

Kinetics and mechanism of the reaction of nitrous acid with 2,4-dinitrophenylhydrazine



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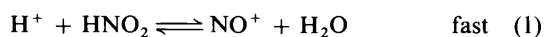
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Arylhydrazines react with excess nitrous acid to form mixtures of the diazonium ion and aryl azide. By use of the weakly basic 2,4-dinitrophenylhydrazine (DNP), $pK_a = 1.55$, information about the mechanism of the diazotisation reaction has been obtained. Three successive stages can be observed. The initial reaction consists of parallel nitrosations by N_2O_3 and NO^+ of the free base DNP at the terminal nitrogen. This is followed by a stage with the rate independent of $[HNO_2]$, almost certainly a tautomerisation, probably to form $ArN=NNHOH$ and $ArNHN=NOH$. The former is converted to ArN_3 , while the latter undergoes a further electrophilic nitrosation by NO^+ of a conjugate base species to yield a di- N,N' -nitrosoarylhydrazine, a precursor to the diazonium ion.

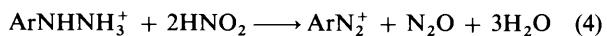
The reaction between nitrous acid and arylhydrazines yields different products, depending upon reaction conditions. In aqueous acid media where the arylhydrazine exists as the conjugate acid there is an encounter controlled reaction¹ to form the α - N -nitroso derivative by reactions (1) and (2).



The primary product undergoes an acid-catalysed decomposition to form the aryl azide reaction (3), and the kinetics of this



process have been reported² by Belyaev *et al.* They found that the rate of formation of aryl azide was favoured by electron-withdrawing substituents and from a Hammett plot they found $\rho = 0.66$. A plausible mechanism for this would be the sequence $ArN(NO)NH_2 \rightarrow ArNHNHNO \rightarrow ArN=NNHOH \rightarrow ArN_3 + H_2O$. Clusius has used ^{15}N tracer techniques to show³ that $C_6H_5N(^{15}NO)NH_2$ yields about 93% of the expected $C_6H_5NN^{15}N$, but also 7% of $C_6H_5N^{15}NN$. With 2,4-dinitrophenylhydrazine, however,⁴ more than 98% of the product is the terminally labelled compound. In the presence of excess nitrous acid the diazonium ion can be formed as shown in reaction (4). With $Ar = C_6H_5$ and $2-CH_3C_6H_4$ and at low



acidities, pH 2.5, the yield of diazonium ion can be¹ almost 100%. With $Ar = 4-NO_2C_6H_4$, under the same conditions, the yield of ArN_2^+ drops to 26.6%.

The mechanism of reaction (4) has not been established. The only case¹ for which there is any kinetic evidence on the formation of the diazonium ion is for $Ar = 4-NO_2C_6H_4$. The final stage of the reaction, followed by absorbance changes at 410 nm gave kinetics that were first-order with respect to $[HNO_2]$. It was suggested that the initial product, $ArN(NO)NH_2$ underwent a second nitrosation to form $ArN(NO)NHO$, possibly through a conjugate base form.

The present paper describes a study of the reaction of excess nitrous acid with 2,4-dinitrophenylhydrazine (DNP) where the tracer evidence of Clusius suggests a simpler system with only one isotopic product. The lower basicity of DNP and reduced nucleophilicity of the α -nitrogen atom results in a simpler system with N -nitrosation occurring only at the β -nitrogen, enabling more details of the mechanism to be deduced.

Experimental

Materials

Sodium nitrite, sodium perchlorate, perchloric acid and 2,4-dinitrophenylhydrazine were AnalaR products, used without further purification; 2,4-dinitroaniline (DNA) from Aldrich was purified by recrystallisation from ethanol. Both the DNP and DNA are very sparingly soluble in water and standard solutions were prepared by dissolving a weighed quantity of the arylhydrazine or arylamine in 1 mol dm⁻³ perchloric acid, followed by accurate dilution.

Kinetic methods

Stopped-flow measurements were made on a Nortech Canterbury SF-3A instrument, fitted with a transient recorder. Conventional UV-VIS spectrophotometry used Phillips Pye-Unicam SP 8600 and SP 8700 instruments. Repeat scan spectra were run on an SP-8720 and a Shimadzu 2101PC UV. Colorimetric analysis for the diazonium ion was carried out by pipetting aliquots of reaction mixture into a solution of 2-naphthol-3,6-disulfonic acid (1 g dm⁻³) in borax (20 g dm⁻³) and measuring the azo dye at 490 nm. Calibration was carried out by diazotisation of standard solutions of 2,4-dinitroaniline, followed by diazo coupling. Our system involved a series of consecutive reactions. The first reaction was much faster than the second, and the second faster than the third and first-order rate constants were easily obtained by standard methods. However, the third reaction was followed by a slower fourth process and under some conditions it was necessary to use a deconvolution program (Enzfitter, Biosoft) to obtain rate constants from the absorbance-time curves. Reaction solutions were made up to an ionic strength of 0.3 mol dm⁻³ with perchloric acid, sodium nitrite and sodium perchlorate. The

concentrations $[H^+]$ and $[HNO_2]$ in the table headings are formal values assuming protonation of the nitrite ion, *i.e.* $[H^+] = [HClO_4] - [NaNO_2]$. For our lower acidities it was necessary to correct for partial dissociation of nitrous acid using a pK_a value of 2.95. All calculations of rate constants have used values of $[H^+]$ and $[HNO_2]$ corrected for changes due to ionisation. The concentrations of DNP used were so low that no corrections were necessary for uptake of protons to form $DNPH^+$.

Results and discussion

Products

The normal products of the reaction between arylhydrazines and excess nitrous acid are the aryl azides and diazonium ions. The presence of diazonium ions was confirmed by the standard diazonium ion coupling reaction to form a red azo dye. The increase in azo dye absorbance with time was monitored at 490 nm in a few runs and a typical plot is shown in Fig. 1. The diazonium ion yield, corrected for decomposition, was calculated to be 10% over the range $[H^+] = 0.075$ – $0.175 \text{ mol dm}^{-3}$.

Evidence for the formation of the aryl azide was obtained by extracting a portion of reaction solution with dichloromethane, separating and drying the organic layer, and then removing the solvent by evaporation. Mass spectra of the product were characterised by an intense peak at mass number 181. Authentic 2,4-dinitrophenyl azide was prepared by diazotisation of 2,4-dinitroaniline, reacting the diazonium ion with excess sodium azide and solvent extraction in the same way. Our product and the authentic azide gave similar electron impact mass-spectra with the principal peak at 181. This is the expected mass number for the corresponding benzfuroxan, known⁵ to be formed readily on heating *ortho*-nitrophenyl azides, by elimination of N_2 and ring closure. No sign of the molecular ion of 2,4-dinitrophenyl azide was observed. As 10% of the arylhydrazine forms diazonium ion we assume the remaining 90% is aryl azide.

Acid–base equilibria of DNP

An essential preliminary to this work was a study of the acid–base equilibria of DNP. The spectra of solutions of DNP as a function of acidity are shown in Fig. 2. Analysis of the data by standard methods at three wavelengths yielded values for the pK_a of 1.54 ± 0.06 (315 nm), 1.59 ± 0.04 (380 nm) and 1.53 ± 0.05 (400 nm). The mean of 1.55 is reasonable when compared with the values of 3.94 and 3.50 for the 4-nitro- and 2-nitro-phenylhydrazines, but is markedly lower than the figure of 2.68 for 50% v/v aqueous dioxane quoted⁶ by Stroh and Westphal. Our value lies very close to a good linear plot of the pK_a of substituted anilinium ions *versus* pK_a of the corresponding substituted phenylhydrazinium ions.

Kinetics

Because of the very low solubility of DNP in water, *ca.* $2 \times 10^{-4} \text{ mol dm}^{-3}$ at 25 °C, all kinetic runs were carried out with a large excess of nitrous acid over DNP. The reaction was monitored by measuring the absorbance at 400 nm. Longer wavelengths gave lower absorbance values, while below 400 nm there can be complications due to overlapping absorption by HNO_2 . Stopped-flow studies showed that there were two rapid initial reactions, followed by a slower third process. Conventional spectrophotometry showed that this was in turn followed by a fourth, even slower reaction.

First reaction

For experiments at $[H^+] = 0.042$ and $[HNO_2] = 0.025 \text{ mol dm}^{-3}$ the absorbance changes gave good first-order plots of $\ln(A_\infty - A_t)$ *versus* time and the resulting rate constants k_{obs}/s^{-1} were found to be independent of $[DNP]_0$. At high acidities,

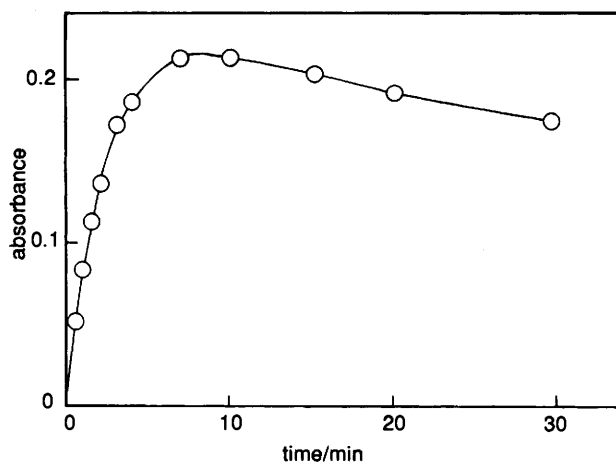


Fig. 1 Kinetics of formation of diazonium ion at 25 °C; $[H^+] = 0.035$, $[HNO_2] = 0.025$ and $[ArNHNH_2] = 5 \times 10^{-4} \text{ mol dm}^{-3}$

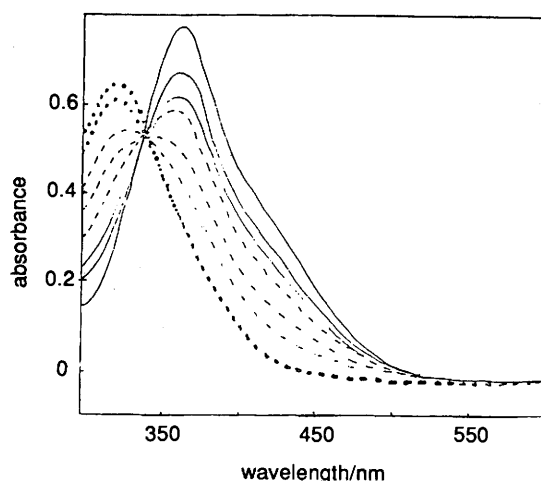


Fig. 2 Effect of acidity on the UV–VIS spectra of 2,4-dinitrophenylhydrazine. Successive curves of decreasing absorbance at 360 nm correspond to pH values 3.48, 2.87, 1.97, 1.67, 1.37, 1.07, -0.40 and -1.2 .

$[H^+] = 0.13$ – 0.25 mol dm^{-3} , the initial reaction showed a marked increase in absorbance, but for runs at low acidities $[H^+] = (0.8$ – $2.2) \times 10^{-2} \text{ mol dm}^{-3}$ the initial reaction showed a decrease. This reflects the marked change in absorbance at 400 nm with pH due to the shift in the acid–base equilibrium of DNP, the extinction coefficient of $DNPH^+$ being *ca.* $1400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ while that of DNP is $7100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The variation of k_{obs} with $[H^+]$ and $[HNO_2]$ is shown in Table 1. For the low acidity region the results appear simple and clearcut. Plots of $\log k_{obs}$ *versus* $\log [HNO_2]$ give orders in the range 2.1–2.2, while the order with respect to $[H^+]$ is zero. For the high acidity experiments, at the lowest nitrous acid concentrations, the order with respect to $[HNO_2]$ is very close to 1, but the order increases somewhat as $[HNO_2]$ rises. The order averaged from 0.005 to $0.025 \text{ mol dm}^{-3}$ nitrous acid lies in the range 1.3–1.4.

Kinetics that are the second-order in nitrite strongly suggest⁷ a mechanism involving N_2O_3 as the nitrosating agent at low acidities. The apparently simple kinetic orders require more detailed consideration because nitrous acid has a rather low pK_a and it is necessary to correct for its partial ionisation in the low acidity experiments; this can modify both $[HNO_2]$ and $[H^+]$. We also need to consider whether the arylhydrazine reacts as the free base DNP or its conjugate acid. Dinitrogen trioxide is a relatively selective nitrosating agent, much less reactive than NO^+ , and it seems unlikely that it will react with $DNPH^+$. Thus

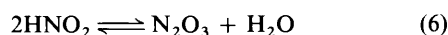
Table 1 Pseudo-first-order rate constants, $k_{\text{obs}}/\text{s}^{-1}$, for the first stage at 25 °C

$[\text{HNO}_2]/10^{-2} \text{ mol dm}^{-3}$	$k_{\text{obs}}/\text{s}^{-1}$							
	$[\text{H}^+]/10^{-3} \text{ mol dm}^{-3}$							
	6.8	8.9	15.8	21.4	130	150	250	1000
2.5	10.5	10.2	10.3	9.4	4.4	4.1	3.6	3.5
2.0	6.4	7.5	6.6	6.8	2.8	2.7	2.6	2.9
1.5	3.4	3.8	3.5	3.6	1.9	1.8	1.5	2.2
1.0	1.4	1.7	1.5	1.4	1.0	0.98	0.87	0.84
0.5	0.30	0.33	0.35		0.49	0.46	0.45	0.41

the expected rate law is shown in eqn. (5), where K_a is the dissociation constant of DNPH⁺

$$k_{\text{obs}} = k_1 \{K_a / (K_a + [\text{H}^+])\} [\text{HNO}_2]^2 \quad (5)$$

This equation gives a good straight line plot of $[\text{HNO}_2]^2/k_{\text{obs}}$ versus $[\text{H}^+]$ with $k_1 = 2.92 \times 10^4 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$, using values of $[\text{H}^+]$ and $[\text{HNO}_2]$ corrected for ionisation of nitrous acid. A plot based on the assumption that DNPH⁺ was the substrate, replacing $K_a/(K_a + [\text{H}^+])$ by $[\text{H}^+]/(K_a + [\text{H}^+])$ gave a large scatter. In view of the fact⁸ that the arylhydrazines protonate almost 100% on the β -nitrogen, and in view of the powerful conjugative electron-withdrawing properties of the *ortho*- and *para*-nitro groups, which should move electron density away from the α -nitrogen, it seems certain that nitrosation occurs on the terminal nitrogen of the free base as shown in reactions (6) and (7). This is consistent with Clusius' observation that more



than 98% of the ¹⁵N tracer was located in the terminal position in his azide product.

It is interesting to note that the apparent lack of dependence of k_{obs} on $[\text{H}^+]$ is actually due to a cancellation of effects, the increased ionisation of HNO₂ at low acidities cancelling out the increased proportion of the free base DNP. For the high acidity kinetics the order of 1.3–1.4 with respect to $[\text{HNO}_2]$ suggests the occurrence of a parallel pathway for nitrosation involving NO⁺. The main difficulty is in deciding whether the substrate is DNP or DNPH⁺. A decision is important. If DNPH⁺ is the substrate the likely product is 2,4-(NO₂)₂C₆H₃N(NO)NH₂, and hence the first reaction would produce a mixture of two products, the α - and β -*N*-nitrosoarylhydrazines. These would have different UV–VIS spectra and different reactivities and the change in absorbance in the second process might be due to parallel decomposition of a mixture of the α - and β -isomers which could be difficult to interpret with certainty; if DNP is the substrate, attack is expected at the more basic terminal nitrogen and then there is only one product of the first reaction, the β -isomer. The two possible rate laws are shown in eqns. (8) and (9), where k_2 and k_3 are the rate constants for the nitrosation of DNP and DNPH⁺ by NO⁺, respectively.

$$k_{\text{obs}} = k_1 \{K_a / (K_a + [\text{H}^+])\} [\text{HNO}_2]^2 + k_2 \{K_a / (K_a + [\text{H}^+])\} [\text{H}^+][\text{HNO}_2] \quad (8)$$

$$k_{\text{obs}} = k_1 \{K_a / (K_a + [\text{H}^+])\} [\text{HNO}_2]^2 + k_3 \{[\text{H}^+] / (K_a + [\text{H}^+])\} [\text{H}^+][\text{HNO}_2] \quad (9)$$

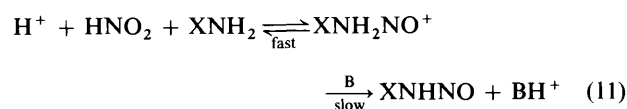
Each of these equations can be manipulated to convert them to forms suitable for a linear plot, but unfortunately the fits are not significantly different; for eqn. (8) $R^2 = 0.989$ while for eqn. (9) $R^2 = 0.984$. The calculated values for k_2 and k_3 from these plots are 1913 and 389 dm⁶ mol⁻² s⁻¹, respectively. Neither

of these is an impossible value in as much as they both are below the encounter limits of *ca.* 5000 and 1500 dm⁶ mol⁻² s⁻¹ for NO⁺ reacting with neutral and cationic nucleophiles. A distinction can, however, be drawn on chemical grounds. The rate constant for the nitrosation⁹ of the free base form of 2,4-dinitroaniline, analogous to k_3 , is 2.5 dm⁶ mol⁻² s⁻¹ at 25 °C and it seems most unlikely that 2,4-(NO₂)₂C₆H₃NHNH₃⁺ could be more reactive than 2,4-(NO₂)₂C₆H₃NH₂ by two orders of magnitude; indeed one would expect it to be much less reactive because of the neighbouring NH₃⁺ group. Thus we conclude that NO⁺ attacks DNP at the terminal nitrogen. The modified value of k_1 from plotting a linearised form of eqn. (8) is $2.67 \times 10^4 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$, a little lower than the value calculated from the low acidity points only. The corresponding plot is shown in Fig. 3. Thus the rate equation for the first stage is shown in eqn. (10).

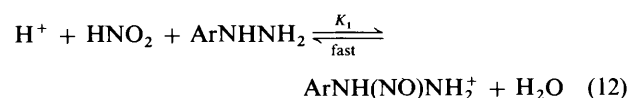
$$\text{Rate} = k_4 [\text{HNO}_2]^2 [\text{ArNHNH}_2] + k_5 [\text{H}^+][\text{HNO}_2][\text{ArNHNH}_2] \quad (10)$$

The equilibrium constant for reaction (6) is reported as $3 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}$ and on substituting this value in eqn. (10), the bimolecular rate constant for the attack of N₂O₃ on DNP is found to be $8.9 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The only reported rate¹⁰ constant for attack of dinitrogen trioxide on a free base arylhydrazine is $1.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for 3-chlorophenylhydrazine, the difference reflecting the much greater electron-withdrawing power of the *ortho/para* nitro substituents. Unpublished data¹¹ gives a rate constant of $8 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the reaction of N₂O₃ with the free base form of 2-(NO₂)C₆H₄NHNH₂. The rate constant of 1913 dm⁶ mol⁻² s⁻¹ for reaction of DNP with NO⁺ is much closer to that found for an encounter reaction of NO⁺ with neutral nucleophiles (*ca.* 5000 dm⁶ mol⁻² s⁻¹).

Before concluding this section we must consider an alternative interpretation of eqn. (10). It is well established that when there are strongly electron-attracting groups bound to an amino group, the initial addition of NO⁺ in electrophilic nitrosation can be reversible and the rate-determining stage becomes proton loss, as in reaction (11).



Williams has suggested⁷ that 2,4-dinitroaniline undergoes *N*-nitrosation by such a mechanism and this accounts for the low value of 2.5 dm⁶ mol⁻² s⁻¹ mentioned above. We need to consider, therefore, the mechanism shown in reactions (12)–(14). This mechanism leads to rate law (15), which is kinetically



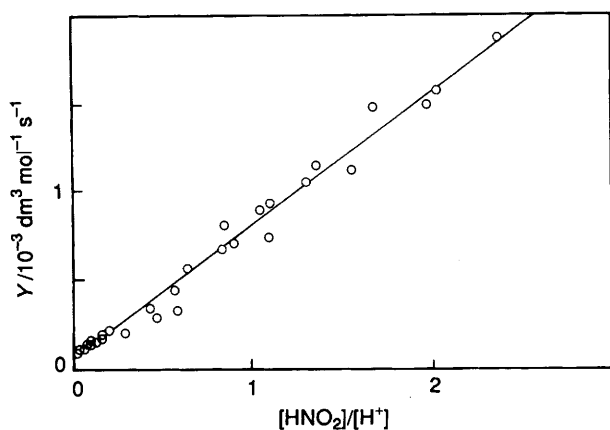
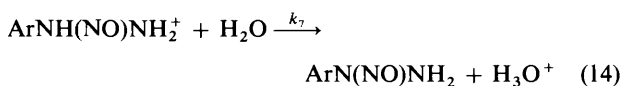
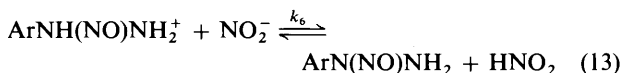


Fig. 3 Linearised plot of eqn. (8) $Y = k_{\text{obs}}(K_a + [\text{H}^+])/([\text{HNO}_2][\text{H}^+])$



$$\text{Rate} = K_1[\text{H}^+][\text{HNO}_2][\text{ArNHNH}_2] \times (k_6[\text{NO}_2^-] + k_7[\text{H}_2\text{O}]) \quad (15)$$

equivalent to eqn. (10) when allowance is made for the HNO_2 - NO_2^- equilibrium.

A similar ambiguity in the nitrosation of amides¹² has been noted. It is important to resolve this ambiguity, because if the process occurred by reactions (12)–(14), then the starting material for the second reaction would be $\text{ArN}(\text{NO})\text{NH}_2$ and the second process would be an isomerisation to ArNHNHNO .

The arguments against such an interpretation are that it seems unlikely that electrophilic nitrosation would occur at the deactivated α -nitrogen when the less deactivated β -nitrogen is available. More cogently the rate constant of $1913 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ is close to the expected encounter limit, whereas if the initial addition of NO^+ is to be a reversible equilibrium, as in reaction (12), then the rate of reaction must be substantially less than the rate of initial addition of the nitroso group. Conclusive evidence comes from the observation that the initial reaction is powerfully catalysed by added bromide ion. If reaction (12) had been a rapid pre-equilibrium, then the presence of Br^- , which provides the additional nitrosating agent ONBr , would have had no effect on the rate. Bromide ion is an exceedingly weak base ($\text{p}K_a$ of HBr has been estimated¹³ to be -8), and so would not be involved in a step analogous to reaction (13). The rate law for the bromide-catalysed reaction is shown in eqn. (16) and

$$\text{Rate} = 2.9 \times 10^6 [\text{H}^+][\text{HNO}_2][\text{Br}^-] \times [\text{ArNHNH}_2] \text{ mol dm}^{-3} \text{ s}^{-1} \quad (16)$$

by use of the formation constant for nitrosyl bromide of $0.051 \text{ dm}^6 \text{ mol}^{-2}$ the bimolecular rate constant for attack of ONBr on ArNHNH_2 is calculated as $5.6 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C . This is substantially more than the value for N_2O_3 , in line with what is observed for other substrates. It is similar to the reactivity of 4-nitroaniline ($4.3 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and well below the encounter rate. Bromide ion does not catalyse the nitrosation of 2,4-dinitroaniline, further evidence by analogy that 2,4-dinitrophenylhydrazine attack does not occur on the α -nitrogen.

Thus we conclude that the first reaction leads to the formation of $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{NHNHNO}$ as a primary product even at higher acidities. It is, of course, possible that the initial

nitrosation is followed by a very rapid tautomerisation, too rapid for us to follow by stopped-flow and that the intermediate that we actually observe is a species of the type $\text{ArN}=\text{NNHOH}$.

Second reaction

The first reaction is followed by a much slower second process with a much smaller change in absorbance. We have only been able to study it by stopped-flow as the half-life is *ca.* 5 s. The rate constants are shown in Table 2. It is clear that k_{obs} is independent of nitrous acid concentration, and that there is a relatively small variation with acidity. Over the range $[\text{H}^+] = 1.6\text{--}13 \times 10^{-2} \text{ mol dm}^{-3}$ the value of k_{obs} is *ca.* 0.13 s^{-1} with small increases at lower acidities. The experiments in 1 mol dm^{-3} perchloric acid show a very distinct increase in rate, but this measurement was made at a much higher ionic strength than the others.

One reasonable interpretation of the data is that we are seeing a tautomerisation reaction such as $\text{ArNHNHNO} \rightarrow \text{ArN}=\text{N}-\text{NHOH}$ or $\text{ArNHNHNO} \rightarrow \text{ArNHN}=\text{NOH}$. Such processes commonly have a rate law with a 'neutral' term due to H_2O acting as a catalyst, with additional acid and base catalysed terms. Because the acid and alkali catalysed 'arms' of our curve do not extend very far it has not been possible to establish the detailed kinetic form or to obtain reliable values for the rate constants of the acid and base catalysed terms. There is no evidence for general acid–base catalysis over a five-fold variation in nitrite concentration. Another possibility is that one of these tautomers reacts further to form the aryl azide. The species $\text{ArN}=\text{NNHOH}$ has been suggested as an intermediate in the reaction between diazonium ion and hydroxylamine to form the azide, reactions (17) and (18). In addition there must be



another species that does not convert to azide, but undergoes a much slower reaction in the third stage, which is described below. The kinetics in the next stage are first-order with respect to $[\text{HNO}_2]$ and as two molecules of nitrous acid are required to form the diazonium ion, reaction (4), this strongly suggests that ArN_2^+ is formed in stage 3; this is confirmed by direct diazo coupling experiments.

By suitable choice of conditions, low $[\text{H}^+]$ and low $[\text{HNO}_2]$, it is possible to obtain the UV spectrum at the end of stage two. Under such conditions the rate of the initial nitrosation can become much slower than the rate of the second stage, which should still have a half-life of *ca.* 5 s. Fig. 4 shows such a series of repeat scan spectra, where 10 half-lives for the second reaction is considerably shorter than the scan repeat time of 90 s. Thus one sees here the conversion of DNP, λ_{max} *ca.* 357 nm, to the products of stage two λ_{max} *ca.* 323 nm. The spectrum of 'authentic' $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{N}_3$ has $\lambda_{\text{max}} = 312 \text{ nm}$, and it seems likely that the spectrum with $\lambda_{\text{max}} = 323 \text{ nm}$ is the sum of the spectrum due to 2,4-dinitrophenyl azide plus the spectrum of the intermediate that is a precursor of the diazonium ion, probably $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{NHN}=\text{NOH}$. When a reaction solution at the end of stage two is quenched with added sulfamic acid to destroy the excess nitrite, and then rapidly extracted with dichloromethane the organic extract has a maximum at 308 nm [λ_{max} for $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{N}_3$ in 95% ethanol at 304 nm] suggesting that the aryl azide has been formed in the second stage.

Third reaction

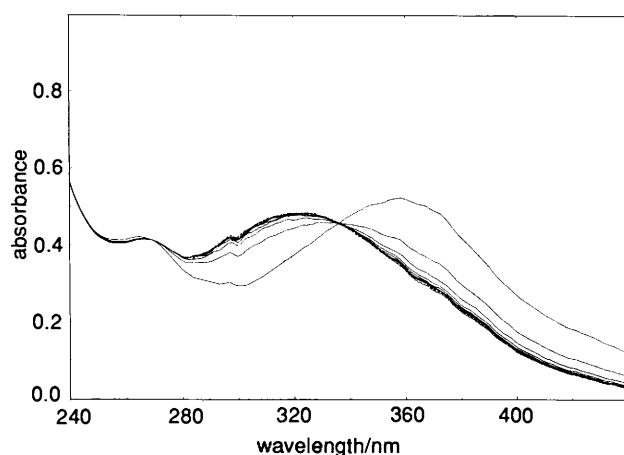
This slow reaction has been followed by two techniques, direct spectrophotometry and by removing samples for colorimetric analysis by the diazo-coupling method. The absorbance due to the azo dye increased and reached a maximum within *ca.* 8 min, and this was followed by a slow decay, presumably due to

Table 2 Pseudo-first-order rate constants, $k_{\text{obs}}/\text{s}^{-1}$, at varying concentrations of $[\text{H}^+]$ and $[\text{HNO}_2]$ for the second stage at 25 °C

$[\text{HNO}_2]/10^{-2} \text{ mol dm}^{-3}$	$k_{\text{obs}}/\text{s}^{-1}$							
	$[\text{H}^+]/10^{-3} \text{ mol dm}^{-3}$							
	6.8	8.9	15.8	21.4	130	150	250	1000
2.5	0.23	0.20	0.14	0.13	0.14	0.17	0.22	1.19
2.0	0.21	0.18	0.13	0.12	0.14	0.16	0.23	1.14
1.5	0.18	0.16	0.13	0.13	0.13	0.17	0.22	1.05
1.0	0.20	0.17	0.12	0.12	0.13	0.15	0.21	1.62
0.5	0.20	0.21	0.14	0.20	0.08	0.13	0.20	1.50

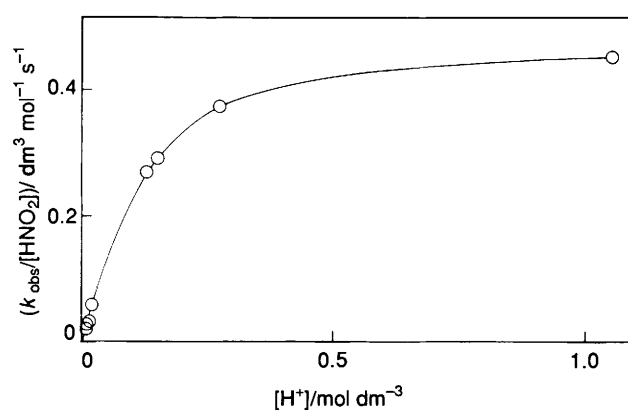
Table 3 Second-order rate constants, k_8 for the third stage at 25 °C

$[\text{H}^+]/10^{-3} \text{ mol dm}^{-3}$ $k_8/10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$k_8/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$						
	8.9	15.8	21.4	130	150	250	1000
	2.44	2.82	5.76	27.1	29.2	37.1	45.4

**Fig. 4** Repeat scan spectra at low $[\text{HNO}_2]$ and $[\text{H}^+]$; $[\text{H}^+] = 5.3 \times 10^{-3}$, $[\text{HNO}_2] = 5 \times 10^{-4}$ and $[\text{DNP}] = 5 \times 10^{-5} \text{ mol dm}^{-3}$. Scans repeated at 90 s intervals.

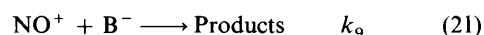
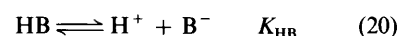
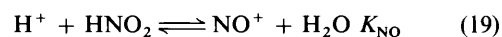
decomposition of 2,4-(NO₂)₂C₆H₃N₂⁺, as shown in Fig. 1. It is clear that the diazonium ion, or a precursor thereof, is formed in the third reaction.

Reaction was also followed by repeat scan spectrophotometry. At low values of $[\text{HNO}_2]$, $5 \times 10^{-4} \text{ mol dm}^{-3}$, and $[\text{H}^+]$, $5.2 \times 10^{-3} \text{ mol dm}^{-3}$, reaction was characterised by two well defined isosbestic points, one at 337 nm, and the other at 270 nm. These changes, which were complete in *ca.* 5–20 min at the higher acidities were followed by a very much slower process in which only relatively small changes in the spectrum were observed. The very slow process could be followed over a period of days. Machackova *et al.* have studied the decomposition of the 2,4-dinitrophenyldiazonium ion and claim¹⁴ that at pH 2.54 (only a little less acid than our lowest acidity) loss of the *ortho*-nitro group takes place, while between pH 4.05 and 6.02 the diazonium ion also loses N₂. According to Machackova the rate constants for decomposition at 20 °C and pH 1.05 and 2.05 are 1.38×10^{-3} and $1.44 \times 10^{-3} \text{ min}^{-1}$ respectively (a half-life of 8.25 h). Another process that would contribute to the very slow reaction is the decomposition of 2,4-dinitrophenyl azide by loss of N₂ and ring closure to form a benzfuroxan. Dyllal has studied the kinetics of this type of process in aromatics containing *ortho*-azido- and nitro-substituents. He has shown that the rate of reaction has very little dependence upon solvent. For 2,4-(NO₂)₂C₆H₃N₃ in decalin the first-order rate constant for decomposition at 25 °C can be calculated¹⁵ to be *ca.* $2.2 \times 10^{-6} \text{ s}^{-1}$, corresponding to a half-life of 3.6 days. It seems likely that these processes are involved in the very slow changes that follow our third stage, but we have not studied them in any detail. The processes we discuss were normally followed over

**Fig. 5** Variation of $k_{\text{obs}}/[\text{HNO}_2]$ with $[\text{H}^+]$ for the third reaction

less than 30 min and we do not expect significant loss of the *ortho*-nitro group in the timescale of our experiments.

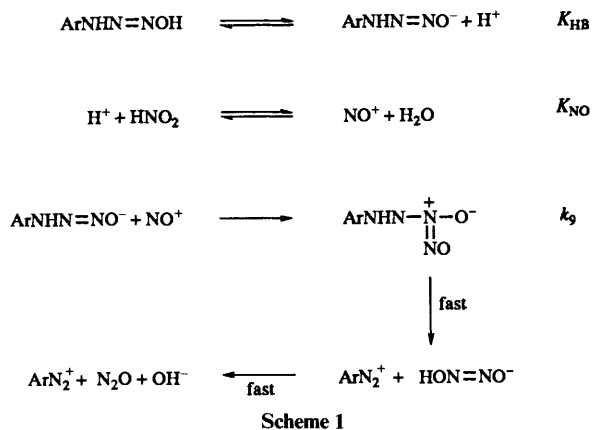
Single wavelength measurements showed that in the third stage k_{obs} was proportional to $[\text{HNO}_2]$ and values of $k_{\text{obs}}/[\text{HNO}_2] = k_8$ increased with an increase in $[\text{H}^+]$ (Table 3), linearly at low acidities but tending to level off at high acidities, as shown in Fig. 5 (which includes the point at 1 mol dm⁻³ perchloric acid). We know from the azo dye experiments that the diazonium ion, or a precursor, is formed in the third stage, and that the stoichiometry requires a second molecule of nitrous acid to react as in reaction (4). Thus the observation that the kinetics are first-order with respect to $[\text{H}^+]$ and $[\text{HNO}_2]$ at low acidities suggests an electrophilic nitrosation by NO⁺. The levelling off at high acidities could be due to an acid–base equilibrium, in which the active species become largely protonated to an inactive form at high acidities. Such a scheme is set out in reactions (19)–(21), with the resulting rate equation given in eqn. (22).



$$v = k_8[\text{HNO}_2][\text{B}]_{\text{total}} = k_9 K_{\text{NO}}[\text{H}^+] \times [\text{HNO}_2][\text{B}]_{\text{total}} / \{K_{\text{HB}} + [\text{H}^+]\} \quad (22)$$

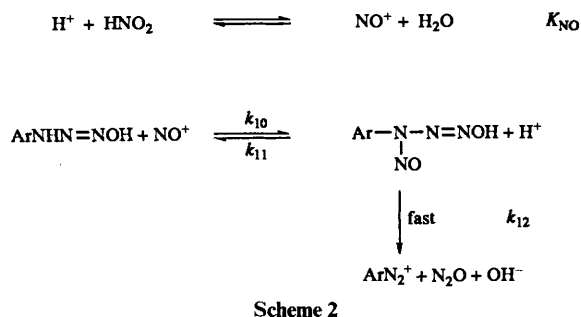
At low acidity, where $K_{\text{HB}} \gg [\text{H}^+]$, $k_8 = k_9 K_{\text{NO}}[\text{H}^+]$, while at high acidity where the inequality is reversed, $k_8 = k_9 K_{\text{NO}} K_{\text{HB}}$. A plot of $1/k_8$ versus $1/[\text{H}^+]$ for all the points gives a straight line with $k_9 K_{\text{NO}} = 3.3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $K_{\text{HB}} = 0.15 \text{ mol dm}^{-3}$. However the values of k_{obs} for low acidities and low nitrous acid

concentrations were obtained by deconvolution techniques and as they were obtained for slow reactions with small absorbance changes the values are less precise than those at high acidities. If we use only the high acidity data obtained at 0.3 mol dm⁻³ ionic strength we find $k_9 K_{NO} = 3.8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $K_{HB} = 0.17 \text{ mol dm}^{-3}$. A possible interpretation of this is shown in Scheme 1, where HB is suggested to be ArNHN=NOH. The product



HON=N-O⁻ is the anion of hyponitrous acid. The *cis* isomer is known to decompose very rapidly to dinitrogen monoxide and water, while the *trans* isomer decomposes more slowly.¹⁶ If ArNHN=NOH were sufficiently basic to exist largely as an unreactive conjugate acid at high acidities, obviously the same kinetic form as eqn. (22) would be obtained.

An alternative explanation for the levelling off in rates at high acidity is the possibility of the second nitrosation being reversible. Challis and Ridd have shown¹⁷ that for aromatic amines the initial nitrosation is reversible in concentrated mineral acids. Williams has found that in the nitrosation of amines with strongly electron-attracting groups by nitrosyl halides, the catalysis by halide ion can level off at high [halide] due to reversibility of the nitrosation step, and he has argued⁷ that the absence of bromide and thiocyanate catalysis in the nitrosation of 2,4-dinitroaniline is due to reversibility. Thus a mechanism such as that in Scheme 2 would fit the results



with ArN(NO)-N=N-OH as a steady-state intermediate. If $k_{12} \gg k_{11}[\text{H}^+]$ then the nitrosation reaction is rate-determining and $k_8 = k_{10}K_{NO}[\text{H}^+]$, while if $k_{11}[\text{H}^+] \gg k_{12}$ then $k_8 =$

$(k_{10}k_{12}K_{NO}/k_{11})$ and the rate becomes independent of acidity. Such a scheme would yield $k_{10}K_{NO} = 3.8 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ and $k_{12}/k_{11} = 0.17 \text{ mol dm}^{-3}$, again using the more accurate high acidity data.

A choice between these schemes is difficult. A K_{HB} value of 0.17 mol dm⁻³ seems very large for the ionisation of the hydroxy group of an -N=N-OH fragment. The first ionisation constant¹¹ for (*E*)-HO-N=N-OH is 10⁻⁷ mol dm⁻³. If HB is a conjugate acid of ArNHN=NOH then the K_{HB} is not so implausible. The value of 3.8 dm⁶ mol⁻² s⁻¹ for $k_{10}K_{NO}$ is similar to the rate constant of 2.5 dm⁶ mol⁻¹ s⁻¹ for the nitrosation of 2,4-dinitroaniline where both nitrogen atoms being attacked are bound to the same strongly electron-attracting aromatic fragment. However, there is no sign of the rate of nitrosation of 2,4-dinitroaniline levelling off at acidities around 1 mol dm⁻³. The second scheme seems rather more probable. A distinction between the two schemes might be possible with the use of Na¹⁵NO₂. Scheme 1 would produce ¹⁵N¹⁵NO whereas Scheme 2 would form N¹⁵NO. Both schemes lead to the formation of a dinitroso compound which is assumed to decompose rapidly to diazonium ion + dinitrogen monoxide.

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