# Kinetics and Mechanism of the Nitroamine–Nitrous Acid Reaction

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Nitroamine and nitrous acid react in aqueous perchloric acid to give nitrate ion and nitrogen. The rate equation is Rate = $(k_4[NH_2NO_2] + k_5[NHNO_2^-])[H^+][HNO_2]$ where $k_4 = 2.8 \times 10^{-3}$ and $k_5 = 1.6 \times 10^3$ dm$^6$ mol$^{-2}$ s$^{-1}$ at 0 °C, corresponding to attack of the nitrosating agent on the neutral and deprotonated nitroamine molecules. Mechanisms for these reactions are discussed, and the lack of reactivity of the neutral nitroamine molecule is considered.

NITROAMINE, $NH_2NO_2$, is usually prepared by the action of sulphuric acid on potassium nitrocarbamate[1] or of nitric acid on sulphamic acid.[2] While kinetic studies of its acid-[3] and base-catalysed decomposition[4] are well known, little information is available on other aspects of its chemistry. The structure of $NH_2NO_2$

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[1] C. A. Marlies, V. K. La Mer, and J. Greenspan, *Inorg. Synth.*, 1939, **1**, 68.

[2] S. Tellier-Pollon and J. Heubel, *Rev. Chim. minérale*, 1967, **4**, 413.

[3] C. A. Marlies and V. K. La Mer, *J. Amer. Chem. Soc.*, 1935, **57**, 1812.

[4] R. P. Bell and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1949, 1288.

has been confirmed by *X*-ray diffraction[5] and infrared spectroscopy.[6] We have studied its reaction with nitrous acid.

## EXPERIMENTAL

Nitroamine was prepared by the action[2] of nitric acid on sulphamic acid, followed by extraction of the resulting solution with diethyl ether. In early preparations the stability of the product was unpredictable. Following literature recommendations, the product was stored in open containers over a $P_4O_{10}$ desiccator which was kept in a refrigerator, but some batches still decomposed suddenly after a few hours. We found that $NH_2NO_2$ may be stored much more successfully under light petroleum, portions being filtered off and dried as required. Using this procedure, no problems were experienced with decomposition, and samples were kept up to 6 weeks before use. Melting points lay in the range 68—70 °C. All other chemicals were of the best grade available.

In the stoicheiometry studies, analyses for $NH_2NO_2$ and nitrate were carried out, after appropriate dilution, by measuring optical densities on a Unicam SP 500 spectrometer at 208 and 301 nm respectively ($\varepsilon_{max.}$ 6 300 and 7 $dm^3 mol^{-1} cm^{-1}$). Nitrate was also determined by reduction to ammonia with Devarda's alloy, distillation into excess of acid, and back titration with standard alkali. The two methods for nitrate analysis gave identical results. Gaseous products of the reaction were identified using a Centronic Q 806 mass spectrometer. Nitrite solution was placed in one arm of a Y tube, with all the other components in the second arm. After cycles of freezing, evacuating, and thawing to ensure thorough degassing of the solutions, the Y tube was rotated to start the reaction. The gaseous products were analysed after 10 half-lives.

Kinetic runs were started by adding a known volume of sodium nitrite solution at 0 °C to the other components which were also thermostatted at 0 °C. Nitroamine was weighed out for each run. Reactions were followed by withdrawing samples at various times and analysing for nitrite by standard colorimetric methods.

## RESULTS

Studies on the stoicheiometry of the reaction at $[H^+] = 0.025, 0.05,$ and $0.250 \text{ mol dm}^{-3}$ showed that $HNO_2$ and $NH_2NO_2$ were consumed on a 1 : 1 basis. The only products identified were nitrate ion and nitrogen gas, with $\Delta[NO_3^-]/\Delta[NO_2^-] = 1.0$.

$$HNO_2 + NH_2NO_2 \longrightarrow HNO_3 + N_2 + H_2O \qquad (1)$$

The kinetics of the reaction were studied at 0 °C and $I = 0.25 \text{ mol dm}^{-3}$, the latter being maintained with sodium perchlorate. Nitroamine was present in large excess over $HNO_2$, and the reaction was followed by measuring the change in nitrous acid concentration with time. Excellent plots of log (optical density) against time were obtained, usually over three half-lives, showing the reaction to be first order in the concentration of $HNO_2$. This was confirmed by the independence of the measured first-order rate constant of $[HNO_2]$. Rate constants are listed in the Table. The reaction was also shown to be first order in $[NH_2NO_2]$ by varying the nitroamine concentration and noting the effect on $k_1$, the measured first-order rate constant. Values of $k_2 = k_1/[NH_2NO_2]$ were constant.

Rate constants for the $HNO_2$–$NH_2NO_2$ reaction at 0 °C

| Batch | $\frac{[H^+]}{\text{mol dm}^{-3}}$ | $\frac{[NH_2NO_2]}{\text{mol dm}^{-3}}$ | $\frac{10^4k_1}{s^{-1}}$ | $\frac{10^4k_2}{\text{dm}^3\text{ mol}^{-1}\text{ s}^{-1}}$ | $\frac{10^3k_4}{\text{dm}^6\text{ mol}^{-2}\text{ s}^{-1}}$ |
|---|---|---|---|---|---|
| 3a | 0.10 | 0.0561 | 0.456 | 8.13 | |
| | 0.10 | 0.098 | 0.796 | 8.12 | |
| | 0.10 | 0.111 | 0.940 | 8.47 | |
| | 0.10 | 0.401 | 3.19 | 7.95 | |
| 3b | 0.025 | 0.110 | 0.457 | 4.15 | 2.92 |
| | 0.050 | 0.113 | 0.537 | 4.75 | 2.66 |
| | 0.150 | 0.099 | 0.762 | 7.70 | 2.85 |
| | 0.200 | 0.103 | 0.928 | 9.01 | 2.80 |
| | 0.250 | 0.102 | 1.04 | 10.2 | 2.67 |

The value of the intercept at $[H^+] = 0$ ($k_3$) is $3.42 \times 10^{-4}$ $dm^3 mol^{-1} s^{-1}$ (batch 3b); $k_4 = (k_2 - k_3)/[H^+]$. $[HNO_2] = 10^{-3}$–$10^{-4}$ mol $dm^{-3}$.

$$\text{Rate} = k_1[HNO_2] = k_2[NH_2NO_2][HNO_2] \qquad (2)$$

While runs using $NH_2NO_2$ from one preparation gave reproducible rate constants, identical runs from various preparations showed a 25% overall variation in the rate constant $k_2$. This was not affected by the addition of radical traps such as ethanol or metal chelating agents, and the source of the irreproducibility is not known. Recrystallisation did not lead to systematic changes in the rates. It is clear, however, that the results at each acidity are represented by rate equation (2) for each batch of $NH_2NO_2$.

The acidity was varied over the perchloric acid concentration range 0.025—0.25 mol $dm^{-3}$. The reaction was dependent on acidity, but plots of $k_2$ against $[H^+]$ gave an intercept on the $k_2$ axis of between $3.4 \times 10^{-4}$ and $4.5 \times 10^{-4}$ $dm^3 mol^{-1} s^{-1}$, depending on the batch of $NH_2NO_2$. All extrapolations involved excellent linear plots. It appears, therefore, that the rate law for the nitrous acid–nitroamine reaction involves two terms corresponding to acid-independent and -dependent reactions [equation (3)], where $k_3$ is the value of $k_2$ at zero acidity and $k_4 = (k_2 - k_3)/[H^+]$. Rate law (3) may be written as (4),

$$\text{Rate} = k_3[HNO_2][NH_2NO_2] + k_4[H^+][HNO_2][NH_2NO_2] \qquad (3)$$

$$\text{Rate} = k_5[H^+][HNO_2][NHNO_2^-] + k_4[H^+][HNO_2][NH_2NO_2] \qquad (4)$$

where $k_5 = k_3/K_a$ and $K_a$ is the acid dissociation constant for $NH_2NO_2$; $K_a = 2.55 \times 10^{-7}$ mol $dm^{-3}$ at 15 °C.[7] Values of $k_4$ and $k_5$ are *ca.* $3 \times 10^{-3}$ and $1.6 \times 10^3$ $dm^6 mol^{-2} s^{-1}$ respectively and relate to electrophilic attack of the nitrosating agent on the neutral and deprotonated forms of nitroamine.

## DISCUSSION

An immediate point of interest lies in the considerable difference in reactivity between nitroamine and its anion towards the nitrosating agent, which is either the nitrite acidium ion, $[H_2NO_2]^+$, or the nitrosyl cation,

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[5] C. A. Beevers and A. F. Trotman-Dickenson, *Acta Cryst.*, 1957, **10**, 34.

[6] M. Davis and N. Jonathan, *Trans. Faraday Soc.*, 1958, **54**, 469.

[7] J. N. Bronsted and C. V. King, *J. Amer. Chem. Soc.*, 1927, **49**, 193.

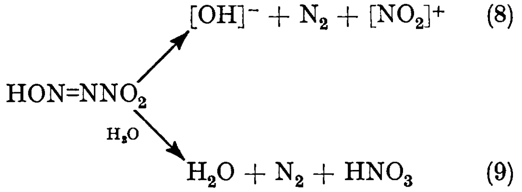
[NO]$^+$. A complication lies in the fact that, while the molecular form of nitramide is $NH_2NO_2$, it has been suggested that the anion may be derived from the acid form NH=NO$_2$H. However, the overall rate constant for attack at the anion compares well with those[8] for similar nitrosation reactions at other negative substrates which are thought to be diffusion controlled. Attack at neutral substrates is usually a factor of 10—100 slower, reflecting the effect of charge on the encounter rate, but attack at $NH_2NO_2$ is a factor of $10^6$ slower. Clearly $NH_2NO_2$ is unreactive towards the nitrosating agent and the reaction is not diffusion controlled.

$$H^+ + HNO_2 \rightleftharpoons [H_2NO_2]^+ \rightleftharpoons [NO]^+ + H_2O \qquad (5)$$

$$[NO]^+ + NH_2NO_2/[NHNO_2]^- \longrightarrow \text{Products} \qquad (6)$$

Reaction at the anion probably involves N-nitrosation at the deprotonated nitrogen atom, followed by proton transfer and breakdown to products, possibly through attack of a water molecule. The scheme is more satisfactory than if the *aci*-form of $[NHNO_2]^-$ had been invoked. The lack of reactivity of nitroamine itself is in accord with its lack of basicity, resulting from the presence of the adjacent nitro-group. This is emphasised by the planar structure[5] of the molecule. The rate-determining step is probably attack of the nitrosating agent to give the positively charged N-nitroso-species.

$$[NO]^+ + [NHNO_2]^- \longrightarrow ONNHNO_2 \longrightarrow HON{=}NNO_2 \qquad (7)$$



$$HON{=}NNO_2 \longrightarrow [OH]^- + N_2 + [NO_2]^+ \qquad (8)$$

$$HON{=}NNO_2 \xrightarrow{H_2O} H_2O + N_2 + HNO_3 \qquad (9)$$

Later steps cannot be rate determining as these, presumably, are identical to those involved in the much faster reaction of the deprotonated nitroamine.

$$[NO]^+ + NH_2NO_2 \xrightarrow{\text{slow}} [ONNH_2NO_2]^+ \xrightarrow{\text{fast}} \text{Products} \qquad (9)$$

Further detailed studies on this reaction, such as deuterium–isotope solvent effects, have not been carried out in view of the complications resulting from the lack of reproducibility in the kinetic studies.

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[8] J. H. Ridd, *Quart. Rev.*, 1961, **15**, 418.