Hydrogen-isotope Exchange in Substituted Anilinium Ions

By J. R. BLACKBOROW and J. H. RIDD

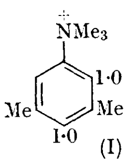
(*William Ramsay and Ralph Forster Laboratories, University College, Gower Street, London, W.C.*1)

THE substituent effects of nitrogen poles in aromatic nitration have recently been discussed:[1] here is an extension of the study of such substituent effects to hydrogen-isotope exchange. The aromatic exchange was followed from the changes in the peak areas in the proton magnetic resonance (p.m.r.) spectrum of the anilinium ions in deuterosulphuric acid using a 60Mc./sec. Perkin–Elmer spectrometer.

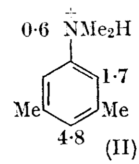
Hydrogen-isotope exchange in the aromatic ring of the anilinium ion and the trimethylanilinium ion occurs too slowly to follow conveniently at room temperature. The presence of one methoxy-substituent or of two methyl substituents (when *meta* to each other) gives rise to a measurable rate of hydrogen-isotope exchange at the activated positions and, in general, leads to a p.m.r. spectrum in which the peaks corresponding to the different aromatic protons can be distinguished.

Exchange rates have been measured for a series of anisidinium and *meta*-xylidinium bisulphates using several concentrations of the aromatic substrate and a range of acidities. The relative substituent effects can be seen from the relative rates outlined below for substitutions in 95% deuterosulphuric acid using 0·4 M-substrate at 35°. At this acidity, the *ortho*- and *para*-protons in the ion (I) give rise to a single peak and a single rate coefficient for isotope exchange of $1{\cdot}4 \times 10^{-4}$ $\text{l.mole}^{-1}\ \text{sec.}^{-1}$. The assignment of equal rates of substitution to the *ortho*- and *para*-positions is based on experiments at lower acidities, where the aromatic proton absorption can be resolved and the two reactions can be followed separately.

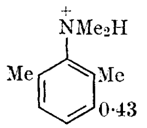
Although the kinetic technique is not capable of high accuracy, the above results permit two conclusions to be drawn. First, the protonated substrates are reacting as such and not through the corresponding free amines. This is shown by the similarity in the rates of substitution of such pairs as (I) and (II) or (IV) and (V). Secondly, there is no obvious directing effect of the positive pole; thus substitution *ortho* to the methoxy-group occurs at much the same rate whether the nitrogen pole is *ortho*-, *meta*-, or *para*- to the position of substitution [compare the results for (V) and (VI)]. Similar conclusions could be drawn for substitution in the xylidines. Because of the probable breakdown of the additivity principle in these systems,[2] it would be unwise to generalise from these results to substitution in anilinium ions without activating substituents; however, it is interesting that no relative retardation of substitution *ortho*- to the nitrogen pole is observed.



(I)



(II)



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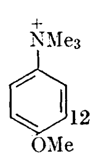
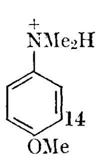
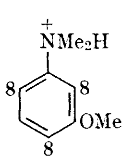


(IV)

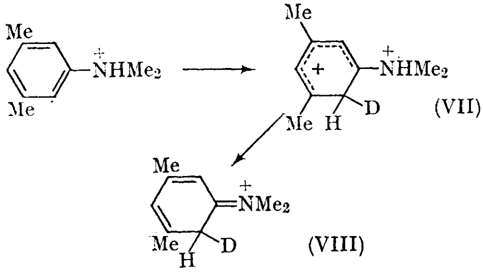


(V)



(VI)

The rate of N–H exchange in the substrates containing an $-\overset{+}{\text{N}}\text{Me}_2\text{H}$ group can be easily followed from the change in the absorption of the N–Me groups: with the $-\overset{+}{\text{N}}\text{HMe}_2$ group, this absorption is a doublet because of coupling with the N–H proton (J = 5c./sec.) but, with the $-\overset{+}{\text{N}}\text{DMe}_2$ group, this absorption is a singlet. As expected from the reactions of aliphatic amines,[3] the rate of NH exchange in the *NN*-dimethylanilinium ion decreases rapidly with acidity and in 95% D_2SO_4 is very slight over several days. This is true for most of the substrates studied but not for the ions (II) and (IV): the N–H exchange then occurs by an acid-catalysed mechanism which for the xylidinium ion has a similar dependence on the acidity of the medium to that of the C–H exchange. The relative



(VII)
(VIII)

rate of this exchange is included in those given above. It may be significant that this acid catalysis of N–H exchange is important only in the systems where C–H exchange is occurring *ortho-* or *para-* to the positive pole, for N–H proton loss from the σ-complex (VII) then provides a possible reaction path leading to a quinoid intermediate (VIII).

Such a mechanism for N–H hydrogen exchange would join the growing class of reactions where electrophilic substitution at an aromatic side chain is initiated by attack on the π-electrons of the aromatic ring.[4]

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