

Chemical Polarisation of ^{15}N Nuclei as a Mechanistic Criterion for Nitration Reactions

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Summary The *para*-nitro-product obtained from the nitration of *NN*-dimethylaniline with H^{15}NO_3 in 85–90% sulphuric acid shows strong polarisation of the ^{15}N nuclei, probably as a result of catalysis of the reaction by nitrous acid.

THE possible formation of aromatic radical-cations as intermediates in aromatic nitration has been a matter of speculation for many years.¹ The presence of chemically induced dynamic nuclear polarisation in the products of aromatic nitration would provide evidence of such intermediates; such polarisation has been sought, but it has not hitherto been found.²

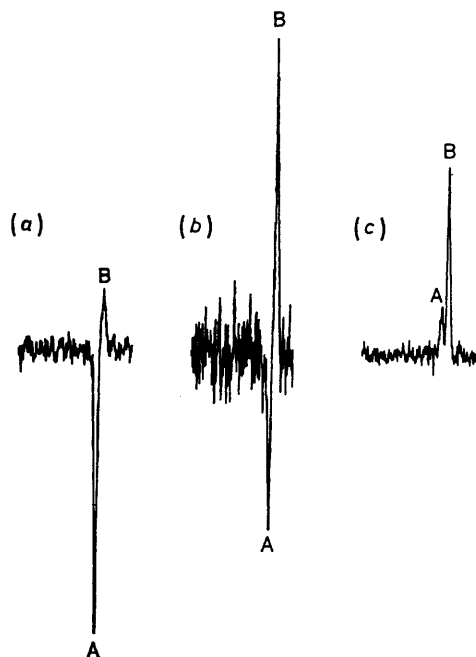
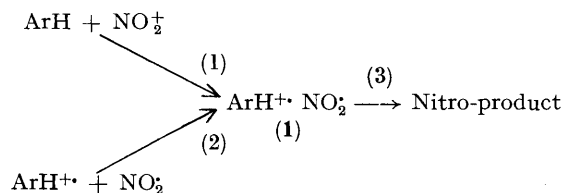


FIGURE. The variation with time of the ^{15}N n.m.r. spectra for the products of nitration of dimethylaniline (0.55 mol dm^{-3}) with H^{15}NO_3 (0.53 mol dm^{-3}) in aqueous sulphuric acid (88%) at 25°C . (a) 3 min (50 pulses); (b) 12 min (100 pulses); (c) 55 min (500 pulses); pulse angle 30° ; pulse repetition time 3 s. A; *p*- $^{15}\text{NO}_2\text{C}_6\text{H}_4\text{NMe}_2$ (δ 8.44); B; *m*- $^{15}\text{NO}_2\text{C}_6\text{H}_4\text{NMe}_2$ (δ 8.90). Values of δ are in p.p.m. for solutions in 72% sulphuric acid up-field from the value for external saturated aqueous $\text{NH}_4^{15}\text{NO}_3$.

We have studied the nitration of *NN*-dimethylaniline with H^{15}NO_3 (95% ^{15}N) in aqueous sulphuric acid at 25°C and have found clear evidence of ^{15}N nuclear polarisation in the *para*-nitro-product. Some results from a typical experiment are illustrated in the Figure. The initial spectrum (a) of this product involves emission with an enhanced signal to noise (S/N) ratio. As the reaction proceeds, this spectrum changes to a weaker absorption signal (c). The *meta*-nitro-product gives an absorption signal with a steady increase in the S/N ratio as the reaction proceeds. This lack of polarisation in the *meta*-nitro-product (and, apparently, also in nitric acid) shows that the polarisation is not generated by an ancillary reaction of the nitric acid and then merely carried over into the nitro-product; the polarisation must

arise from the presence of radical pairs on the reaction path for *para*-nitration.

A commonly suggested path¹ for the formation of radical-cations in nitration involves electron transfer to a nitronium ion to form the radical pair (1) (see the Scheme); competition between the dissociation and recombination reactions of this radical pair could then lead to nuclear polarisation. However, from Kaptein's rules,³ as modified for ^{15}N nuclei,⁴ the recombination product formed in this way [reactions (1) + (3)] should show enhanced absorption in the ^{15}N n.m.r. spectrum.† The observed result would be consistent with the formation of the radical pair (1) from the preformed radicals [reactions (3) + (2)], but the polarisation could also arise in other ways.



SCHEME

The reaction stages which give rise to the observed polarisation have not yet been identified, but we know that the extent of polarisation increases with decreasing acidity and with conditions favouring nitrous acid-catalysed nitration. Indirect evidence for the formation of the radical-cation of *NN*-dimethylaniline during nitrous acid-catalysed nitration has already been given⁶ and the suggested reaction path includes reactions (2) and (3) above. Hence, both the direction of the observed polarisation and the absence of polarisation in the *meta*-nitro-product (which is not formed in the catalysed reaction⁶) are consistent with polarisation *via* nitrous acid-catalysed nitration, even though this catalysis probably contributes little, under the conditions described herein, to the overall rate and product composition.‡

We conclude, therefore, that the polarisation is clear evidence that at least part of the *para*-nitro-product is formed by a reaction involving radical pairs and that this part probably involves the nitrous acid-catalysed reaction.

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† This conclusion follows from the reasonable assumption that the *g*-value of NO_2^{\ddagger} is less than that of the radical-cation under these conditions (see ref. 5). The coupling constant $a(^{15}\text{N})$ in NO_2^{\ddagger} should be negative because of the negative magnetogyric ratio of the ^{15}N nucleus.

‡ The reaction rate and product composition are reasonably close to the values expected for the uncatalysed reaction (ref. 6), but it is difficult to eliminate completely the nitrous acid-catalysed reaction under the conditions described herein since, in such highly acidic media, the conventional nitrous acid scavengers (*e.g.* hydrazine) become relatively ineffective. Comparison with earlier work under slightly different conditions (ref. 6) suggests that the half-life of the reaction described herein should be *ca.* 2–3 min.

¹ For a recent review see Z. V. Todres, *Usp. Khim.*, 1978, **47**, 260.

² I. P. Beletskaya, S. V. Rykov, and A. L. Buchachenko, *Org. Magn. Reson., Spec. Suppl.*, 1973, **5**, 595.

³ R. Kaptein, *Chem. Commun.*, 1971, 732.

⁴ N. A. Porter, G. R. Dubay, and J. G. Green, *J. Am. Chem. Soc.*, 1978, **100**, 920.

⁵ Landolt-Bornstein's 'Numerical Data and Functional Relationships in Science and Technology,' ed. K.-H. Hellwege, Springer-Verlag, Vol. 9, part d2, p. 22 *et seq.*; P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, 1967, p. 129.

⁶ J. C. Giffney and J. H. Ridd, *J. Chem. Soc., Perkin Trans. 2*, 1979, 618.