The Kinetics of Hydrogen-isotope Exchange at the Nitrogen Atom of Substituted Anilinium Ions. Part 2.[1] The Nitrosonium-ion-catalysed Reaction

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Nitrosonium ions catalyse hydrogen-isotope exchange between the N–H protons of *NN*-dimethylanilinium ions and aqueous sulphuric acid (83—93%). At the acidities used, the subsequent chemical reactions between the amines and nitrosonium ions occur much more slowly. The rate of the catalysed exchange is proportional to the concentration of nitrosonium ions and inversely proportional to the appropriate acidity function (h_0'''). A mechanism is put forward for the catalysed exchange based on the formation of a loose complex between the nitrosonium ion and the anilinium ion followed by proton loss from the nitrogen pole. This process is shown to be related to the direct diazotisation of some anilinium ions and to the nitrous-acid-catalysed nitration and oxidation of the *NN*-dimethylanilinium ion. Substituent effects on the nitrosonium-ion-catalysed exchange are much less than those on the acid-catalysed exchange and resemble those on the acid-catalysed mechanism of diazotisation.

THE results in the preceding paper established that hydrogen-isotope exchange at the nitrogen atom of certain *NN*-dimethylanilinium ions in aqueous sulphuric acid can be initiated by proton donation to the aromatic ring. The results in the present paper concern the catalysis of such hydrogen-isotope exchange by nitrosonium ions under similar conditions. The acidities of the reaction media were sufficient to prevent the hydrolysis of nitrosonium ions to nitrous acid and related species.[2]

As before,[1] the work has been carried out using *N*-deuterio-*NN*-dimethylanilinium ions and the exchange has been followed from the change in the coupling pattern of the *N*-methyl peak in the ^{1}H n.m.r. spectrum of the anilinium ions when the deuteron is replaced by a proton. At lower acidities, there are well known reactions between nitrosating agents and *NN*-dimethylanilines leading mainly to nitrosation in the aromatic ring[3] but, at the acidities used here, the rate of such reactions are much slower than the hydrogen-isotope exchange. The rate of exchange at a given acidity shows first-order kinetics in the presence or absence of nitrosonium ions. The first-order rate coefficient [k_1, equation (1)] is, in general, a measure of the combined contributions of the nitrosonium-ion-catalysed reaction and the underlying base- and acid-catalysed mechanism of exchange.

$$\text{Rate} = k_1[\text{Ar}\overset{+}{\text{N}}\text{Me}_2\text{D}] \qquad (1)$$

To study the catalysis of exchange by nitrosonium ions, it is desirable to choose conditions so that the rate of exchange by the base- and acid-catalysed mechanisms is negligible. The previous work[1] shows that this is true for exchange in the *NN*-dimethylanilinium ion at concentrations of sulphuric acid $>82\%$. Results for the nitrosonium-ion-catalysed exchange under these conditions are shown in Table 1. Values of the second-order rate coefficient k_2 in the final column are obtained by dividing k_1 by the concentration of nitrosonium ions. The constancy of k_2 for the set of experiments carried out in 92.6% sulphuric acid shows that, at a given acidity, the catalysed reaction follows equation (2).

$$\text{Rate} = k_2[\text{Ar}\overset{+}{\text{N}}\text{Me}_2\text{D}][\text{NO}^+] \qquad (2)$$

The other results in Table 1 show that k_2 increases as the acidity decreases: a plot of log k_2 *versus* $-H_0'''$ has slope -1.01 ± 0.03 [*r* (correlation coefficient) 0.997]. The full kinetic form of the catalysed exchange is therefore that of equation (3) where $k_3 = (9.8 \pm 0.9) \times 10^{-8}$ s^{-1}.

$$\text{Rate} = k_3[\text{Ar}\overset{+}{\text{N}}\text{Me}_2\text{D}][\text{NO}^+]/h_0''' \qquad (3)$$

The values of k_2 for the substituted ions $\text{XC}_6\text{H}_4\overset{+}{\text{N}}\text{Me}_2\text{D}$ where X = 3-Me, 4-Me, and 3-Cl have been calculated in the same way and are given in Table 2. The calculation of k_2 for the ion with X = 3-OMe is a little more complex since hydrogen-isotope exchange in this ion shows strong acid catalysis[4] in addition to the normal base catalysis: in consequence, there is no acidity at which the rate of exchange in the absence of nitrosonium ions is negligible. The values of k_2 (Table 2) have therefore been calculated from the difference between the first-order rate coefficients (k_1) in the absence and presence of nitrosonium

TABLE 1

Second-order rate coefficients k_2 [equation (2)] for the nitrosonium ion catalysed protiodedeuteriation of the *NN*-dimethylanilinium ion at 33 ± 0.5 °C

H_2SO_4 (%)	$10^2[\text{NO}^+]$ / mol dm^{-3}	10^5k_1 / s^{-1}	10^3k_2 / mol^{-1} s^{-1} dm^3
84.8		(0.12) [a]	
84.8	0.388	20.1	51.8
85.8	0.267	8.84	33.1
85.8	0.385	12.8	33.2
86.6	0.688	22.5	32.7
86.6	0.707	21.2	30.0
89.0	0.773	8.85	11.4
90.15	1.39	10.7	7.70
92.6	1.98	5.5	2.78
92.6	2.22	6.3	2.84
92.6	4.44	12.0	2.70
92.6	8.88	24.2	2.73

[a] Extrapolated from the results in Part 1, Table 1.

ions using an acidity at which the combined rate of exchange by the base- and acid-catalysed paths is near its minimum value. The mean values of k_2 for the substituted *NN*-dimethylanilinium ions have been divided by that for the *NN*-dimethylanilinium ion at the appropriate acidity to give the substituent effects in Table 3.

TABLE 2

First-order and second-order rate coefficients [equations (1) and (2)] for the protiodedeuteriation of substituted *NN*-dimethylanilinium ions at 33 ± 0.5 °C

Substituent	H_2SO_4(%)	$10^2[NO^+]$/mol dm^{-3}	10^5k_1/s^{-1}	10^3k_2/mol^{-1} s^{-1} dm^3
3-Me	92.6	0.537	12.1	22.5
3-Me	92.6	0.480	9.11	19.0
4-Me	89.85	0.387	37.6	97.1
3-Cl	89.0	3.42	10.7	3.13
3-Cl	89.0	3.49	8.95	2.56
3-OMe	83.5		46.7	
3-OMe	83.5		49.6	
3-OMe	83.5	0.0499	84.1	801
3-OMe	83.5	0.0551	84.6	661

TABLE 3

Comparison of substituent effects in the diazotisation of substituted anilinium ions and in the nitrosonium-ion-catalysed hydrogen-isotope exchange in substituted *NN*-dimethylanilinium ions

Substituent	Relative rate	
	Diazotisation [a]	Isotope exchange [b]
None	1.0 [c]	1.0 [c]
3-Me	6.8	7.3
4-Me	7.4	13
3-Cl	0.41	0.26
4-Cl	0.20	
3-OMe	18.6	8.1
4-OMe	9.5	

[a] In mol dm^{-3} perchloric acid at 2 °C, E. C. R. de Fabrizio, E. Kalatzis, and J. H. Ridd, *J. Chem. Soc.* (*B*), 1966, 533.
[b] In 83.6—92.6% sulphuric acid at 33 °C. [b] By definition.

DISCUSSION

The nitrosonium-ion-catalysed reaction described in this paper and the acid-catalysed reaction described in the preceding paper are both examples of electrophilic catalysis of hydrogen-isotope exchange but the substituent effects show that the reaction paths are quite different. The acid-catalysed reaction occurs only where the aromatic ring has electron-donating substituents and the substituent effect of a methyl group accords with that expected for the attack of the electrophile on the aromatic ring leading to the formation of a Wheland intermediate. In contrast, the nitrosonium-ion-catalysed reaction is easily observed with the *NN*-dimethylanilinium ion and the substituent effect of the methyl group (Table 3) is far less than would be expected for the formation of a Wheland intermediate from a weak electrophile.

Our interpretation of this difference is that the nitrosonium-ion-catalysed reaction involves a weaker interaction between the nitrosonium ion and the aromatic ring in the transition state of the exchange reaction. The unit slope of the plot of log k_2 against H_0 suggests that the nitrosonium-ion catalysis represents a modification of the base-catalysed reaction [5] (*cf.* Part 1) [1] in which electron donation from the aromatic ring to the nitrosonium ion facilitates the proton transfer. This is illustrated for a water molecule as the initial proton acceptor in equations (4)—(6). At these high acidities, another species (*e.g.* HSO_4^-) may also act in this way.

$$\mathrm{NO^+ + Ar\overset{+}{N}Me_2D\cdots OH_2 \xrightleftharpoons{K_4} NO^+{\cdot}Ar\overset{+}{N}Me_2D\cdots OH_2} \qquad (4)$$

$$\mathrm{NO^+{\cdot}Ar\overset{+}{N}Me_2D\cdots OH_2 + B \xrightleftharpoons{K_5} NO^+{\cdot}ArNMe_2\cdots DOH + HB^+} \qquad (5)$$

$$\mathrm{NO^+{\cdot}ArNMe_2\cdots DOH \xrightarrow{k_6} NO^+{\cdot}ArNMe_2 + DOH} \qquad (6)$$

In these equations, the complex formation between the nitrosonium ion and the anilinium ion is shown as preceding the initial proton transfer because, from the dissociation constant of the $\mathrm{Ph\overset{+}{N}Me_2H}$ ion (pK_a 5.07),[6] the encounter of the nitrosonium ions with the unprotonated species $\mathrm{ArNMe_2\cdots DOH}$ would be too infrequent to explain the observed reaction rate. If equation (3) is rewritten in terms of the concentrations of the unprotonated amine and the nitrosonium ion, the corresponding rate coefficient (1.1×10^{14} mol^{-1} s^{-1} dm^3) greatly exceeds that for a bimolecular encounter in this medium (*ca.* 3×10^8 mol^{-1} s^{-1} dm^3).[7]

The extent of catalysis by nitrosonium ions provides a measure of the interaction between the nitrosonium ions and the aromatic ring. On the base-catalysed mechanism, the rate coefficient k_1 is related to the dissociation constant of the anilinium ion (K) and the rate coefficient (k_d) for the diffusion apart of $\mathrm{ArNMe_2}$ and DOH by equation (7) (*cf.* Part 1). On the above mechanism for

$$k_1 = k_dK/h_0''' \qquad (7)$$

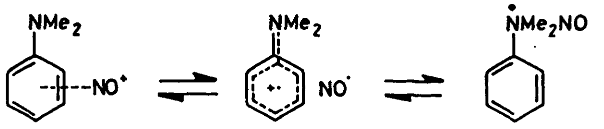
nitrosonium-ion catalysis the corresponding relationship is (8) [*cf.* equations (4)—(6)]. From the comparison of

$$k_1 = k_6K_5K_4[\mathrm{NO^+}]/h_0''' \qquad (8)$$

the base-catalysed and nitrosonium-ion-catalysed reactions in 84.8% sulphuric acid (Table 1), it follows that $k_6K_5K_4/k_dK = 4.3 \times 10^4$ mol^{-1} dm^3. This implies that the nitrosonium-ion catalysis decreases the free energy of activation by *ca.* 27 kJ mol^{-1} as a result of the interaction between the nitrosonium ion and the aromatic ring in the transition state. This is more than the value of $\Delta G°$ in forming most π-complexes and suggests a significant extent of electron transfer between these components. The substituent effects (Table 3) are also greater than observed in π-complex formation and in the direction expected for a reaction involving electron donation from the aromatic ring.

The existence of this nitrosonium-ion-catalysed mechanism of hydrogen-isotope exchange was foreseen from earlier experiments on the diazotisation of aniline at lower acidities. Over the range 1—6 mol dm^{-3} perchloric acid, the diazotisation of aniline appears to involve proton loss from a complex of the nitrosonium ion * and the anilinium ion followed by the formation of the $\mathrm{Ph\overset{+}{N}H_2NO}$ ion and the fast conversion of this to the diazonium ion.[8] At higher acidities, the rate of diazotisation falls off rapidly and this was interpreted as the reversible formation of the $\mathrm{Ph\overset{+}{N}H_2NO}$ ion followed by slow prototropic rearrangements to give the diazonium ion.[9] This mechanism requires that nitrosonium ions catalyse N–H hydrogen-isotope exchange between anilinium ions and highly acidic media. Thus, the present observations provide support for the earlier conclusions. The differences in the substrate used and the experimental conditions make it difficult to attempt a more quantitative comparison but the extent of nitrosonium-ion catalysis is approximately as expected and the similarity in the substituent effects for diazotisation and hydrogen-isotope exchange (Table 3) points to a similarity in the two reaction paths.† This comparison also implies that the reactions in equations (4)—(6) are followed by the migration of the nitrosonium ion to the nitrogen atom of the amine.

The reactions leading to the nitrosonium-ion-catalysed exchange are also important in the nitrous-acid-catalysed nitration and oxidation of the *NN*-dimethylanilinium ion with nitric acid in 80—90% sulphuric acid.[10] When sufficient nitric acid is present, the combined rate of disappearance of the *NN*-dimethylanilinium ion in these reactions has the kinetic form of equation (3) and, for reaction of the deuteriated ion ($\mathrm{Ph\overset{+}{N}Me_2D}$) in 84.8% sulphuric acid at 34 °C, the value of k_3 ($9 \times 10^8\ \mathrm{s^{-1}}$) is very close to that for hydrogen-isotope exchange ($9.8 \times 10^8\ \mathrm{s^{-1}}$). This equivalence in the rate and kinetic forms of the two reactions implies that, in the presence of sufficient nitric acid, the intermediate formed in the exchange reaction is quantitatively captured and deflected along different reaction paths. The initial products of the nitrous-acid-catalysed nitration and oxidation appear to be *p*-nitro-*NN*-dimethylaniline and *NNN'N'*-tetramethylbenzidine in a ratio that is very dependent on the acidity. The product composition has been explained [10] by assuming a rapid equilibration



(9)

between the species shown in equation (9) followed by the oxidation of the nitric oxide in the radical pair by nitronium ions and molecular nitric acid. Nitrosonium ions are certainly capable of generating such radical cations under these conditions for the e.s.r. spectra of the radical cations $\mathrm{4\text{-}MeC_6H_4NMe_2^{+\cdot}}$ and $\mathrm{4\text{-}MeOC_6H_4NMe_2^{+\cdot}}$ have been detected in the reactions of the corresponding amines with nitrous acid in *ca.* 76% sulphuric acid.[11]

We conclude therefore that the nitrosonium-ion-catalysed exchange reported in this paper is the simplest manifestation of a process of great importance in the reactions of anilinium ions and nitrous acid. The simplicity arises from the high acidity of the medium and the absence of strong oxidising agents for these cause the reprotonation of the intermediates to compete successfully with the possible subsequent reactions.

EXPERIMENTAL

Materials.—Nitrosonium hydrogensulphate was prepared by passing sulphur dioxide through fuming nitric acid at 0 °C.[12] The extinction coefficient at 230 nm in 75.4% sulphuric acid was 2 905 (lit.,[13] 2 900). The *NN*-dimethylanilinium hydrogensulphates and their *N*-deuteriated derivatives were prepared as described in Part 1. The preparation and standardisation of the sulphuric acid solutions were also as described in Part 1.

Kinetics.—The reaction was started by adding a solution of nitrosonium hydrogensulphate (2 ml) in the required concentration of sulphuric acid at 33 °C to a solution of the anilinium hydrogensulphate ($0.4\ \mathrm{mol\ dm^{-3}}$; 2 ml) in the same concentration of sulphuric acid at the same temperature. After mixing, part of the solution was transferred to an n.m.r. tube which was then sealed with Parafilm to exclude moisture. The remaining details were as described in Part 1. The variation of the height of the N–Me peak with time in a typical kinetic run is shown in Table 4.

TABLE 4

Variation in the height (h_t) of the N–Me peak in the protiodeuteriation of the *N*-deuterio-*NN*-dimethylanilinum ion in sulphuric acid (92.6%) at 33 °C

[NO $\mathrm{HSO_4}$] $8.88 \times 10^{-2}\ \mathrm{mol\ dm^{-3}}$ [$\mathrm{Ph\overset{+}{N}Me_2D}$] $0.2\ \mathrm{mol\ dm^{-3}}$

t/min	h_t/cm	t/min	h_t/cm
10	16.8	39	12.2
15	15.9	42	11.7
18	15.5	45	11.3
21	14.8	48	11.1
24	14.5	51	10.6
27	13.8	54	10.2
30	13.4	57	10.1
33	13.1	60	9.8
30	12.7	∞	3.0

k_1 (least squares) $= (24.2 \pm 0.3) \times 10^{-5}\ \mathrm{s^{-1}}$

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* In the earlier studies,[8] we thought it more probable that the attacking agent was the nitrous acidium ion but that distinction is not relevant to the present discussion.

† The acidity dependence of the diazotisation reaction in 1—3 $\mathrm{mol\ dm^{-3}}$ perchloric acid requires the initial proton loss [equation (5)] to be part of the rate-determining step [8] whereas the analogy between the nitrosonium-ion-catalysed exchange and the base-catalysed exchange implies that the initial proton transfer is reversible and that reaction (6) is rate determining. The rate-determining step in the nitrosonium-ion-catalysed exchange may vary with the acidity but it is also possible that the analogy with the base-catalysed mechanism is misleading and that reaction (5) is always rate determining on this reaction path.

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