Secondary Hydrogen-isotope Effects in the Nitration of Anilinium Ions

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THE slow rate of N–H hydrogen isotope exchange reported in the preceding Communication for the dimethylanilinium ion in concentrated deuterosulphuric acid applies also to the anilinium ion: the half-life for the N–H exchange of a 1M solution of *NNN*-trideuteroanilinium bisulphate in 89% sulphuric acid at 35° is $\sim$ 100 min. and this rate decreases rapidly with acidity. Hence, at this and higher acidities, the nitration of the anilinium ion can be made to occur much more rapidly than the rate of N–H hydrogen isotope exchange.

The difference in the rates of these reactions permits the nitration of the anilinium ion and of the *NNN*-trideuteroanilinium ion to be studied in both sulphuric acid and deuterosulphuric acid; solvent isotope effects on the rate of nitration and the effect of replacing $-N^+H_3$ by $-N^+D_3$ can therefore be studied separately.

The results, obtained by spectrophotometric studies,[1] are listed below in terms of the product composition ($\pm 1\%$) and the second-order rate coefficient (k_2).

These results accord with the earlier experiments[1] on the trimethylanilinium ion in that there is no significant solvent-isotope effect on the rate of nitration, but there now appears to be a significant change in the rate of reaction and in the product composition when the protonated pole is replaced by the deuterated one. The rate of substitution at the *meta*-position is reduced by 20% and that at the *para*-position by 39%. It is now clear that the exchange at the $-N^+H_3$ group would have been far from complete under the conditions used previously for studying the nitration of the anilinium ion in deuterosulphuric acid; the earlier results[1] therefore refer to the substituent effect of the $-N^+H_3$ pole.

The isotope effect could be considered either as a small primary effect resulting from the partial transfer of one proton to a base in the transition state or as a secondary effect deriving from the decrease in the stretching frequency of all three N–H bonds in the transition state. In this connection, it is significant that the isotope effects on the rate and orientation are much less in the

TABLE

Nitration in sulphuric acid and deuterosulphuric acid at the same composition (4·8 *moles* % H_2O *or* D_2O); *temperature* 25°.

Substrate	Solvent	k_2 (l.mole^{-1} sec.$^{-1}$)	Product Comp. (%) *meta*	Product Comp. (%) *para*
$Ph\overset{+}{N}H_3$	H_2SO_4	0·44 $\pm$ 0·01	63	37
	D_2SO_4	0·45 $\pm$ 0·01	63	37
$Ph\overset{+}{N}D_3$	H_2SO_4	0·32 $\pm$ 0·01	69	31
	D_2SO_4	0·33 $\pm$ 0·01	70	30
$Ph\overset{+}{N}Me_2H$	H_2SO_4	0·032 $\pm$ 0·001	79	21
$Ph\overset{+}{N}Me_2D$	D_2SO_4	0·030 $\pm$ 0·001	81	19

nitration of the dimethylanilinium ion where only one hydrogen can be exchanged (see Table). This suggests that the isotope effects observed with the anilinium ion are derived from contributions from all three hydrogens, giving $k_H/k_D = 1{\cdot}08$ per hydrogen for *meta*-substitution and $k_H/k_D = 1{\cdot}18$ per hydrogen for *para*-substitution. Little is known of secondary hydrogen isotope effects in such systems[2] but these values do not seem unreasonable.

Thus the above isotope effects accord with the conclusion[3] from substituent effects that no one hydrogen of the $-N^+H_3$ group is singled out for a special role in the transition state. The difference between the rates of nitration and N–H isotope exchange also provides perhaps the clearest evidence that reaction through the equilibrium concentration of the free amine is not significant for nitration in strongly acidic media.

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