Kinetic and Product Study of the Reaction Between Nitrous Acid and Hydrazine

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The reaction between nitrous acid and hydrazine is a normal *N*-nitrosation reaction, and does not involve oxidation at NH_2NH_2 to N_2H_2 as previously postulated. The *N*-nitrosohydrazine decomposes by two parallel routes, to HN_3 at high acidities and to ammonia and N_2O at low acidities. An intermediate in the decomposition has been detected spectrophotometrically. Revised values are provided for the relative reactivity of some nucleophiles to nitrosating agents, and the relation between reactivity and charge in nitrosation reactions is discussed.

PREVIOUS studies on the reaction of nitrous acid with the alkylhydroxylamines have shown the existence of an unusual reaction mechanism involving attack by a cationic reagent, $[NO]^+$ or $[H_2NO_2]$,$^+$ on cationic substrates $[RNH_2OH]^+$. Attack occurs at the oxygen atom, followed by migration of the nitrosyl group to the nitrogen.[1] This has similarities to the mechanism of diazotisation of aromatic amines proposed by Challis and Ridd [2] for moderately concentrated mineral acid solution, where nitrosation occurs by initial electrophilic attack on the π electrons of the aromatic ring of $[RNH_3]^+$ (R = aryl). Hydrazine exists as the cation $[NH_3NH_2]^+$ over the range pH 0—8, and having both a cationic $[NH_3]^+$ group and a nucleophilic NH_2 group seemed a good model compound with which to investigate the reaction of positively charged nucleophiles with nitrosating agents. The reaction of HNO_2 with NH_2NH_2 is also of some technological interest, as hydrazine has been proposed as a scavenger for nitrous acid in the Purex process for the separation of uranium and plutonium.[3]

The oxidation of hydrazine in aqueous solutions has been studied by many workers, the products being nitrogen, ammonia, and hydrogen azide. This has been discussed in terms of the action of the oxidising reagent as a one-equivalent or a two-equivalent reagent and mechanisms involving N_2H_3, N_2H_2, N_4H_4, and N_4H_6 as reaction intermediates have been postulated. Hydrogen azide is thought to arise from two-equivalent oxidising agents *via* the formation of N_2H_2. The subject has been reviewed by Higginson.[4] The kinetics of the reaction with nitrous acid have been briefly studied by Biddle and Miles [3] using a flow technique. They assumed a stoicheiometry of the form (1) and showed

$$[N_2H_5]^+ + HNO_2 \longrightarrow HN_3 + H_2O + [H_3O]^+ \quad (1)$$

that the reaction was strongly acid catalysed. They could not find any u.v. evidence for the formation of a reaction intermediate, although their method did enable them to detect such a species in the sulphamic acid–nitrous acid reaction.

A much more detailed study has been reported by Koltunov and Marachenko,[5] who found that over the range $[H^+] = 0.1$—0.5 mol dm^{-3} the stoicheiometry was as in (2). They found a rate law $-d[HNO_2]/dt = 408[H^+][HNO_2][N_2H_5^+]$ mol dm^{-3} s^{-1} at 9 °C and 0.5 mol dm^{-3} ionic strength, and proposed the mechanism below:

$$7N_2H_4 + 12\ HNO_2 + H^+ \longrightarrow [NH_4]^+ + HN_3 + 5\ N_2 + 6\ N_2O + 18\ H_2O \quad (2)$$

$$[N_2H_5]^+ + [NO]^+ \xrightarrow{\text{slow}} N_2H_2 + HNO + 2H^+$$

$$2\ N_2H_2 \longrightarrow H_2N\text{-}N\text{-}N\text{-}NH_2 \xrightarrow{\text{fast}} N_2 + N_2H_4$$

$$2\ N_2H_2 \longrightarrow HN{=}N\text{-}NH\text{-}NH_2 \xrightarrow{\text{fast}} NH_3 + NH_3$$

$$2\ HNO \longrightarrow N_2O + H_2O$$

Although they used hydrochloric acid as a reaction medium, they did not report any catalytic effect due to chloride ion, in contrast to what has been observed in many other reactions of nitrous acid. Much work has been done on the products of the reactions of nitrous acid with hydrazine, and with the alkylhydrazines. Smith [6] has summarised much of the previous work from the viewpoint of an organic chemist. A number of workers have found evidence for the formation of ammonia and dinitrogen mono-oxide as products, although no evidence has been obtained for the formation of intermediate nitrosohydrazines.

EXPERIMENTAL

All the chemicals used were of AnalaR grade.

Kinetic Methods.—Four methods were used. In the early work, method (*i*), the disappearance of nitrous acid was followed spectrophotometrically at 360 nm using a Unicam SP 700 spectrophotometer. Sodium nitrite solutions were injected from a syringe into a solution of hydrazine in perchloric acid. For very fast runs, a spring-powered syringe gun was used. Method (*ii*) was similar, except that a Unicam SP 600 instrument was used, with a Servoscribe recorder. Method (*iii*) involved quenching aliquot portions from the reaction mixture with a small volume of a concentrated alkaline phosphate buffer. The absorbance due to the nitrite ion at 355 nm was recorded on a Unicam SP 600 instrument. This method was only suitable for reactions that were sufficiently slow to be followed by sampling with a pipette, and these experiments

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[1] M. N. Hughes, T. D. B. Morgan, and G. Stedman, *J. Chem. Soc.* (*B*), 1968, 344.

[2] B. C. Challis and J. H. Ridd, *J. Chem. Soc.*, 1962, 5208.

[3] P. Biddle and J. H. Miles, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1929; C. S. Schlea, M. R. Caverly, H. E. Henry, and W. J. Jenkins, U.S.A.E.C. document DP8D8, 1963; E. K. Dukes and R. M. Wallace, U.S.A.E.C. document DP728, 1963.

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

[5] V. S. Koltunov and V. I. Marachenko, *Kinetika i Kataliz*, 1966, **7**, 224.

[6] P. A. S. Smith, 'Open Chain Nitrogen Compounds,' Benjamin, New York, 1965, vol. 2, p. 14.

were made at 0 °C with low concentrations of hydrazine and perchloric acid. The final experiments (*iv*) were carried out with a Nortech stopped-flow apparatus at 360 nm. The conditions were not ideal because the light intensity at this wavelength was much lower than in the visible, and the molar absorption coefficient of molecular nitrous acid is not very high. Because of the shorter reaction times that could be followed, measurements were extended to higher acidities than were used with the first three methods.

Product Analyses.—Analyses for hydrogen azide were made by adding a sample of reaction mixture to a solution of iron(III) nitrate in perchloric acid, and measuring the absorbance at 460 nm. The method was calibrated by use of standard azide solutions. Analyses for ammonia were made by destroying the hydrazine with potassium iodate, removing the excess of iodate with iodide, and reducing the liberated iodine with thiosulphate. The solution was then made alkaline, and the ammonia separated by distillation. Liberation of gas was followed by means of a Warburg apparatus, using conventional methods, calibrating the apparatus by measurements on the nitrous acid–hydroxylamine reaction. Because the rates of our reactions were comparable to the rate of attainment of equilibrium between N_2O dissolved in the aqueous phase and in the vapour space, we were not able to obtain reliable rate constants by this method. Even for stoicheiometric measurements there were problems when the rate of reaction was comparable with the rate at which the solutions were mixed.

Calculation of Loss of Hydrogen Azide.—At acidities greater than 0.5 mol dm^{-3} our product is almost entirely HN_3. This can undergo a second reaction with nitrous acid [equation (3)]. At constant acidity there is thus a

$$HN_3 + HNO_2 \longrightarrow N_2 + N_2O + H_2O \qquad (3)$$

system of two consecutive second-order reactions, (2) and (3). The kinetics have been worked out,[7] and with known values of the rate constants it is possible to calculate the loss of HN_3 due to (2). Identical results were obtained by standard numerical integration procedures using a Runge–Kutta method on an ICT 1905 computer.

TABLE 1

Rate constants for the reaction between nitrous acid and hydrazine at 25 °C, in the presence of 0.1 mol dm^{-3} chloride ion

$10^3[N_2H_5^+]$/mol dm^{-3}	5.04	10.08	25.2	50.4	50.4	50.4	50.4	50.4
$10^2[H^+]$/mol dm^{-3}	25.0	25.0	25.0	25.0	20.0	15.0	9.9	4.9
k_1/s^{-1}	1.05	1.87	4.62	8.41	6.82	5.22	3.59	1.63
$k_1[H^+]^{-1}[N_2H_5^+]^{-1}$/dm^6 mol^{-2} s^{-1}	831	741	733	668	675	692	717	746

RESULTS

The kinetics of reaction were investigated in solutions buffered with excess of perchloric acid, and containing a large excess of hydrazine over nitrous acid. Individual runs gave good pseudo-first-order kinetics (k_1). A typical plot is in Figure 1. By varying the initial concentrations of hydrazine and perchloric acid the complete rate law (corrected for chloride catalysis) was shown to be $-d[HNO_2]/dt = 611[H^+][HNO_2][N_2H_5^+]$ mol dm^{-3} s^{-1} at 25 °C and 0.3 mol dm^{-3} ionic strength. The Arrhenius activation energy of 56.5 kJ mol^{-1} (measured over the range 0—25 °C) is in agreement with values for other nitrosation reactions but markedly greater than Koltunov and Marachenko's value of 36.1 kJ mol^{-1}. In the experiments described so far hydrazine hydrochloride was used as a substrate and this introduced a small amount of chloride-ion catalysis. The effect was small, but in order to avoid complications additional sodium chloride was added to maintain a constant chloride-ion concentration, and a correction was made to the rate constant. Results are shown in Table 1 and were obtained by method (*iv*).

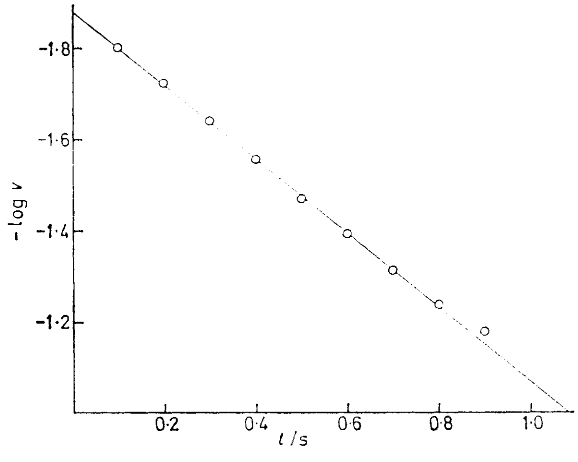

FIGURE 1 First-order plot for a typical reaction between nitrous acid and hydrazine at 25°C; $[H^+] = 0.25$, $[N_2H_5^+] = 0.101$, $[Cl^-] = 0.1$, and $[HNO_2]_0 = 0.001$ mol dm^{-3}. The parameter v is proportional to the absorbance due to HNO_2 at 360 nm

Measurements of the solvent isotope effect at 6 °C (to give a lower rate) over the range $[H^+] = 0.004$—0.008 mol dm^{-3} using method (*i*) gave values of $k_D/k_H = 1.4$. Chloride, bromide, and thiocyanate ions catalysed the reaction, method (*iii*), and plots of the second-order rate constant $v/[N_2H_5^+][HNO_2]$ as a function of the concentration of the catalytic anion at 0 °C are shown in Figure 2. The relative catalytic powers are $Cl^- : Br^- : SCN^- = 1 : 1 : 8$. A similar set of experiments at 25 °C [method (*ii*)] gave relative reactivities of 1 : 1 : 5. As can be seen from Figure 2 the increase in rate due to added chloride and bromide ion is small. In order to increase the fraction of reaction proceeding by the anion-catalysed path, experiments were made with a much higher chloride-ion concentration, 1.15 mol dm^{-3}. The data in Table 2 establish that the total rate of reaction under these conditions is first order with respect to $[H^+]$,

TABLE 2

Rate constants for the reaction between nitrous acid and hydrazine at 25 °C in the presence of 1.15 mol dm^{-3} chloride ion [method (*iv*)]

$10^2[H^+]$/mol dm^{-3}	2.4	4.9	9.9	1.49	1.99	2.49
k_1/s^{-1}	0.66	1.42	2.74	4.53	5.62	6.96
$k_1[H^+]^{-1}$/dm^3 mol^{-1} s^{-1}	27.6	28.9	27.7	30.4	28.3	28.0

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[7] S. Benson, ' Foundations of Chemical Kinetics,' 1st edn., McGraw-Hill, London, 1960, p. 45.

and similar experiments showed it was also first order with respect to $[N_2H_5^+]$.

As the uncatalysed + the chloride-catalysed reaction is first order with respect to $[H^+]$ and $[N_2H_5^+]$, and the same is true of the uncatalysed reaction on its own, then this is also true for the chloride-catalysed reaction. Because both reactions are subject to large salt effects, and at concentrations of the order of 1 mol dm^{-3} these are likely to vary from salt to salt, we did not try to split the rate constants in Table 2 into parts due to the uncatalysed and chloride-catalysed reactions. Much more marked catalytic effects can be seen with thiocyanate ion, and the dependence of the anion-catalysed rate on $[H^+]$ and $[N_2H_5^+]$ was examined over a four-fold change in each of these variables. The rate law found was $-d[HNO_2]/dt = k_4^{SCN^-}[H^+][HNO_2][SCN^-][N_2H_5^+]$. The rate constants obtained at 0 °C and 0.3 mol dm^{-3} ionic strength are $k_4^{X} = 420$ (Cl), 420 (Br), and 3 600 dm^9 mol^{-3} s^{-1}. Attempts to confirm this by working at 25 °C and with high concentrations of thiocyanate, and following the rather rapid reaction by the stopped-flow method, were unsuccessful. Individual runs gave good first-order plots, but the first-order rate constants were poorly reproducible, $\sigma = 7\%$. Other systems involving equally rapid reactions of nitrous acid and hydrazine (but not thiocyanate) were quite self-consistent, and so were experiments in the thiocyanate-catalysed nitrosation of hydroxylamine. Under the conditions used a significant fraction of the nitrite exists as nitrosyl thiocyanate, and this is known to decompose to form NO and thiocyanogen [equation (4)]. We suspect

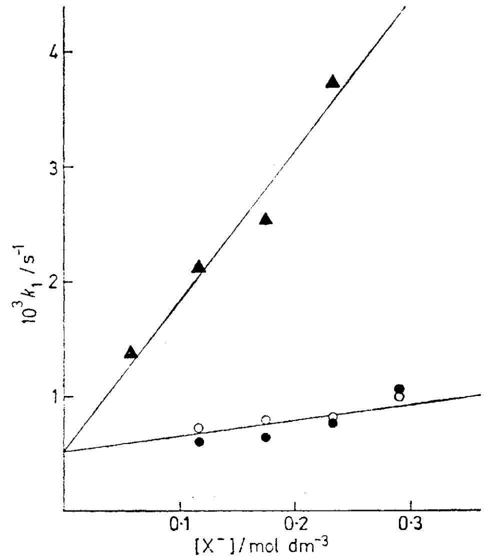

FIGURE 2 Variation of first-order rate constant for the disappearance of nitrous acid with concentration of the catalytic anion at 0° C, $[N_2H_5^+] = 0.004$ and $[H^+] = 0.004$ mol dm^{-3}: $X^- = Cl^-$ (●), Br^- (○), or SCN^- (▲)

$$H^+ + HNO_2 + [SCN]^- \longrightarrow NOSCN + H_2O \longrightarrow NO + \tfrac{1}{2}(SCN)_2 \quad (4)$$

that NO or thiocyanogen (or species derived from subsequent reactions of these compounds) are responsible for the complications. The lack of reproducibility may indicate the involvement of free radicals.

This form of rate law is commonly found for a rate-determining attack by a nucleophile ($[N_2H_5]^+$) on an equilibrium concentration of a nitrosyl halide. The effect of ionic strength on the acid-catalysed reaction (no halide present) was investigated by adding sodium perchlorate up to 1 mol dm^{-3} ionic strength (I). A plot of log k against $I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ had a gradient of 1.23. Some runs were carried out at lower acidities, pH 3.40—4.31, in acetate buffers. The reaction was found to show buffer catalysis, as has been observed in diazotisation. The present discussion will be solely concerned with the results in perchloric acid, where there were no complications due to nucleophilic buffer anions.

The u.v. spectra of the reaction solution showed the formation of an intermediate species with an absorption maximum at 225 nm. This peak slowly disappeared, following first-order kinetics. The reaction was acid catalysed, the overall rate law being $v = 1.05\,[H^+][\text{Intermediate}]$ dm^3 mol^{-1} s^{-1} at 25 °C and 0.3 mol dm^{-3} ionic strength. Typical results are shown in Table 3. The deuterium solvent-isotope effect was $k_D/k_H = 1.2$. Thus for runs with constant hydrazine concentration, at constant acidity we have a system of two consecutive first-order reactions $A \longrightarrow B \longrightarrow C$ with known rate constants. Using the familiar expression for the variation of [B] with time, we calculated the absorption coefficient of our intermediate to be *ca.* 1 200 dm^3 mol^{-1} cm^{-1}, on the basis of the initial concentration of nitrous acid. As HN_3 is often described as the product of the nitrous acid–hydrazine reaction, our first product analyses were directed towards its determination. The yield of azide was close to 100% at greater than 0.2 mol dm^{-3} perchloric acid, but decreased with lower acidities. Analyses for ammonia accounted quantitatively for the ' missing ' azide as shown in Figure 3. The results fitted the equation $[HN_3]_\infty/([HNO_2]_0 - [HN_3]_\infty) = 0.44 + 25[H^+]$ for experiments at 1.5 mol dm^{-3} ionic strength and 0 °C. This corresponds to a yield of 69.5% ammonia at $[H^+] = 0$. Because our results at low perchloric-acid concentration were not accurate enough for us to be sure about this intercept, we determined the yield in acetate buffers over the range pH 3.7—4.4, obtaining a yield of ammonia of 70.5%. Experiments in phosphate buffers gave 72.5%. Assuming a 1 : 1 nitrous acid : hydrazine stoicheiometry, the remaining nitrogen must be in an average oxidation state of +I. Measurements with a Warburg apparatus showed that gas evolution occurred. In acetate buffers a yield (assumed to be N_2O) of 64% was obtained. In 0.2 mol dm^{-3} perchloric acid the yield was 26 ± 5% (the corresponding ammonia yield was 16%). This discrepancy is discussed below.

TABLE 3

Rate constants at 25 °C for the disappearance of the intermediate absorbing at 225 nm

$10^3[H^+]$/mol dm^{-3}	1.5	4.5	8.5	11.5	17.5
$10^3\,k_1$/s^{-1}	1.38	4.05	9.87	10.7	19.0
$k_1[H^+]^{-1}$/dm^3 mol^{-1} s^{-1}	0.92	0.90	1.16	0.94	1.09

The above results refer to reaction with the nitrite acidium or nitrosonium ion as the electrophile. A few experiments were made where large concentrations of bromide or thiocyanate ion were present, so that reaction proceeded largely through nitrosyl bromide and nitrosyl thiocyanate as electrophiles. At 0.03 mol dm^{-3} perchloric acid, 1.5 mol dm^{-3} ionic strength, and 20 °C, the yields of ammonia were 55 and 60% respectively, compared with a figure of 45% for the nitrite acidium or nitrosonium ion (at 0 °C).

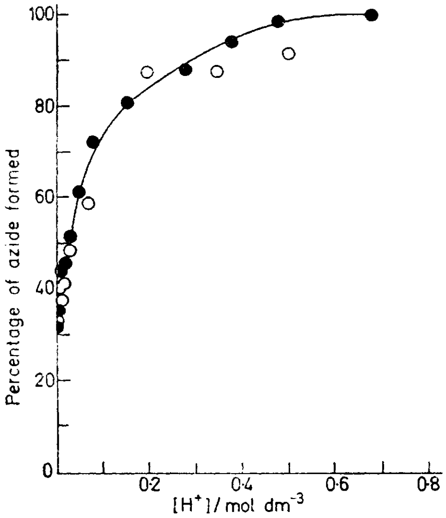

FIGURE 3 Variation of product composition with acidity at 0° C: (●), azide analyses; (○), ammonia analyses

DISCUSSION

The most complete study of this reaction is undoubtedly that of Koltunov and Marachenko, but the evidence for their mechanism is basically the variety of nitrogenous products that they observed. There is no other compelling evidence. Their mechanism is based largely on analogies with other reactions in which hydrazine is oxidised, but it is interesting to note that N_2O, which is one of their main products, is not normally a product of the oxidation of hydrazine. They concluded from their stoicheiometry that nitrous acid is acting as a two-electron oxidising agent, and that the nitrosonium ion oxidised the hydrazinium ion to N_2H_2. Their stoicheiometric results referred to acidities between $[H^+] = 0.1$ and 0.5 mol dm^{-3}. Our own results show the formation of *ca.* 100% HN_3 under these conditions, as assumed by Biddle and Miles. The rate law for reaction (3) has been shown[8] to be $-d[HNO_2]/dt = 33.7[H^+][HNO_2][HN_3]$ mol dm^{-3} s^{-1} at 0 °C. Thus in the hydrazine–nitrous acid reaction there is likely to be some loss of HN_3 by this path, with consequent formation of nitrogen and N_2O. Calculations show that, for initially equimolar concentrations of hydrazine and nitrous acid, *ca.* 32% of HN_3 is expected to be lost in this way.

For higher values of $[N_2H_5^+]_0/[HNO_2]_0$ naturally the loss is much less, and for a ten-fold excess of hydrazine is only 2%. These figures are independent of the acidity, because the reactions with the hydrazinium ion and hydrogen azide are similarly acid catalysed. In all of our work we used a sufficiently large excess of hydrazine to ensure that these losses were negligible. Koltunov and Marachenko do not give sufficient details to enable us to decide how important this was in their system, but it seems significant that they report nitrogen and N_2O as formed in nearly equivalent amounts. If we assume that the nitrogen arises from the nitrous acid–hydrogen azide reaction, and allow for the same amount of N_2O, then from equation (2) we find that ammonia and the remaining N_2O are formed in equivalent amounts in agreement with our own observations. There is an additional complication. In our early experiments we noted some scatter, ±10%, in our yields of HN_3. This proved to be due to mixing factors. Even with hydrazine concentrations as low as 0.01 mol dm^{-3} the half-life for the consumption of nitrous acid in 0.1 mol dm^{-3} perchloric acid at room temperature is *ca.* 1 s. Thus with normal pipetting techniques the mixing time may be comparable with or greater than the half-life of the reaction. There may thus be portions of the solution where $[HNO_2]/[N_2H_5^+]$ is much higher for a short period of time than calculated stoicheiometrically for the whole solution. We solved this problem by doing experiments at 0 °C to slow the reaction down, and mixing with a spring-powered syringe with which mixing times may be as short as a few centiseconds. Little or no scatter was observed under these conditions. This factor should also lead to loss of HN_3 and formation of nitrogen and N_2O, and the yields of HN_3 that we observed with rapid mixing were *ca.* 15% higher than those observed with normal mixing methods. This is probably the cause of the apparently large amount of gas evolved for reaction in 0.2 mol dm^{-3} perchloric acid.

The kinetic form of the rate law for the uncatalysed reaction, the catalysis of the reaction by chloride, bromide, and thiocyanate ions, its kinetic form, and the relative magnitudes of the values of k_4^X are all consistent[9] with electrophilic nitrosation of the hydrazinium ion by equilibrium concentrations of the nitrosonium or nitrite acidium ions or the nitrosyl halide NOX. There thus seems no reason on grounds of either products or of kinetics to postulate a mechanism involving the oxidation of hydrazine to N_2H_2 or related species.

The observed rate law, $-d[HNO_2]/dt = k_3[H^+][HNO_2][NH_3NH_2^+]$, has the form expected for electrophilic nitrosation by the nitrosonium or nitrite acidium ion at the hydrazinium ion. For singly charged anions the rate constants corresponding to k_3 are *ca.* 10 000—20 000 dm^6 mol^{-2} s^{-1} at 25 °C and are thought[9] to correspond to an encounter-controlled process. The effect of charge on the encounter rate has been calculated by Debye, and for two singly charged cations the rate should be less than for a singly charged cation and a

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

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

singly charged anion, the factor depending on the distance of closest approach.[10] The factors are 2.7 (0.75), 4.2 (0.5), and 37 (0.2 nm). Taking the nitrosating agent to be the nitrosonium ion, we estimate an encounter rate with the hydrazinium ion of *ca.* 1 300 $dm^6 mol^{-2} s^{-1}$ at 25 °C. Thus the observed rate is not much less than the encounter limit.

Thompson and Kaufmann [11] have also studied the reaction of cationic nucleophiles with the nitrosonium (or nitrite acidium) ion in their work on azido-complexes of Cr^{III} and Co^{III}. For *cis*- and *trans*-$[Co(en)_2(N_3)(OH_2)]^{2+}$ (en = ethylenediamine) they found rate constants of 440 and 100, which compare with an encounter limit that we calculate to be *ca.* 1 000 $dm^6 mol^{-2} s^{-1}$. Clearly, even with a doubly charged species one can get close to a diffusion-controlled reaction. Reactivity differences are brought out much more clearly by using less reactive nitrosating agents such as the nitrosyl halides. For $[Cr(N_3)(OH_2)_5]^{2+}$ they find k_4^{Cl} and k_4^{Br} to be 65 000 and 120 000, whereas for $[N_2H_5]^+$ at the same temperature we find k_4^{Cl} and k_4^{Br} to be *ca.* 800 and 1 200 $dm^9 mol^{-3} s^{-1}$ respectively. It is clear that even allowing for activity-coefficient corrections for different charge types, the azide complexes are far more reactive nucleophiles than the hydrazinium ion, despite their 2+ charge. These results may be compared with earlier data on hydroxylamine.[1]

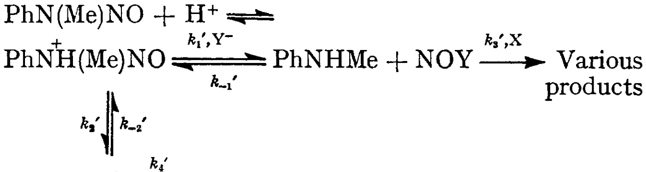
Comparison of bimolecular rate constants ($dm^3 mol^{-1} s^{-1}$) for reaction of NH_2OH and $[NH_3NH_2]^+$ with nitrosyl halides at 0 °C

NH_2OH	3.5×10^7 (Cl)	3.7×10^7 (Br)	3.6×10^6 (SCN)
$[NH_3NH_2]^+$	7.5×10^5 (Cl)	1.9×10^3 (Br)	7.8×10 (SCN)

The hydrazinium ion is a much less reactive nucleophile than hydroxylamine, as might be expected from its basicity and the fact that the latter has a lone pair of electrons on the oxygen atom adjacent to the nucleophilic nitrogen centre. The hydrazinium ion also discriminates much more between the different electrophiles. The reason that hydrazine is so successful as a nitrite scavenger is not that it is intrinsically reactive, but that at moderate acidities virtually all the hydrazine is present in the reactive form $[NH_3NH_2]^+$. Hydroxylamine and many other amino-compounds which are intrinsically much more reactive, exist in acid solution mainly as the much less reactive conjugate acids, with very little of the active free base present.

An interesting approach to the determination of the relative reactivity of a range of nitrosating agents towards various nucleophiles has come out of work [1] on the kinetics and mechanism of the Fischer–Hepp rearrangement in the presence of added nitrite scavengers. The experiments were made under very different conditions to the present work, 3.0 mol dm^{-3} hydrochloric acid, 2.7 mol dm^{-3} sulphuric acid containing 0.2 mol dm^{-3} of sodium bromide, and 4.8 mol dm^{-3} H_2SO_4. We agree with a number of the conclusions reached, for example that hydrazine nitrosates *via* the hydrazinum ion and not the neutral base, that nitrosyl chloride is a less discriminating reagent than nitrosyl bromide, and that in general these latter species do not nitrosate at rates approaching the encounter limit. However, when quantitative comparisons are made the agreement is not good. Thus for the relative reactivities of $[N_2H_5]^+$ to NH_2OH the present work gives the ratios as 0.024 (NOCl) and 0.000 62 (NOBr), whereas the data from the Fischer–Hepp rearrangement are interpreted to give 0.000 04 (NOCl) and 0.000 038 (NOBr). Aniline is suggested to be less reactive than free hydroxylamine towards nitrosyl chloride, the ratio being 0.17, whereas a comparison of Schmid's data [13] for aniline with our own work on hydroxylamine suggests the reactivity ratio to be 5.2. Our own data on the reaction of nitrosyl chloride with hydroxylamine might be criticised on the grounds that we were looking at a rather small catalytic effect. However, in the chloride-catalysed nitrosation of *O*-methyl, *ON*-dimethyl, and *O*-isopentyl hydroxylamine the reactivity of the free base was found to be within a factor of 2.7 of that of hydroxylamine, and in these three cases chloride catalysis was a marked feature, which could easily be accurately measured. Similarly in support of our data on hydrazine we find [14] that the chloride-ion-catalysed nitrosation of $[NMeH_2NH_2]^+$ and $[NMe_2HNH_2]^+$ are within a factor of 3 of our value for $[NH_3NH_2]^+$; here again the chloride catalysis is easy to measure in the case of the alkyl compounds.

The cause of this discrepancy is not clear. One possibility is that the kinetic scheme used to analyse the data for the Fischer–Hepp rearrangement should be extended slightly. The basic scheme may be written as follows:



We follow here the system used in the original paper [12] for numbering rate constants; (I) represents a Wheland-type intermediate with the nitroso-group bonded to a tetrahedral carbon atom *para* to the methylamino-group, Y^- is a nucleophile such as chloride or bromide ion, and X is a nitrite scavenger such as hydrazinium ion. The modification we suggest is to include the hydrolysis reaction (5) of NOY. If we take the case of Y = Cl then the equilibrium constant for (5) is $[NOCl]/[H^+]$-

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[10] E. F. Caldin, 'Fast Reactions in Solution,' Blackwell, Oxford, 1964, p. 12.

[11] R. C. Thompson and E. J. Kaufmann, *J. Amer. Chem. Soc.*, 1970, **92**, 1540.

[12] D. L. H. Williams, *J.C.S. Perkin II*, 1975, 655.

[13] H. Schmid and G. Muhr, *Ber.*, 1937, **70**, 421.

[14] N. Uysal, Ph.D. Thesis, University of Wales, 1975.

$[HNO_2][Cl^-] = 5.6 \times 10^{-4}$ dm^6 mol^{-2} at 0 °C. Taking a value for the rate constant for the formation of nitrosyl chloride by the reverse reaction of (5) as *ca.* 1 000 dm^6

$$NOY + H_2O \rightleftharpoons H^+ + HNO_2 + Y^- \qquad (5)$$

mol^{-2} s^{-1} at 0 °C then the pseudo-first-order rate constant for the hydrolysis of NOCl is 1.8×10^6 s^{-1}. This hydrolysis must be very much faster than the rate of the reverse reaction between *N*-methylaniline and nitrosyl chloride because in solutions as acidic as 3 mol dm^{-3} HCl the former species will be almost completely protonated. Taking the pK_a of the conjugate acid to be 4.85, the Hammett acidity function H_0 to be -1.05, and the total concentration of *N*-methylaniline to be 4×10^{-3} mol dm^{-3} (described [15] as a large excess), then the rate of hydrolysis of NOCl should be *ca.* 10^4 times as great as the rate of reaction with *N*-methylaniline. There will, of course, also be a rapid formation of NOCl by the reverse of (5), but the net effect will be that equilibrium (5) will be rapidly established and the standing concentration of molecular nitrous acid will be much greater than that of nitrosyl chloride. There will therefore be other routes by which X will scavenge the liberated nitrite, reactions involving the nitrosonium ion as an electrophile. The possibility of nitrosation of the *N*-methylanilinium ion was mentioned, but not quantitatively allowed for.[12] There may be other factors operating as well. Medium effects could well be substantial in view of the difference in acidities. These ideas are currently being examined.[15]

$$H^+ + HNO_2 + X \longrightarrow \text{Various products} \qquad (6)$$

We do not in any way question that this is an interesting and potentially useful approach to the determination of the relative efficiencies of various nitrite scavengers, but we think a more complex kinetic treatment is necessary in order to obtain relative rate constants characteristic of a particular electrophile. In particular we think it necessary to know quantitatively the position of equilibrium (5). It is also necessary to be cautious in extrapolating kinetic behaviour from one acidity to another. Thus the nitrosation of hydroxylamine at low acidities, say pH 4, undoubtedly proceeds through the free base. However, at pH 1 the reactive species is the conjugate acid, and the rate law is $-d[HNO_2]/dt = k[H^+][HNO_2][NH_3OH^+]$; at *ca.* 1.8 mol dm^{-3} H_2SO_4, k reaches a maximum and then decreases with increased acidity.[1] Hydrogen azide on the other hand has a rate constant that increases rapidly with acid concentration up to 4.2 mol dm^{-3} $HClO_4$.[16] The behaviour of sulphamic acid is complicated by the fact that both the sulphamate ion and undissociated NH_2SO_3H are nitrosated.[17]

Turning to the details of the mechanism we note that the yield of ammonia varies with the nature of the nitrosating agent. This is a similar result to that observed in the nitrosation of hydroxylamine, where the yields of *cis*- and *trans*-hyponitrous acid varied with the nitrosating agent.[18] Results of this sort imply that the reactions do not proceed through a common intermediate, the *N*-nitroso-compound. The explanation is that *N*-nitroso-compounds of this type exist in *cis* and *trans* forms due to partial double-bond character of the N–N bond ($NH_2{-}NH{-}N{=}O \longleftrightarrow NH_2{-}NH{=}N{-}O$). There is n.m.r. evidence for the existence of such isomers among the alkyl derivatives of the nitrosohydrazines, nitrosohydroxylamines, and nitrosamines. Furthermore the evidence shows that the rate of *cis–trans* interconversion is slow on the n.m.r. time scale, and is slow enough for the isomers to be separated at low temperatures in some cases. As the bond between the nitroso-group and the amino-nitrogen is being formed in the transition state at the same time as the N–X bond of the nitrosating agent ON–X is being broken, we may expect the relative rates of formation of *cis* and *trans* products to depend on the nature of X. If the rate of *cis–trans* isomerisation is much faster than the rate of breakdown of nitrosohydrazine, then clearly the relative proportions of the final products will be independent of the nature of the nitrosating agent. If however, this is not the case, then one may expect the different proportions of *cis*- and *trans*-nitrosohydrazines to give rise to different proportions of the products, in this case ammonia and hydrogen azide. We assume that in general we may expect *cis*- and *trans*-nitrosohydrazines to give rise to different proportions of NH_3 and HN_3 acid in their decomposition.

N-Nitroso-compounds usually show a weak absorption band, ε *ca.* 10^2 dm^3 mol^{-1}, in the 350—380 nm region, and although we have looked carefully for such a band we were unable to find any trace of it. It seems likely that the nitrosohydrazine rapidly tautomerises to $NH_2{-}N{=}N{-}OH$, a similar reaction to that postulated in the mechanisms of diazotisation and deamination. The absorption band at 225 nm is probably due to this species. It is analogous to *trans*-hyponitrous acid, HO–N=NOH, which absorbs [19] at 208 nm (ε 2 740 dm^3 mol^{-1} cm^{-1}), and undergoes an acid-catalysed decomposition to N_2O and water, $v = (k + k'[H^+])[H_2N_2O_2]$. At pH < 1 the k' term can be neglected in comparison with the k term.

The decomposition of $NH_2{-}N{=}N{-}OH$ can readily be visualised as leading to NH_3 and N_2O, or alternatively to HN_3 and water. The latter reaction, which is analogous to what is thought to happen in diazotisation and deamination, must be acid catalysed in order to account for the 100% yield of HN_3 at high acidities. There cannot be an acid catalysed path leading to ammonia and N_2O of any significance; if there were, then we would observe a significant yield of ammonia at high acidities. The simplest scheme is set out below:

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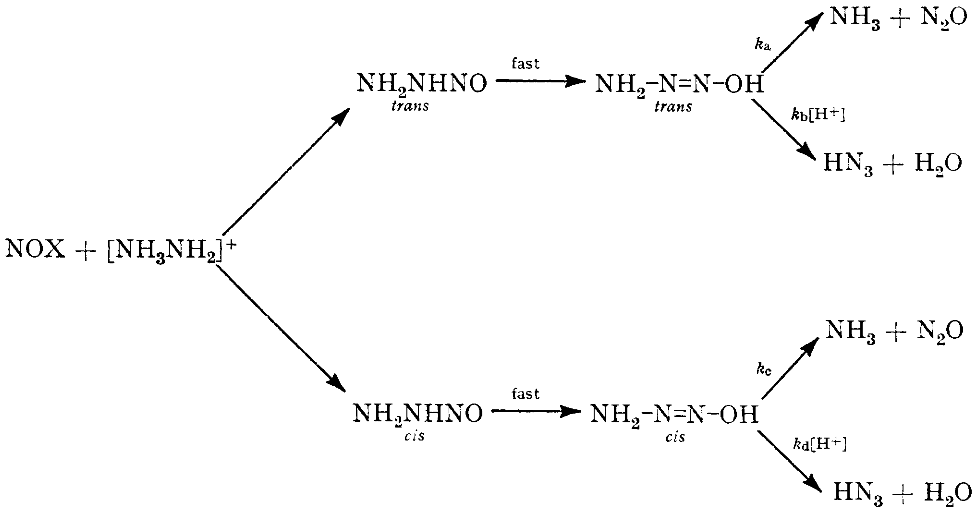
[15] D. L. H. Williams, personal communications.

[16] G. Stedman, unpublished work.

[17] M. N. Hughes, *J. Chem. Soc.* (*A*), 1967, 902.

[18] G. Stedman and M. A. Hussain, *J. Chem. Soc.* (*B*), 1968, 597.

[19] M. N. Hughes and G. Stedman, *J. Chem. Soc.*, 1963, 1239.



If α is the fraction of reaction going to the *trans* isomer, then expression (7) follows. This simplifies to the observed dependence on acidity if either k_a or k_c can be neglected. Now *cis*-hyponitrous acid decomposes to N_2O and water very rapidly, whereas at pH < 1 *trans*-$H_2N_2O_2$ dehydrates rather slowly [20] ($t_{\frac{1}{2}}$ 1.5 h at 70 °C).

$$\frac{[HN_3]}{[NH_3]} = \frac{\alpha k_b[H^+](k_a + k_b[H^+])^{-1} + (1 - \alpha)k_d[H^+](k_c + k_d[H^+])^{-1}}{\alpha k_a(k_a + k_b[H^+])^{-1} + (1 - \alpha)k_c(k_c + k_d[H^+])^{-1}}$$

We suggest that k_a is small and can be neglected. This leads us to suggest that the peak observed at 225 nm is due to *trans*-NH_2-N=N-OH, which decomposes by an acid-catalysed mechanism to form NH_3: thus k_b would be 1.05 $dm^3\ mol^{-1}\ s^{-1}$ at 25 °C. Again by analogy with hyponitrous acid, we suggest that *cis*-NH_2-N=N-OH decomposes rapidly. When k_a is set equal to zero, then $[HN_3]/[NH_3] = (\alpha k_c + k_d[H^+])/k_c(1 - \alpha)$. This leads to a value of $\alpha = 0.30$, and $k_d/k_c = 56.9$.

This mechanism seems reasonable in the light of the known organic chemistry of alkyl- and aryl-hydrazines. The nitrosation product of phenylhydrazine gives phenyl azide in excellent yield in the presence of acid, but on heating gives aniline and N_2O. Gassman and Shudo [21] reported the decomposition of the *N*-nitroso-derivative of dialkylhydrazines to yield the secondary amine and N_2O. Our own work on the mechanism of nitrosation of the alkylhydrazines will be reported shortly. Although the products of the nitrosation of hydrazine (and hydroxylamine) are more complex than observed in diazotisation, this can be an advantage in trying to obtain information about the post-nitrosation stages of reaction. We hope to investigate the nitrosation of other inorganic systems.

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[20] M. N. Hughes and G. Stedman, *J. Chem. Soc.*, **1964**, 163.

[21] P. G. Gassman and K. Shudo, *J. Amer. Chem. Soc.*, 1971, **93**, 5899.