiments, so are M4 and M5, and also M6 and M11. The agreement within each group is good. The consistency of the last pair of results is significant because M6 involved mixing <sup>15</sup>N<sub>2</sub>H<sub>5</sub><sup>+</sup> + HClO<sub>4</sub> with NaNO<sub>2</sub> while M11 involved mixing <sup>15</sup>N<sub>2</sub>H<sub>4</sub> + NaNO<sub>2</sub> with HClO<sub>4</sub>. This suggests that mixing effects are not important. Experiments M1-M3 and M7-M9 show that there is no significant trend in the isotope distribution from 1 to 4 mol dm<sup>-3</sup> perchloric acid. The result for M10 at pH 3.7 shows a large increase in the yield of <sup>15</sup>NNO, and also a marked increase in the yield of <sup>15</sup>N<sub>2</sub>. It is well established<sup>1</sup> that at low acidities the initial nitrosation no longer gives rise to 100% HN<sub>3</sub> and the stoichiometry changes from (1) to (6). This arises from the

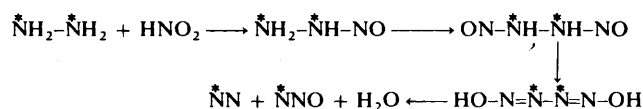


fact that at low acidities the initial nitrosation product can decompose in two ways depending on whether water or ammonia is lost. The 100% yield of azide at higher acidities is due to acid catalysis of the azide-forming pathway. Reaction by the ammonia route would, in the limiting case, lead to 70% of <sup>15</sup>NNO, while of the 30% hydrazoic acid reacted completely with nitrous acid by (3) this would produce an additional 15% of terminally labelled nitrous oxide, making 85% in all. However, this does not account for the tracer distribution in the dinitrogen, which contains 62.5% <sup>15</sup>N<sub>2</sub> and 32.7% <sup>15</sup>NN. In discussions of the mechanism of oxidation of hydrazine it is commonly postulated that diazene is an intermediate, and this could provide a route for the formation of excess of <sup>15</sup>N<sub>2</sub>.

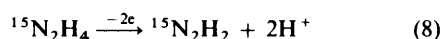




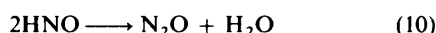
Scheme 1



Scheme 2



Stanbury<sup>8</sup> has recently measured the kinetics of reaction (9) in aqueous solution. If diazene were derived from  $\text{NH}_2\text{NHNO}$  then the other product would presumably be  $\text{HNO}$ , which would produce unlabelled  $\text{N}_2\text{O}$  [equation (10)]. This is not,



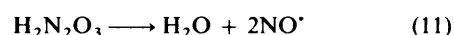
however, the only route by which doubly labelled dinitrogen might be formed. If the first nitrosation product could undergo a second nitrosation before it decomposed, as shown in Scheme 1, the formation of  $\text{N}_2$  + hyponitrous acid would be envisaged. *cis*-Hyponitrite is known to break down very fast to nitrous oxide and water, but *trans*-hyponitrous acid is much more stable.

The most striking feature of the results in Table 1 is the variation in the distribution of tracer with the ratio  $\text{HNO}_2/\text{N}_2\text{H}_5^+$ . The relevant results are summarised in Table 2. For M12, M6 and M11 which have the lower ratios of nitrous acid to hydrazine there is a substantial excess of  $^{15}\text{NN}$  and  $^{15}\text{NNO}$ . The reactions in Scheme 1 do not account for such a result. If, however, there was a second nitrosation at the other nitrogen of hydrazine, as shown in Scheme 2, then this could account for the formation of singly labelled  $\text{N}_2$  and  $\text{N}_2\text{O}$ . Arguments for double nitrosation in the reaction of methylhydrazine<sup>9</sup> and phenylhydrazine<sup>10</sup> with excess of nitrous acid have been given previously.

Reaction by a mixture of the expected pathway *via* the intermediate  $\text{HN}_3$ , (4) + (5), and Scheme 2 can account satisfactorily for the results for  $[\text{HNO}_2]_0/[\text{N}_2\text{H}_5^+]_0 = 0.5, 1.0$  and 2.5. In each case the amount of doubly labelled dinitrogen is matched, within experimental error, with the amount of unlabelled nitrous oxide and the results correspond to 66, 80 and 86% reaction by the hydrazoic acid route, respectively.

The results for a five-fold excess of nitrous acid over hydrazine, M4 and M5, are different. An excess of doubly labelled nitrogen, over 50%, implies reaction either by Scheme 1, or a pathway involving diazene, (8) + (9); however, if stoichiometry (2) is obeyed, there should be an equal amount of unlabelled  $\text{N}_2\text{O}$  and there is not. As M4 and M5 were independent experiments, and the isotopic distributions are very similar, this cannot be dismissed as an erroneous result. The argument that the extra amount of doubly labelled  $\text{N}_2$  should be matched by an increase in unlabelled  $\text{N}_2\text{O}$  assumes that all the  $\text{H}_2\text{N}_2\text{O}_2$  in Scheme 1 (or all the  $\text{HNO}$  formed in the diazene mechanism) give rise to  $\text{N}_2\text{O}$ . If, however, Scheme 1 were to result in the formation of a sizeable amount of *trans*-

hyponitrous acid, then this would only decompose to  $\text{N}_2\text{O}$  very slowly, and the doubly labelled  $^{15}\text{N}_2$  (which is formed rapidly) may not be matched by an equal amount of  $\text{N}_2\text{O}$ . Other explanations are possible. The  $\text{NO}^-$  ion and nitrous acid can form the anion of Angeli's salt,  $\text{HN}_2\text{O}_3^-$ , as was shown by Hughes and Wimbledon,<sup>11</sup> and under acidic conditions in the presence of nitrous acid this very rapidly forms nitric oxide [equation (11)]. This would again lead to a deficiency of



unlabelled  $\text{N}_2\text{O}$ . Another possibility is that  $\text{HNO}$  could be reduced by hydrazine. A one-electron step would lead to the formation of  $\text{NHOH} + ^{15}\text{N}_2\text{H}_3$  (or their conjugate acid forms). The decomposition of  $\text{NHOH}$  leads<sup>12</sup> to  $0.50\text{N}_2$ , while  $2\text{N}_2\text{H}_3$  decomposes to  $\text{N}_2\text{H}_4 + \text{N}_2\text{H}_2$ . This route should lead to the formation of unlabelled  $\text{N}_2$ , and as the high yield of  $^{15}\text{N}_2$  is accompanied by only a very low yield of  $^{14}\text{N}_2$  we think the explanation is unlikely.

We conclude from this work that the cyclic azide hypothesis has to be abandoned, and that we are forced to the conclusion that there are at least three routes for the nitrous acid reaction with hydrazine, one involving the formation of hydrazoic acid which subsequently reacts with nitrous acid, one which involves a dinitrosation of hydrazine, probably forming  $\text{ON}-\text{NH}-\text{NH}-\text{NO}$ , and a third which may involve  $\text{HN}=\text{N}-\text{N}(\text{NO})\text{OH}$ .

### Acknowledgements

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