Nitration of *NN*-Dimethylanilinium Ion. Evidence for a New Reaction Path in Nitrous Acid-catalysed Nitrations

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Summary The nitration of the *NN*-dimethylanilinium ion in 85% sulphuric acid is catalysed by nitrous acid but the reaction does not involve C-nitrosation followed by oxidation.

The nitration of certain highly reactive aromatic compounds has long been known to be catalysed by nitrous acid and, following the studies of Ingold *et al.*,[1] this catalysis has been considered to involve preliminary C-nitrosation followed by oxidation. Whilst this is probably the normal explanation of such catalysis, we now have evidence that catalysis can occur through a different reaction path.

In the absence of nitrous acid, the nitration of *NN*-dimethylaniline in aqueous H_2SO_4 (91–100%) follows the rate profile expected for the attack of NO_2^+ on the *NN*-dimethylanilinium ion[2] and our recent work shows that this remains true down to 84% H_2SO_4. In 85% H_2SO_4 the observable reaction of the *NN*-dimethylanilinium ion with nitrous acid is very slow, little change being observed in the n.m.r. spectrum after 4 h, even when the concentration of nitrous acid is as high as 0·1 M. Nevertheless, at this acidity, nitrous acid (0·02–0·1 M) markedly catalyses the nitration reaction, increases the *para*/*meta* ratio in the mononitro-product, and causes the formation of substituted benzidines as side-products (see Table). The extent of formation of these side-products increases as the acidity is decreased.

The catalysis does not arise from C-nitrosation by the

TABLE. Nitration of the *NN*-dimethylanilinium ion (0·1 M) with HNO_3 (0·1 M) in aqueous H_2SO_4 (85·1%) at 33 °C.

$[NO^+]/mol\ l^{-1}$	$t_{\frac{1}{2}}$/min[a]	Products isolated/%[b] *m*-NO_2	*p*-NO_2	2,4-$(NO_2)_2$	other
—	15	45	38	11	
0·02	6	11	54	11	5[c]
0·1	2	4	42	11	14[d]

[a] Approximate values derived from change in the n.m.r. spectrum of the amine. [b] Calculated from the fraction of amine consumed. [c] *p*-Nitroso-*NN*-dimethylaniline. [d] 6% *p*-Nitroso-*NN*-dimethylaniline, 4% tetramethylbenzidine, 2% 3-nitrotetramethylbenzidine, 2% 3,3′-dinitrotetramethylbenzidine.

nitrosonium ion followed by oxidation, for the rate of C-nitrosation by this means is far too slow. The catalysis does not arise from a reaction between nitrous acid and nitric acid to form a more effective nitrosating agent or from a nitric acid catalysed nitrosation, for studies using ^{15}N labelled nitric acid have shown that >80% of the nitro-group in the *para*-nitro-derivative formed is derived from the stoicheiometric HNO_3. We suggest that the *NN*-dimethylanilinium ion is attacked by the nitrosonium ion to form a small concentration of an intermediate which normally breaks down to reform the reactants, but which, in the presence of nitric acid, yields the products listed in the Table.

Support for this comes from the fact that the rate of *N*-deuterium exchange between the ion $PhNDMe_2^+$ and H_2SO_4 is greatly increased in the presence of nitrosonium ions and that, in 85% H_2SO_4, this rate of catalysed deuterium exchange is about equal to the rate of the catalysed nitrations. The deuterium exchange could be explained if the ion $PhNMe_2NO^+$ were the intermediate but the formation of benzidine derivatives among the products of the catalysed nitrations suggests a reaction path involving cation radicals. The main point we now make is that the rates and products of nitration reactions may be sensitive to the amount of nitrous acid present even when there is no obvious reaction between the aromatic substrate and the nitrous acid in the medium used for nitration.

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[1] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Cornell University Press, 2nd Edn, 1969, p. 337.
[2] M. Brickman, J. H. P. Utley, and J. H. Ridd, *J. Chem. Soc.*, 1965, 6851.