The Nitration of the *NN*-Dimethylanilinium Ion. A New Mechanism for Catalysis by Nitrous Acid

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The reaction of the *NN*-dimethylanilinium ion with nitric acid in *ca.* 85% sulphuric acid is catalysed by nitrous acid but this catalysis does not occur through the formation and oxidation of the *C*-nitroso derivative. The initial products of the catalysed reaction are *p*-nitro-*NN*-dimethylaniline and *NNN'N'*-tetramethylbenzidine, the proportion of the former decreasing with decreasing acidity. The catalysed reaction is first order with respect to the *NN*-dimethylanilinium ion and the nitrosonium ion but zeroth order with respect to nitric acid for $[HNO_3] > 0.15$ mol dm^{-3}; this kinetic form and rate are the same as those for the nitrous acid catalysed mechanism for hydrogen isotope exchange at the nitrogen pole of the amine. These observations are interpreted as involving the rate-determining formation of the $PhNMe_2^{+\bullet}NO^{\bullet}$ radical pair followed by the fast reactions of this species with nitronium ions and molecular nitric acid.

THE rates and products of nitration of the *NN*-dimethylanilinium ion have been reported previously for reaction in 91.1—100% sulphuric acid;[1] the kinetic form and the products then accord with the direct attack of the nitronium ion on the protonated amine. The present work involves an extension of that study to reaction in less acidic media. With lower concentrations of sulphuric acid (83—90%), the characteristics of nitration of the *NN*-dimethylanilinium ion are, in general, consistent with the above mechanism although the amount of *para*-substitution increases more rapidly than would be expected from analogous experiments on the nitration of the anilinium ion.[2] At concentrations of sulphuric acid below 83%, the reaction rate is initially very slow, as expected from the low concentration of nitronium ions, but the reaction also shows auto-catalysis after an induction period of several minutes. The auto-catalysis appears to derive from nitrous acid, produced by oxidation of the amine, for the induction period is absent if some nitrous acid is present initially. The nitration of amines is known to be catalysed by nitrous acid in less acidic media,[3] and this catalysis has been ascribed to *C*-nitrosation followed by oxidation.[3,†] However, this explanation cannot apply to the catalysis of nitration now reported, for the rate of *C*-nitrosation of *NN*-dimethylaniline is far too slow at the acidities used here.[4] We have therefore made a study of the kinetics and products characteristic of this new reaction path.

Products.—The determination of the product composition for the catalysed nitrations is complicated by the number of products formed. In addition to the ring-nitrated derivatives of *NN*-dimethylaniline (4-nitro, 3-nitro, 2,4-dinitro), some demethylated products are formed (mainly 4-nitro-*N*-methylaniline and *N*-nitroso-*N*-methyl-4-nitroaniline) and, at the lower acidities, there is extensive formation of *NNN'N'*-tetramethylbenzidine and its nitro derivatives (3-nitro, 3,3'-dinitro). All the above compounds have been isolated from the reaction mixtures by t.l.c. and determined separately. However, for the interpretation of these results, it is more helpful to look at the balance between the various nitroanilines formed and the extents of demethylation and benzidine formation (Table 1).

TABLE 1

Percentage composition of the product of nitration of the *NN*-dimethylanilinium ion in aqueous sulphuric acid at 33 °C. The concentrations of the amine and nitric acid were 0.1 mol dm^{-3}

H_2SO_4/%	87.1	85.8	85.1	83.6	81.8	80.0	74.7
$3-NO_2C_6H_4NMe_2$	57	48	45	30	2		
$4-NO_2C_6H_4NMe_2$	28	35	38	45	40	10	2
$2,4-(NO_2)_2C_6H_3NMe_2$	6	10	11	10	1		
Demethylation [a]					9	13	
Tetramethylbenzidines [b]					26	56	63
Yield isolated (%)	91	93	94	85	78	79	65

[a] Determined from the yields of $4-NO_2C_6H_4NHMe$ and $4-NO_2C_6H_4N(NO)Me$. [b] Determined from the yields of *NNN'N'*-tetramethylbenzidine and its 3-nitro and 3,3-dinitro derivatives.

The increase in the yield of the *p*-nitro compound as the acidity is decreased from 87.1 to 83.6% sulphuric acid could be caused by the medium effect observed in the nitration of the anilinium ion[2] or could represent some contribution from the autocatalytic reaction path. When the acidity is further decreased to 81.8% sulphuric acid, the product composition changes markedly, associated with the appearance of autocatalysis in the kinetic form. At this acidity, the autocatalytic reaction appears to lead mainly to *p*-nitro-*NN*-dimethylaniline. However, the composition of the product from the autocatalytic reaction is strongly dependent on the acidity of the medium, for the reaction in 74.7% sulphuric acid gives mainly tetramethylbenzidines.

Further evidence concerning the products of the catalysed nitrations has been obtained from reactions carried out in the presence of nitrosonium ions (Table 2). When the concentration of nitrosonium ions is 0.1 mol dm^{-3}, the catalysed reaction is predominant even in 85.1% sulphuric acid. This is shown both by the increase in the reaction rate produced by the nitrosonium ions (the half-life is decreased from 15 to 2 min) and by the low yield of the *m*-nitro product. At this acidity the catalysed reaction gives little of the products derived from tetramethylbenzidine.

[†] We have no reason to doubt that this mechanism is correct for the conditions previously studied.

TABLE 2

Percentage composition of the product from the *NN*-dimethylanilinium ion in the presence of nitrosonium hydrogensulphate (0.1 mol dm^{-3}). Other conditions as for Table 1

H_2SO_4 (%)	85.1	85.1 [a]	83.6	81.8
3-$NO_2C_6H_4NMe_2$	4	11		
4-$NO_2C_6H_4NMe_2$	42	54	26	20
2,4-$(NO_2)_2C_6H_3NMe_2$	11	11	3	
4-$NOC_6H_4NMe_2$	6	5	2	
Demethylation [b]	15		18	13
Tetramethylbenzidines [c]	8		27	46
Total yield (%)	86	81	76	79

[a] With [$NOHSO_4$] = 0.02 mol dm^{-3}. [b] See footnote *a*, Table 1. [c] See footnote *b*, Table 1.

In considering how the products of the catalysed reaction vary with the acidity of the medium it is helpful to realise that the 2,4-dinitro-*NN*-dimethylaniline is almost certainly derived from the further nitration of *p*-nitro-*NN*-dimethylaniline for no *o*-nitro-*NN*-dimethylaniline has been detected in these experiments and the further nitration of *o*-nitro-*NN*-dimethylaniline is slower than that of the *para*-isomer.[5] Furthermore, previous work at lower acidities has suggested that the demethylation observed in the nitrous acid catalysed nitration of *NN*-dimethylaniline is subsequent to nitration at the *para*-position [6] and this accords with the two demethylated products observed here [*p*-$NO_2C_6H_4NHMe$, *p*-$NO_2C_6H_4N(NO)Me$]. Thus the multiplicity of products in the nitrous acid catalysed reaction can be understood as deriving from two initial products: *p*-nitro-*NN*-dimethylaniline and *NNN'N'*-tetramethylbenzidine. From the results in Table 2, the initial division into these two products is in the ratio 68 : 8 in 85.1% sulphuric acid and 33 : 46 in 81.8% sulphuric acid. This must reflect a change in the product composition in the catalysed reaction for the small amount of the 3-nitro compound formed shows that the amount of reaction by the uncatalysed path is slight.

Kinetics.—The kinetic study of these reactions is complicated by the number of products formed, by the sensitivity of the product composition to the acidity of the medium, and by the presence of autocatalysis under some conditions. These difficulties have, to some extent, been overcome by following the reaction from the change in the concentration of the *NN*-dimethylanilinium ion using for this purpose the height of the $\overset{+}{N}Me_2H$ peak in the ^1H n.m.r. spectrum. Where the kinetic plot indicates autocatalysis, the rate coefficient has been calculated from the initial part of the kinetic run.

In the absence of added nitrous acid, the form of the individual kinetic runs and the variation of the rate with the initial concentration of nitric acid are consistent with equation (1),* although there is evidence of autocatalysis at the lower acidities. The corresponding values of k_2 are collected in Table 3. For comparison with other kinetic results (see below), it is convenient to plot these values in terms of the corresponding initial rate of reaction with 0.1 mol dm^{-3} amine and 0.1 mol dm^{-3} nitric acid. The least-squares slope of the resulting plot (0.38 ± 0.02, Figure 1) is very similar to those obtained for the *meta*- and *para*-nitration of the anilinium ion (0.38 and 0.36 respectively).[2] The scatter of the experimental points corresponds to an error of ±15%. This large error arises mainly because the n.m.r. method is less accurate than the methods based on u.v. and visible spectroscopy used in the previous work.[2] However, the consistency of rate coefficients obtained at the same time and for the same acidity is greater than the above figure of ±15% would suggest.

$$\text{Rate} = k_2[\mathrm{Ph\overset{+}{N}Me_2H}][\text{nitric acid}] \qquad (1)$$

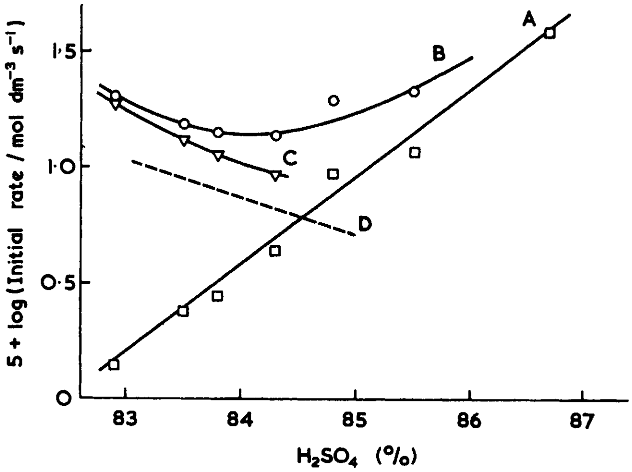

FIGURE 1 Initial rates of reaction with [$\mathrm{Ph\overset{+}{N}Me_2H}$] = 0.1 mol dm^{-3}, [$HNO_3$] = 0.1 mol dm^{-3}. A, Reaction in the absence of nitrous acid; B, reaction in the presence of $NOHSO_4$ (0.01 mol dm^{-3}); C, the nitrous acid catalysed component of the reaction; D, the extrapolated rate of N–H hydrogen isotope exchange in $\mathrm{Ph\overset{+}{N}Me_2D}$ with the above concentrations of $\mathrm{Ph\overset{+}{N}Me_2H}$ and $NOHSO_4$

In the presence of added nitrous acid ([NO^+] = 0.01 mol dm^{-3}), the form of each kinetic run corresponds more closely to first-order kinetics and the slopes of the first-order plots were used to calculate the initial rates given in Table 4 and plotted in Figure 1. Initial rates of reaction for the nitrous acid catalysed reaction have been calculated by subtracting the initial rates of reaction in the absence of nitrous acid (termed the uncatalysed reaction) from those in the presence of nitrous acid (termed the overall reaction). The results are shown in Table 4 and those for the lower acidities (where the accuracy is greatest) are included in Figure 1.

The kinetic form of the nitrous acid catalysed reaction has been established by determining how the initial rate of this reaction varies with the concentrations of the reactants. The results for reaction in 84.8% sulphuric acid (Table 5) show that the reaction is first order with respect to the amine and nitrous acid but that it becomes zeroth order with respect to the concentration of nitric

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* Nitric acid is written in words in this equation to show that the stoicheiometric concentration not the concentration of nitric acid molecules is involved.

acid when the concentration of this species exceeds 0.15 mol dm^{-3}. Because of the importance of the last observation, the experiments have been repeated using 83.8% sulphuric acid with essentially the same conclusion (Table 5). The limiting kinetic form of the catalysed reaction is therefore as equation (2).

TABLE 3

Second-order rate coefficients [k_2, equation (1)] for the nitration of the *NN*-dimethylanilinium ion (0.1 mol dm^{-3}) in aqueous sulphuric acid at 34°

H_2SO_4 (%)	$\frac{[HNO_3]}{\text{mol dm}^{-3}}$	$\frac{10^2 k_2}{\text{mol}^{-1}\text{ s}^{-1}\text{ dm}^3}$
86.7	0.1	3.8
85.5	0.1	1.16
84.8	0.1	0.94
84.8	0.15	0.83
84.8	0.20	0.83
84.8	0.25	0.71
84.8	0.25	0.75 [a]
84.8	0.30	0.76
84.3	0.10	0.44
83.8	0.10	0.28
83.5	0.10	0.24
82.9	0.10	0.14

[a] Using $PhNM_3D$.

TABLE 4

Initial rates of reaction (nitration + oxidation) of the *NN*-dimethylanilinium ion at 34 °C

$[\mathrm{Ph\overset{+}{N}Me_2H}] = [HNO_3] = 0.10$ mol dm^{-3}; $[NO^+] = 0.010$ mol dm^{-3}

	$\frac{10^4\text{ Initial rate}}{\text{mol dm}^{-3}\text{ s}^{-1}}$		
H_2SO_4 (%)	Overall	Uncatalysed [a]	Catalysed
82.9	2.00	0.14	1.86
83.5	1.54	0.24	1.30
83.8	1.41	0.28	1.13
84.3	1.37	0.44	0.93
84.8	1.95	0.94	1.01
85.5	2.12	1.16	0.96

[a] In the absence of the nitrosonium salt.

TABLE 5

Initial rates of reaction (nitration + oxidation) of the *NN*-dimethylanilinium ion at 34 °C. Determination of the kinetic form of the catalysed reaction

				$\frac{10^4\text{ Initial rate}}{\text{mol dm}^{-3}\text{ s}^{-1}}$		
$\frac{H_2SO_4}{\%}$	$\frac{[\mathrm{Ph\overset{+}{N}Me_2H}]}{\text{mol dm}^{-3}}$	$\frac{[HNO_3]}{\text{mol dm}^{-3}}$	$\frac{[NO^+]}{\text{mol dm}^{-3}}$	Overall	Uncatalysed	Catalysed
84.8	0.10	0.10	0.010	1.95	0.94	1.01
84.8	0.15	0.10	0.010	3.00	(1.41) [a]	1.59
84.8	0.20	0.10	0.010	3.84	(1.88) [a]	1.96
84.8	0.30	0.10	0.010	5.76	(2.82) [a]	2.94
84.8	0.10	0.10	0.010	1.95	0.94	1.01
84.8	0.10	0.15	0.010	2.64	1.25	1.39
84.8	0.10	0.20	0.010	3.01	1.66	1.35
84.8	0.10	0.25	0.010	3.21	1.77	1.44
84.8	0.10	0.30	0.010	3.69	2.28	1.41
84.8	0.10	0.10	0.010	1.95	0.94	1.01
84.8	0.10	0.10	0.015	2.28	0.94	1.34
84.8	0.10	0.10	0.020	2.89	0.94	1.95
84.8	0.10	0.10	0.030	4.05	0.94	3.11
84.8	0.10	0.10	0.040	4.76	0.94	3.82
83.8	0.10	0.10	0.010	1.41	0.28	1.13
83.8	0.10	0.15	0.010	1.52	(0.42) [a]	1.19
83.8	0.10	0.20	0.010	1.94	(0.56) [a]	1.35
83.8	0.10	0.25	0.010	2.15	(0.70) [a]	1.45
83.8	0.10	0.30	0.010	2.27	(0.84) [a]	1.43
83.8	0.10	0.40	0.010	2.52	(1.12) [a]	1.40

[a] Calculated from the known kinetic form of the uncatalysed reaction.

$$\text{Rate} = k_2'[\mathrm{Ph\overset{+}{N}Me_2H}][NO^+] \qquad (2)$$

At the acidities used, the rate of N–H hydrogen isotope exchange is slow [7] and so the reactivity of the $\mathrm{Ph\overset{+}{N}Me_2D}$ can also be studied. The results in Table 3 show that, as expected, the replacement of N–H by N–D in the *NN*-dimethylanilinium ion causes no significant change in the rate of the uncatalysed reaction. This is not true of the catalysed reaction and the results in Table 6 show that the corresponding value of (k_H/k_D) is *ca.* 2. Unfortunately, this value cannot be expressed very precisely because of the errors in the kinetic method: thus, if the observed rates of reaction are considered to have errors of ±15%, the value of the isotope effect for reaction with 0.1 mol dm^{-3} nitric acid in 83.8% sulphuric acid lies between 1.7 and 3.9.

TABLE 6

Isotope effects on the initial rates of reaction (nitration + oxidation) of the *NN*-dimethylanilinium ion at 34°

$[\mathrm{Ph\overset{+}{N}Me_2L}] = 0.10$ mol dm^{-1}, L = H or D; $[NO^+] = 0.010$ mol dm^{-3}

			$\frac{10^4\text{ Initial rate}}{\text{mol dm}^{-3}\text{ s}^{-1}}$			
$\frac{[H_2SO_4]}{\%}$	$\frac{[HNO_3]}{\text{mol dm}^{-3}}$	L	Overall	Uncatalysed	Catalysed	$\frac{k_H}{k_D}$
84.8	0.25	H	3.21	1.77	1.44	2.9
		D	2.27	(1.77) [a]	0.50	
83.8	0.10	H	1.41	0.28	1.13	2.5
		D	0.73	(0.28) [a]	0.45	
83.8	0.2	H	1.94	0.56	1.38	2.2
		D	1.18	(0.56) [a]	0.62	

[a] Assumed to have this value from the absence of an isotope on the uncatalysed reaction.

DISCUSSION

The kinetic analysis has established that the reaction of *NN*-dimethylaniline with nitric acid (>0.15 mol dm^{-3}) containing some nitrous acid in 82—87% sulphuric acid has the kinetic form of equation (3) where k_2 and k_2' are dependent on the acidity and where the second term leads to both oxidation and nitration.

$$\text{Rate} = k_2[\mathrm{Ph\overset{+}{N}Me_2H}][\text{nitric acid}] + k_2'[\mathrm{Ph\overset{+}{N}Me_2H}][NO^+] \qquad (3)$$

The relative importance of these terms for a given set of initial concentrations can be seen from the initial rates in Figure 1: the line A represents the contribution of the first term and the line C that of the second. The acidity dependence of k_2 is as expected for the reaction of the protonated amine with the nitronium ion [1,2] and so the present interest lies in the second term. The magnitude of k_2' is far too great for this term to derive from a reaction of the nitrosonium ion with the equilibrium concentration of the free amine (the corresponding rate coefficient would have to be *ca.* 10^{14} mol^{-1} s^{-1} dm^3) and so reaction must involve the protonated amine. The much slower rate of reaction with nitrous acid in the absence of nitric acid shows that the second term cannot derive from the formation of the *C*-nitroso derivative of the amine.

The clearest evidence on the source of this second term has come from a parallel study of hydrogen-isotope exchange at the nitrogen poles of amines.[7,8] In concentrations of sulphuric acid >80%, the rate of exchange between the N–H protons of the *NN*-dimethylanilinium ion and the solvent is very slow ($t_{\frac{1}{2}} > 15$ h at 33 °C). The exchange is, however, catalysed by nitrosonium ions and this catalysed reaction has the same kinetic form [equation (2)] and dependence on acidity as the catalysed nitration + oxidation. The dependence on acidity is illustrated in Figure 1 where the broken line is calculated from a slight extrapolation of the rate profile for exchange (determined for 85—92% sulphuric acid). The rate coefficients of the two reactions are also very similar when both refer to the deuteriated substrate (Table 7). It is therefore reasonable to assume that the two catalysed reactions have a common rate-determining step and that this involves the formation of an intermediate which, in the presence of the nitric acid, leads to nitration + oxidation and, in the absence of the nitric acid, reforms the reactants with hydrogen-isotope exchange at the nitrogen pole.

Substituent effects on the catalysed hydrogen-isotope exchange[7] are very similar to those observed at lower acidities on the direct diazotization of anilinium ions[9] and on the direct *N*-nitrosation of *N*-methylanilinium ions.[9] The last two reactions have been considered[9,10] to involve the initial interaction of NO^+ or H_2ONO^+ with the aromatic π-electrons of the anilinium ion followed by proton loss from the nitrogen and the migration of NO^+ to form the nitrosammonium ion $Ph\overset{+}{N}R_2NO$ (R = H or Me). Such an interpretation can easily be extended to explain the nitrosonium ion catalysis of N–H hydrogen-isotope exchange but it is less easy to understand why the nitrosammonium ion $Ph\overset{+}{N}Me_2NO$ should react readily with nitric acid or the species derived from it. The formation of *NNN′N′*-tetramethylbenzidine is a characteristic reaction of the radical cation[11] $PhNMe_2^{+\cdot}$ and so we suggest that the interaction of the nitrosonium ion with the *NN*-dimethylanilinium ion leads to the radical pair $ArNMe_2^{+\cdot}$ $NO^{\cdot}$ possibly through the intermediate formation of $Ar\overset{+}{N}Me_2NO$ and that the radical pair undergoes the subsequent reactions with nitric acid (Scheme). There is some evidence for the formation of the radical pair in this way, for the salts $Ar\overset{+}{N}Me_2NO$ X^- (X = Cl, NO_3) can be prepared at −78 °C in tetrachloroethane but decompose at higher temperatures in reactions considered to involve homolytic fission of the N–N bond.[12] The very slow rate of formation of benzidine in the absence of nitric acid makes it necessary to assume that the radical pair is stabilised by electron exchange so that the dissociation of the radical pair is slower than its reactions with other species in the solution. The possible association of the radical pair by bond formation at the amino nitrogen atom or the 4-carbon atom should be reversible and so should not affect the overall reaction rate.

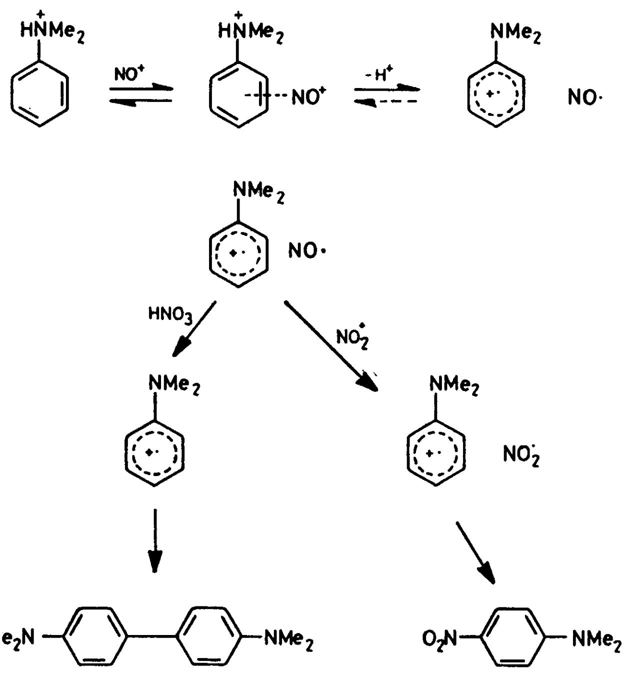
Table 7

Reactions of $Ph\overset{+}{N}Me_2D$. Comparison of second-order rate coefficients [k_2' equation (2)] for nitration + oxidation at 34° and for exchange at 33°

$\frac{H_2SO_4}{\%}$	$\frac{10^2k'_2}{mol^{-1}\ s^{-1}\ dm^3}$	
	Nitration + Oxidation	Exchange
83.8	4.5 [a] 6.2 [b]	7.9 [c]
84.8	5.0 [a]	5.5 [c]

[a] For $[HNO_3] = 0.1$ mol dm^{-3}. [b] For $[HNO_3] = 0.2$ mol dm^{-3}. [c] Extrapolated value, see text.

It is next necessary to consider why the product composition from the catalysed nitration + oxidation is so dependent on the acidity of the medium. As outlined above, the initial products appear to be *p*-nitro-*NN*-dimethylaniline and *NNN′N′*-tetramethylbenzidine. If these are taken as products of the nitration and oxidation reactions then the ratio of the amounts of nitration and oxidation changes by a factor of 12 over the range 85.1—81.8% sulphuric acid (see above and Table 2). This is similar to the change in the ratio $[NO_2^+]:[HNO_3]$ as judged from the variation with acidity of the rate coefficients for nitration by the nitronium ion. We suggest therefore that there are two reaction paths for the oxidation of NO to NO^+ in the radical pair: oxidation by the nitronium ion to form the radical pair $ArNMe_2^{+\cdot}$ $NO_2^{\cdot}$ followed by association of the radicals to form the *p*-nitro derivative; and oxidation by nitric acid to form NO^+ and a species that does not lead to substitution in the ring but instead frees the $ArNMe_2^{+\cdot}$ cation radical for



Scheme

dimerisation to give eventually *NNN'N'*-tetramethylbenzidine. These reactions are illustrated in the Scheme. The implication that the nitro-group in the *p*-nitro-*NN*-dimethylaniline formed derives from the nitric acid not the nitrosonium salt accords with the fact that reaction with equal concentrations of ^{15}N labelled nitric acid and unlabelled nitrosonium hydrogensulphate in 85.1% sulphuric acid yields mainly the labelled *p*-nitro-*NN*-dimethylaniline (>80% ^{15}N).

Attempts to establish the cation radical pathway by the detection of CIDNP in the ^1H and ^{13}C n.m.r. spectra of the reaction products were unfortunately inconclusive. The catalysed nitration of *NN*-dimethylaniline gives an e.s.r. signal but it is too complex to derive from the cation radical of *NN*-dimethylaniline and is probably that of the cation radical of tetramethylbenzidine. E.s.r. spectra corresponding to the cation radicals of *p*-methoxy-*NN*-dimethylaniline and *p*-methyl-*NN*-dimethylaniline have been detected in the reactions of these amines with nitrous acid in aqueous sulphuric acid:[7] an account of this work together with the related studies on NO^+-catalysed hydrogen-isotope exchange will be presented shortly.

EXPERIMENTAL

Materials.—*NN*-Dimethylanilinium hydrogensulphate was prepared by the dropwise addition of sulphuric acid (98%) to a vigorously stirred solution of *NN*-dimethylaniline in acetone (1 : 9 v/v). The solution was filtered and the precipitated salt was recrystallised from acetone–methanol (1 : 9) and dried over phosphorus pentaoxide (Found: C, 43.6; H, 5.9; N, 6.3. Calc. for $C_8H_{13}NSO_4$: C, 43.8; H, 6.0; N, 6.4%). The *N*-deuterio-*NN*-dimethylanilinium hydrogensulphate was prepared in a similar way using deuteriosulphuric acid but the recrystallisation stage was omitted. Nitric acid (100%) was prepared by vacuum distillation from a solution of nitric acid in concentrated sulphuric acid (1 : 2 v/v). Nitrosonium hydrogensulphate was provided by Dr. D. J. Mills.[7] The extinction coefficient (230 nm; 75.4% H_2SO_4) was in excellent agreement with that reported (2 900).[13]

Products.—Separate solutions (15 ml) in aqueous sulphuric acid of the amine, nitric acid, and, where required, nitrosonium hydrogensulphate were brought together at the same time to start the reaction. When reaction was complete the solutions were poured onto ice and partially neutralised with ammonium hydroxide so as to precipitate the nitro-compounds formed. These were extracted with chloroform, dried ($MgSO_4$), and separated by t.l.c. using plates coated with Merck Kieselgel GF_{254} (type 60) and light petroleum–methylene chloride–ethyl acetate (80 : 17.5 : 2.5) as the eluant. The individual bands were removed from the plates, and the products were dissolved in chloroform, isolated by evaporation, weighed, and identified by comparison with authentic samples. The mixture was then fully neutralised to precipitate the more basic products, mainly *NNN'N'*-tetramethylbenzidine, and the isolation procedure was repeated. The products isolated but not specified individually in Tables 1 and 2 can be illustrated by the results for nitration of *NN*-dimethylaniline (0.1 mol dm^{-3}) with nitric acid (0.1 mol dm^{-3}) in 80.0% sulphuric acid: *p*-nitro-*N*-methylaniline (9%), *p*-nitro-*N*-nitroso-*N*-methylaniline (4%), *NNN'N'*-tetramethylbenzidine (24%), 3-nitro-*NNN'N'*-tetramethylbenzidine (24%), 3.3'-dinitro-*NNN'N'*-tetramethylbenzidine (8%). The extent of *N*-nitrosation is not reproducible and is believed to occur during the isolation procedure.

One experiment was carried out using ^{15}N labelled nitric acid (0.1 mol dm^{-3}; 95% ^{15}N) with dimethylaniline (0.1 mol dm^{-3}) and nitrosonium hydrogensulphate (0.1 mol dm^{-3}) in 85.1% sulphuric acid. The three solutions containing the reactants were brought together at the same instant to start the reaction. Mass spectrometric analysis showed that 80—85% of the *p*-nitro-*NN*-dimethylaniline formed was labelled with ^{15}N.

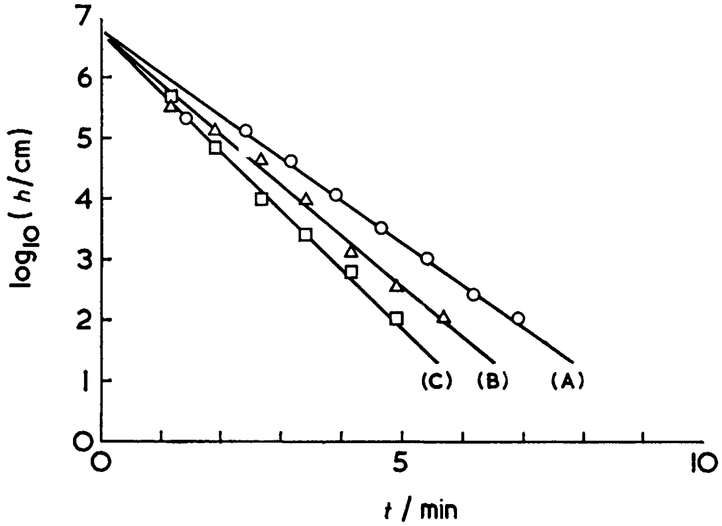


FIGURE 2 The variation with time in the height (*h*) of the methyl peak in the ^1H n.m.r. spectrum of $Ph\overset{+}{N}Me_2H$ at 34 °C. H_2SO_4 = 84.8%; [$Ph\overset{+}{N}Me_2H$] = 0.1 mol dm^{-3}; [$NOHSO_4$] = 0.01 mol dm^{-3}; [HNO_3] = 0.15 mol dm^{-3} (A), 0.25 mol dm^{-3} (B), 0.35 mol dm^{-3} (C)

Kinetics.—Separate solutions in sulphuric acid of *NN*-dimethylanilinium hydrogensulphate, nitric acid and, where appropriate, nitrosonium hydrogensulphate were prepared and equal volumes (2—5 ml) were placed in the three fingers of the reaction vessel. The solutions were brought to 34 °C and then mixed by shaking. A sample was immediately extracted and placed in an n.m.r. tube at the same temperature. The course of the reaction was followed from the change in the n.m.r. absorption (60 MHz) of the methyl proton of the $\overset{+}{N}Me_2H$ group. The ratio of the height of this doublet (h) to that at zero time (h_0) was taken as proportional to the amount of the *NN*-dimethylanilinium ion present since there is no evidence of broadening of the spectrum or of a loss in resolution during the reaction. The value of h_0 was, in general, determined by an extrapolation to zero-time of plots of log h (for first-order reactions) or $1/h$ (for second-order reactions). This procedure is illustrated for three runs in Figure 2. Where the plots showed some curvature, the rate coefficients were calculated from the first part of the run and used to calculate the initial rates given in Tables 4 and 5. The temperature of the n.m.r. probe was shown to be 34 ± 1 °C by the difference in the chemical shifts of the C–H and O–H protons in methanol.[14] Some kinetic runs were carried out using deoxygenated solutions but the reaction rates were unchanged.

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