The Mechanism of Nitration of 2,3-Dinitroaniline in Aqueous Sulphuric Acid. Evidence for Bamberger's Hypothesis of *N*-Nitration followed by Rearrangement

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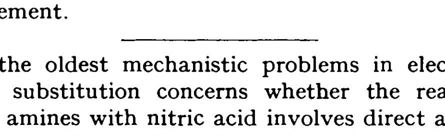
Summary Product analyses and tracer studies involving $H^{15}NO_3$ show that the 6-nitration of 2,3-dinitroaniline by nitric acid in aqueous sulphuric acid occurs mainly by attack on the amino nitrogen atom followed by rearrangement.

One of the oldest mechanistic problems in electrophilic aromatic substitution concerns whether the reaction of aromatic amines with nitric acid involves direct attack on the ring [reaction (1)] or formation of the nitroamine followed by rearrangement [reactions (2) + (4)].[1] The marked discrepancy between the product composition for the nitration of aniline in 85% sulphuric acid (*ortho*, 6%; *meta*, 34%; *para*, 59%) and that for the rearrangement of phenylnitroamine under the same conditions (*ortho*, 93%; *para*, 7%)[2] has long been held to show that the nitroamine is not involved in nitration by nitric acid in aqueous sulphuric acid. However, the recent evidence[3] that aniline undergoes nitration as the conjugate acid under these conditions reopens this mechanistic problem as far as the reactions of free amines are concerned. We have therefore repeated this comparison of the reaction products for nitration and for the nitroamine rearrangement using a substrate which, from kinetic studies,[4] undergoes reaction as the free amine.



The substrate chosen was 2,3-dinitroaniline for this has free *ortho* and *para* positions. In concentrations of sulphuric acid > 90% the n.m.r. spectra of mixtures of 2,3-dinitroaniline and nitric acid indicate complete conversion into a mixture of 2,3,4- and 2,3,6-trinitroanilines: there is no evidence of any intermediate. The nitration and rearrangement reactions have been studied at 0 °C and at two acidities (98 and 90% sulphuric acid). In contrast to the studies using aniline, the composition of the nitrated product (2,3,4-trinitro, 34 ± 2%; 2,3,6-trinitro, 66 ± 2%) is the same for the nitration and rearrangement reactions within experimental error; the product composition is the same at the two acidities. At a lower acidity (78·5% sulphuric acid), where the rearrangement rate is much slower, the nitroamine can be isolated in a yield of 90% from the reaction of nitric acid with the amine.

This isolation of the nitroamine suggests that the nitrogen atom is the most reactive centre in the free amine. This is consistent with the identical product compositions from the nitration and rearrangement reactions. These results suggest that what appears to be direct nitration at the higher acidities is instead an *N*-nitration followed by a fast rearrangement [reactions (2) + (4)].

The results are also consistent with some dissociation of the protonated nitroamine to form nitronium ions and the free amine followed by a reaction between the last two species [reactions (3) + (1)]. Such heterolyses in nitroamines are not normally observed,[5] but the reaction could be facilitated in this nitroamine by the electron-withdrawing groups present.

To distinguish between these interpretations, the rearrangement has been carried out in 78·5% sulphuric acid at room temperature in the presence of 0·64 equivalents of $H^{15}NO_3$ (98·5% ^{15}N) and the isotopic composition the major product (2,3,6-trinitroaniline) has been determined. After 30 min (much less than 50% reaction), this product contained 2·4% of ^{15}N. If the *C*-nitration had involved free nitronium ions, the enrichment would have been > 39%. We conclude therefore that this nitroamine rearrangement is essentially intramolecular and hence that what appears to be direct *C*-nitration at somewhat higher acidities is almost certainly *N*-nitration followed by a fast rearrangement. The rates and kinetic forms of nitration of *p*-nitroaniline and 2-chloro-4-nitroaniline in concentrated sulphuric acid are consistent with this reaction path[6] and so *N*-nitration followed by rearrangement may be the normal reaction path for amines undergoing nitration *via* the neutral molecule in aqueous sulphuric acid.

The percentage of ^{15}N in 2,3,6-trinitroaniline increases during reaction apparently as a result of exchange between the nitroamine and the labelled nitronium ions.

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