

## The Nitration of *N*-Methyl-*N*-nitrosoaniline in Carbon Tetrachloride

By T. G. BONNER and R. A. HANCOCK

*(Royal Holloway College, Englefield Green, Surrey)*

and R. L. WILLIAMS and J. C. WRIGHT

*(Ministry of Aviation, Explosives Research and Development Establishment, Waltham Abbey, Essex)*

AROMATIC nitration by nitric acid in carbon tetrachloride does not appear to have been previously reported, although studies with dinitrogen pentoxide in the presence of nitric acid in this

solvent have been carried out.<sup>1</sup> The present report is concerned with a kinetic study of the mononitration of *N*-methyl-*N*-nitrosoaniline in dilute solutions of pure nitric acid in carbon

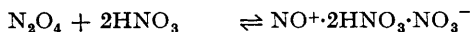
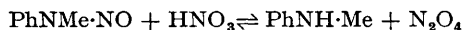
tetrachloride. The reaction order with respect to the aromatic substrate was found to be unity while third-order dependence on the nitric acid concentration is apparent in the range of 5-fold—30-fold excess over the nitrosamine.

Although the *o*-nitro-isomer has received little mention as a concomitant product in nitrations leading to *N*-methyl-*N*-nitroso-*p*-nitroaniline,<sup>2</sup> we have found the two isomers to be formed in almost equimolecular concentration in carbon tetrachloride. This fact was established by chromatographic analysis of the reaction products and by observation of the wavelength of the isobestic point from ultraviolet examinations of the reaction solution.

In order to aid differentiation between the most likely mechanisms (see Scheme) for the nitration of *N*-methyl-*N*-nitrosoaniline (the routes to the *o*-isomer are assumed to be similar to those shown for the *p*-isomer) this compound has been prepared with a 31% <sup>15</sup>N-isotopically-enriched nitroso-group. The isotopic exchange rate between nitric acid and the nitroso-group of the substrate was measured simultaneously with the rate of nitration; the exchange rate for the *p*-nitro-isomer, prepared with a similar percentage enrichment of the nitroso-group, was separately measured under the same conditions.

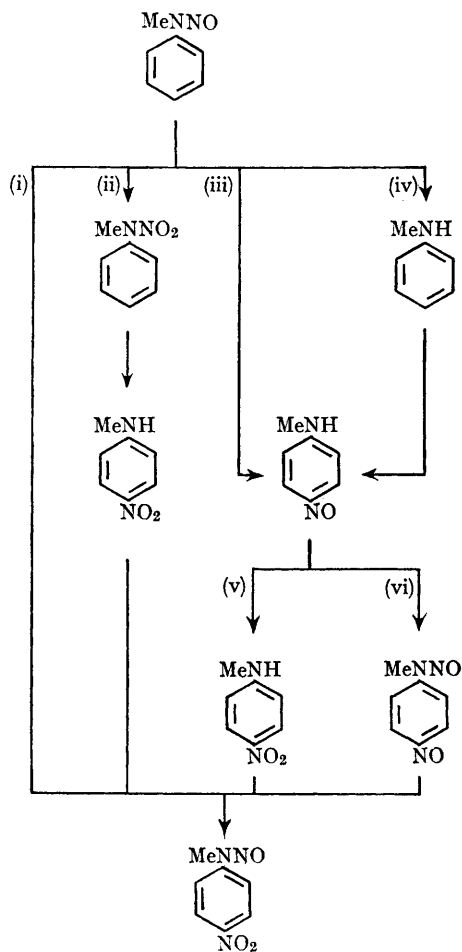
With a ten-fold excess of nitric acid, analysis of the isolated *p*-nitro-product showed that an increase in percentage <sup>15</sup>N-labelling occurred with time, *viz.*, 2% and 5% after 74% and 88% reaction respectively. Slow separation of the NO group from the substrate is evident and hence it appears that route (iv) is operative. Further, pathway (vi) is preferred to (v) by analogy with the results of a separate study<sup>3</sup> on the oxidation of 4-nitrosodiphenylamine by nitric acid.

One interpretation of the third-order dependence of the reaction rate on nitric acid concentration is that two molecules of nitric acid are required to solvate the N<sub>2</sub>O<sub>4</sub> produced in the first step of route (iv) in order to make it an effective *C*-nitrosating species in the aprotic solvent.



A similar interpretation<sup>1</sup> has previously been proposed for the enhancement of aromatic nitration by nitrogen pentoxide with added nitric acid

in carbon tetrachloride in which second- and third-order dependence of the rate on nitric acid concentration was found according to the concentration range employed. Also, association of two molecules of nitric acid with the nitrate ion has been proposed by Gillespie<sup>4</sup> and confirmed by Lynn<sup>5</sup> in 100% nitric acid.



- (i) Direct nitration without denitrosation.
- (ii) Intramolecular nitramine rearrangement.
- (iii) Intramolecular nitrosation.
- (iv) Intermolecular nitrosation.
- (v) Oxidation before *N*-nitrosation.
- (vi) *N*-Nitrosation before oxidation.

(Received, January 5th, 1966; Com. 009.)

<sup>1</sup> V. Gold, E. D. Hughes, C. K. Ingold, and G. H. Williams, *J. Chem. Soc.*, 1950, 2452.

<sup>2</sup> M. Battegay and W. Kern, *Bull. Soc. chim. France*, 1928, 43, 114; H. H. Hodgson and G. Turner, *J. Chem. Soc.*, 1942, 584.

<sup>3</sup> To be published.

<sup>4</sup> R. J. Gillespie, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1950, 2552.

<sup>5</sup> S. Lynn, D. M. Mason, and W. H. Corcoran, *J. Phys. Chem.*, 1955, 59, 238.