^{15}N Nuclear Polarisation in Nitration and Related Reactions. Part 6.[1] A Comparison of ^{15}N and ^{13}C CIDNP Effects in the Nitration of Phenols

John H. Ridd,*[a] **Susan Trevellick**[a] **and John P. B. Sandall***[b,†]
[a] *Chemistry Department, University College, 20 Gordon Street, London WC1H 0AJ, UK*
[b] *Chemistry Department, Royal Holloway and Bedford New College, Egham Hill, Egham, Surrey TW20 0EX, UK*

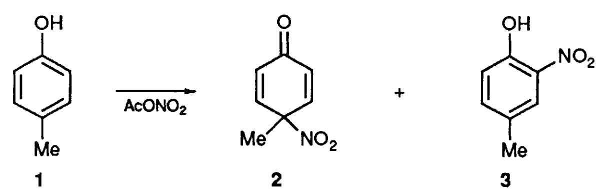
In the nitration of 4-methylphenol in acetic anhydride, the products from nitration at the 2-position and *ipso*-attack at the 4-position show strong emission signals in the ^{15}N NMR spectrum during reaction. In the same reaction, the ^{13}C NMR spectrum shows emission and enhanced absorption signals for the substrate and both products. The nitration of 2-methyl-6-nitrophenol under similar conditions shows similar ^{15}N nuclear polarisation and similar ^{13}C nuclear polarisation in the substrate but the polarisation in the product is complicated by the fast rearrangement of the *ipso*-intermediate. The pattern of nuclear polarisation in these substrates identifies the phenoxy radical as one component of the radical pair generating the polarisation and accords with the accepted mechanism for nitrous acid catalysed nitration.

The previous parts of this series[1,2] have presented evidence from CIDNP effects that a number of nitration reactions occur through the radical pair $ArH^{\cdot+}NO_2^{\cdot}$. This conclusion has been supported by kinetic studies[3] and is in general, but not complete, accord with the conclusions of electrochemical and related work.[4]

However, with the exception of a few studies on ^{15}N-labelled amines,[2d] the above arguments from CIDNP effects have been based entirely on the polarisation deriving from the NO_2 component of the radical pair. In principle, the ^{15}N CIDNP effects should be accompanied by ^1H and ^{13}C nuclear polarisation deriving from the aromatic component of the radical pair. Unfortunately, these effects are more difficult to detect as a consequence of the shorter relaxation times and lower hyperfine coupling constants found with these nuclei (in comparison with the $^{15}NO_2$ group and $^{15}NO_2$ radical). The ^{13}C CIDNP effects have now been detected in the nitration reactions of some phenols.

Results

Three phenols were studied (4-methylphenol, 2-methyl-6-nitrophenol and 4-nitrophenol) and all showed ^{13}C CIDNP effects during nitration in acetic anhydride. The nitration of 4-methylphenyl acetate was also investigated but no ^{15}N or ^{13}C CIDNP effects were found.



Scheme 1

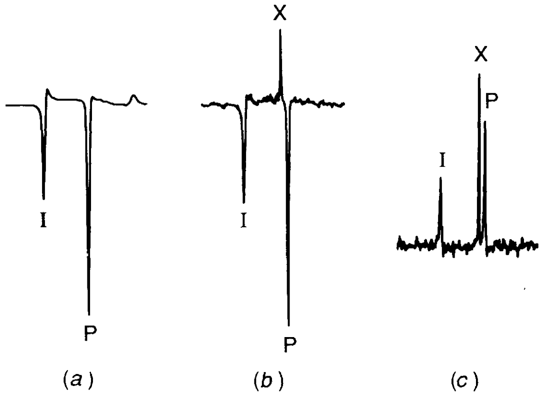


Fig. 1 ^{15}N NMR spectra taken during the nitration of 4-methylphenol with ^{15}N-labelled acetyl nitrate in acetic anhydride with the NMR spectrometer set at 2 °C: (*a*) 1.00–2.16 min; (*b*) 12–13.3 min; (*c*) 22.3–24 min. *I*, *ipso*-intermediate **2**; P, 4-methyl-2-nitrophenol; X, standard ([$^{15}N_2$]dinitromesitylene); for chemical shifts, see Experimental section.

4-*Methylphenol*.—The nitration of 4-methylphenol in aqueous sulfuric acid is known[5] to give rise to both 2-substitution and *ipso*-attack (Scheme 1). In the present work, 4-methylphenol was nitrated in acetic anhydride and the same two products were formed together with a small amount of 4-methyl-2,6-dinitrophenol. The major product is 4-methyl-2-nitrophenol (70%). The reaction was followed from the change in the ^1H NMR absorption of the aromatic protons[6] and our values of the chemical shifts of the signals for the *ipso*-intermediate **2** accord well with those reported previously.[7] The *ipso*-intermediate **2** is known[8] to rearrange to give 4-methyl-2-nitrophenol but, at the temperature used in the present work (at or below 22 °C), that rearrangement is too slow to interfere with the results reported here. From the ^1H NMR spectra, the nitration at 22 °C of 4-methylphenol (1 mol dm^{-3}) with acetyl nitrate (1 mol dm^{-3}) prepared from 100% nitric acid in acetic anhydride has a half-life of *ca.* 3.5 min.

When the reaction is carried out using ^{15}N labelled nitric acid, very strong emission signals are seen for the labelled nitrogen atom in the *ipso*-intermediate **2** and in the 2-nitro product **3** (Fig. 1). The strength of these signals can be seen from the absence of the signal for the standard ([$^{15}N_2$]-dinitromesitylene) from the first spectrum. These strong emission signals are characteristic of nitration by the nitrous acid catalysed mechanism[2a,b] (in contrast, electron transfer to the nitronium ion gives enhanced absorption[1]) and so it appears that nitrous acid catalysed nitration is a significant component of the overall reaction. This is consistent with earlier studies, for the nitration of phenol in acetic anhydride shows auto-

---

[†] *Present address:* Chemistry Department, University of Exeter, Stocker Road, Exeter EX4 4QD, UK.

Table 1 Assignment of the ^{13}C chemical shifts for the aromatic carbon atoms in the nitration of 4-methylphenol (Scheme 1) and 2-methyl-6-nitrophenol (Scheme 3)

	$\delta_C(Ac_2O)$					
Compound	C-1	C-2	C-3	C-4	C-5	C-6
1	154.6	115.2	130.0	128.9	130.0	115.2
2	184.2	130.0	143.9	85.0	143.9	130.0
3	152.9	133.4	124.3	130.5	139.0	119.7
5	153.5	129.5	138.5	119.8	112.8	133.6
7	157.7	131.9	131.5	139.4	119.3	132.8

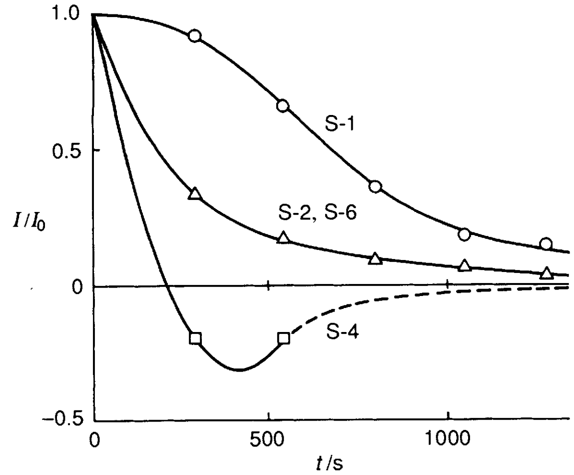


Fig. 2 The changes with time in the intensities of the ^{13}C signals (relative to $t = 0$) for 4-methylphenol **1** during nitration by acetyl nitrate in acetic anhydride at 22 °C. The assignment of the signals is indicated by S (starting material) followed by the number of the carbon atom.

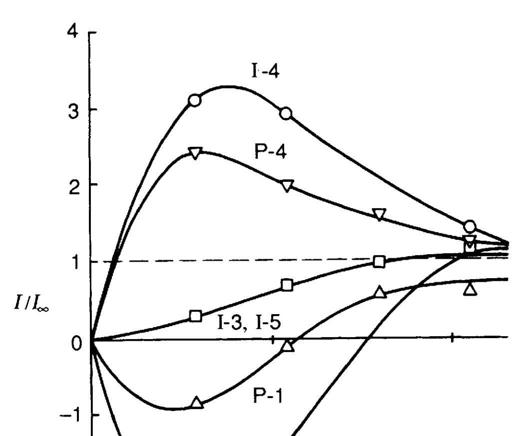


Fig. 3 The changes with time in the intensities of the ^{13}C signals (relative to $t = \infty$) for the *ipso*-intermediate **2** and 4-methyl-2-nitrophenol **3** during the formation of these compounds in the nitration of 4-methylphenol by acetyl nitrate in acetic anhydride at 22 °C. The assignment of the signals is indicated by I (*ipso*-intermediate) and P (2-nitro product) followed by the number of the carbon atom.

catalysis and the reaction rate is greatly increased by traces of nitrous acid.[9] The mechanism that has been proposed[2b,3] for this nitrous acid catalysed nitration of phenols is shown in Scheme 2. In this scheme, the middle reaction is enclosed in parentheses since this is considered to show only the stoichiometry of this stage; the mechanism must be more complex.[2a] The nuclear polarisation is considered to be generated by the radical pair **4**.

Table 2 Comparison of the observed and (in parentheses) calculated phases of ^{13}C nuclear polarisation for the aromatic carbon atoms in the nitration of 4-methylphenol (Scheme 1) and 2-methyl-6-nitrophenol (Scheme 3). A = Enhanced absorption; E = emission

	Phase of nuclear polarisation					
Compound	C-1	C-2	C-3	C-4	C-5	C-6
1	A (A)	– (E)	– (A)	E (E)	– (A)	– (E)
2	E (E)	– (A)	– (E)	A (A)	– (E)	– (A)
3	E (E)	A (A)	– (E)	A (A)	– (E)	– (A)
5	A (A)	E (E)	– (A)	– (E)	– (A)	E (E)

$$ArO^- + NO^+ \rightleftharpoons ArO^{\bullet} + NO^{\bullet}$$

$$(NO^{\bullet} + NO_2^+ \rightleftharpoons NO^+ + NO_2^{\bullet})$$

$$NO_2^{\bullet} + ArO^{\bullet} \rightleftharpoons \underset{\mathbf{4}}{\overline{NO_2^{\bullet}\ ArO^{\bullet}}} \longrightarrow \text{Nitro products}$$

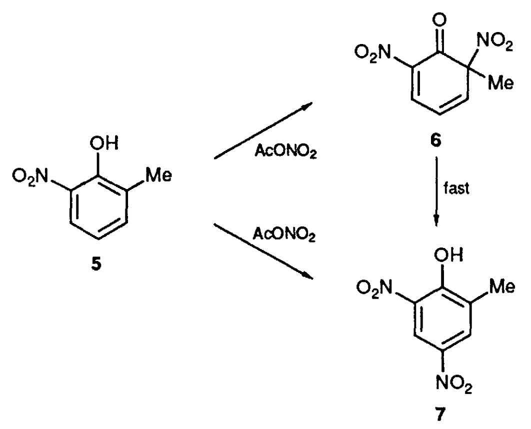
Scheme 2

The reaction has also been followed by ^{13}C NMR spectroscopy and our assignment of the signals is shown in Table 1. The value of δ_C 85.0 for C-4 in the *ipso*-intermediate is very similar to the values for the corresponding carbon atoms in the *ipso*-intermediates derived from the nitration of 4,*N*,*N*,-trimethylaniline and 2,4,6,*N*,*N*,-pentamethylaniline (δ_C 86.2, 87.7).[10] The conditions for the ^{13}C runs differed from those for the ^{15}N runs in the temperature and in the concentration of nitric acid used to prepare the nitrating mixture (see Experimental Section), but both nitrating solutions were left for sufficiently long (25 min at 0 °C) to ensure essentially complete conversion of the nitric acid into acetyl nitrate.

The ^{13}C NMR signals for the carbon atoms bonded to hydrogen showed no obvious evidence of nuclear polarisation but the signals for C-1 and C-4 (and, for 4-methyl-2-nitrophenol, also C-2) changed in an unusual way during the course of the reaction. The variation of the signal intensity (I) with time is shown for the starting material in Fig. 2 (in terms of I/I_0) and for the two main products in Fig. 3 (in terms of I/I_∞). To avoid complications from the subsequent rearrangement of the *ipso*-intermediate, the 'infinity time' was taken as 1746 s.

The Figures show that, for the starting material, the signal for C-4 appears initially in emission, and that for C-1 shows evidence for enhanced absorption (in comparison with the signal for C-2 and C-6). For the products, the signals for C-1 appear initially in emission and those for C-4 clearly show enhanced absorption. The maximum enhancement in the intensity of the signals (a factor of *ca.* 3) is, however, much less than that observed in the ^{15}N NMR studies. Some of the spectra were reproduced in our preliminary publication[11] and the complete set of results is compared in Table 2 with the results expected on the basis of Kaptein's rules.[12]

2-*Methyl*-6-*nitrophenol*.—The ^{13}C NMR spectra taken during the nitration of 2-methyl-6-nitrophenol by acetyl nitrate in acetic anhydride at 8 °C showed only the signals arising from the starting material and the 4,6-dinitro product. The assignment of the signals is included in Table 1 and some typical spectra are shown in Fig. 4. However, this does not mean that the extent of *ipso*-attack at the methyl group is negligible. When the reaction was followed by ^{15}N NMR spectroscopy using ^{15}N labelled acetyl nitrate at −25 °C, two strong emission signals



Scheme 3

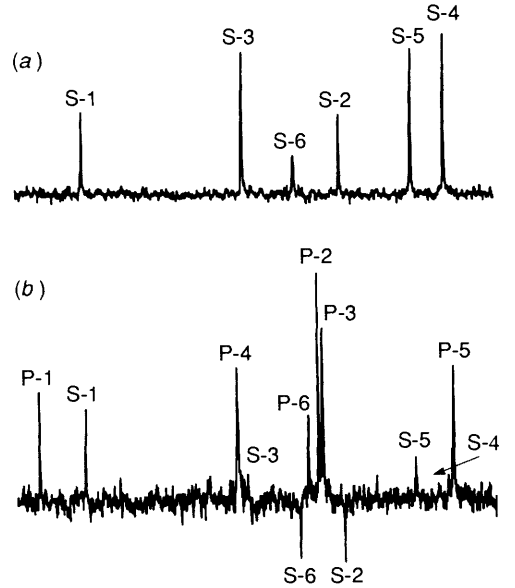


Fig. 4 ^{13}C NMR spectra taken during the nitration of 2-methyl-6-nitrophenol by acetyl nitrate in acetic anhydride at 8 °C: (*a*) before addition of the acetyl nitrate and (*b*) 4.35–8.55 min after mixing. The assignment of the signals is indicated by S (starting material, **5**) and P (2,4-dinitro product, **7**) followed by the number of the carbon atom. For chemical shifts, see Table 1.

were seen analogous to those shown for the nitration of 4-methylphenol in Fig. 1; these have been assigned to the *ipso*-intermediate **6** and the 4,6-dinitro product **7** (Scheme 3). Separate studies[6] have shown that the rate of rearrangement of the *ipso*-intermediate **6** is much faster than that of the *ipso*-intermediate **2**. It appears therefore that, at 8 °C, the rate of this rearrangement is too fast for the ^{13}C NMR signals of the *ipso*-intermediate to appear in the spectra.

The signals for the starting material in Fig. 4 show obvious evidence of CIDNP effects: emission signals are seen for C-2 and C-6, and enhanced absorption for C-1 (relative to the absorption for C-3, C-4 and C-5). A comparison of these results with those calculated on the basis of Kaptein's rules[12] is included in Table 2. A similar analysis has not been attempted for the signals corresponding to the product because this is formed in two ways (Scheme 3) and a comparison of the ^{15}N NMR spectra for the overall reaction and the separate rearrangement of the *ipso*-intermediate shows that the two pathways have opposing CIDNP effects.[6]

Other Substrates.—Measurements have been made[13] on the ^{13}C NMR spectra of reaction mixtures during the nitration of 4-nitrophenol in aqueous trifluoroacetic acid under the same conditions as used previously for studying the ^{15}N CIDNP effects in nitrous acid catalysed nitration.[2b] For the 2,4-dinitrophenol formed, the ratios of the intensities of the signals for the C-2 and C-4 atoms to that of the C-3 atom was greater at the start of the reaction than at the end of reaction by a factor of up to 1.6. These are the carbon atoms that would be expected to show enhanced absorption[12] but the effect is not much greater than experimental error. No ^{13}C nuclear polarisation was detected in the substrate.

The nitration of 4-methylphenyl acetate in acetic anhydride has been studied under the same conditions as that of 4-methylphenol but no ^{15}N or ^{13}C CIDNP effects were detected. Since this could be a consequence of the slower rate of reaction, the work was repeated using sulfuric acid (0.2% w/w) as a catalyst but again no CIDNP effects were found.

Discussion

Since the ^{15}N CIDNP effects reported here accord with those for nitrous acid catalysed nitration[2] and since no CIDNP effects were found in the nitration of 4-methylphenyl acetate, the observed CIDNP effects almost certainly reflect the incursion of the nitrous acid catalysed mechanism of nitration and not the underlying mechanism of nitration by acetyl nitrate. One of the substrates studied (4-nitrophenol) is already known to be subject to nitrous acid catalysed nitration,[2b,3a] and the other substrates should be equally, or more, easily oxidised. The CIDNP effects will therefore be discussed in terms of the reaction path for nitrous acid catalysed nitration shown in Scheme 2.

In this Scheme, the nuclear polarisation is considered to derive from the radical pair **4**. An emission signal in the ^{15}N NMR spectrum during nitration has been shown previously to be consistent with this mechanism[2a,b] and so the ^{15}N signals shown in Fig. 1 will not be discussed further. The principal purpose of the present discussion is to consider to what extent the observed CIDNP effects in the ^{13}C NMR spectrum are also consistent with this interpretation.

The rule[12] for determining the phase of the ^{13}C polarisation at atom *i* in the reactions studied here is given by eqn. (1). In this

$$\Gamma = \mu\varepsilon(g_{\mathrm{ArO}\cdot} - g_{\mathrm{NO_2}\cdot})a_i \qquad (1)$$

equation, the sign of Γ determines the phase of the polarisation (+, A; −, E), the sign of μ is determined by how the radical pair is formed (+, encounter of free radicals; −, direct electron transfer), and the sign of ε is determined by how the products are formed (+, by radical combination; −, by escape from cage). When the polarisation is derived from the radical pair **4** in Scheme 2, μ must be positive and ε is positive for the products and negative for the substrate. The sign of the *g*-factor difference is known to be positive because phenoxy radicals[14] have *g*-factors in the range 2.003–2.007 and there are good reasons[2a,15] for believing that the *g*-factor of the $NO_2^{\cdot}$ radical is 2.000. Thus, for atoms in the products, the sign of the ^{13}C polarisation should be the same as that of the hyperfine coupling constant a_i, and for the atoms in the substrate, the opposite should be true.

Unfortunately, there is little direct evidence on the signs of these hyperfine coupling constants and so the results have been obtained from AM1 calculations[16] of the sign of the spin populations in the C(2s) orbitals (Table 3). The use of the C(2s) orbitals for this purpose accords with earlier discussions of the derivation of ^{13}C hyperfine coupling constants by semi-empirical MO calculations.[17] The signs are the same for all three radicals (C-1, C-3, C-5, negative; C-2, C-4, C-6, positive) and have been combined with the other quantities above to give the calculated phases of nuclear polarisation in Table 2. For those atoms for which polarisation can be detected, the

Table 3 AM1 calculations of the spin populations in the C(2s) orbitals of the aromatic carbon atoms of substituted phenoxy radicals

	Spin population × 10^2					
Substituents	C-1	C-2	C-3	C-4	C-5	C-6
4-Me	−2.33	3.66	−3.28	4.21	−3.28	3.66
2-Me,6-NO_2	−2.35	4.03	−3.40	3.89	−2.98	3.98
4-NO_2	−2.47	3.74	−3.23	4.67	−3.23	3.74

Table 4 Assignment of the ^1H chemical shifts for the aromatic hydrogen atoms in the nitration of 4-methylphenol (d = doublet; s = singlet)

Compound (Scheme 1)	$\delta_H(Ac_2O)$			
	2-H	3-H	5-H	6-H
1	7.05(d)	6.77(d)	6.77(d)	7.05(d)
2	6.37(d)	7.2(d)	7.2(d)	6.37(d)
3	—	7.89(s)	7.45(d)	7.05(d)

Table 5 ^{15}N Chemical shifts[a] in acetic anhydride measured relative to [^{15}N]nitrobenzene

Compound	δ
ipso-Intermediate **2**	−19.0
4-Methyl-2-nitrophenol	−2.0
ipso-Intermediate **6**	−10.0 (N-2)
2-Methyl-6-nitrophenol	−2.4
2-Methyl-4,6-dinitrophenol	4.7 (N-4)
	1.7 (N-6)

[a] Low field values negative.

agreement between the observed and calculated results is complete. The absence of obvious polarisation on the carbon atoms of CH groups is as expected from the shorter relaxation times of these nuclei. The results are entirely consistent with the identification of the phenoxy radical as the other component of the radical pair and also with the formation of the radical pair by the diffusion together of the two radicals (and not by direct electron transfer to nitronium ions). Also, since the *g*-value of nitric oxide[18] is also less than that of the phenoxy radicals, the radical pair formed by electron transfer to the nitrosonium ion (Scheme 2, line 1) can be eliminated as the source of the polarisation since this would give the opposite phase to that observed (since μ would then be negative).

The very considerable polarisation found in the substrate when this is 4-methylphenol (Fig. 2) shows not only that there must be a significant probability of escape from the radical pair **4** but also that the initial oxidation (Scheme 2, line 1) must be reversible under the conditions of reaction. For nitrous acid catalysed nitration in aqueous nitric acid, this has already been deduced from kinetic studies[3a] but it is helpful to have this further evidence of reversibility from ^{13}C nuclear polarisation.

Experimental

Materials.—4-Nitrophenol, 4-methylphenol, 4-methyl-2-nitrophenol, 4-methyl-2,6-dinitrophenol, 4-methylphenyl acetate and 2-methyl-4,6-dinitrophenol were obtained from Aldrich in grades of the highest purity available. 2-Methyl-6-nitrophenol was prepared by a conventional nitration[19] of 2-methylphenol followed by separation of the 4-nitro and 6-nitro isomers by steam distillation and sublimation. The product had m.p. 69–70 °C (lit.,[20] 70 °C). Acetic anhydride (BDH) was purified by distillation (b.p. 138–140 °C). The sulfuric acid was AnalaR grade (98%). Nitric acid (100%) was obtained by vacuum distillation at 0 °C of a 1:1 (v/v) mixture of fuming nitric acid (AnalaR, *d.* 1.5) and sulfuric acid (AnalaR, 98%). [^{15}N]Nitric acid (99% ^{15}N) was obtained from M. S. D. Isotopes as a 45% aqueous solution; the 100% acid was obtained by vacuum distillation of a 2.3:1 mixture of sulfuric acid and the aqueous acid as described above. The [$^{15}N_2$]dinitromesitylene was prepared by Dr. A. H. Clemens.

Nitration Reactions.—For the runs using 4-methylphenol and followed by ^1H and ^{13}C NMR spectroscopy, a solution (1 cm^3, 2 mol dm^{-3}) of nitric acid (100%) in acetic anhydride was maintained at 0 °C for 20 min and then added to a solution (1 cm^3, 2 mol dm^{-3}) of 4-methylphenol also at 0 °C. The reaction mixture was then heated to 22 °C and the ^1H or ^{13}C NMR spectra observed. The ^{13}C NMR spectra involved 128 pulses with a pulse angle of 28° and a pulse repetition time of 1.9 s. The chemical shifts were measured relative to dichloromethane as an internal standard taking this to have δ_H 5.48; δ_C 54.7. The assignment of the ^1H chemical shifts is shown in Table 4; in addition a small signal was observed at δ_H 8.13 corresponding to 4-methyl-2,6-dinitrophenol. Weak ^1H and ^{13}C NMR signals for 4-methyl-2-nitrophenyl acetate were also found after *ca.* 30 min resulting from the slow acetylation of the 4-methyl-2-nitrophenol formed. The identification of all of the above signals (with the exception of those for the *ipso*-intermediate **2**) is based on comparison with the NMR spectra of authentic compounds.

The nitration of 2-methyl-6-nitrophenol was carried out in a similar way but the concentrations of the reactants had to be halved because of the low solubility of the product (2-methyl-4,6-dinitrophenol). Also, to speed up the nitration reaction, some sulfuric acid (0.2%) was added to the nitrating solution giving a final concentration of 0.1% (w/w) in the final reaction mixture. The solutions of nitric acid in acetic anhydride and of 2-methyl-6-nitrophenol in acetic anhydride were cooled to −78 °C before mixing and allowed to warm up to 8 °C in the NMR spectrometer.

The ^{15}N NMR study of the nitration of 4-methylphenol was carried out by mixing aqueous solutions of $H^{15}NO_3$ (as supplied) with acetic anhydride and, in consequence, the final reaction mixture in acetic anhydride also contained acetic acid (3.5 mol dm^{-3}). For concentrations of nitric acid $\geq$ 1 mol dm^{-3}, the catalytic effect of added acetic acid on nitration by the normal mechanism in acetic anhydride is very slight[21] (at least up [HOAc] = 2.2 mol dm^{-3}) but, possibly because the present reactions involve nitrous acid catalysis, the rate of reaction was markedly greater than for the runs described above. In consequence, it was found more convenient to arrange for the two reactant solutions to mix within the NMR instrument.

A solution of 4-methylphenol (1 cm^3, 2 mol dm^{-3}) in acetic anhydride was placed in an NMR tube containing a glass rod and frozen in liquid nitrogen in such a way as to leave a coaxial cylindrical cavity. The solution of nitric acid (1 cm^3, 2 mol dm^{-3}) in acetic anhydride was then injected into this cavity using a syringe and the whole system frozen again in liquid nitrogen. The reaction mixture was then brought to 2 °C within the NMR instrument and the ^{15}N NMR spectra measured. The spectra (Fig. 1) involved 16 pulses with a pulse angle of 45° and a pulse repetition time of 4.4 s.

For the ^{15}N NMR study of the nitration of 2-methyl-6-nitrophenol, [^{15}N]nitric acid (100%) was used and the procedure followed that described above for the study by ^{13}C NMR spectroscopy except that the temperature was reduced to −25 °C to observe the signal for the *ipso*-intermediate **6**. The spectra involved 24 pulses with a pulse angle of 45° and a pulse repetition time of 10.8 s. The ^{15}N chemical shifts are given in Table 5.

The studies on 4-nitrophenol were carried out in aqueous trifluoroacetic acid (90% w/w) at 25 °C using nitric acid (0.38 mol dm^{-3}) and 4-nitrophenol (0.4 mol dm^{-3}). The nitration of 4-methylphenyl acetate was carried out as described for 4-methylphenol except that sulfuric acid (0.2%) was present in some runs to increase the reaction rate. For the ^{13}C NMR spectra, the reactants were mixed at 0 °C and the reaction mixture brought to 22 °C in the NMR instrument.

MO Calculations.—The calculations (Table 3) were carried out by the MNDO self-consistent field method (AM1 Hamiltonian[16]) running MOPAC (Version 5.00) on a VAX 8600 at Royal Holloway and Bedford New College. A complete geometry optimisation was carried out with an unrestricted Hartree–Fock (UHF) calculation for each radical. As expected, spin annihilation was incomplete ($\langle S^2 \rangle$ *ca.* 1.1) but the sign of the spin density should be reliable.

Instruments.—The ^1H NMR spectra were run on a JEOL JS-100 spectrometer; the ^{13}C and ^{15}N NMR spectra were run on a Varian XL200 spectrometer.

Acknowledgements

One of us (S. T.) thanks the SERC for a studentship.

References

1 Part 5. J. F. Johnston, J. H. Ridd and J. P. B. Sandall, *J. Chem. Soc., Perkin Trans. 2*, 1991, 623.
2 (*a*) A. H. Clemens, J. H. Ridd and J. P. B. Sandall, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1659; (*b*) 1984, 1667; (*c*) 1985, 1227; (*d*) A. H. Clemens, P. Helsby, J. H. Ridd, F. Al-Omran and J. P. B. Sandall, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1217.
3 (*a*) M. Ali and J. H. Ridd, *J. Chem. Soc., Perkin Trans. 2*, 1986, 327; (*b*) U. Al-Obaidi and R. B. Moodie, *J. Chem. Soc., Perkin Trans. 2*, 1985, 467; (*c*) L. R. Dix and R. B. Moodie, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1097.
4 For a summary of the present position, see J. H. Ridd, *Chem. Soc. Rev.*, 1991, **20**, 149.
5 R. G. Coombes, J. G. Golding and P. Hadjigeorgiou, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1451.
6 S. M. Trevellick, PhD. Thesis, London, 1989.
7 C. E. Barnes, K. S. Feldman, M. W. Johnson, H. W. H. Lee and P. C. Myhre, *J. Org. Chem.*, 1979, **44**, 3925.
8 C. E. Barnes and P. C. Myhre, *J. Am. Chem. Soc.*, 1978, **100**, 973.
9 J. G. Hoggett, R. B. Moodie and K. Schofield, *J. Chem. Soc., Chem. Commun.*, 1969, 605.
10 F. Al-Omran, K. Fujiwara, J. C. Giffney, J. H. Ridd and S. R. Robinson, *J. Chem. Soc., Perkin Trans. 2*, 1981, 518.
11 M. Ali, J. H. Ridd, J. P. B. Sandall and S. Trevellick, *J. Chem. Soc., Chem. Commun.*, 1987, 1168.
12 R. Kaptein, *J. Chem. Soc., Chem. Commun.*, 1971, 732.
13 M. Ali, PhD. Thesis, University of London, 1991.
14 Landolt-Bornstein, *Numerical Data and Functional Relationships in Science and Technology*, ed. H. Fischer, Springer-Verlag, Berlin, 1988, New Series, Vol. II/17, Part e, pp. 38–44.
15 J. R. Morton, K. F. Preston and S. J. Strach, *J. Phys. Chem.*, 1979, **83**, 533.
16 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
17 J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, 1970, p. 128.
18 Landolt-Bornstein, *Numerical Data and Functional Relationships in Science and Technology*, ed. K.-H. Hellwege, Springer-Verlag, Berlin, 1980, Vol. II/9, Part a, pp. 96.
19 A. I. Vogel, *Textbook of Practical Organic Chemistry*, Longman, 1st edn., 1948, p. 648.
20 M. J. Astle and W. P. Cropper, *J. Am. Chem. Soc.*, 1943, **65**, 2395.
21 S. R. Hartshorn, R. B. Moodie and K. Schofield, *J. Chem. Soc. B*, 1971, 1256.

Paper 1/05655G
Received 6*th November* 1991
Accepted 16*th January* 1992