Nitrogen-tracer Experiments on the Reaction of Hydrazine with an Excess of Nitrous Acid

By **Kieran G. Phelan** and **Geoffrey Stedman**,* Chemistry Department, University College of Swansea, Singleton Park, Swansea SA2 8PP

Mass-spectrometric analysis of the dinitrogen and dinitrogen monoxide evolved from the reaction between $[^{15}N_2H_5]^+$ and excess of HNO_2 are consistent with scrambling occurring between two nitrogens of hydrazine and one nitrogen of nitrous acid. A cyclic form of hydrazoic acid is postulated as a reaction intermediate, although other explanations are possible. At low acidities, pH 3.7, substantial yields of ammonia and N_2O are formed. This would be expected to disturb the pattern of tracer distribution in the evolved gases, but in fact the isotopic results were virtually the same as at higher acidities.

THE present investigation began as an attempt to study the mechanism of reaction of hydrazine with excess of nitrous acid in aqueous acidic solutions. The mechanism of reaction in solutions containing a large excess (tenfold) of hydrazine over nitrous acid has been previously investigated, and shown [1] to occur by a rate-determining N-nitrosation [equation (1)]. The nitrosohydrazine is

$$H^+ + HNO_2 + [N_2H_5]^+ \xrightarrow[\text{slow}]{} [H_3O]^+ + [NH_2NHNO] \xrightarrow[\text{fast}]{} HN_3 + H_2O \quad (1)$$

written as a neutral molecule in (1), but it may exist in a conjugate acid form such as $[NH_3NHNO]^+$. In solutions where $[H^+] > 1$ mol dm^{-3}, hydrazoic acid is virtually the only product; in less acidic solutions a proportion of the products appears as $[NH_4]^+ + N_2O$. Hydrazoic acid also reacts with nitrous acid, and the kinetics of this reaction have been studied. The postulated [2] mechanism is shown in (2). Thus for the reaction of hydrazine with excess of nitrous acid a combination of (1) and (2)

$$H^+ + HNO_2 + HN_3 \xrightarrow[\text{slow}]{} [H_3O]^+ + [N_3NO] \xrightarrow[\text{fast}]{} N_2 + N_2O \quad (2)$$

might plausibly be expected to describe the reaction giving an overall stoicheiometry (3).

$$2HNO_2 + [N_2H_5]^+ \longrightarrow N_2 + N_2O + 2H_2O + [H_3O]^+ \quad (3)$$

Methylhydrazine [3] and phenylhydrazine [4] also react with excess of nitrous acid with rather similar stoicheiometries to (3), equations (4) and (5). However it seems

$$[CH_3NHNH_2{\cdot}H]^+ + 2HNO_2 \longrightarrow CH_3OH + N_2 + N_2O + H_2O + [H_3O]^+ \quad (4)$$

$$[C_6H_5NHNH_3]^+ + 2HNO_2 \longrightarrow [C_6H_5N_2]^+ + N_2O + 3H_2O \quad (5)$$

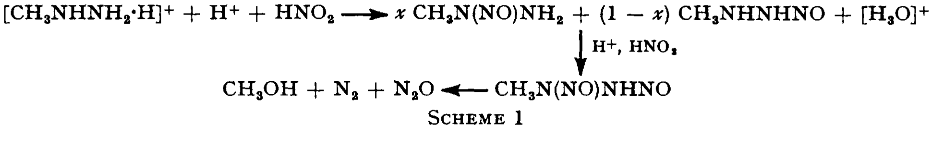
unlikely that methyl azide and phenyl azide are reaction intermediates, as these species do not react at all rapidly with nitrous acid. It has been proposed that reaction (4) proceeds by a double-nitrosation process of the type shown in Scheme 1, and a similar pathway has been suggested for reaction (5).

An analogous process for hydrazine could account for reaction (3). In addition to these explanations it should be noted that an alternative interpretation has been offered by Koltunov and Marchenko,[5] in terms of a mechanism involving N_2H_2 and N_4H_4 as reaction intermediates. It was hoped that a ^{15}N tracer study would enable us to distinguish between these possibilities. A preliminary account of some of this work has already appeared.[6]

EXPERIMENTAL

Materials.—The enriched hydrazine, doubly labelled with ^{15}N to more than 95 atom %, was obtained from Prochem Ltd. and was used without further purification.

Isotopic Experiments.—Reactions were carried out in two-legged reaction vessels, the hydrazine and perchloric acid being placed in one leg and the sodium nitrite solution in the other. The solutions were degassed by a series of freeze, pump-out, and thaw cycles. The tap connecting the vessel to the vacuum line was then closed, and the reagents were mixed by repeated tipping of the solution from one leg of the vessel to the other. The evolved gas was partially transferred by expansion into another evacuated tube, where it was stored over alkali in order to remove acidic gases. Use of this simple technique meant that only a portion of the gaseous products was analysed, but as we were measuring the isotopic composition this should not have mattered apart from a possible loss in accuracy due to the smaller sample size for the mass spectrometer. The tube was then cooled in liquid nitrogen to condense any nitrogen monoxide and dinitrogen monoxide and the residual gas was shared with another tube; this sample was then analysed mass spectrometrically for peaks m/e = 28, 29, and 30. The tube containing the gases that had been condensed in liquid nitrogen was then immersed in a pentane slush-bath and pumped out. At this temperature nitrogen monoxide can be pumped off while dinitrogen monoxide remains behind. In this pro-



$$\begin{tikzcd}[CH_3NHNH_2{\cdot}H]^+ + H^+ + HNO_2 \arrow[r] & x\,CH_3N(NO)NH_2 + (1-x)\,CH_3NHNHNO + [H_3O]^+ \arrow[d, "H^+,\ HNO_2"] \\ CH_3OH + N_2 + N_2O & CH_3N(NO)NHNO \arrow[l]\end{tikzcd}$$

SCHEME 1

cedure there were some losses of dinitrogen monoxide, and it was important not to pump the sample too long. Pumping times of up to 15 min were used. The residual frozen gas was allowed to warm up, and was analysed mass spectrometrically for peaks *m/e* = 46, 45, 44, 31, and 30. Mass-spectrometric analyses were carried out at AERE Harwell on two different instruments, a V.G. Micromass 602C and a V.G. Micromass 16F.

TABLE 1

Mass-spectrometric analyses of gases evolved in the reaction of $[^{15}N_2H_5]^+$ with excess of HNO_2. The hydrazine was 95% ^{15}N-labelled

No.	$[H]^+$	[nitrite]	[hydrazine]		Dinitrogen analyses (%) uncorrected			Dinitrogen analyses (%) corrected		Dinitrogen monoxide analyses (%)				
		mol dm^{-3}		*m/e*	28	29	30	29	30	44	45	46	30	31
9	pH 3.7 [a]	0.40	0.05		7.7	62.0	30.3	67.2	32.8	36.1	63.9	0.0	100	0
7	pH 3.7 [a]	0.04	0.0198		no gas					36.4	63.6	0.0	100	0
8	pH 3.7 [a]	0.20	0.05		72.7	18.6	8.7	68.1	31.9	36.0	64.0	0.0	100	0
6	0.035	0.04	0.02		11.4	61.5	27.1	69.4	30.6	47.5	52.5	0.0	100	0
5 [b]	0.43	0.04	0.02		7.1	61.5	31.3	66.3	33.7					
4	0.95	0.04	0.02		47.7	34.5	17.6	66.2	33.8	39.7	60.3	0.0	100	0
12	0.98	0.0225	0.0075		42.0	44.9	13.1	77.4	22.5	22.8	76.7	0.4	96	4
13	2.51	0.0225	0.0075		49.9	37.6	12.6	74.9	25.1	32.5	67.5	0	100	0
15	3.42	0.0225	0.0075		43.1	39.4	17.5	69.2	30.8	37.1	62.9	0	100	0
10	8.43	0.0225	0.0075		37.0	42.1	20.9	66.8	33.2	no gas				
11	8.43	0.0225	0.0075		27.5	53.4	19.1	73.7	26.3	no gas				

[a] Solution was an HNO_2–$NaNO_2$ buffer. [b] For the N_2O samples peaks 44 and 45 were reported as 63.9 and 36.1%. A transcription error is suspected.

TABLE 2

Effect of the ratio $[HNO_2]/[N_2H_5^+]$ on the isotopic composition of the gaseous products of the reaction between $[^{15}N_2H_5]^+$ and HNO_2 in 0.06 mol dm^{-3} $HClO_4$

$[HNO_2]_0$	$[N_2H_5^+]$		Dinitrogen analyses (%) uncorrected			Dinitrogen analyses (%) corrected		Dinitrogen monoxide analyses (%)				
mol dm^{-3}		*m/e*	28	29	30	29	30	44	45	46	30	31
0.30	0.10		7.8	50.8	41.4	55.1	44.9	35.4	64.3	0.3	94.1	5.9
0.20	0.10		26.2	49.8	24.0	67.3	32.5	33.5	66.2	0.3	97.6	2.4
0.10	0.10		6.9	66.5	26.6	71.4	28.6	35.0	64.7	0.3	95.7	4.3
0.05	0.10							31.3	68.4	0.3	97.5	2.5
0.0098	0.10		55.0	30.9	14.1	68.7	31.3	34.4	65.4	0.3	96.9	3.1

In most cases the samples had to wait a considerable period of time, up to several weeks, before they were analysed, and in some cases there was undoubtedly leakage of air into the sample tubes. Fortunately, as we were using highly enriched $[^{15}N_2H_5]^+$ (99% for experiments in Table 1, 95% for experiments in Table 2), this did not cause a serious problem.

Stoicheiometric Experiments.—Ammonia analyses were carried out by allowing a solution of hydrazine plus a suitable excess of nitrous acid to react to completion. The solution was made alkaline and ammonia was distilled off and collected in a known excess of standard mineral acid, which was then back-titrated. Measurements of the pressure of evolved gas were carried out by reacting hydrazine and nitrous acid solutions in a closed system fitted with a pressure transducer. This was calibrated by using reaction (2) as a standard. Measurements of the consumption of nitrous acid, $\Delta[HNO_2]/\Delta[N_2H_5^+]$, were made by reacting hydrazine with a more than two-fold excess of nitrous acid in a Canterbury SF 3A stopped-flow apparatus. The consumption of nitrous acid was calculated from the initial and final absorbances at 370 nm, assuming complete destruction of hydrazine.

RESULTS

The results of the mass-spectrometric analyses are summarised in Tables 1 and 2. All of the experiments in Table 1 involved at least a two-fold excess of nitrous acid over hydrazine. In order to check whether the ratio of nitrite to hydrazine affected the results we also carried out the experiments shown in Table 2. In a few cases the gas samples were too small for accurate analysis, and this is indicated in the tables. The technique that we used for removing possible traces of nitrogen monoxide from dinitrogen monoxide certainly involved loss of the latter species during the pumping process, and this probably contributed to the small size of the gas sample in some cases. One complication was that in many cases the samples of gas stood for a period of weeks before a mass-spectrometric analysis could be carried out, and in some cases there was certainly some leakage of air as shown by the presence of the argon peak at *m/e* = 40, and the unexpectedly high pressure of gas found in the tube.

Samples 10—15 were a group that had a particularly long wait before analysis and this is reflected in the large size of the peak at *m/e* = 28. For the analysis of dinitrogen monoxide this did not present a difficulty as any carbon dioxide that leaked in would have been absorbed by the alkali and we are sure that the peaks at *m/e* = 44, 45, and 46 do represent N_2O. For the dinitrogen analyses however, this leakage represented a significant problem, and we have not made any use of the peaks at *m/e* = 28 because of possible contamination by atmospheric dinitrogen. Instead we have used only the results for peaks of mass number 29 and 30, and the ' corrected ' results in columns 8 and 9 of Table 1 are percentage figures calculated from the ion currents for these two peaks only. It appears that all the dinitrogen obtained from the nitrous acid–hydrazine reaction contains at least one atom derived from hydrazine, and thus the only peaks of interest are those at mass number 29 and 30. Contamination by dinitrogen from the atmosphere affects the peak at 28, but has negligible effects on those at 29 and 30. Our use of highly enriched, doubly labelled $[N_2H_5]^+$ was particularly fortunate; had we used ^{15}N-labelled nitrite, contamination of our samples by leakage of air would have been a serious difficulty.

ratio is varied from 3.0 (comparable to experiments in Table 1) to 0.1 : 1, and we do not attribute any significance to this difference. It is reported in the literature [7] that a rearrangement of the type $^{15}N^{14}NO \longrightarrow {}^{15}NO^+$ can occur in the mass spectrometry of dinitrogen monoxide. The results in Table 2 were measured on a different instrument to those shown in Table 1 and it may be that the ionisation conditions promoted the rearrangement. We are somewhat surprised that a peak at mass number 31 was not observed in the results shown in Table 1.

TABLE 3

Measurements of the stoicheiometry of the reaction between nitrous acid and hydrazine *

$[H^+]$	$[N_2H_5^+]$	$[\text{nitrite}]_0$	R_1	pH	$[N_2H_5^+]_0$	$[\text{nitrite}]_0$	Y	$[H^+]$	$[N_2H_5^+]_0$	$[HNO_2]_0$	R_2
	mol dm^{-3}				mol dm^{-3}				mol dm^{-3}		
8.46	0.040	0.118	2.04	3.41	0.050	0.20	0.39	0.90	0.002 04	0.004 62	2.03
8.46	0.020	0.050	1.94	3.8	0.079	0.38	0.42	0.45	0.002 04	0.005 35	2.22
0.91	0.040	0.084	2.15	3.8	0.050	0.40	0.60	0.18	0.002 04	0.004 64	2.00
0.41	0.040	0.084	1.98	3.9	0.062	0.38	0.49	0.046	0.002 04	0.004 32	1.73
0.15	0.040	0.091	1.85	3.9	0.020	0.042	0.45	0.0049	0.002 04	0.004 71	1.84
0.05	0.045	0.020	1.87	3.9	0.040	0.084	0.58				
pH 3.7	0.048	0.020	1.47	3.9	0.079	0.108	0.47				
pH 3.6	0.110	0.040	1.34								
pH 5.5	0.101	0.040	1.21								
pH 5.7	0.211	0.080	1.23								

* R_1 = Number of moles gas evolved/moles of $[N_2H_5]^+$; $Y = [NH_4^+]_\infty/[N_2H_5^+]_0$; $R_2 = ([HNO_2]_0 - [HNO_2]_\infty)/[N_2H_5^+]_0$.

A brief comment on the dinitrogen monoxide analyses seems appropriate. Different groups of experiments were analysed on different mass spectrometers by different operators. In all the early work there was no sign of any peak at $m/e = 46$, although a small peak (0.2%) due to $^{14}N^{14}N^{18}O$ might have been anticipated. In the last set of analyses shown in Table 2 there was a report of a small peak, 0.3%, at a mass number of 46. We used markedly larger amounts of reactants in these experiments, and we provided larger samples of gas for isotopic analysis, which made it easier to detect small peaks.

In addition to the isotope experiments we also made measurements on the stoicheiometry of the reaction of hydrazine with excess of nitrous acid. These results are recorded in Table 3.

DISCUSSION

If we examine the results in Table 1 a fairly clear pattern emerges for the analyses of dinitrogen monoxide, with the peaks of mass number 44 and 45 constituting approximately 36 and 64% of the total. The peak of mass number 45 is presumably due to dinitrogen monoxide singly labelled with ^{15}N. The fact that the peaks due to the fragment ions $[NO]^+$ at $m/e = 30$ and 31 give virtually 100% of peak 30 suggests that the dinitrogen monoxide is almost completely $^{15}N^{14}NO$. The nitroso-group of N_2O should be derived from isotopically normal nitrous acid, and thus should contain about 0.35% of ^{15}N. The fact that no peak was observed at $m/e = 31$ must reflect the limitations of the mass-spectrometric analyses shown in Table 1 possibly partly due to small sample size. The results in Table 2 show a significant peak at mass number 31. There is no sign of any trend in the relative size of this peak as the $[HNO_2]_0/[N_2H_5^+]_0$

No clear pattern can be seen from raw mass-spectrometric data for dinitrogen, $m/e = 28$, 29, and 30. If, however, we assume that leakage from the atmosphere is likely to have led to the introduction of $^{14}N_2$ and we ignore the peak $m/e = 28$ then a rather similar pattern to the dinitrogen monoxide results emerges, with peaks of mass numbers 29 and 30 constituting 67 and 33% of the dinitrogen.

Inspection of the results in Table 1 shows that for a limited number of experiments there are results that do not fit this pattern, *e.g.* experiments 6, 12, and 13, and there is also a certain amount of scatter among the majority of results that do fit the pattern. Apart from imperfections in our mass-spectrometric analyses we also have problems in mixing our reaction mixtures under reproducible conditions. For a reaction mixture with $[H^+] = 0.5$ and $[N_2H_5^+] = [HNO_2]_0 = 0.02$ mol dm^{-3} at 25 °C the first half-lifetime for the nitrosation of hydrazine can be calculated from the known kinetics [1] to be *ca.* 0.16 s. As the reactants are mixed by tipping the contents of one leg of an evacuated reaction vessel into the other leg, then it is clear that the rate of mixing may be comparable with or slower than the rate of reaction. Thus the local conditions under which reaction occurs will not be uniform. If, for example, a significant amount of the first nitrosation product $^{15}NH_2{}^{15}NHNO$ were to decompose to $^{15}NH_4^+ + {}^{15}NNO$ then this would increase the percentage of the peak of mass number 45. We cannot suggest any obvious explanation for the contrary observation in experiment 6, where the percentage of peak of mass number 44 is unusually high, apart from the speculation that there might have been contamination by carbon dioxide (although this should have been absorbed by alkali). Our early experiments involved mixing of the reaction solutions at ambient temperatures, *ca.* 20 °C, but when the possible importance of the mixing process was realised we mixed the reactants immediately after the frozen solutions had melted, so that the temperature would be close to 0 °C and the reaction rate be correspondingly lower.

Turning to the interpretation of the results, we note first of all that they are not consistent with the alternative mechanism proposed by Koltunov and Marchenko.[5] These workers reported the stoicheiometry (6), and proposed the mechanism shown below involving intermediates such as $\mathrm{N_2H_2}$ and $\mathrm{N_4H_4}$ which have frequently been invoked in discussions of the oxidation of hydrazine, particularly by metal-ion oxidants.[8] From this mechanism we would predict that with doubly labelled hydrazine the dinitrogen monoxide would be unlabelled, while the dinitrogen should be 100% doubly labelled. This does not fit the observed results. If both the ammonia and the hydrazoic acid in (6) reacted completely with nitrous acid then the dinitrogen would be 85.7% doubly labelled and 14.3% singly labelled, while the dinitrogen monoxide would be 85.7% unlabelled and 14.3% singly labelled (in the terminal position). This isotope distribution does not fit the observed results either. This confirms our previous conclusion [1] that the mechanism in Scheme 2 is incorrect. Other workers have reached a similar conclusion.[9]

$$\begin{aligned}&\mathrm{7N_2H_4 + 12HNO_2 + H^+ \longrightarrow}\\&\qquad\mathrm{[NH_4]^+ + HN_3 + 5N_2 + 6N_2O + 18H_2O}\end{aligned}\qquad(6)$$

$$\begin{array}{rl}\mathrm{H^+ + HNO_2} & \rightleftharpoons \mathrm{[NO]^+ + H_2O}\\ \mathrm{[N_2H_5]^+ + [NO]^+} & \longrightarrow \mathrm{N_2H_2 + HNO + 2H^+}\\ \mathrm{2N_2H_2} & \longrightarrow \mathrm{N_4H_4} \longrightarrow \mathrm{N_2H_4 + N_2}\\ \mathrm{2N_2H_2} & \longrightarrow \mathrm{N_4H_4} \longrightarrow \mathrm{NH_3 + HN_3}\\ \mathrm{2HNO} & \longrightarrow \mathrm{N_2O + H_2O}\end{array}$$

SCHEME 2

Turning to the mechanism summarised in equations (1) and (2), the predicted isotope distribution in the products is summarised in equation (7). Again it is apparent that this does not fit the present observations. The alternative mechanism involving a double nitrosation would produce the isotope distribution shown in equation (8), which again is not consistent with the observed results.

$$\begin{aligned}&\mathrm{[{}^{15}N_2H_5]^+ + [NO]^+ \longrightarrow {}^{15}NH_2{}^{15}NHNO \longrightarrow H[{}^{15}N{}^{15}NN]} \xrightarrow{\mathrm{[NO]^+}}\\&\qquad\tfrac{1}{2}\mathrm{ON{}^{15}N{}^{15}NN} + \tfrac{1}{2}\mathrm{{}^{15}N{}^{15}NNNO} \longrightarrow \tfrac{1}{2}\mathrm{{}^{15}N{}^{15}N} + \tfrac{1}{2}\mathrm{NNO} + \tfrac{1}{2}\mathrm{{}^{15}NNO} + \tfrac{1}{2}\mathrm{{}^{15}NN}\end{aligned}\qquad(7)$$

$$\begin{aligned}&\mathrm{[{}^{15}N_2H_5]^+ + [NO]^+ \longrightarrow {}^{15}NH_2{}^{15}NHNO} \xrightarrow{\mathrm{[NO]^+}}\\&\qquad\mathrm{ON{}^{15}NH{}^{15}NHNO \longrightarrow {}^{15}NNO + {}^{15}NN + H_2O}\end{aligned}\qquad(8)$$

A possible rationalisation of these points is to postulate parallel reactions forming dinitrogen and dinitrogen monoxide by reactions (7) and (8) assuming products to be formed in the ratio 2 : 1 respectively. This would certainly lead to an isotope distribution of 66.6% $\mathrm{{}^{15}NN}$, 33.3% $\mathrm{{}^{15}N{}^{15}N}$ and 66.6% $\mathrm{{}^{15}NNO}$, 33.3% NNO, close to what we observe. However, we find that the pattern of tracer distribution is independent of acidity and of the concentrations of nitrous acid and hydrazine over a wide range of values, and it seems improbable that the relative rates of two processes should be so constant. The formation of hydrazoic acid as a product is known to be favoured by increased acidity, and the rate of a nitrosation process such as (9) might well be acid catalysed; thus acidity might affect the rates of (9) and (10) similarly. Against this one should note that in the reaction of phenylhydrazine with excess of nitrous acid the double-nitrosation mechanism appeared to be favoured by low acidities whereas the formation of phenyl azide was favoured by high acidities. A more cogent objection is that one might expect the rate of a reaction such as (9) to be dependent upon the nitrous acid concentration whereas (10) should be independent of $\mathrm{[HNO_2]}$. This difficulty would be avoided if reaction (9) involved two consecutive processes, a rate-determining reaction independent of $\mathrm{[HNO_2]}$ followed by a fast reaction in which nitrous acid took part.

$$\mathrm{NH_2NHNO + HNO_2 \longrightarrow ONNHNHNO + H_2O}\qquad(9)$$

$$\mathrm{NH_2NHNO \longrightarrow HN_3 + H_2O}\qquad(10)$$

By far the simplest and most direct interpretation of our isotopic data is to assume a mechanism whereby the two labelled nitrogen atoms from hydrazine and one unlabelled nitrogen from nitrous acid become scrambled in the formation of hydrazoic acid. Reaction with nitrous acid (in the form of the active electrophilic species $\mathrm{[NO]^+}$) leads to the results set out in Scheme 3. A plausible way in which such scrambling could occur is shown in Scheme 4. Formation of hydrazoic acid from *N*-nitrosohydrazine must involve tautomerisation and loss of water. The postulated intermediate ***trans***-$\mathrm{NH_2N{=}N{-}OH}$ is a plausible species; analogous compounds *trans*-hyponitrous acid (HO–N=N–OH) and tetrazene [10] ($\mathrm{NH_2N{=}N{-}NH_2}$) are known species. The postulated mode of decomposition of $\mathrm{NH_2N{=}N{-}OH}$ involves neighbouring-group participation with the nucleophilic amino-group helping the expulsion of the hydroxyl group (which is probably protonated and leaves as water). Such a process is postulated to result in the formation of a cyclic azide species in which all three nitrogens become equivalent. Breakdown of this to a linear azide would form isotopically scrambled hydrazoic acid. A modification of this explanation would involve attack by $\mathrm{[NO]^+}$ on the cyclic azide to form $\mathrm{N_3NO}$: this would lead to the same result, isotopic scrambling.

An alternative explanation, for which we are indebted to a referee of our earlier paper,[6] is that scrambling might occur in the decomposition of nitrosyl azide. If homolytic cleavage produced the azide radical and nitrogen monoxide, then combination of two $N_3^{\bullet}$ to form a symmetric cyclic N_6 species would induce scrambling. An example of this is known in the literature.[11] The difficulty with this explanation is that if N_6 were formed and then decomposed to 3 N_2 then nitrogen monoxide would be a product of the reaction between nitrous acid and hydrazoic acid, as shown below. This has not been

$$2\,HNO_2 + 2\,HN_3 \longrightarrow 2\,H_2O + 2\,NO + 3\,N_2$$

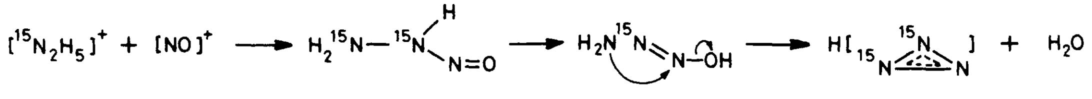
observed. If we suppose that N_6 redissociated to 2 $N_3^{\bullet}$, and that the azide radicals diffused apart and recombined quantitatively with nitrogen monoxide, then this would fit the observed results. It seems, however, a complex scheme and we doubt whether there would not be some loss of N_6 to form 3 N_2. An alternative explanation involving the azide radical is to suppose that homolytic fission of nitrosyl azide occurs, and that the cyclic azide radical scrambles its nitrogen atoms by cyclisation, followed by return to a linear species within the solvent cage. Leaving aside the question of whether a cyclic azide radical species is any more plausible than the cyclic HN_3 species we have postulated, a major difficulty with this explanation is that in the classic study by Clusius and Effenberger[12] of ^{15}N labelling in the hydrazoic acid–nitrous acid reaction there was no sign of this scrambling.

$$\tfrac{2}{3}H[^{15}N^{15}NN] + \tfrac{1}{3}H[^{15}NN^{15}N] + [NO]^+ \longrightarrow \tfrac{1}{3}(^{15}N^{15}NNNO) + \tfrac{1}{3}(N^{15}N^{15}NNO) + \tfrac{1}{3}(^{15}NN^{15}NNO)$$

$$\downarrow$$

$$\tfrac{1}{3}(^{15}N^{15}N) + \tfrac{2}{3}(^{15}NN) + \tfrac{1}{3}(NNO) + \tfrac{2}{3}(^{15}NNO)$$

SCHEME 3



SCHEME 4

The Stability of Cyclic Azide Structures.—Cyclic structures were suggested in the early days of azide chemistry, but the linear structure has been long established. There are not, so far as the authors are aware, any stable compounds with a three-nitrogen ring system. Wright[13] has reported *ab initio* calculations indicating that there may be a minimum in the potential-energy surface for $[N_3]^+$ corresponding to a cyclic species, although of higher energy than the linear symmetric and linear asymmetric species. He also reports calculations on cyclic N_4 and N_6 species. There are, however, several pieces of evidence in the literature[14] that suggest a high-energy cyclic azide species may exist. When solid alkali-metal azides are irradiated with u.v. light there is spectroscopic evidence for the formation of a species with D_{3h} symmetry, possibly a cyclic form of $N_3^{\bullet}$. This must be a high-energy species and so it cannot be claimed that these observations show that such cyclic species are likely to be formed in thermal reactions at ambient temperatures. Bonner and co-workers[9] have searched for evidence of isotopic scrambling when aqueous solutions of $Na[^{15}NNN]$ and $H[^{15}NNN]$ were irradiated with u.v. light, but without success. Turning now to theoretical considerations, a cyclic azide ion would have four π electrons, and be anti-aromatic. Theoretical calculations by the MINDO 3 method give ΔH_f for cyclic $HN_3(g)$ to be +11.7 kJ mol^{-1} and for the open-chain molecule $HN_3(g)$ to be −60.7 kJ mol^{-1}. The MINDO 3 method is known to be not very successful for nitrogen compounds, and the absolute values must be treated with reservation. Differences in ΔH_f values are probably more reliable, so this certainly suggests that cyclic hydrazoic acid is markedly less stable than the familiar form. Calculations on cyclic $N_3^-(g)$, linear $N_3^-(g)$, cyclic $N_3^{\bullet}(g)$, and linear $N_3^{\bullet}(g)$ gave ΔH_f values of +75.5, −3.7, +35.9, and +9.4 kJ mol^{-1} respectively, again indicating the lower stability of the cyclic species. Recent measurements by ion cyclotron resonance spectroscopy[15] have led to values of ΔH_f of 201 and 468 kJ mol^{-1} for the linear species $N_3^-(g)$ and $N_3^{\bullet}(g)$, which may be compared with the thermochemical values[16] of 146 and 439 kJ mol^{-1} respectively. Clearly the MINDO 3 calculation does not work well for azide species, so we cannot put much weight on the calculation for cyclic $HN_3(g)$.

Reaction Stoicheiometry.—The discussion so far has been based upon the assumption that the stoicheiometry is given by equation (3). A detailed study of the stoicheiometry under rather different conditions to the present work, with a large excess of hydrazine over nitrous acid in solutions at 1.8 mol dm^{-3} ionic strength at 0 °C, showed[1] that the yield of hydrazoic acid is described by (11). Thus for $[H^+] \geqslant 0.34$ mol dm^{-3} the yield of hydrazoic acid is more than 90%, and (3) will be a reasonable approximation. However at lower acidities there are substantial yields of ammonia, suggested to be formed by (12). Dinitrogen monoxide obtained by this reaction might well have a different isotopic composition to that derived from the route (1) + (2). Another potential complication is that the relative proportions of NH_3 and HN_3 may be different in excess of nitrous acid compared to excess of hydrazine. Thus a pathway such as (8) might be favoured by excess of nitrous acid, and the disappearance of NH_2NHNO by this route would reduce the

$$[HN_3]_\infty/([HNO_2]_0 - [HN_3]_\infty) = 0.44 + 25\,[H^+] \quad (11)$$

$$NH_2NHNO \longrightarrow NH_3 + N_2O \quad (12)$$

amount of ammonia formed by (12). We therefore turn to the results of the stoicheiometric studies summarised in Table 3.

The most direct evidence comes from the ammonia yields Y in column 8 of Table 3 where it appears that around pH 4 there are yields of around 50%. The limiting low-acidity yield calculated from (11) is 69.4%. We may in some cases have lost some ammonia through the familiar reaction between ammonia and nitrous acid, although we would expect such losses to be small, but it is clear that even in the presence of a large excess of nitrite there is a substantial conversion of hydrazine into ammonia at low acidities. This is confirmed by the gas-evolution experiments. The ratio of the number of moles of gas evolved to the number of moles of hydrazine consumed is close to 2 : 1, the value expected from equation (3) at acidities down to $[H^+] = 0.05$ mol dm^{-3}. At acidities comparable to those used in the ammonia experiments R_1 drops to *ca.* 1.4, and in still less acidic solutions it goes to 1.22. The limiting value of R_1 expected from (11) is 1.31. The third set of experiments set out in Table 3 are measurements of the consumption of nitrous acid relative to hydrazine. These are not strictly comparable with the other two sets of stoicheiometric measurements because the concentrations of hydrazine and nitrous acid are about an order of magnitude lower. At high acidities the ratio R_2 ($\Delta[HNO_2]/\Delta[N_2H_5^+]$) is close to 2 : 1, the value expected from (3), while at lower acidities there are signs of a decrease. Our conclusion is that for reaction of excess of nitrite with hydrazine at about pH 3.7 a substantial amount of ammonia is formed, probably around 50%. Independent evidence for this view comes from a stoicheiometric study of the hydrazine–nitrous acid reaction by Bonner and co-workers.[9] These workers have shown that for reaction at acidities $[H^+] > 0.5$ mol dm^{-3} the ratio $[N_2O]/[N_2]$ in the evolved gases is close to 1 : 1 as required by (3). When the acidity is reduced to 0.001 mol dm^{-3} the ratio $[N_2O]/[N_2]$ rises to 4.2 : 1 (excess of hydrazine) and 3.2 : 1 (excess of nitrite).

The fact that reaction at pH 3.7 produces some 50% of ammonia and some dinitrogen monoxide (presumably an equal amount) suggests that this might affect the results of the tracer experiments at these acidities. The dinitrogen monoxide formed from $^{15}NH_2{}^{15}NHNO$ would reasonably be expected to be ^{15}NNO, and a mixture of 50% of this species and 50% of the scrambled dinitrogen monoxide from the 'cyclic' azide pathway would yield a mixture that is overall 16.7% NNO and 83.3% ^{15}NNO for a mixture that initially has $[HNO_2] : [N_2H_5^+] = 2 : 1$. In experiments 8 and 9 of Table 1 the ratio of nitrite to hydrazine is 4 : 1 and 8 : 1 respectively and so in these cases dilution by the excess of isotopically normal nitrous acid could have minimised this effect (although it is not clear how such a dilution could occur). However experiment 7 with 2 : 1 ratio shows the 'usual' 45 : 44 (mass number) ratio of 2 : 1. If the nitrogen atoms in $^{15}NH_2{}^{15}NHNO$ could scramble by *reversible* formation of our postulated cyclic azide then one would expect the dinitrogen monoxide formed in (12) to be a mixture of $^{15}N^{15}NO$, $N^{15}NO$, and ^{15}NNO. There was no sign of any significant peak at mass number 46, as would be expected for $^{15}N^{15}NO$, and at most only a relatively small peak at mass number 31, expected for $^{15}NO^+$ derived from $^{15}N^{15}NO$ and $N^{15}NO$. The small peak at 31 was only reported for one group of experiments (Table 2), and may be due to a mass-spectrometric rearrangement, as mentioned above. If 50% of the dinitrogen monoxide were derived from the ammonia route, one would expect the 30 : 31 (mass number) ratio to be 66.6 : 33.3, much higher than the average 96 : 4 ratio in Table 2. This seems to be an unsatisfactory explanation. If one postulates a route whereby nitrous acid attacks cyclic azide with the formation of dinitrogen monoxide and ammonia, with the NO group of the N_2O derived from the nitrous acid, then one could account for the formation of N_2O of the observed isotopic composition. This is shown in equation (13), with *N

$$H[\textit{cyclo}\text{-}{*N_3}] + HNO_2 + H_2O \longrightarrow {*NH_3} + H{*NO_2} + {*NNO} \qquad (13)$$

representing isotopically scrambled nitrogen, 66.6% ^{15}N and 33.3% of N. However this results in the introduction of ^{15}N tracer into the nitrite, which would lead in turn to the formation of $*N*NO$ and $N*NO$, whose existence we have just discounted. Another source of dinitrogen monoxide is hyponitrous acid, but reactions such as (14) can be rejected on the grounds that they

$$H[\textit{cyclo}\text{-}N_3] \xrightarrow{2H_2O} NH_3 + HON{=}NOH \longrightarrow N_2O + H_2O \qquad (14)$$

would result in the formation of N_2O with ^{15}N tracer in in the nitroso-group. We have also considered mechanisms involving $HNO^{\bullet}$ as a postulated source of dinitrogen monoxide, but have not succeeded in finding one that fits the facts. These difficulties are not peculiar to the postulated cyclic azide mechanism. If one assumes that the isotope results are due to parallel reactions by (7) and (8) in the ratio 2 : 1, then one still expects changes in the isotopic composition of the products under conditions where some 50% of the dinitrogen monoxide is derived from the ammonia route.

In conclusion, therefore, the isotopic results suggest a common pattern of behaviour over a wide range of acidity and relative concentrations of reactants. We can account for the results at hydrogen-ion concentrations above *ca.* 0.3 mol dm^{-3} either by a nitrogen-scrambling mechanism, possibly involving a cyclic form of azide, or by parallel reactions involving the nitrosation of HN_3 and NH_2NHNO. Neither explanation appears to account for the fact that, at low acidities where substantial yields of ammonia are observed, the pattern of the isotope distribution seems to be the same as at higher acidities.

We are indebted to the S.R.C. for a maintenance award (to K. G. P.), and to AERE Harwell and BNFL for financial support. We thank Professor F. T. Bonner for helpful discussion and prior communication of results, and Drs. R. K.

Webster and J. H. Miles for helpful discussion and for arranging mass-spectrometric analyses. We are indebted to Mr. C. Sweeney for the MINDO 3 calculations.

[2/092 *Received*, 18*th January*, 1982]

REFERENCES

[1] J. R. Perrott, G. Stedman, and N. Uysal, *J. Chem. Soc., Dalton Trans.*, 1976, 2058.

[2] G. Stedman, *J. Chem. Soc.*, 1959, 2943.

[3] J. R. Perrott, G. Stedman, and N. Uysal, *J. Chem. Soc., Perkin Trans. 2*, 1977, 274.

[4] G. Stedman and N. Uysal, *J. Chem. Soc., Perkin Trans. 2*, 1977, 667.

[5] V. S. Koltunov and V. I. Marchenko, *Kinet. Katal.*, 1966, **7**, 224.

[6] K. G. Phelan and G. Stedman, *J. Chem. Soc., Chem. Commun.*, 1981, 299.

[7] L. Friedman and J. Bigeleisen, *J. Chem. Phys.*, 1950, **18**, 1325; G. M. Begun and L. Landu, *ibid.*, 1961, **35**, 547.

[8] W. C. E. Higginson, *Spec. Publ. Chem. Soc.*, 1975, **10**, 95.

[9] F. T. Bonner, personal communication.

[10] N. Wiberg, H. Bayer, and H. Bachhuber, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 177.

[11] R. C. Thompson and J. C. Sullivan, *Inorg. Chem.*, 1970, **9**, 1590; C. F. Wells and D. Mays, *J. Chem. Soc. A*, 1969, 2175.

[12] K. Clusius and E. Effenberger, *Helv. Chim. Acta*, 1955, **38**, 1843.

[13] J. S. Wright, *J. Am. Chem. Soc.*, 1974, **96**, 4753.

[14] J. I. Bryant, *Spectrochim. Acta*, 1966, **22**, 1475; H. A. Papazian, *J. Phys. Chem. Solids*, 1969, **30**, 462.

[15] M. J. Pellerite, R. L. Jackson, and J. I. Brauman, *J. Phys. Chem.*, 1981, **85**, 1624.

[16] P. Gray, *Q. Rev. Chem. Soc.*, 1963, **17**, 441.