Kinetics and Mechanism of the Reaction between Nitrous Acid and Arylhydrazines

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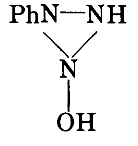
The kinetics of the reaction between nitrous acid and phenylhydrazine and its ring-substituted derivatives correspond to an encounter controlled nitrosation by the nitrosonium or nitrous acidium ion with the arylhydrazinium ion. The primary product, 1-aryl-1-nitrosohydrazine, is converted into aryl azide in an acid-catalysed step, the rate of which is very little affected by *meta*- or *para*-substituents. In the presence of excess of nitrous acid substantial yields of diazonium ion are obtained, probably through the formation of a 1-aryl-1,2-dinitrosohydrazine, which can also decompose to give aryl azide.

THE reaction between nitrous acid and phenylhydrazine is most commonly thought of as a convenient route for the preparation of aryl azides,[1] though a nitrogen-15 study by Clusius [2] provided convincing evidence that an *N*-nitroso-compound is involved as an intermediate [reaction (i)]. The distribution of tracer among the three nitrogens of the azide group lead to a suggestion that a species (A) containing a three-membered ring might be involved.

$$PhNHNH_2 \longrightarrow PhN(NO)NH_2 \longrightarrow PhN_3 + H_2O \quad (i)$$

Following our kinetic studies [3] on the nitrosation of hydrazine and its methyl derivatives we have examined a range of substituted phenylhydrazines.


(A)

RESULTS

Products.—The products were found to be different for reaction with an excess of arylhydrazine over nitrous acid, and *vice versa*. In the former case the product was found to be the aryl azide as is commonly reported in the literature. They were identified in solution by their u.v. spectra, and could be extracted by non-polar solvents and identified by i.r. and mass spectra. In the latter case, with an excess of nitrous acid, quite large yields of diazonium ion could be obtained, up to 100%. The most direct evidence for this was by adding portions of reaction mixture to an alkaline solution of a coupling reagent, when the characteristic red colour of an azo-dye could be observed. When the infinity solution was sampled at various times, the absorbance of the azo-dye reached a maximum and then decreased. The rate of decay correlated semi-quantitatively with the known [4] rate constants for the decomposition of the arenediazonium ions. The u.v. spectra of the infinity solutions also contained the expected peaks due to the diazonium ions, though, because of overlap with the spectra of the aryl azides, this was only really useful when there was a large yield of the diazonium ion. The yield of this species was a function of acidity, but apparently not of the excess of nitrous acid concentration, and at high acidities the yield tended towards a limiting value. Data are shown in Table 1.

Kinetics.—For reaction in the presence of an excess of arylhydrazine repeated scans of the u.v. spectrum showed that there were at least two consecutive processes. At wavelengths in the region of 360 nm the initial absorbance was almost entirely due to molecular nitrous acid. In the first reaction this disappeared, and was replaced by a much more intense u.v. spectrum. This reached a maximum and then slowly faded to give a final spectrum close to that of the aryl azide. A typical plot of absorbance (A) against time is shown in Figure 1. Because the first reaction was so rapid, it was possible to follow the later stages of the second reaction without interference from the first. Plots of $\log(A - A_\infty)$ *versus* time were linear and from the slopes the first-order rate constant k_1 was calculated. This proved to be independent of the concentration of nitrite and arylhydrazine, and also of the presence of nucleophilic anions that normally catalyse nitrosations (chloride, bromide, thiocyanate). Typical data are shown in Table 2. The rate law is $v = 2.7\,[H^+][\text{intermediate}]$. A solvent isotope effect study gave k_H/k_D 1.35. Values of $10k_1/[H^+]$ for substituted phenylhydrazines at 25° are 1.9 (p-CH_3), 2.5 (m-CH_3), 3.2 (p-Cl), 3.0 (p-Br), and 11.4 (m-Cl).

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[1] P. A. S. Smith, 'Open Chain Nitrogen Compounds,' Benjamin, New York, Vol. II, 1966, p. 129; I. T. Millar and H. D. Springall, 'Sidgwick's Organic Chemistry of Nitrogen,' 1966, Clarendon, Oxford, 3rd edn., p. 493.

[2] K. Clusius and K. Schwarzenbach, *Helv. Chim. Acta*, 1959, **81**, 739.

[3] J. R. Perrott, G. Stedman, and N. Uysal, *J.C.S. Dalton*, 1976, 2058, *J.C.S. Perkin II*, 1977, 274.

[4] M. K. Crossley, R. H. Kienle, and C. H. Benbrach, *J. Amer. Chem. Soc.*, 1940, **62**, 1400.

The kinetics of the first reaction presented much more of a problem because reaction was too fast to follow satisfactorily by conventional techniques. The procedure finally adopted made use of the fact that if perchloric acid and arylhydrazine are present in virtually constant excess, then provided that the initial reaction is first-order in nitrous acid, one has a system of two consecutive first-order processes A $\longrightarrow$ B $\longrightarrow$ C with rate constants k_a and k_b respectively. The maximum concentration of the intermediate B, and the time at which the concentration is a maximum can be related to k_a/k_b. If the value of k_b is known (and it corresponds to k_1) then that of k_a can be obtained. By varying the initial concentrations of reagents it is possible to determine the rate law for the process A $\longrightarrow$ B. In practice we found that the absorbance changes were not always large enough at the wavelengths we investigated, and this limited the accuracy with which we could determine $t_{max.}$. Results for phenylhydrazine are shown in Table 3, the k_3 values being rounded off to the nearest ten. The rate law is $v = k_3[H^+][HNO_2][PhNHNH_3^+]$ mol dm^{-3} s^{-1}.

TABLE 1

Yield of diazonium ion obtained from the reaction of $XC_6H_4NHNH_3^+$ with excess of nitrous acid (0.001M) at 25°

$10^3[H^+]$/M	3	3	5	10	20	40	100	150	150
X	Yield (%)								
p-H	102	101 [a]	97.0	91.9	78.7	63.0	57.4	55.0	55.0 [a]
p-NO_2	26.6		24.0	17.4	14.5	12.5	11.0	10.1	
o-CH_3	95	97.5 [a]						42.6	
o-Cl	82.5							53.7	

[a] $[HNO_2]$ 0.01M.

TABLE 2

First-order rate constants for the secondary process in the reaction between excess of phenylhydrazine and nitrous acid (0.000 1M) at 25°

$10^3[H^+]$/M	5	5	5	15	25
$10^3[PhNHNH_3^+]$/M	1.04	10.1	10.1	1.03	1.03
10^3k_1/s^{-1}	1.30	1.56	1.56 [a]	4.02	6.67
$10k_1[H^+]^{-1}$/M^{-1} s^{-1}	2.6	3.1	3.1	2.7	2.7

[a] $[HNO_2]$ 0.000 04 M.

It can be seen that k_3 is reasonably constant considering the limitations of the method. Indeed it is rather better than we expected. Experiments in which sodium chloride, bromide, and thiocyanate were added showed that these species catalysed the first reaction in the sequence $SCN^- \gg Br^- > Cl^-$. The same technique has been applied to several substituted arylhydrazines, though only a few runs were done with each compound, varying the acidity by a factor of 1.5—2. Assuming the same form of rate law we find k_3 = 1 100 (*p*-Cl), 1 300 (*m*-CH_3), 1 700 (*p*-Cl), 1 400 (*p*-CH_3), and 800 (*p*-Br) dm^6 mol^{-2} s^{-1} at 25°. These values are rounded off to the nearest hundred. The obvious way to measure a relatively fast reaction is by the stopped-flow technique. Only a limited amount of time was available on this apparatus, and a few measurements were made of the first reaction in the presence and absence of thiocyanate catalysis.

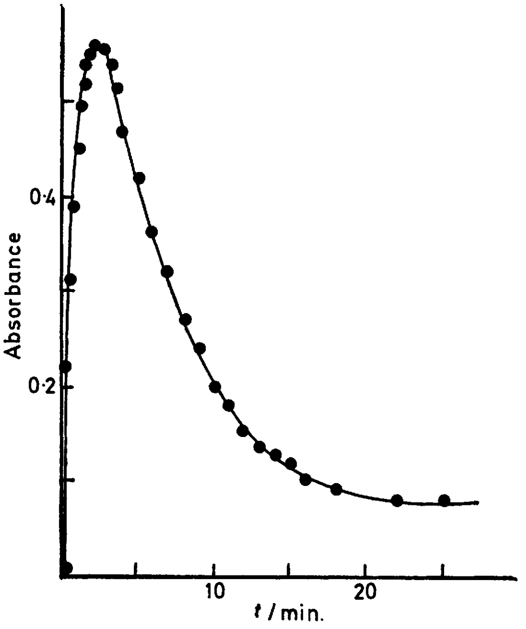


FIGURE 1 Variation of absorbance at 310 nm with time for the reaction of 0.000 1M-nitrous acid with 0.001M-phenylhydrazine in 0.015M-perchloric acid at 25°

TABLE 3

Kinetics of reaction of nitrous acid with phenylhydrazine at 25°

$10^3[PhNHNH_3^+]$/M	$10^3[H^+]$/M	$10^4[HNO_2]$/M	10^3k_b/s^{-1}	$10k_b[H^+]^{-1}$/M^{-1} s^{-1}	10^2k_a/s^{-1}	k_3/dm^6 mol^{-2} s^{-1}
1.04	5	1	1.30	2.6	0.44	850
2.12	5	1	1.15	2.3	0.91	860
0.53	5	1	0.95	1.9	0.25	940
10.1	5	1	1.56	3.1	4.27	850
1.03	15	1	4.02	2.7	1.27	820
1.03	25	1	6.67	2.7	2.38	920
10.1	5	0.4	1.56	3.1	4.27	850
10.1	5	0.7	1.47	2.9	4.27	850

In calculating k_4^{SCN} it has been assumed that thiocyanate catalysis follows the same rate law found for nucleophilic anion catalysis of nitrosation in previous studies,[3] *viz* $v = k_4^{SCN}[H^+][HNO_2][SCN^-][PhNHNH_3^+]$. Values of k_3

of 970 (o-CH_3) and 2 000 (o-Cl) were also obtained by the stopped-flow method from single runs at 300 nm and 0.1M-perchloric acid at 25°, by assuming the form of the rate law.

Only a limited amount of work has been done on the reaction in the presence of excess of nitrous acid. Repeated u.v. scans of the spectrum of reacting solutions show that there are at least two consecutive processes. A typical trace for the second process is shown in Figure 2. Colourimetric measurements, using the diazo-coupling reaction show that for runs at low acidity where the diazonium ion constitutes virtually 100% of the product, the rate of formation of diazonium ion is catalysed by nitrous acid for phenylhydrazine, and its *ortho*-methyl derivative, though the form of the rate law was not established. More detailed studies on *para*-nitrophenylhydrazine show that plots of the diazonium ion concentration against time are sigmoid shaped, as shown in Figure 3, confirming that it is a secondary product. Measurements of the absorbance of the reacting solution at 410 nm as a function of time showed a small increase in absorbance for several minutes, followed by a decay to a small infinity reading. Plots of $\log(A - A_\infty)$ *versus* time for this last reaction gave good linear plots yielding a first-order rate constant k_2. The dependence of k_2 upon acidity is shown in Figure 4. Variation of the nitrous acid concentration showed that $k_2 = k_5[HNO_2]$.

TABLE 4

Stopped-flow studies of the reaction between nitrous acid and excess of phenylhydrazine at 25°

$[H^+]/M$	0.05 [a]	0.05 [a]	0.05 [a]
k_a/s^{-1}	0.67	1.32	2.07
$k_3/dm^6\ mol^{-2}\ s^{-1}$	1 340	1 320	1 380
$[SCN^-]/M$	0.010 [b]	0.015 [b]	0.020 [b]
k_a/s^{-1}	0.66	0.95	1.14
$10^{-6}k_4^{SCN}/dm^9\ mol^{-1}\ s^{-3}$	1.18	1.17	1.07

[a] $[PhNHNH_3^+]$ 0.01M. [b] $[PhNHNH_3^+]$ 0.005; $[H^+]$ 0.01M.

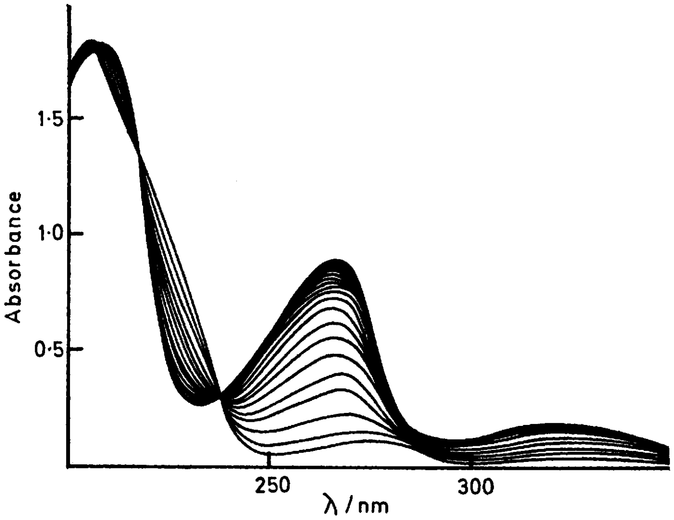


FIGURE 2 U.v. traces for the reaction of 0.000 1M-o-chlorophenylhydrazine with 0.000 5M-nitrous acid in 0.005M-perchloric acid at 25°

DISCUSSION

The kinetic evidence for phenylhydrazine suggests the rate law $v = k_3[H^+][HNO_2][PhNHNH_3^+]$. This agrees well with the rate laws found for hydrazine and the methylhydrazines,[3] and the numerical value of k_3 is reasonable. It is somewhat greater than the figure for hydrazine, 611, which was thought to approach the encounter limit. It suggests a diffusion controlled nitrosation by the nitrous acidium or nitrosonium ion. The catalysis of reaction by nucleophilic anions, and the sequence SCN $\gg$ Br $>$ Cl supports the idea of an electrophilic nitrosation, and the very similar rate constants for a variety of substituted phenylhydrazines are consistent with the levelling effect expected for species reacting at close to the encounter rate. We will not attempt any discussion of the differences, which are probably within the uncertainties of the $t_{max.}$ method. The value of k_4^{SCN} of $1.1 \times 10^6\ dm^9\ mol^{-3}\ s^{-1}$ for the phenylhydrazinium ion is much greater than the values of 2.3×10^4, 7.3×10^3, and $5.7 \times 10^2\ dm^9\ mol^{-3}\ s^{-1}$ for the NN dimethyl-, N-methyl-,

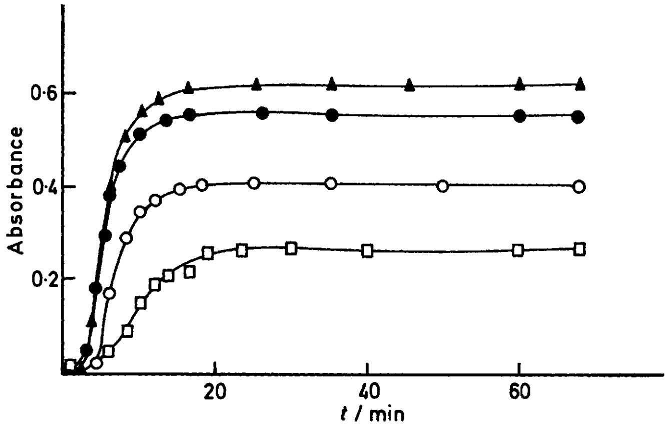


FIGURE 3 Variation with time of the absorbance due to the diazonium ion (measured by the diazo-coupling reaction) in the reaction between 0.005M-nitrous acid and 0.000 128M-p-nitrobenzenediazonium ion at 25°: $[H^+] = 0.003$, ▲; 0.005, ●, 0.001, ○; 0.003M, □

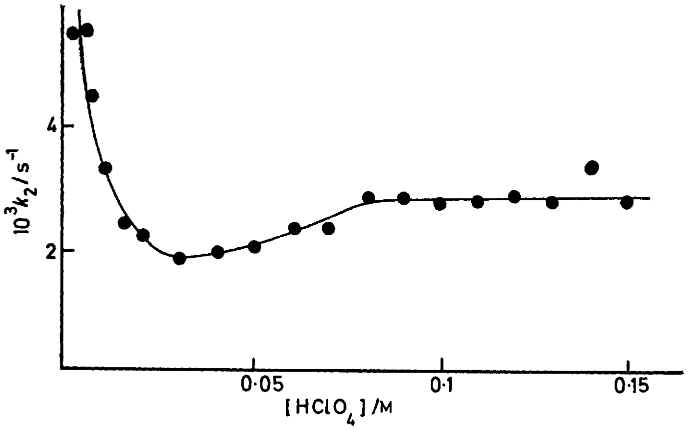


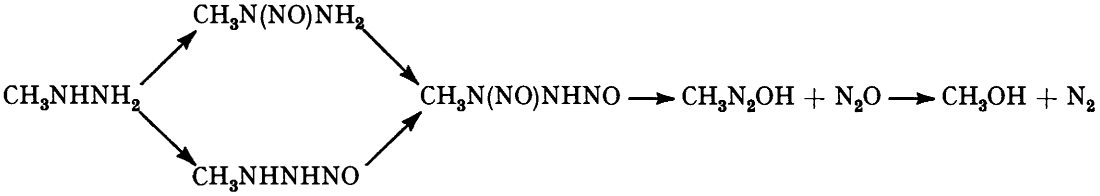
FIGURE 4 Variation of k_2 with acidity at 25°

and hydrazinium ions respectively. It is known from previous work [3] that nitrosyl thiocyanate is a relatively weak electrophile, and that it reacts with nucleophiles at rates many orders of magnitude below the encounter limit. Thus these rates reflect different nucleophilicities. The obvious difference is the polarisibility of the aromatic ring. If one interprets this on a soft–hard acid–base approach, nitrosyl thiocyanate is a relatively soft electrophile and prefers to react with the soft phenylhydrazinium ion.

It is well established [5] that phenylhydrazine is protonated virtually 100% on the terminal nitrogen, 99.92% according to Condon,[6] so there is no reason to doubt that the electrophile will attack the other nitrogen bearing a lone pair of electrons and yield $PhN(NO)NH_2$ (or its conjugate acid) as the inital product, as was concluded by Clusius. The second reaction leads to the formation of an aryl azide, and involves an acid-catalysed migration of the nitrosyl group to the terminal nitrogen. Now

$$ArNHNH_3^+ \longrightarrow ArN(NO)NH_2 \longrightarrow ArNHNHNO \longrightarrow N_2O + ArNH_2 \longrightarrow ArN_2^+ \quad \text{(ii)}$$

D_3O^+ is a stronger acid in D_2O than H_3O^+ is in H_2O; however reaction was slower in D_2O. This implies substantial stretching of some bond(s) to hydrogen in the transition state, probably the proton displaced from the terminal amino-group. The absence of substituent effects may reflect opposing influences on the basicity of the arylnitrosohydrazine and the migrating tendency of the nitroso-group



$$\begin{tikzcd}[column sep=small] & CH_3N(NO)NH_2 \arrow[dr] & & & \\ CH_3NHNH_2 \arrow[ur] \arrow[dr] & & CH_3N(NO)NHNO \arrow[r] & CH_3N_2OH + N_2O \arrow[r] & CH_3OH + N_2 \\ & CH_3NHNHNO \arrow[ur] & & & \end{tikzcd}$$

(iii)

Turning now to the reaction in excess of nitrous acid, one obvious route for the formation of the diazonium ion is (ii). However this can be eliminated as the rate of diazotisation of *p*-nitroaniline is strongly acid-catalysed [7] whereas the disappearance of the absorbance at 410 nm is independent of acidity. Furthermore from the known rate constant, the diazotisation of *p*-nitroaniline under our conditions would be a very much faster process than the changes in the u.v. spectrum and the rate of formation of diazonium ion that we observed. Another possibility, the electrophilic nitrosation of aryl azide to form $[ArN_3NO]^+$ which could break down to nitrogen(I) oxide and the diazonium ion was checked, and found not to occur under our conditions.

A more likely explanation is that a second nitrosation is involved. It is known that alkyl-*N*-nitrosohydrazines are destroyed by excess of nitrous acid. For the reaction of methylhydrazine with excess of nitrous acid the corresponding pathway *via* methylamine was eliminated,[3] and reaction was suggested to go by sequence (iii). Dinitroso-compounds of *NN'*-dialkylhydrazines have been isolated. Nitrogen(I) oxide was identified as a gaseous product for experiments with *o*-methyl-, *o*-chloro-, and *p*-nitro-phenylhydrazine by mass spectrometry. If this pathway occurred with arylhydrazines, the diazonium ion derived from ArN_2OH would be observed as a product, whereas for the alkyl compound its existence is only inferred as a precursor to the end product, methanol. The main difficulty is that the rate law is independent of acidity, whereas nitrosations are normally acid catalysed processes, $v = k[H^+][HNO_2][\text{substrate}]$. This could be accounted for if another acid–base equilibrium (iv) was involved. A reasonable value for k_c for an anionic nucleophile is 15 000 dm^6 mol^{-2} s^{-1} (the encounter limit); as k_cK_1 is 2.8 this gives a value of K_1 of *ca.* 2×10^{-4}. This seems far too large to be reasonable. An alternative explanation would be to suppose that the nitrosoarylhydrazine exists as the conjugate acid $ArN(NO)NH_3^+$. A reasonable value for k_d for a neutral nucleophile is 5 000 dm^6 mol^{-1} s^{-1} giving K_2 as *ca.* 6×10^{-4}. Now the pK_a value of *p*-nitrophenylhydrazinium ion is 3.7, so this value is much more plausible. If this idea is correct, then at sufficiently low acidities there should be deviations from the simple rate

$$ArN(NO)NH_2 \rightleftharpoons ArN(NO)NH^- + H^+ \quad K_1 \quad \text{(iv)}$$

$$H^+ + HNO_2 + ArN(NO)NH^- \longrightarrow ArN(NO)NHNO \quad k_c \quad \text{(v)}$$

law observed for the acid-catalysed conversion of the arylnitrosohydrazine to the aryl azide. The lowest acidity at which we have studied this reaction is 0.005M-perchloric acid, too high to detect any sizeable effect.

$$ArN(NO)NH_3^+ \rightleftharpoons ArN(NO)NH_2 + H^+ \quad K_2 \quad \text{(vi)}$$

$$H^+ + HNO_2 + ArN(NO)NH_2 \longrightarrow ArN(NO)NHNO \quad k_c \quad \text{(vii)}$$

Further work is proceeding on the reaction in excess nitrous acid.

EXPERIMENTAL

The substituted arylhydrazines were commercial materials. Solutions were prepared freshly each day before each group of experiments. Spectrophotometric measurements were made using a Unicam SP 500 instrument with a

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[5] R. F. Evans and W. Kynaston, *J. Chem. Soc.*, 1963, 3151.

[6] F. E. Condon, R. T. Reece, D. G. Shapiro, D. C. Thakker, and T. B. Goldstein, *J.C.S. Perkin II*, 1974, 1112.

[7] L. F. Larkworthy, *J. Chem. Soc.*, 1959, 3304.

thermostatted cell-block. For rapid reactions the solutions were mixed by syringe injection through a small hole in the cell compartment lid. Repetitive scan measurements were made on a Unicam SP 800 instrument. Stopped-flow measurements were carried out on a Canterbury SF 3-A instrument with a Tetronix storage oscilloscope. Mass spectra and ^{1}H n.m.r. spectra were obtained by a departmental service, using an MS9 and a Varian HA 100 instrument respectively.

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