ipso-Attack at the 4-Position in the Nitration of 4-Nitrophenol

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The nitrous acid catalysed nitration of 4-nitrophenol in trifluoroacetic acid leads to *ca.* 22% *ipso*-attack at the 4-position followed by a 1,3-rearrangement that appears to be intramolecular.

The nitration of 4-nitrophenol (0.39 mol dm^{-3}) with nitric acid (0.39 mol dm^{-3}) in trifluoroacetic acid at 21 °C goes cleanly to 2,4-dinitrophenol but shows some auto-catalysis. The reaction is inhibited by azide ions and catalysed by nitrous acid. When the reaction is carried out using ^{15}N-labelled 4-nitrophenol and unlabelled nitric acid, the ^{15}N n.m.r. spectrum of the product shows that the 2-nitro-group is 11% labelled with ^{15}N [based on integration of a spectrum with 2400 pulses; *cf.* Figure 1(a)]. The use of a two-fold excess of nitric acid does not significantly reduce the extent of labelling at this position; the main reaction cannot therefore involve the exchange of the labelled nitrogen with the nitric acid. When the reaction is carried out using ^{15}N-labelled nitric acid and unlabelled 4-nitrophenol, the final ^{15}N n.m.r. spectrum shows a similar extent of ^{15}N-labelling at the 4-position [Figure 1(b)].

By analogy with earlier work on nitrous acid catalysed nitration[1] and on the 1,3-rearrangement of nitro-groups,[2] we

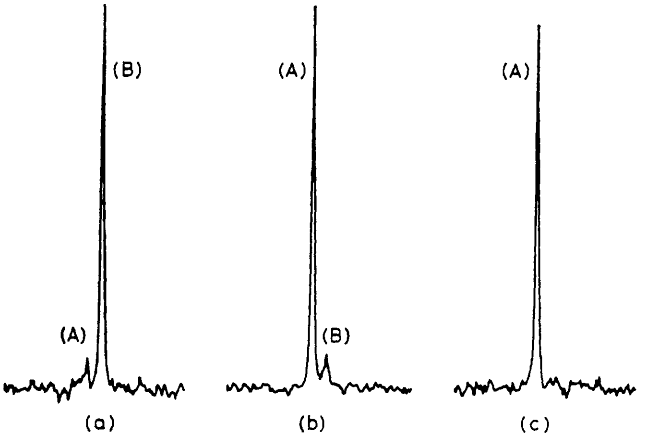
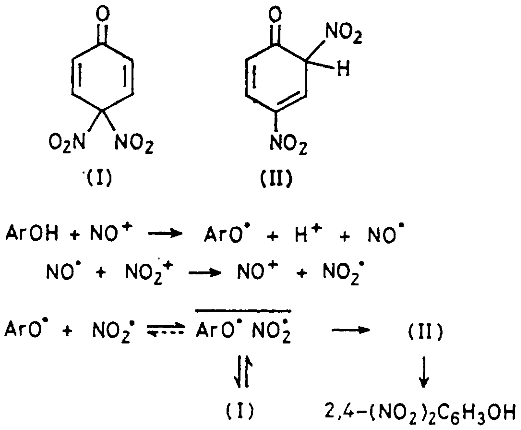


Figure 1. ^{15}N N.m.r. spectra of 2,4-dinitrophenol after the completion of the reaction in trifluoroacetic acid at 21 °C of (a) 4-$^{15}NO_2C_6H_4OH$ + HNO_3; (b) 4-$NO_2C_6H_4OH$ + $H^{15}NO_3$; and (c) 4-$NO_2C_6H_4OMe$ + $H^{15}NO_3$ followed by demethylation. (A) 2-$^{15}NO_2$ (δ 5.64); (B) 4-$^{15}NO_2$ (δ 7.39). Number of pulses *ca.* 300, pulse delay 30 s, pulse angle 25°. Values of δ are in p.p.m. upfield from $Ph^{15}NO_2$ as an internal standard.

interpret the nitro-group migration in terms of the radical pair $\overline{\mathrm{ArO^{\bullet}NO_2^{\bullet}}}$ (Scheme 1).† Since the *ipso* intermediate (I) should be partitioned almost equally between rearrangement of the labelled and unlabelled nitro-groups, the 11% exchange observed implies that 22% of the reaction occurs by *ipso*-attack.



Scheme 1

We have attempted to compare this result with that for attack by nitronium ions but the observation of C.I.D.N.P. effects in the nitration of 4-nitrophenol under various conditions suggests that it is difficult to eliminate radical reactions with this substrate. The nitration of 4-nitroanisole to 2,4-dinitroanisole in trifluoroacetic acid appears however to be a conventional nitronium ion nitration; this substrate is much less reactive than 4-nitrophenol and gives no nuclear polarisation and no significant amount of nitro-group migration [<2% from a spectrum with 4140 pulses; *cf.* Figure 1(c)]. The marked difference in the amounts of nitro-group migration with these two substrates is most easily attributed to a difference between the extents of *ipso*-attack at C–NO_2 in the ionic and radical pathways for nitration.

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† This interpretation is supported by the C.I.D.N.P. effects observed. For Figure 1(a), signal A appears initially with enhanced absorption: for Figure 1(b), this signal appears initially in emission. These observations are consistent with the application of Kaptein's rules (ref. 3) to the reactions in Scheme 1. We recognise that many of the phenoxy radicals will be protonated (ref. 4).

References

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