^{13}C Nuclear Polarisation in the Nitrous Acid Catalysed Nitration of Phenols

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The nitrous acid catalysed nitration of the phenols p-XC$_6$H$_4$OH (X = Me, NO$_2$) gives ^{13}C nuclear polarisation in the products and (for X = Me) also in the starting material.

Evidence from kinetic studies and ^{15}N CIDNP effects[1] has suggested that some nitrous acid catalysed nitrations of phenols involve an ArO$\cdot$ NO$_2\cdot$ radical pair. The corresponding ^{13}C nuclear polarisation from the aromatic component of this radical pair has now been observed.

The nitration of p-cresol by nitronium ions is known to involve both direct attack at the 2-position and *ipso*-attack at the 4-position followed by rearrangement.[2] This appears to be true also for the nitrous acid catalysed nitration of p-cresol in acetic anhydride[3]† and signals characteristic of such *ipso*-intermediates appear in the ^{13}C n.m.r. spectra during reaction but are absent when rearrangement is complete. Our assignment of these signals is shown in Table 1. For the C-3, C-4, and methyl carbons, the signals are close to those found for the corresponding *ipso*-intermediate in the nitration of N,N-dimethyl-p-toluidine.[5]

These n.m.r. spectra show nuclear polarisation in the starting material, the *ipso*-intermediate, and the product. This nuclear polarisation is observed at those carbons which do not carry hydrogen atoms, presumably because of the longer relaxation times involved. Thus the results for the aromatic region (see Figure 1) show the signals P1 and S4 to be initially in emission. The evidence for enhanced absorption comes from the changes in the relative peak heights during reaction. The signals I3, P5, P3, and P6, coming from the C–H groups, grow steadily during nitration but the signals P2 and P4 are initially strong and then decrease. The relative peak heights of signals P4 and P5 change by a factor of 9 during reaction. The phase of the nuclear polarisation at the seven centres involved is indicated in Table 1.

The present work supports and provides further details concerning the radical pair interpretation[1] of nitrous acid catalysed nitration. Taking, as before,[1b] $(g_{\mathrm{ArO}} - g_{\mathrm{NO2}})$ as positive and using MNDO calculations for the signs of the hyperfine coupling constants in the phenoxyl radical, the phase of the polarisation at each of the seven centres indicated in Table 1 accords with the application of Kaptein's rules[6] to the mechanism in Scheme 1. This agreement provides the clearest evidence that the phenoxyl radical is one component of the radical pair (**4**) that generates the polarisation and shows also that the polarisation does not derive from the radical pair generated by the initial electron transfer (**1**) → (**5**) since, by Kaptein's rules, the opposite polarisation should then be found. In addition, the presence of polarisation in the starting material indicates that the formation of the phenoxyl radical must be reversible; this step cannot therefore, under these conditions, be rate-determining.

The above reactions are followed by the rearrangement[3a] of the *ipso*-intermediate (**2**) to the nitro-product (**3**), but this reaction is considerably slower and we do not believe that it

Table 1. ^{13}C Chemical shifts (p.p.m. from Me$_4$Si) for p-cresol (**1**, R = Me), the *ipso*-intermediate (**2**, R = Me), and 2-nitro-p-cresol (**3**, R = Me). The capital letters indicate the phase of the nuclear polarisation (A, enhanced absorption: E, emission).

Compound	C-1	C-2	C-3	C-4	C-5	C-6	Me
(**1**), R = Me	154.6A	115.2	130.0	128.9E	130.0	115.2	19.8
(**2**), R = Me	184.2E	130.0	143.9	85.0A	143.9	130.0	25.1
(**3**), R = Me	152.9E	133.4A	124.3	130.5A	139.0	119.7	19.5

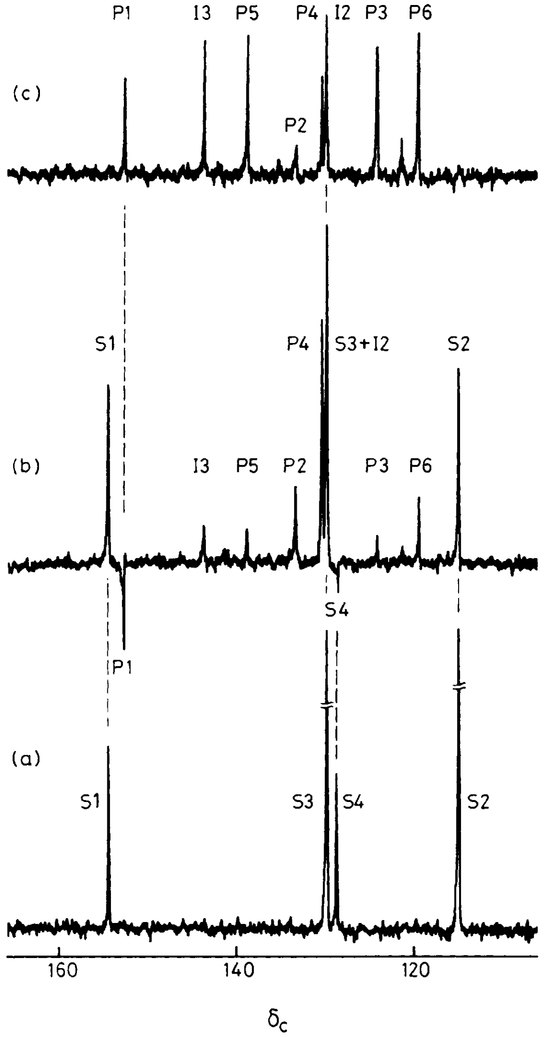

Figure 1. ^{13}C N.m.r. spectra taken during the nitration of p-cresol (1 mol dm^{-3}) with acetyl nitrate (1 mol dm^{-3}) in acetic anhydride at 22 °C: (a) before addition of the acetyl nitrate; (b) at 2—7 min, and (c) at 27—32 min after mixing. The assignment of the signals is indicated by S (starting material), I (*ipso*-intermediate), and P (2-nitro-p-cresol) followed by the number of the carbon atom. All spectra involved 128 pulses, pulse angle 28°, pulse repetition time 1.9 s.

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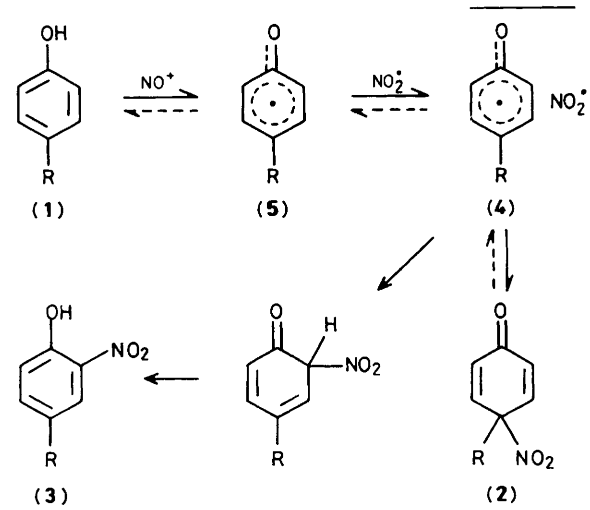
† The high reaction rate and the ^{15}N nuclear polarisation indicate nitrous acid catalysis; this accords with earlier evidence on the nitration of phenols in this medium.[4]



Scheme 1

contributes to the polarisation reported above. Another slower reaction is the acetylation of the phenol and some weak peaks, deriving from the ester formed, are present in Figure 1(c).

Less intense ^{13}C nuclear polarisation of the same phase has been observed in the product of the nitrous acid catalysed nitration of *p*-nitrophenol under the conditions used previously for studies by ^{15}N n.m.r. spectroscopy[1b] but there was no obvious ^{13}C-polarisation in the starting material.

One of us (M. A.) thanks the C.V.C.P. for the award of an Overseas Research Studentship and another (S. T.) thanks the S.E.R.C. for a studentship.

Received, 15th April 1987; Com. 511

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