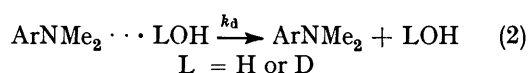
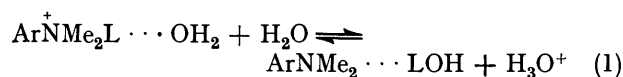


The Kinetics of Hydrogen-isotope Exchange at the Nitrogen Atom of Substituted Anilinium Ions. Part 1. The Acid-catalysed Reaction

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The rate of N-H hydrogen-isotope exchange in *NN*-dimethylanilinium ions has been studied in the solvents sulphuric acid and deuteriosulphuric acid using the difference in the ^1H n.m.r. absorption of the NMe_2H^+ and NMe_2D^+ groups. With the *N*-deuterio-*NN*-dimethylanilinium ion, the reaction rate decreases steadily with acidity as expected from previous studies of the reaction mechanism at lower acidities. However, the rate of N-D exchange in the *N*-deuterio-*NN*-dimethyl-3,5-xylidinium ion reaches a minimum in 83% sulphuric acid and then increases steadily with the acidity. Under the same conditions, hydrogen-isotope exchange occurs in the aromatic ring. The effect of methyl substituents on the rate of the acid-catalysed N-H exchange indicates that this reaction and the C-H exchange have a common initial step involving the donation of a proton or deuteron to the positions in the aromatic ring *ortho* or *para* to the nitrogen. The Wheland intermediate, so formed, is considered to be able to lose a proton from either the carbon or the nitrogen. This interpretation of the acid-catalysed exchange is supported by the effect of isotopic substitution in the aromatic ring on the rate of N-H exchange and by preliminary studies on the range of this reaction mechanism.

PROTON exchange between alkyl-substituted ammonium ions and aqueous acids has been investigated by a number of workers¹ and more limited studies have been carried out on the corresponding reactions of substituted anilinium ions.^{2,3} The latter reactions, at least when studied in moderately concentrated aqueous acids, are first order with respect to the aromatic substrate and the rate coefficients vary approximately inversely with the corresponding acidity function which, for the tertiary amines used, is h_0''' . This kinetic form has been interpreted in terms of the reactions shown in the equations (1) and (2).



Since the reverse of the first reaction is considered to be fast at the acidities used, the overall rate of proton exchange by this mechanism can be written in terms of the dissociation constant (K) of the substituted anilinium ion and the rate coefficient (k_a) for the diffusion apart of the amine and the adjacent water molecule [equation (3)].

$$\text{Rate} = k[\text{ArNMe}_2\text{L}^+] = k_a K [\text{ArNMe}_2\text{I}]/h_0''' \quad (3)$$

The present paper is concerned with an extension of the previous studies^{1,2} to higher acidities and with the incursion of a new, acid-catalysed, path for N-H exchange. The reaction giving rise to the kinetic form of equation (3) will therefore be termed the base-catalysed exchange.

Most previous workers¹⁻³ have followed the reaction from the variation in the line shape of n.m.r. signals with the rate of exchange. The acidities used in the present work are sufficient for the n.m.r. spectrum to correspond essentially to that of the protonated amine and the rate

of exchange has therefore been followed from the change in the form of the NMe_2^+ methyl signal when the N-H proton is replaced by a deuteron. Providing the acidity is sufficient for the rate of proton exchange to be slow, the coupling between the N-H and C-H protons splits the methyl peak to a doublet (J 5 Hz). When the nitrogen is deuteriated, the methyl peak should be split to a triplet but this was not resolved by our instruments. The progress of the exchange has therefore been followed from the variation in the height of the methyl peak as a result of the conversion of the doublet into a singlet when the protonated salt is placed in deuteriosulphuric acid and by the reverse change when the deuteriated salt is placed in sulphuric acid. This method has been used previously⁴ for following the exchange reaction between the trimethylammonium ion and deuteriosulphuric acid. A preliminary account of part of the present work has been published⁵ based on a more approximate method of following the kinetics.

The resulting first-order rate coefficients (k) obtained from the reaction of the PhNMe_2D^+ ion in sulphuric acid are listed in Table 1. A plot of $\log k$ against H_0''' has slope 1.31 ± 0.03 [r (correlation coefficient) 0.998]. Previous authors³ have pointed out that part of the variation of k with acidity should come from the decrease in k_a with the viscosity (η) of the medium. Following their suggestion,³ we have also plotted values of $\log (\eta k/\eta_0)$ against H_0''' where η_0 is the viscosity of water. The resulting slope [1.13 ± 0.03 (r 0.997)] is much nearer to the value of unity expected from the previous studies at lower acidities. From the interpolated value of the first-order rate coefficient ($1.22 \times 10^{-3} \text{ s}^{-1}$) in 72% sulphuric acid ($H_0''' - 8.02$) and the dissociation constant of the *NN*-dimethylanilinium ion (7.9×10^{-6}),² the value of k_a calculated from equation (1) is $1.6 \times 10^{10} \text{ s}^{-1}$ at this acidity. This is close to the value ($1.45 \times 10^{10} \text{ s}^{-1}$) reported previously² for proton exchange in 40—

60% sulphuric acid at 25 °C when followed from the line-shape technique but this similarity must owe something to the accidental cancelling of errors and other factors because of the difference in the experimental conditions. These results show that exchange in the *NN*-dimethylanilinium ion occurs by the base-catalysed mechanism up to 78% sulphuric acid.

TABLE 1

First-order rate coefficients k [equation (3)] for N-H hydrogen-isotope exchange in the *N*-deuterio-*NN*-dimethylanilinium ion (0.22 mol kg⁻¹) in sulphuric acid at 33 ± 0.5 °C

Acid (%)	$-H_0'''$ ^{a,b}	$10^3 k/s^{-1}$	$10^4 \eta/N$ m ⁻² b	$10^3 \eta k \eta_0^{-1}/s^{-1}$
69.22	7.51	6.68	84.5	63.4
		5.89		55.9
70.71	7.78	2.94	94.1	31.1
		2.55		27.0
71.29	7.89	1.61	98.2	17.8
		1.53		16.9
72.31	8.07	0.94	105.8	11.2
		1.03		12.2
74.63	8.49	0.307	125.1	4.31
76.63	8.85	0.109	144.1	1.76
		0.104		1.68
77.80	9.05	0.0557	156.2	0.978

^a Interpolated from the results of E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, 1964, **86**, 2671. ^b At 25 °C.

A kinetic run was attempted using 98% sulphuric acid but no evidence of exchange was found over a period of several weeks. The H_0''' function has not been determined at this acidity but the extrapolation of the plot of $\log(\eta k/\eta_0)$ against H_0''' to 95% sulphuric acid ($H_0''' = 11.89$) gives a half-life of *ca.* 300 days. This absence

TABLE 2

First-order rate coefficients for N-H hydrogen-isotope exchange in substituted *NN*-dimethylanilinium ions at 33.5 ± 0.5 °C

Acid (%)	$-H_0'''$	$10^3 k/s^{-1}$	Acid (%)	$-H_0'''$	$10^3 k/s^{-1}$
3-MeC ₆ H ₄ ⁺ NMe ₂ D (0.21 mol dm ⁻³) in H ₂ SO ₄					
70.35	7.72	123	77.80	9.05	1.49
70.35	7.72	108	98.00		0.0104
73.05	8.21	41.2			
76.30	8.79	3.58			
3,5-Me ₂ C ₆ H ₃ ⁺ NMe ₂ D (0.21 mol kg ⁻¹) in H ₂ SO ₄					
70.71	7.78	67.3	84.66	10.23	0.209
72.31	8.07	32.9	87.29	10.67	0.455
74.63	8.49	6.93	89.44	11.02	0.977
76.63	8.85	3.88	95.00	11.91	2.67
77.50	9.00	1.61	98.00		4.72
81.93	9.77	0.142	98.76		5.34
3,5-Me ₂ C ₆ H ₃ ⁺ NMe ₂ H (0.40 mol dm ⁻³) in D ₂ SO ₄					
70.38	8.04	33.9	77.30	9.22	1.43
72.04	8.33	12.1	81.64	9.93	0.384
72.18	8.36	12.2	89.34	11.13	3.6
74.96	8.83	3.38	90.84	11.36	4.6
75.55	8.93	1.55			

of exchange in the *NN*-dimethylanilinium ion is therefore as expected from the base-catalysed mechanism outlined above.

At acidities below 78% sulphuric acid, the results with the *NN*-dimethyl-3-toluidinium ion (Table 2) accord with those of the *NN*-dimethylanilinium ion. The plot of $\log k$ against H_0''' has slope 1.44 ± 0.10 (r 0.993) and the reaction is a little slower than that with the *NN*-

dimethylanilinium ion (by a factor of *ca.* 2 in 72% H₂SO₄) as expected from the slightly greater basicity of the amine (K 4.53×10^{-6}).⁶ However, in 98% H₂SO₄, the rate of hydrogen-isotope exchange is slow but measurable (Table 2). In consequence of the results discussed below we consider this to represent the incursion of the acid-catalysed mechanism of exchange.

The acid-catalysed mechanism of exchange is seen much more clearly in the reactions of the *NN*-dimethyl-3,5-xylidinium ion. The first-order rate coefficients for the reaction of 3,5-Me₂C₆H₃⁺NMe₂D in H₂SO₄ are given in Table 2 and plotted logarithmically against the acid composition in Figure 1. At acidities up to 82% H₂SO₄, the plot of $\log k$ against H_0''' accords with the base catalysed mechanism of exchange for the slope is 1.34 ± 0.06 (r 0.996). The reaction rate is slower than that with the *NN*-dimethylanilinium ion by a factor of *ca.* 3.5.

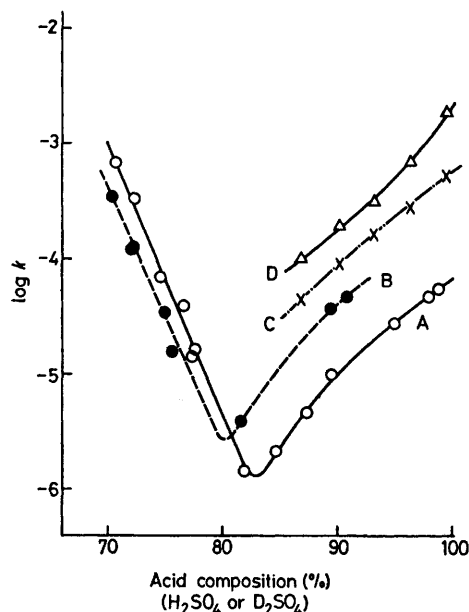


FIGURE 1 Rate profiles for the hydrogen-isotope exchange reactions of the *NN*-dimethyl-3,5-xylidinium ion: A, protio-deuteriation at nitrogen in H₂SO₄; B, deutero-deuteriation at nitrogen in D₂SO₄; C, aromatic deuteration at the 2- and 6-positions in D₂SO₄; D, aromatic deuteration at the 4-position in D₂SO₄.

However, in *ca.* 83% H₂SO₄, the reaction rate passes through a minimum and then increases steadily with acidity.

The reverse reaction involving the 3,5-Me₂C₆H₃⁺NMe₂H ion in D₂SO₄ has also been studied and the results are included in Table 2 and Figure 1. When plotted against acid composition by weight, the base-catalysed exchange in D₂SO₄ is a little slower than that in H₂SO₄ but the difference almost disappears when comparison is carried out at the same H_0''' values.* This comparison is unfortunately complicated by differences in the

* The H_0''' values in D₂SO₄-D₂O mixtures have been assumed to be the same as those of H₂SO₄-H₂O mixtures of the same molecular composition. This is true for the H_0 acidity function at these acidities.⁷

concentrations of substrates used. However, in reaction by the acid-catalysed mechanism, the reaction in D_2SO_4 is faster than that in H_2SO_4 by much more than that expected from the difference in the acidity of solutions of the same acid composition by weight. The acid-catalysed reactions in D_2SO_4 also show some deviations from first-order kinetics (see below); the values in Table 2 are averaged over about the first half-life.

This exchange reaction is accompanied by deuterio-deprotonation at the 2-, 4-, and 6-positions of the aromatic

TABLE 3

First-order rate coefficients k for C-H hydrogen-isotope exchange between xylidinium ions (0.5 mol dm^{-3}) and deuteriosulphuric acid at 34.9°C

3,5-Me ₂ C ₆ H ₃ NMe ₂ ⁺ H					
D ₂ SO ₄ (%)	86.8	90.2	93.2	96.4	99.6
10 ⁵ k/s ⁻¹ { 2,6-positions	4.4	8.9	16	27	51
{ 4-position	10	19	31	68	180
3,5-Me ₂ C ₆ H ₃ NMe ₃ ⁺					
D ₂ SO ₄ (%)	88.6	90.9	93.5	96.9	99.3
10 ⁵ k/s ⁻¹ (2-, 4-, and 6-positions) ^a	2.4	3.7	7.9	19	43
2,6-Me ₂ C ₆ H ₃ NMe ₂ ⁺ H					
D ₂ SO ₄ (%)	90.2	94.1	96.4	97.1	99.6
10 ⁵ k/s ⁻¹ (3,5-positions)	1.2	4.4	8.4	9.7	20

^a At the lower acidities (<94% D₂SO₄), the peaks for the 2-, 6-, and 4-positions in the ¹H n.m.r. spectrum are separate but the rates of exchange are similar: at the higher acidities, the peaks merge and only the overall rate of exchange can be followed.

ring. The rates of these reactions have been followed from the variation in the areas of the corresponding C-H signals in the ¹H n.m.r. spectrum and the resulting rate coefficients are given in Table 3 together with those for some related substrates.

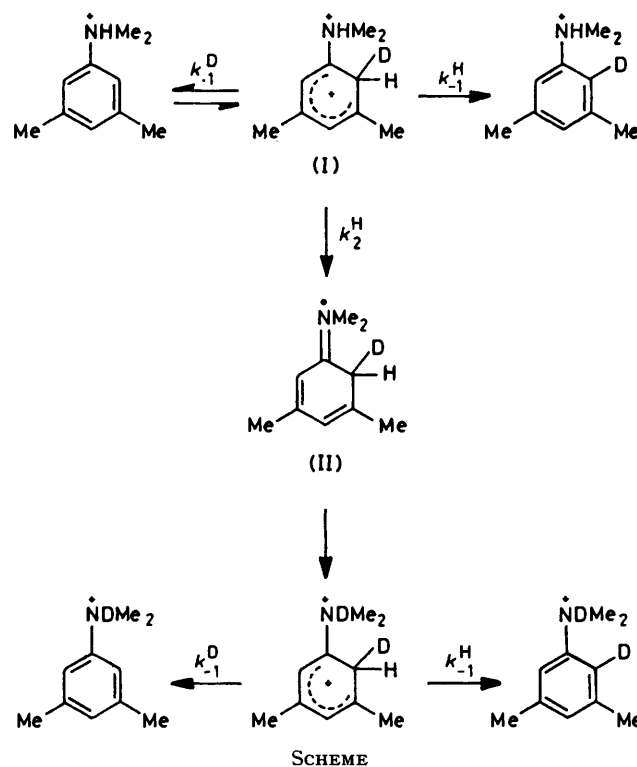
DISCUSSION

The results concerning the base-catalysed N-H exchange reaction in this paper are in general accord with the previous studies and need no further consideration. This discussion is therefore limited to the mechanism and range of the acid-catalysed N-H exchange.

The key observation concerning the mechanism of the acid-catalysed reaction is the sensitivity of the reaction rate to methyl substituents in the aromatic ring. In 98% sulphuric acid, the rate coefficient for acid-catalysed N-H exchange in the 3,5-Me₂C₆H₃NMe₂D⁺ ion is greater than that in the 3-MeC₆H₄NMe₂D⁺ ion by a factor of *ca.* 450 (Table 2). This is very similar to the effect of a methyl group on the rate of protiodedeuteration of benzene at the *ortho*- and *para*-positions in 80% sulphuric acid (a factor of *ca.* 300).⁸ Since the acid-catalysed N-H exchange in 3,5-Me₂C₆H₃NMe₂H is accompanied by exchange in the aromatic ring, we suggest that the two processes have a common initial step involving proton transfer to the positions *ortho* or *para* to the nitrogen atom. Some of the consequences of this interpretation are most easily seen by considering the reverse reaction of 3,5-Me₂C₆H₃NMe₂H in D₂SO₄ and the suggested

reaction path following *ortho*-attack on this substrate is set out in the Scheme. The initial addition of a deuteron to the aromatic ring is shown as a reaction of the conjugate acid of the substrate because of the similarity between the rate profiles for C-H exchange in 3,5-Me₂C₆H₃NMe₂H⁺ and 3,5-Me₂C₆H₃NMe₃⁺ (Table 3).

On this mechanism, the Wheland intermediate (I) can undergo reaction by heterolysis of the C-D bond (reforming the reactants), heterolysis of the C-H bond (leading to C-H exchange without N-H exchange), and heterolysis of the N-H bond leading to the quinonoid intermediate (II). It is probably reasonable to assume that the life-time of this intermediate is long in comparison with that required for the diffusion apart of the amine and the base that has accepted the proton and, if so, the formation of (II) should always lead to N-H exchange. The formation of (II) should also normally lead to C-H exchange because of the isotope effect on the relative rates of C-H and C-D heterolysis. Hence, on this mechanism for deuterio-deprotonation at nitrogen the rate



of N-H exchange can be less than that of C-H exchange but cannot be much greater than that of C-H exchange. The rates of these reactions in Figure 1 show that this condition is satisfied.

This mechanism has a less obvious consequence concerning the kinetic form of the deuterio-deprotonation at nitrogen. When the initial addition of the deuteron is to an aromatic carbon atom bearing a hydrogen atom, the fraction (f_H) of the intermediate (I) giving rise to N-H exchange is given by equation (4). When this addition is to a carbon atom that has already been

deuteriated, the corresponding fraction (f_D) is given by equation (5).^{*} Since $k_{-1}^D < k_{-1}^H$, the fraction of initial deuterium transfers leading to N-H exchange and hence the first-order rate coefficient for N-H exchange should increase during a kinetic run. The extent and form of this increase is complicated by the fact that the initial deuterium transfer could be to either the *ortho*- or *para*-position and by the fact only C-H exchange without N-H exchange is effective in changing the kinetic form of the reaction.

$$f_H = k_2^H / (k_{-1}^H + k_{-1}^D + k_2^H) \quad (4)$$

$$f_D = k_2^H / (2k_{-1}^D + k_2^H) \quad (5)$$

Kinetic runs with a large number of experimental points have been carried out using the $3,5\text{-Me}_2\text{C}_6\text{H}_3\text{N}^+\text{Me}_2\text{H}$ and $3,5\text{-Me}_2\text{C}_6\text{D}_3\text{N}^+\text{Me}_2\text{H}$ ions in D_2SO_4 at 28°C in an attempt to analyse these deviations from a first-order form. The results indicate that the expected deviations occur and this is illustrated by the two Guggenheim plots⁹ in Figure 2. The ordinate of these plots is the

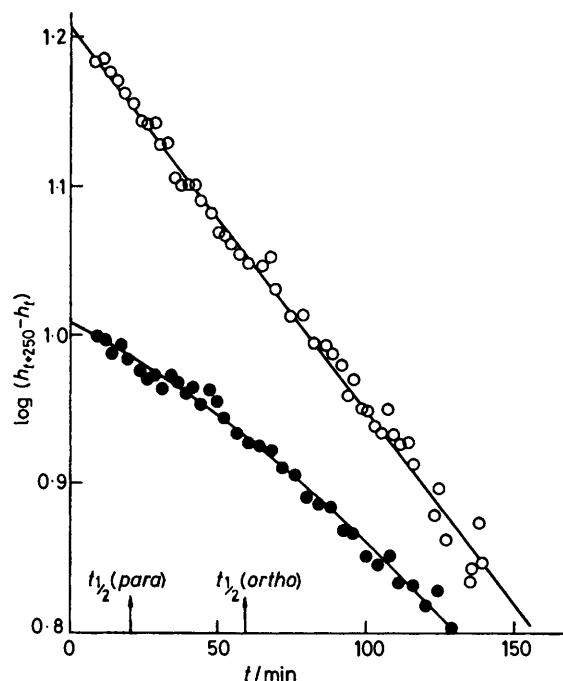


FIGURE 2 Guggenheim plots showing the effect of ring deuteration on the kinetic form of N-N hydrogen isotope exchange in 96.01% D_2SO_4 . The half-lives for exchange in the aromatic ring are also shown. $3,5\text{-Me}_2\text{C}_6\text{D}_3\text{N}^+\text{Me}_2\text{H}$, \circ ; $3,5\text{-Me}_2\text{C}_6\text{H}_3\text{N}^+\text{Me}_2\text{H}$, \bullet

logarithm of the difference in the peak heights (h) (measured relative to a standard) at two times 250 min apart. The results with the initially deuteriated ion show the linear form expected for a first-order reaction ($k\ 9.86 \times 10^{-5}\ \text{s}^{-1}$). The results with the initially undeuteriated ion give a curve corresponding to a rate

^{*} This and some following arguments ignore secondary isotope effects deriving from the replacement of C-H by C-D.

coefficient of $4.4 \times 10^{-5}\ \text{s}^{-1}$ at 10 min and $7.9 \times 10^{-5}\ \text{s}^{-1}$ at 120 min. This evidence that the concurrent aromatic deuteration modifies the rate of the N-H deuteration supports the mechanism outlined in the Scheme but unfortunately the scatter of the experimental points makes a more detailed analysis unprofitable. The proposed mechanism is analogous to those for substitution reactions in aromatic methyl groups reviewed by Hartshorn,¹¹ for these reactions are also initiated by electrophilic attack on the aromatic ring.

A preliminary survey has been carried out on the range of this acid-catalysed mechanism for N-H exchange. It does not always accompany C-H exchange, for the $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N}^+\text{Me}_2\text{H}$ ion undergoes C-H exchange at the 3,5-positions at *ca.* 1/3 of the rate of that in the 2,6-positions of the $3,5\text{-Me}_2\text{C}_6\text{H}_3\text{N}^+\text{Me}_2\text{H}$ ion (Table 3) but, in the former ion, the acid-catalysed mechanism for N-H exchange could not be detected. Presumably, the aromatic exchange must be at the positions *ortho* or *para* to the nitrogen pole for the acid-catalysed mechanism of N-H exchange to be effective. This accords with the fact that both the *meta*- and *para*-*NN*-dimethylanisidinium ions undergo C-H exchange in 95% D_2SO_4 at 35°C but only the former shows the acid-catalysed mechanism of N-H exchange.⁵

EXPERIMENTAL

Materials.—Sulphuric acid was the AnalaR reagent (98%). Deuteriosulphuric acid was either the commercial product or was prepared by the slow distillation of sulphur trioxide at 0.1 mmHg into stirred deuterium oxide to give a final composition of *ca.* 100% D_2SO_4 . The acids were diluted with H_2O or D_2O and estimated by the titration of weighed samples.

NN-Dimethylaniline, *p*-toluidine, 2,6-xylylidine, and 3,5-xylylidine were laboratory reagents. The *NN*-dimethyl derivatives were prepared by the treatment of the primary amines with trimethyl orthophosphate¹¹ or methyl sulphate.¹² The corresponding hydrogensulphates were prepared by the dropwise addition of an equivalent amount of sulphuric acid (98%) to a stirred solution of the tertiary amine (0.05 mol) in acetone (50 cm^3) at 0°C . The addition of ether (5 cm^3) facilitates precipitation of the salt. The salts were filtered off, recrystallised from methanol-acetone, dried *in vacuo* over P_2O_5 , and analysed (Table 4). The corresponding *N*-deuterio-salts were prepared in the same way using deuteriosulphuric acid and dry acetone followed by washing with dry acetone but the recrystallisation was omitted. The absence of the doublet corresponding to the NMe_2H group in the n.m.r. spectrum taken immediately after the salt was dissolved in 98% H_2SO_4 was taken as evidence of complete *N*-deuteriation. The ring-deuteriated salt $3,5\text{-Me}_2\text{C}_6\text{D}_3\text{N}^+\text{Me}_2\text{H HSO}_4^-$ was prepared by the treatment of *NN*-dimethyl-3,5-xylylidine with excess of D_2SO_4 (*ca.* 100%) for 24 h at room temperature followed by neutralisation with aqueous sodium carbonate (saturated) and extraction with ether. The corresponding hydrogensulphate was then prepared as outlined above. The hydrogensulphate of the quaternary ion $3,5\text{-Me}_2\text{C}_6\text{H}_3\text{N}^+\text{Me}_3$ was prepared by methylation of 3,5-xylylidine with methyl iodide to give the

quaternary iodine followed by the replacement of the iodide ion by the hydroxide ion using an ion exchange resin (Amberlite IRA 400) and acidification of the resulting solution to pH 2 with sulphuric acid. Evaporation of the solution followed by recrystallisation of the resulting solid gave the quaternary hydrogensulphate as deliquescent prisms. This was dried over P_2O_5 and analysed (Table 4).

Kinetics.—The majority of the kinetic runs were carried out by dissolving *ca.* 100 mg of the appropriate anilinium hydrogensulphate in sulphuric acid or deuteriosulphuric acid of the stated composition at 33.5 °C to give a solution of known molarity or molality. A sample was then pipetted into an n.m.r. tube and the height at the position of the NMe_2D methyl peak (h_t) followed using a Perkin-Elmer R10 60 MHz spectrometer. For the slower runs, the relative peak height was measured using another peak as a standard (usually the methyl peak of toluene present in a sealed capillary) to compensate for slow changes in the characteristics of the spectrometer. The reaction was followed for

TABLE 4
Analytical results on substituted anilinium hydrogensulphates

Cation	Found (%)			Calculated (%)		
	C	H	N	C	H	N
$C_6H_5NMe_2H$	43.6	5.9	6.3	43.8	6.0	6.4
3-Me $C_6H_4NMe_2H$	46.0	6.2	5.7	46.3	6.5	6.0
3,5-Me $_2C_6H_3NMe_2H$	48.7	6.7	5.9	48.6	6.9	5.7
2,6-Me $_2C_6H_3NMe_2H$	48.5	7.0	5.8	48.6	6.9	5.7
3,5-Me $_2C_6D_3NMe_2H$	47.8		5.8	48.0		5.6
3,5-Me $_2C_6H_3NMe_2$	50.0	7.8	5.8	50.6	7.3	5.4

ca. one half-life and the rate coefficient was obtained from a least-squares calculation of the slope of a plot of $\ln(h_t - h_\infty)$ against time using 10–30 experimental points. A typical kinetic run is shown in Table 5. The standard error calculated from such runs was usually *ca.* $\pm 4\%$ but the mean rate coefficients from some fast runs carried out under the same conditions often differed by more than this (see Table 1).

A few kinetic runs were carried out on a Varian H 100 spectrometer taking about 200 experimental points per run and calculating the rate coefficients from Guggenheim plots based on two sets of experimental points separated by 250 minutes. Two kinetic runs of this type are shown in Figure 2, every second point being omitted for clarity. The methyl peak of toluene was again used as a standard since the concurrent deuteration of the ring was found to lead to a slight increase in the sharpness and hence the height of the C-Me peaks in the substrate.

The kinetic runs on C-H exchange were followed from the relative areas of the corresponding peaks in the 1H n.m.r. spectra using the integrated areas of the methyl peak of added methyl sulphate as a standard. A series of runs were done for each acidity using substrate concentrations in the

TABLE 5
Hydrogen-isotope exchange at nitrogen in the 3-Me $C_6H_4-NMe_2D$ ion (0.21 mol dm $^{-3}$) in H_2SO_4 (73.05%) at 33.5 °C followed from the height (h_t) of the NMe_2D methyl peak

t/min	h_t/mm	t/min	h_t/mm
12.25	88	27.00	66.5
14.00	87	29.00	67
16.50	80.5	32.00	61
18.50	80	36.00	60
21.00	76	40.00	56.5
23.00	76	44.00	52
25.00	72	48.00	51
		∞	23

$$k = (4.12 \pm 0.13) \times 10^{-4} s^{-1}$$

range 0.2–0.8 mol dm $^{-3}$ and the values in Table 3 obtained by interpolation. The standard errors are *ca.* $\pm 10\%$ for this is not a very accurate kinetic technique.

The n.m.r. spectra of the reaction mixtures were also examined for evidence of new peaks resulting from sulphonation. The results showed that this was insignificant for the compounds and conditions discussed above.

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