# Decomposition of Hydrazoic Acid in Nitric Acid

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Hydrazoic acid in solution in nitric acid at 97 °C decomposes to form a mixture of $N_2$, $N_2O$, and NO. The reaction is strongly acid catalysed and the kinetics of decomposition are first order with respect to hydrazoic acid concentration. The mechanism proposed involves electrophilic attack by $NO_2^+$ on hydrazoic acid to form $N_3ONO$, which can then fragment to $N_2 + 2NO^{\cdot}$ or dissociate to $N_3^{\cdot} + NO_2^{\cdot}$. Dinitrogen monoxide is thought to arise from the reaction sequence: $2NO_2^{\cdot} \longrightarrow N_2O_4$; $N_2O_4 + HN_3 \longrightarrow N_3NO + HNO_3$; $N_3NO \longrightarrow N_2 + N_2O$.

During the course of an investigation of the reaction of hydrazine with hot, moderately concentrated nitric acid, it became necessary to consider possible side reactions of one of the products, hydrazoic acid. Very little work has been done on this reaction. Caronna and Sansone[1] studied the oxidation by concentrated, fuming nitric acid, and found that a mixture of dinitrogen, dinitrogen monoxide, and nitrogen monoxide was formed. As however there would probably have been some nitrous acid or related species in concentrated fuming nitric acid, these results may have been complicated by the presence of products formed by the well known nitrous acid–hydrazoic acid reaction. Masek[2] has reported a very brief study of the reaction of hydrazoic acid and nitric acid in sulphuric acid solution, and proposed the stoicheiometry (1). He postulated the mechanism in equations (2)—(4).

$$4HN_3 + 2[NO_2]^+ \longrightarrow 4N_2 + 3N_2O + H_2O + 2H^+ \quad (1)$$

$$HN_3 + [NO_2]^+ \longrightarrow 2NO^{\cdot} + N_2 + H^+ \quad (2)$$

$$2NO^{\cdot} + [NO_2]^+ + 2H^+ \longrightarrow 3[NO]^+ + H_2O \quad (3)$$

$$[NO]^+ + HN_3 \longrightarrow N_2O + N_2 + H^+ \quad (4)$$

This paper describes an investigation of the kinetics and stoicheiometry of the decomposition.

## Experimental

It was necessary to investigate the decomposition of hydrazoic acid in nitric acid at the same temperature as had been used in a study of the reaction between hydrazine and nitric acid. CAUTION: At this temperature, 97 °C, hydrazoic acid is volatile and as it is both explosive and toxic special care was needed. Reaction vessels were thermostatted in an oil-bath, which was placed in a fume cupboard. Reactions were carried out using closed reaction vessels; in most cases there was an alkali trap connected between the reaction vessel and the atmosphere. The explosive properties of hydrazoic acid are known[3] to be significant at concentrations above *ca.* 4 mol $dm^{-3}$, but the present experiments involved solutions approximately two orders of magnitude lower in concentration.

Measurements of the vapour pressure of hydrazoic acid in solutions of $NH_3$ in nitric acid were made by the technique of King and Templeton,[4] passing a stream of fine bubbles of dinitrogen carrier gas through an aqueous solution, and analysing for the amount of hydrazoic acid carried away in the gas stream by absorbing it in sodium hydroxide solution. Azide concentrations were determined by the standard cerium(IV) sulphate method of analysis.[5]

Product analyses were carried out by allowing degassed solutions of sodium azide and nitric acid to mix in an evacuated vessel, with a large vapour:solution volume ratio. A sample of the evolved gas was transferred to another vessel, and its pressure was measured with the vessel immersed to a fixed mark in (*a*) liquid $N_2$, (*b*) in a solid–liquid n-pentane slush-bath, and (*c*) at ambient temperatures. The analysis basically assumed a mixture of $N_2$, $NO^{\cdot}$, and $N_2O$, and at these temperatures the gas phase should be (*a*) $N_2$, (*b*) $N_2 + NO^{\cdot}$, and (*c*) $N_2 + NO^{\cdot} + N_2O$ respectively. We checked our calibration by analysing the equimolar mixture of $N_2$ and $N_2O$ obtained from the azide–nitrite reaction, and found that 1 mol of $HNO_2$ produced on average 0.96 mol $N_2$ and 1.02 mol $N_2O$. Thus, although this is a very simple method of analysis, it seems to produce reasonable results; the analysis for $NO^{\cdot}$ is probably[6] not as good as that for $N_2$ and $N_2O$.

Kinetic measurements were made by removing aliquots and quenching them in a solution containing a known excess of cerium(IV) sulphate. The excess of cerium(IV) was back-titrated with ammonium iron(II) sulphate solution using an iron(II) phenanthroline indicator.

## Results and Discussion

The results of our measurements of the gaseous products of the reaction between hydrazoic acid and 9.18 mol $dm^{-3}$ nitric acid are summarised in Table 1. We find close to 2 mol of gas formed per mol of azide consumed, although no significance is attached to this integral number. The only other familiar compound of nitrogen that might be stable under our reaction conditions of hot, moderately concentrated nitric acid is the ammonium ion. We treated samples of the infinity solutions with excess of sodium hydroxide, and distilled the alkaline solution into a known amount of standard acid. We could find no evidence for the presence of ammonia. Any nitrous acid or dinitrogen tetroxide would be destroyed

**Table 1.** Gas analysis measurements of the decomposition of $HN_3$ in 9.18 mol $dm^{-3}$ $HNO_3$ at 97 °C: number of moles of product per mol of $HN_3$ reacted

| | | | | | *x* | |
|---|---|---|---|---|---|---|
| $HN_3$ | $N_2$ | NO | $N_2O$ | Total | *a* | *b* |
| −1 | 1.22 | 0.22 | 0.45 | 1.89 | 0.424 | 0.56 |
| −1 | 1.15 | 0.25 | 0.45 | 1.85 | 0.48 | 0.45 |
| −1 | 1.23 | 0.27 | 0.50 | 2.00 | 0.508 | 0.73 |
| −1 | 1.46 | 0.30 | 0.47 | 2.23 | 0.508 | 1.16 |
| −1 | 1.20 | 0.13 | 0.58 | 1.91 | 0.484 | 0.69 |
| −1 | 1.23 | 0.20 | 0.47 | 1.90 | 0.468 | 0.60 |
| −1 | 1.29 | 0.34 | 0.46 | 2.09 | 0.52 | 0.84 |
| −1 | 1.32 | 0.29 | 0.42 | 2.03 | 0.484 | 0.77 |

[a] Calculated from redox balance. [b] Calculated from mass balance.

**Table 2.** First-order rate constants for the decomposition of hydrazoic acid at 97 °C

| $[HNO_3]$/mol dm$^{-3}$ | 6.12 | 7.65 | 9.18 | 10.7 |
|---|---|---|---|---|
| $10^3 k_1$/min$^{-1}$ | 5.1 | 24.5 | 84 | 249 |

by reaction with hydrazoic acid; hydrazine and hydroxylamine decompose much more readily in nitric acid than does hydrazoic acid. Thus we think the stoicheiometric equation is given by (5). If our assumption that there are no other nitrogenous products is correct, then values of $x$ and $y$ can be obtained either from the material balance or the redox balance of equation (5).

$$x\,HNO_3 + HN_3 \longrightarrow 1.27\,N_2 + 0.27\,NO + 0.46\,N_2O + y\,H_2O \quad (5)$$

Calculation of $x$ by redox balance gives $x = 0.49$, while mass balance yields $x = 0.73$. When we examine the calculations based upon the individual experiments it is apparent that the redox-balance calculation (in which the $N_2$ formed disappears from the equation, as it has a formal oxidation number of zero) is much more self-consistent than the mass-balance calculation as can be seen from the sixth and seventh columns of Table 1. If we take the $x$ value from the redox balance as correct, then the analysis for dinitrogen would have to yield a factor of 1.15 instead of 1.27 in equation (5) to give a mass balance. There are certainly much better analytical systems for $N_2/NO/N_2O$ than our method which could probably improve on our results. For the present we will use equation (6), assuming our analysis for dinitrogen to have been high.

$$0.486\,HNO_3 + HN_3 \longrightarrow 1.15\,N_2 + 0.27\,NO + 0.46\,N_2O + 0.73\,H_2O \quad (6)$$

The kinetics of reaction, followed by the disappearance of hydrazoic acid, obeyed a simple first-order rate law with respect to hydrazoic acid concentration. The first-order rate constant increased markedly with increase in $[HNO_3]$ as can be seen from Table 2. A plot of log $k_1$ against $H_0$ was linear over the range 6.1—10.7 mol dm$^{-3}$ nitric acid at 97 °C with a slope of 1.71. Measurements over the temperature range 50—70 °C in 12.2 mol dm$^{-3}$ nitric acid gave an Arrhenius activation energy of 89 kJ mol$^{-1}$.

Measurements of the interaction of hydrazoic acid with the solvent aqueous nitric acid were made by measuring the Henry's law constant. The results are shown in Table 3. The results for solutions in water are in good agreement with the earlier studies of Feitknecht and Sahli,[7] of D'Orazio and Wood,[8] and of King and Templeton,[4] and do not require further comment. Salt effects on the solubility of non-electrolytes have been reviewed by Long and McDevitt.[9] They are usually rather small, and those observed for nitric acid are commonly unusually small, when compared with other 1 : 1 electrolytes. Thus, the small decrease in the Henry's law constant for $HN_3$ with increase in $[HNO_3]$ is reasonable. It might be argued that the results in Table 3 refer only to relatively low nitric acid concentrations, and that the effects might be different in more concentrated solutions. However, other volatilisation experiments over the range 4.65—7.75 mol dm$^{-3}$ nitric acid at 97 °C showed no detectable variation in rate of volatilisation with acidity. Hydrazoic acid can interact with strong mineral acids and protonate to form $H_2N_3^+$ in relatively concentrated sulphuric acid, and a p$K_a$ of $-6.2$ for this species has been proposed.[10] There would be no significant amount of protonation in our solutions for which the highest acidity corresponds to $H_0 = -3.3$.

**Table 3.** Henry's law constants for hydrazoic acid in aqueous solution

| $\theta_c$/°C | 25 | 25 | 25 | 45 | 45 | 45 | 60 | 60 | 60 |
|---|---|---|---|---|---|---|---|---|---|
| $[HNO_3]$/mol dm$^{-3}$ | 0 | 1.58 | 3.16 | 0 | 1.58 | 3.16 | 0 | 1.58 | 3.16 |
| $10^2 K$/atm dm$^3$ mol$^{-1}$ | 8.5 | 8.0 | 7.0 | 20.0 | 17.3 | 17.5 | 30 | 27 | 26 |

Turning to the interpretation in terms of mechanism, the most striking features of the kinetics is the rapid increase in rate with acidity. This does not seem to involve any interaction of the medium with hydrazoic acid. The effect of acidity on the rate of reaction must be due to an increase in the concentration of the active nitrogen(v) species. The only likely candidates are the nitronium ion, the nitrate–acidium ion, and covalent nitric acid. The slope of a plot of log $k_1$ *versus* $H_0$ is very similar to the value of 1.80 observed [11] for reaction between nitric acid and sulphamic acid at 70 °C, and in this reaction the nitronium ion was considered to be the active species.

Certainly the increase in rate with stoicheiometric concentration of nitric acid is far too great for the active species to be covalent nitric acid. The nitrate acidium ion, $[H_2NO_3]^+$, is a possible electrophile, but has never been identified as an active species. We assume that our active species is $[NO_2]^+$.

The most likely reaction would appear to be an electrophilic substitution to form $N_3NO_2$ [equation (7)]. Two isomeric species may be envisaged,  $\mathrm{NNNN}{<}^{O}_{O}$ and NNNONO. The latter offers an obvious route to the nitrogen monoxide product by a fragmentation reaction (8), the same overall process as postulated by Masek.[2] The formation of $N_2O$ is less easily accounted for without postulating a rather complex rearrangement. Masek's suggestion, equations (3) and (4), appears plausible. However, the reaction between NO and $HNO_3$ to form $HNO_2$ is normally considered [12] to occur as in equations (9)—(12). The reaction of NO$^\cdot$ basically requires $NO_2^\cdot$, which is derived from $N_2O_4$ and its precursor $HNO_2$. It seems doubtful whether in the presence of a powerful nitrite scavenger such as hydrazoic acid there would be a sufficient concentration of $HNO_2$ for reaction by this route. Exchange of $^{15}N$ between NO$\cdot$ (g) and dilute nitric acid certainly requires the presence of traces of $HNO_2$ as a catalyst.[13]

$$[NO_2]^+ + HN_3 \longrightarrow N_3NO_2 + H^+ \quad (7)$$

$$NNNONO \longrightarrow N_2 + 2NO^\cdot \quad (8)$$

$$H^+ + HNO_2 + [NO_3]^- \rightleftharpoons N_2O_4 + H_2O \quad (9)$$

$$N_2O_4 \rightleftharpoons 2NO_2^\cdot \quad (10)$$

$$NO_2^\cdot + NO^\cdot \rightleftharpoons N_2O_3 \quad (11)$$

$$N_2O_3 + H_2O \rightleftharpoons 2HNO_2 \quad (12)$$

An alternative pathway whereby $NO_2$ can be generated without $HNO_2$ as a precursor is set out in equations (13)—(16). This mechanism leads to a stoicheiometry (17). A

$$N_3ONO \longrightarrow N_3^{\cdot} + NO_2^{\cdot} \quad (13)$$

$$2N_3^{\cdot} \longrightarrow 3N_2 \quad (14)$$

$$2NO_2^{\cdot} \longrightarrow N_2O_4 \quad (15)$$

$$N_2O_4 + HN_3 \longrightarrow [N_3NO] + HNO_3 \longrightarrow N_2 + N_2O + HNO_3 \quad (16)$$

$$\tfrac{1}{3}\,HNO_3 + HN_3 \longrightarrow \tfrac{4}{3}\,N_2 + \tfrac{1}{3}\,N_2O + \tfrac{2}{3}\,H_2O \quad (17)$$

combination of (8) and (17) cannot, however, account for the observed stoicheiometry. If we had 77.8% reaction by (8) and 22.2% by (17) we could account for the ratio of $HNO_3$ : $HN_3$ of 0.486 : 1; this would, however, predict 0.259 mol of $N_2O$ and 0.444 mol of NO per mol of $HN_3$, almost the opposite of what is observed.[1] However, we have not allowed for interaction between these two mechanisms, and one possibility that must be considered is shown in equations (18) and

$$NO^{\cdot} + NO_2^{\cdot} \longrightarrow N_2O_3 \quad (18)$$

$$N_2O_3 + 2HN_3 \longrightarrow 2N_2 + 2N_2O + H_2O \quad (19)$$

(19). If this reaction occurred to some extent, then it would increase the proportion of $N_2O$, and decrease that of $NO^{\cdot}$. It is possible to attempt a more quantitative treatment by assuming that an amount $\alpha$ reacts by equation (8), an amount $\gamma$ by equation (17), and that an amount $\beta$ of the NO formed in (8) reacts with $NO_2$ formed as an intermediate in (13) as shown in (18) and (19). Our stoicheiometric equations can then be written as in (20) and (22).

$$\alpha\,HNO_3 + \alpha\,HN_3 \longrightarrow \alpha\,N_2 + 2\alpha\,NO + \alpha\,H_2O \quad (20)$$

$$\gamma\,HNO_3 + 3\gamma\,HN_3 \longrightarrow 4\gamma\,N_2 + \gamma\,N_2O + 2\gamma\,H_2O \quad (21)$$

$$\beta\,HNO_3 + 3\beta\,HN_3 + \beta\,NO \longrightarrow 3.5\,\beta\,N_2 + 2\beta\,N_2O + 2\beta\,H_2O \quad (22)$$

By fitting (20)—(22) to the numbers in (6) one can show that $\alpha/T = 0.229$, $\beta/T = 0.118$, and $\gamma/T = 0.084$ gives a fair fit to (6) ($T = \alpha + 3\beta + 3\gamma$). We do not lay any emphasis on these numbers, other than noting that a combination of these two mechanisms can account for the product distribution. Other explanations are possible; clearly equation (23) would account for an increase in $N_2O$ and a decrease in NO

$$NO^{\cdot} + N_3^{\cdot} \longrightarrow N_3NO \longrightarrow N_2 + N_2O \quad (23)$$

and $N_2$. A similar mathematical treatment shows that the interactive pathway could also account for the results. Clearly both paths (18) + (19) and (23) might occur, and there may be other alternative explanations also.

There is no evidence at the moment to distinguish between these possibilities.

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