

## Is Hydrazoic Acid (HN<sub>3</sub>) an Intermediate in the Destruction of Hydrazine by Excess Nitrous Acid?

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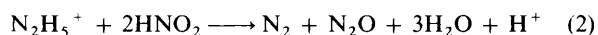
The kinetics of the decomposition of NH<sub>2</sub>N=NOH, the intermediate absorbing at 225 nm formed in the nitrous acid-hydrazine reaction have been studied by stopped-flow spectrophotometry at acidities up to 1 mol dm<sup>-3</sup> H<sup>+</sup>. A substantial amount of protonation occurs at high acidities, and the pK<sub>a</sub> of NH<sub>3</sub><sup>+</sup>N=NOH is 0.57. In excess hydrazine decomposition occurs to form hydrazoic acid (HN<sub>3</sub>), but in excess nitrous acid a rapid second nitrosation occurs by a diffusion-controlled reaction between NO<sup>+</sup> and NH<sub>2</sub>N=NOH which can bypass this pathway, though the possibility of some hydrazoic acid formation cannot be ruled out. Spectrophotometric evidence has been obtained for the formation of a relatively stable species, probably a very minor component, a product of the double-nitrosation reaction.

Hydrazine is frequently used as a nitrite scavenger in reaction systems where it is necessary to remove the last traces of nitrous acid. This is particularly important where the reaction medium is aqueous nitric acid, because nitric and nitrous acids react to form the nitrogen(IV) oxides N<sub>2</sub>O<sub>4</sub> and NO<sub>2</sub>, which can act as powerful redox catalysts. Its excellence as a scavenger arises from the fact that the hydrazinium ion reacts with NO<sup>+</sup> at almost the encounter rate,<sup>1</sup> and as it is only weakly basic it is not significantly deactivated by undergoing a second protonation. Rates of nitrite scavenging by hydrazine in solutions up to 15 mol dm<sup>-3</sup> nitric acid have been measured.<sup>2</sup> Hydrazine reacts only very slowly with nitric acid, and is thus a potential useful nitrite scavenger in nuclear fuel reprocessing.<sup>3</sup> At acidities above 1 mol dm<sup>-3</sup> H<sup>+</sup>, and with excess hydrazine, the product is almost 100% hydrazoic acid, equation (1), though

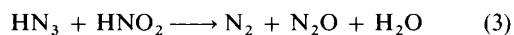


at low acidities ammonia and dinitrogen monoxide are also formed.<sup>1</sup>

At other stages in the reprocessing cycle it may be necessary to destroy unreacted hydrazine, and this can easily be done by reaction with excess nitrous acid, equation (2). Hydrazoic acid



is known<sup>4</sup> to react rapidly with nitrous acid as shown in equation (3), and hence is a plausible intermediate in reaction



(2). However an isotopic tracer study with <sup>15</sup>N-labelled hydrazine has shown<sup>5</sup> that other reaction pathways also exist. In view of the fact that hydrazoic acid is volatile, explosive and toxic it is desirable to understand the detailed mechanism of reaction (2), and to see whether hydrazine can be destroyed without generating hydrazoic acid as an intermediate. Previous work<sup>1</sup> on the hydrazine-nitrous acid reaction concentrated on reaction in excess hydrazine, at acidities below pH 1. The present work is concerned with much more acidic solutions, and the effect of excess nitrous acid on the kinetics of decomposition.

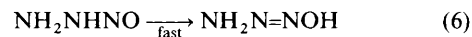
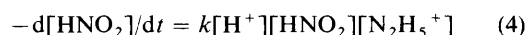
### Experimental

*Materials.*—All of the chemicals were Analar materials and were used without further purification.

*Kinetics.*—Rapid reactions were followed on a Canterbury SF 3A-stopped-flow instrument with a data collection system. The disappearance of nitrous acid was followed at 360 nm where there is a characteristic, low-intensity absorption. The growth of the intermediate was followed at 253 nm, on the long wavelength side of the absorption maximum; our stopped-flow did not function well at lower wavelengths due to scattered light. Repeated scan spectra were run on a Unicam SP8-200 spectrophotometer. Pressure measurements for gas evolution were made with a standard pressure transducer calibrated for the evolution of N<sub>2</sub> + N<sub>2</sub>O by reaction (3). Solutions were made up to constant ionic strength with LiClO<sub>4</sub>.

### Results and Discussion

*Reaction in Excess Hydrazine.*—Previous work<sup>1</sup> has shown that in mildly acidic media, pH 1–3, nitrous acid reacts with excess hydrazine by a rate determining N-nitrosation, following rate-law (4), to form a product absorbing at 225 nm, reactions



(5) and (6) respectively. On the basis of spectroscopic and kinetic arguments this was concluded to be *trans*-NH<sub>2</sub>N=NOH, formed by the rapid tautomerisation of the initially formed *N*-nitrosohydrazine. This is analogous to the well established mechanism of the diazotisation and deamination reactions. To establish that there is no build up of any precursor to NH<sub>2</sub>N=NOH we have followed the kinetics of formation of NH<sub>2</sub>N=NOH and shown that they follow the same rate law, with the same rate constant as for the disappearance of nitrous acid.

Traces showing the growth of NH<sub>2</sub>N=NOH are shown in

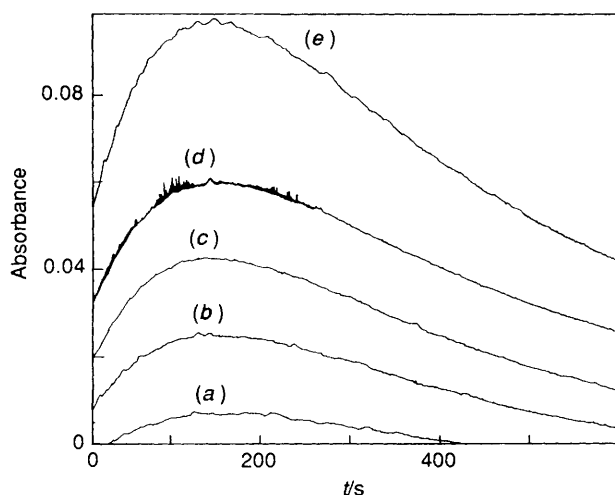


Fig. 1 Absorbance vs. time scans for the hydrazine-nitrous acid reaction at 250 nm:  $10^4[\text{N}_2\text{H}_5^+] = 9.6$ ;  $10^3[\text{H}^+] = 4.8$ ;  $10^5[\text{HNO}_2] = 3.2$  (a), 6.4 (b), 9.6 (c), 11.2 (d), 20.0 (e)  $\text{mol dm}^{-3}$

Table 1 Kinetics of formation ( $k_1$ ) and decomposition ( $k_2$ ) of  $\text{NH}_2\text{N}=\text{NOH}$  at  $0^\circ\text{C}$  ( $[\text{HNO}_2]_0 = 0.004$ ,  $[\text{N}_2\text{H}_5^+]_0 = 0.06$ ,  $I = 1.0$   $\text{mol dm}^{-3}$ )

$[\text{H}^+]/\text{mol dm}^{-3}$	$10^2 k_2/\text{s}^{-1}$	$k_1/\text{s}^{-1}$	$\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$
0.1	1.45		296
0.2	2.24		263
0.4	3.12	7.4	153
0.6	3.71	10.8	123
0.8	4.03	12.1	108
1.0	4.27	14.0	97

Fig. 1, and these also illustrate the fact that the intermediate undergoes a slow, acid-catalysed decomposition, the kinetics of which were previously<sup>1</sup> established at low acidities to follow rate law (7) at  $25^\circ\text{C}$ .

$$v = 1.07[\text{H}^+][\text{NH}_2\text{N}=\text{NOH}] \text{ mol dm}^{-3} \text{ s}^{-1} \quad (7)$$

With conventional spectrophotometry it was not practicable to extend these measurements below about pH 2. To study the reactions at acidities closer to those of industrial interest it was necessary to go to  $1 \text{ mol dm}^{-3} \text{H}^+$ , where the kinetics were much faster. We reduced the rate by working at  $0^\circ\text{C}$ , and used stopped-flow spectrophotometry. With our equipment it was not practicable to work at 225 nm, and measurements on the formation and decay of the intermediate were made at 253 nm. With a fifteen-fold excess of hydrazine over nitrite the rate of formation of  $\text{NH}_2\text{N}=\text{NOH}$  was much faster than its decay. Both reactions followed pseudo-first order kinetics with rate constants  $k_1$  and  $k_2$  respectively shown in Table 1. Measurements at 363 nm for nitrous acid and 253 nm for  $\text{NH}_2\text{N}=\text{NOH}$  confirmed that rate law (4) held at higher acidities and that the rate of loss of nitrous acid was still equal to the rate of formation of the intermediate. The spectrum of the solution at the end of the reaction was that expected for hydrazoic acid, with a broad maximum at 258 nm. From the intensity of this peak we confirmed that at high  $[\text{N}_2\text{H}_5^+]_0$  the product was 98% hydrazoic acid. Its identity was confirmed by making the solution alkaline and observing the expected change to the azide ion spectrum.

*Acid-Base Properties of the Intermediate.*—The kinetics of the decomposition of the intermediate showed a marked change from the low-acidity behaviour. The rate constant  $k_2$  tended to level off at higher acidities, as can be seen from the data in Table 1, and the absorption coefficient  $\epsilon$  of the intermediate decreased

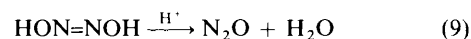
markedly as the acidity increased. This suggests that a sizeable fraction of the intermediate is being protonated, giving rise to a decrease in absorbance, and a levelling off in rate because further increases in  $[\text{H}^+]$  do not significantly increase the concentration of the conjugate acid species. For such a system the rate constant  $k_2$  should vary as shown in equation (8), where

$$k_2 = k_3[\text{H}^+]/([\text{H}^+] + K_a) \quad (8)$$

$K_a$  is the dissociation constant of the conjugate acid and  $k_3$  is the rate constant for the decomposition.

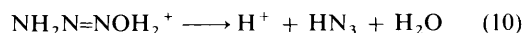
A plot of  $1/k_2$  vs.  $1/[\text{H}^+]$  yields a good straight line with  $k_3 = 0.0532 \pm 0.02 \text{ s}^{-1}$  and  $K_a = 0.268 \pm 0.013 \text{ mol dm}^{-3}$ . At low acidities  $k_2 = (k_3/K_a)[\text{H}^+]$ . Combining the present data with the earlier figure of  $1.07 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for  $k_3/K_a$  at  $25^\circ\text{C}$  yields an activation energy of  $45.6 \text{ kJ mol}^{-1}$ . The absorption coefficient data were not as good as the rate-constant data, and a plot of  $1/\epsilon$  vs.  $1/[\text{H}^+]$  yielded a value of  $K_a = 0.33 \text{ mol dm}^{-3}$ . By setting  $K_a = 0.268 \text{ mol dm}^{-3}$  and assuming that the absorption coefficient for the conjugate acid is much less than for the conjugate base we calculate  $\epsilon_{253} = 460 \pm 80 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  for  $\text{NH}_2\text{N}=\text{NOH}$ .

The acid-base character of  $\text{NH}_2\text{N}=\text{NOH}$  was further examined by quenching a reaction solution with  $[\text{N}_2\text{H}_5^+] = 0.04$ ,  $[\text{HNO}_2]_0 = 0.004$  and  $[\text{H}^+] = 0.026 \text{ mol dm}^{-3}$  in  $1 \text{ mol dm}^{-3} \text{NaOH}$  15 s after mixing. This is sufficient time for all of the nitrous acid to have been consumed ( $t_1 \approx 1.1 \text{ s}$ ) but for very little decomposition of  $\text{NH}_2\text{N}=\text{NOH}$  to have occurred. The quenched solution showed a new peak at 243 nm, which was stable for ca. 1 h. This peak is likely to be due to  $\text{NH}_2\text{N}=\text{NO}^-$ . The compound with the closest structural similarity to  $\text{NH}_2\text{N}=\text{NOH}$  is *trans*-hyponitrous acid,  $\text{HON}=\text{NOH}$ , and it is interesting to compare the two systems. Hyponitrous acid has<sup>6</sup> a  $\text{p}K_1$  of 7, so ionisation of  $\text{NH}_2\text{N}=\text{NOH}$  to  $\text{NH}_2\text{N}=\text{NO}^-$  in  $1 \text{ mol dm}^{-3}$  sodium hydroxide is reasonable. The wavelength maxima for  $\text{HON}=\text{NOH}$  and  $\text{HON}=\text{NO}^-$  are 209 and 233 nm which compare with 225 and 243 nm for  $\text{NH}_2\text{N}=\text{NOH}$  and  $\text{NH}_2\text{N}=\text{NO}^-$ . Hyponitrous acid undergoes a slow acid-catalysed decomposition, (9), as observed for  $\text{NH}_2\text{N}=\text{NOH}$ .



There are differences in behaviour. The anion  $\text{HON}=\text{NO}^-$  is not stable, but decomposes to  $\text{N}_2\text{O} + \text{OH}^-$ , and there is also an acid-independent term in the rate law for the decomposition of hyponitrous acid.<sup>6</sup>

Possible sites for protonation in  $\text{NH}_2\text{N}=\text{NOH}$  are the amino group, the hydroxyl group, the double bond and lone pairs on the double-bonded nitrogens. The reactions of  $\text{HON}=\text{NOH}$  have been studied<sup>7</sup> up to  $11.6 \text{ mol dm}^{-3}$  perchloric acid, with no evidence of the formation of measurable amounts of a conjugate acid, so by analogy we exclude the last three sites. General experience would lead one to predict the amino group as the most basic site anyway. However this does pose a problem of interpretation of the kinetics, as the obvious decomposition products of  $^+\text{NH}_3\text{N}=\text{NOH}$  are  $\text{NH}_3 + \text{N}_2\text{O} + \text{H}^+$ , and ammonia and dinitrogen monoxide are only major products at low acidity.<sup>1</sup> However,  $^+\text{NH}_3\text{N}=\text{NOH}$  will be in equilibrium with a smaller concentration of the O-protonated tautomer  $\text{NH}_2\text{N}=\text{NOH}_2^+$  and decomposition of this to  $\text{H}^+ + \text{HN}_3 + \text{H}_2\text{O}$  seems reasonable with water as a leaving group, equation (10). Thus we conclude that the  $K_a$  value of



$0.268 \text{ mol dm}^{-3}$  refers to the ionisation of the bulk conjugate acid  $^+\text{NH}_3\text{N}=\text{NOH}$ , while the active species in decomposition to hydrazoic acid is a minor tautomer  $\text{NH}_2\text{N}=\text{NOH}_2^+$ .

At low acidities, where the intermediate exists as  $\text{NH}_2\text{N}=\text{NOH}$ , the major decomposition products are  $\text{NH}_3 +$

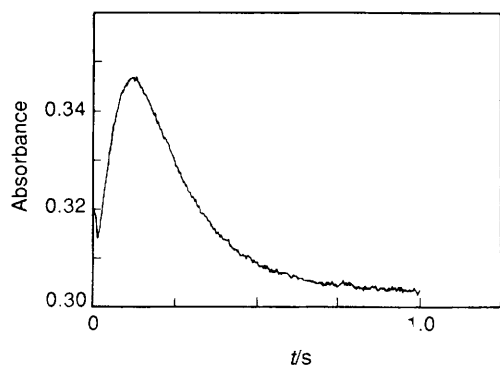


Fig. 2 Absorbance vs. time traces for the reaction of hydrazine with excess nitrous acid:  $[\text{HNO}_2]_0 = 0.05$ ,  $[\text{N}_2\text{H}_5^+]_0 = 0.002$ ,  $[\text{H}^+] = 1.0$  mol dm<sup>-3</sup>

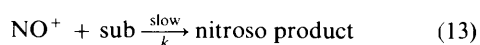
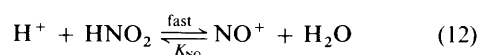
$\text{N}_2\text{O}$ . Both the amide and hydroxide ions are poor leaving groups, and we are indebted to a referee for the suggestion that here also the reactive species may be a minor tautomer, in this case  $\text{NH}_3^+\text{N}=\text{NO}^+$ .

**Reaction with Excess Nitrous Acid.**—This was followed spectrophotometrically at 253 nm by stopped-flow. A typical trace is shown in Fig. 2, which shows the formation of the intermediate and its disappearance. The decomposition reaction was very much faster in the presence of excess nitrous acid than it was for reaction in excess hydrazine. Thus in 1 mol dm<sup>-3</sup> perchloric acid with  $[\text{HNO}_2]_0 = 0.03$  and  $[\text{N}_2\text{H}_5^+]_0 = 0.01$  mol dm<sup>-3</sup> the half-life for the disappearance of the intermediate was 0.48 s, whereas at the same acidity, and with excess hydrazine it was 16.2 s. Although plots of  $\ln(A - A_\infty)$  vs.  $t$  for the absorbance decay were linear we did not use the apparent pseudo first-order rate constants because there was significant overlap between the formation and decay reactions. Thus in the example above, using rate constants for the formation reaction obtained with a large excess of hydrazine, we calculate  $t_1$  for the formation reaction to be ca. 0.14 s which is not sufficiently small to avoid significant overlap with the decay reaction. To obtain the order of reaction with respect to  $[\text{HNO}_2]$  we compared instantaneous rates at absorbances corresponding to a given intermediate concentration, choosing conditions where the formation reaction was essentially complete. This gave an order of 1.06. Variation of the perchloric acid concentration had little effect on the rate of the reaction with nitrous acid, and the rate law is concluded to be of the form (11) at acidities close to  $[\text{H}^+] = 1$  mol dm<sup>-3</sup>. Values for  $k_4$  were

$$\text{rate} = k_4[\text{NH}_3^+\text{N}=\text{NOH}][\text{HNO}_2] \quad (11)$$

obtained by computing concentration vs. time curves by the Gear integration method, using values for  $k_1$  and  $k_2$  obtained by the work with large excess of hydrazine, and trying a range of values for  $k_4$ . We did not have computer optimisation programs available. The best fit was obtained for  $k_4 = 200 \pm 20$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> for 1 mol dm<sup>-3</sup> perchloric acid.

When reaction rate constants are obtained by such indirect methods it is important to check that the values are chemically reasonable. Nitrosation reactions commonly occur by electrophilic attack by  $\text{NO}^+$  on the substrate (sub) as shown in equations (12) and (13). If the substrate is basic, and is almost



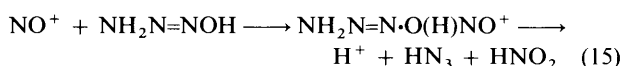
fully protonated at the acidities used, then the rate law takes

form (14) where  $K_a$  is the dissociation constant of the conjugate

$$v = \{kK_{\text{NO}}K_a/(K_a + [\text{H}^+])\}[\text{H}^+][\text{HNO}_2][\text{sub}] \quad (14)$$

acid, where [sub] represents the total, stoichiometric concentration of the substrate. Equation (14) yields a value of  $kK_{\text{NO}}$  of 946 dm<sup>6</sup> mol<sup>-2</sup> s<sup>-1</sup>. Many nitrosations by  $\text{NO}^+$  take place at the encounter rate, with  $kK_{\text{NO}}$  ca.  $2 \times 10^3$  dm<sup>6</sup> mol<sup>-2</sup> s<sup>-1</sup> at 0 °C for anionic nucleophiles.<sup>8</sup> The rate constant for a neutral nucleophile will be expected to be a little smaller, so our rate of 946 dm<sup>6</sup> mol<sup>-2</sup> s<sup>-1</sup> is physically reasonable, and we interpret the nitrous acid catalysed decomposition of the intermediate as involving encounter controlled nitrosation of the free base form  $\text{NH}_2\text{N}=\text{NOH}$  by  $\text{NO}^+$ .

With this rate constant we can now compare the rate of conversion of the intermediate to hydrazoic acid by use of equation (10) with the rate of destruction by excess nitrous acid. For 1 mol dm<sup>-3</sup>  $\text{H}^+$  the rate of azide formation is 0.041  $[\text{NH}_3^+\text{N}=\text{NOH}]$ , while in the presence of 0.02 mol dm<sup>-3</sup> excess nitrous acid the rate of the nitrite path is  $4[\text{NH}_3^+\text{N}=\text{NOH}]$  about two orders of magnitude faster. It is clearly possible to destroy hydrazine with excess nitrous acid without generating significant amounts of hydrazoic acid by reaction (10). The relative rate of destruction by  $\text{HNO}_2$ ,  $v_D$ , and of formation of hydrazoic acid,  $v_A$ ,  $v_D/v_A = 4765 [\text{HNO}_2]$ . Unfortunately the conclusion is not as clearcut as would appear. Another way in which hydrazoic acid could be formed is by nitrosation of  $\text{NH}_2\text{N}=\text{NOH}$  at the hydroxyl group, followed by loss of nitrous acid, reaction (15).



However  $\text{HNO}_2$  is not noted as a good leaving group, and the acid-catalysed reactions of alkyl nitrites,  $\text{RO}(\text{H})\text{NO}^+$  involve the loss of  $\text{NO}^+$  with  $\text{ROH}$  being formed. A closer comparison is with the reaction of nitrous acid and *trans*- $\text{HON}=\text{NOH}$ . There is no sign of an electrophilic nitrosation at oxygen with the formation of  $\text{H}^+$ ,  $\text{N}_2\text{O}$  and  $\text{HNO}_2$  [the analogous process to reaction (15)]. Nitrosation at oxygen at an  $\text{N}-\text{OH}$  group does occur in the nitrosation of  $^+\text{NH}_3\text{OH}$ , but the rate is many orders of magnitude lower than the encounter rate.<sup>9</sup> Thus, although reaction (15) is a possibility it seems unlikely to be a substantial contributor to the rate. The isotopic studies<sup>5</sup> of the distribution of tracer in  $\text{N}_2\text{O}$  and  $\text{N}_2$  in the reaction of  $^{15}\text{N}_2\text{H}_5^+$  with  $\text{HNO}_2$  led to the suggestion that dinitrosation might occur to yield  $\text{ON}^{15}\text{NH}^{15}\text{NHNO}$  (which would form  $^{15}\text{NNO} + ^{15}\text{NN}$ ) and also  $\text{H}^{15}\text{N}=\text{NN}(\text{NO})\text{OH}$  (which was postulated to form  $^{15}\text{N}_2$  and  $\text{N}_2\text{O}$ ). These are the most likely products of our second nitrosation though we cannot exclude a contribution from a reaction such as (15).

**Evidence for a Further Intermediate Species.**—During the above studies it was discovered that the disappearance of the 225 nm peak was followed by another, very much slower process in which a small peak at 230 nm decayed. This had been missed in the original studies<sup>1</sup> because the reaction was very much slower and the absorbance changes were very much smaller than the corresponding features of the 225 nm species. Quenching the solution in 1 mol dm<sup>-3</sup> sodium hydroxide confirmed that we were seeing a distinct species, with the disappearance of the 230 nm peak and the appearance of a new peak at 273 nm with no sign of a peak at 243 nm. On reacidification the 230 nm peak reappeared. In a series of quenching experiments carried out over a range of conditions the ratios of the absorbances at 230 and 273 nm were constant, suggesting that the two species were related by acid-base equilibria.

The kinetics of decay of these species were examined by preparing a stock solution of the 230 nm intermediate in which decomposition had been quenched by making the pH 10.1. At

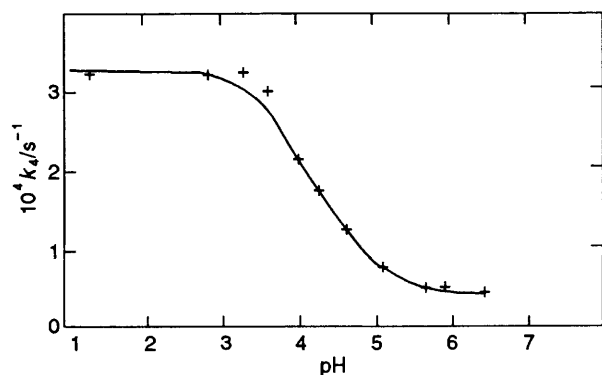


Fig. 3 Variation of  $k_4$  with pH

Table 2 Kinetics of decomposition of the minor product at 25 °C

pH	$10^4 k_4^a/s^{-1}$	$10^4 k_4^b/s^{-1}$	pH	$10^4 k_4/s^{-1}$	$10^4 k_4^a/s^{-1}$
1.27	3.22	3.27	4.62	1.22	1.18
2.83	3.20	3.15	5.11	0.71	0.72
3.27	3.22	2.97	5.66	0.47	0.50
3.59	2.95	2.70	5.87	0.46	0.47
4.03	2.10	2.12	6.37	0.40	0.42
4.25	1.75	1.75			

<sup>a</sup> Experimental. <sup>b</sup> Calculated from  $k_4 = (k_a[H^+] + k_bK_a)/(K_a + [H^+])$ , see text.

this acidity the 273 nm peak did not decay to a measurable extent over a time scale of hours. Aliquots of this stock solution were added to a large excess of buffer solutions of various pH values, and the kinetics of decomposition followed spectrophotometrically. Individual runs gave good first-order plots of  $\ln(A - A_\infty)$  vs.  $t$ ,  $k_4$ , and Fig. 3 shows the variation with pH. This has the characteristic sigmoid shape for a reaction controlled by an acid-base equilibrium, in which both acid and base species decompose with rate constants  $k_a$  and  $k_b$ . The line in Fig. 3 was calculated with  $k_a = 3.27 \times 10^{-4} s^{-1}$ ,  $k_b = 4 \times 10^{-5} s^{-1}$  and  $K_a = 6.33 \times 10^{-5} mol dm^{-3}$  ( $pK_a = 4.2$ ).

Values of  $k_4$  calculated from these figures are compared with the experimentally measured values in Table 2. The spectrum of the base species at pH 6.37 showed a peak at 260 nm. At this pH more than 99% of the intermediate is in the conjugate base form, and has a slow but measurable rate of decomposition,  $k_{obs} \approx 4 \times 10^{-5} s^{-1}$ . When the intermediate is at pH 10.2 the peak is at 273 nm, and there is no observable decomposition. There must therefore be another acid-base equilibrium with a  $pK_a$  between about 7 and 9, but we have not investigated this point any further.

While it is clear that there is a new and distinct species present, its identification is more difficult. The relatively slow decomposition of the 230 nm peak makes it possible to estimate the relative concentrations formed under different conditions by measuring the 'initial' absorbance at the wavelength after the much more rapid decay of the 225 nm peak is complete. Values are shown in Table 3. There is a marked increase in initial absorbance at 230 nm as  $[N_2H_5^+]_0$  decreases. This cannot be due to parallel reaction between hydrazine and nitrous acid, as the concentration of a species formed in this way should be independent of  $[N_2H_5^+]_0$ . At  $[N_2H_5^+]_0 = 0.4 mol dm^{-3}$  the  $t_{1/2}$  for the disappearance of nitrous acid is about 0.017 s, while at  $0.02 mol dm^{-3}$  it is ca. 0.34 s. The longer lifetime of nitrous acid at low hydrazine concentration will favour reaction between nitrous acid and the intermediate  $NH_2N=NOH$ . This has been confirmed by a numerical integration of the system of differential equation by the Gear method. Thus even with a large excess of hydrazine  $[HNO_2]_0 = 0.004$ ,  $[N_2H_5^+]_0 =$

Table 3 Values of the 'initial' absorbance for the species absorbing at 230 nm at 25 °C ( $[H^+] = 0.5$ ,  $[HNO_2]_0 = 0.004 mol dm^{-3}$ )

$[N_2H_5^+]_0/mol dm^{-3}$	$A_{230}$
0.40	0.097
0.08	0.315
0.02	0.414
0.004	0.683

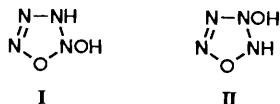
Table 4 *Ab initio* calculations of formation energies for various structures using a 3-21G basis set

	$E_t/au$
<i>trans</i> - $NH_2NH-NO$	-238.450 3540
<i>cis</i> - $NH_2NH-NO$	-238.454 6179
<i>trans</i> - $NH_2N=NOH$	-238.463 075
<i>cis</i> - $NH_2N=NOH$	-238.473 2436
<i>trans,trans</i> - $ON-NHNH-NO$	-366.336 0
<i>trans,trans</i> - $HON=NNH-NO$	-366.340 4
<i>cis,cis</i> - $HON=NN=NOH$	-366.347 0
<i>trans,cis</i> - $HN=NN(OH)-NO$	-366.324 3
I	-366.342 8
II	-366.334 4

The designations *cis* and *trans* refer to the geometry of the nitrogen and/or oxygen atoms about the linkages designated by single or double bonds. Further details of these calculations can be obtained from G.S.; au = Hartree  $\approx 4.360 \times 10^{-18} J$ .

0.06,  $[H^+] = 1 mol dm^{-3}$  the large rate constant for the second nitrosation leads to approximately 2.5% of the nitrite reacts by path (2). Such model calculations confirm that there will be a marked increase in the amount of reaction occurring between  $NH_2N=NOH$  and  $[HNO_2]$  as  $[N_2H_5^+]_0$  decreases. We conclude that the species that absorbs at 230 nm results from the reaction of hydrazine with two molecules of nitrous acid, and that it contains two acidic protons. The final point to note is that hydrazine reacts with an excess of nitrous acid according to the stoichiometry in reaction (2) very rapidly, with 2 moles of gas being released very quickly. The slow decomposition of the 230 nm species suggests it is only a very minor side-product, not on the pathway that leads to the rapid evolution of  $N_2 + N_2O$ . It is formed in such small amounts that it does not significantly disturb the overall stoichiometry, though it can be detected spectrophotometrically. With a  $pK_a$  of 4.2 it seems likely to contain a hydroxyl group, and a possible structure is  $HO-N=N-N=NOH$ . Attempts to isolate it by precipitation as silver(I) or lead(II) salts were unsuccessful. In another experiment hydrazine was treated with a slightly more than two-fold excess of nitrous acid, and the excess nitrous acid destroyed with ascorbic acid. The solution was then made alkaline and treated with Devarda's alloy in an attempt to reduce any nitrogen containing compound to ammonia, which could be distilled off and determined. This gave an amount of ammonia  $1.6 \pm 1.6\%$  of the original hydrazine, indicating that the intermediate is present in small amounts only.

To examine our system by an alternative approach we have carried out *ab initio* calculations<sup>10</sup> on some of the species postulated in our discussions using the GAMESS package<sup>11</sup> at the 3-21G level. The results are summarised in Table 4. The *cis/trans* isomerism in some of the listed structures arises from the partial double bond character of the  $>N-NO$  linkage, leading to restricted rotation. The calculations predict that the tautomerisation product  $NH_2N=NOH$  is more stable than the initial nitrosation product  $NH_2NHNO$ . For the dinitrosated species, and their tautomeric rearrangement products the calculated order of stability is  $HON=N-N=NOH > HON=N-NHNO > ONNHNHNO$ . The isotopic results require<sup>5</sup> that the reaction of  $*N_2H_5^+ + 2HNO_2$  should involve at least one pathway forming  $*N_2 + N_2O$ , and  $H*N=NN(NO)OH$  was suggested as a possible intermediate that could lead to the



isotope distribution, by decomposition to  $^*N_2 + cis\text{-HON=NOH}$ . The calculations suggest that this is less stable than any of the three tetranitrogen species mentioned above. We were also interested in the possible structure of the relatively stable species observed as a minor product of reaction, and we considered the ring structures I and II. The *ab initio* calculations suggest that these are less stable than the open-chain structure  $\text{HON=N-N=NOH}$ . One unexpected feature of the calculations was the prediction at the 3-21G level that *cis*- $\text{NH}_2\text{N=NOH}$  was more stable than the *trans* isomer. The calculations refer to gaseous species, with no allowance for solvation energies, and they refer to thermodynamic and not kinetic stability. Calculations using the same basis set for *cis*- and *trans*- $\text{HON=NOH}$  again predict the *cis* isomer to be marginally more stable than *trans*, although there is no doubt<sup>6</sup> that the *trans* isomer is more kinetically stable than the *cis* form. Calculations with a larger basis set, 4-31G, predict *trans*- $\text{NH}_2\text{N=NOH}$  to be very slightly more stable than the *cis* structure. Such calculations cannot provide conclusive evidence when there are small differences in energies for gas-phase structure, whereas the actual reactions take place in solution, and are governed by kinetic as well as thermodynamic factors. In the absence of

other evidence we suggest that our minor, relatively stable intermediate is  $\text{HON=N-N=NOH}$ .

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