^{15}N Nuclear Polarisation in Nitration and Related Reactions. Part 2.[1] *p*-Nitrophenol

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The nitrous acid-catalysed nitration of *p*-nitrophenol by $H^{15}NO_3$ in aqueous trifluoroacetic acid gives a strong emission signal during reaction for the 2-$^{15}NO_2$ group in the ^{15}N n.m.r. spectrum of the 2,4-dinitrophenol formed: the enhancement is by a factor of up to 600. The reaction is accompanied by 11% migration of the original 4-nitro group to the 2-position and substitution by the labelled nitro group at the 4-position. The ^{15}N n.m.r. spectrum during the related reaction using ^{15}N labelled *p*-nitrophenol and unlabelled nitric acid shows that the migration of the 4-$^{15}NO_2$ group to the 2-position causes a strongly enhanced absorption signal for the 2-$^{15}NO_2$ group in the 2,4-dinitrophenol formed. A strongly enhanced absorption signal for this group is also found for the reaction of *p*-nitrophenol with $H^{15}NO_3$ in the presence of sodium azide. The complete set of results is interpreted in terms of nuclear polarisation deriving from the reactions of the radical pair $ArO^{\bullet}NO_2^{\bullet}$ when formed either by diffusion or from a singlet precursor. The reaction between hydrazoic acid and nitric acid is catalysed by *p*-nitrophenol.

The ^{15}N nuclear polarisation observed in the nitration of *p*-nitrophenol differs in several ways from that seen in the nitration of mesitylene. These differences come partly from the observation of nuclear polarisation in the presence of azide ions and partly from the fact that, with *p*-nitrophenol, it is possible to have ^{15}N labelling in both the substrate and the reactant.

The following characteristics of the nitration of *p*-nitrophenol are already well established. For reaction with the nitronium ion in aqueous nitric acid (50 mole %), the reactivity of *p*-nitrophenol[2] is about half that of the phenylmethanesulphonate ion. Since the latter ion is less reactive than benzene by a factor[3] of *ca.* 18, the rate of reaction of *p*-nitrophenol with the nitronium ion must be well below the encounter rate in all common nitrating media. Thus, from the relative reactivity (88) of mesitylene and benzene in trifluoroacetic acid,[4] *p*-nitrophenol should be less reactive than mesitylene by a factor of *ca.* 3 000 in those nitration reactions that are first order with respect to the aromatic compound.

Despite the low reactivity of *p*-nitrophenol, its nitration by nitric acid (1—6 mol dm^{-3}) in acetic acid is catalysed by nitrous acid.[5] Comparison of the acidity dependence of the nitrous acid-catalysed nitration of *p*-nitrophenol with that of other substrates indicates that this catalysed reaction involves the *p*-nitrophenoxide ion[5] for the rate *decreases* slightly with an increase in the concentration of nitric acid. The direct reaction with the nitronium ion appears however to involve the *p*-nitrophenol molecule.[2,5] The nitronium ion should of course react also with the *p*-nitrophenoxide ion but the product of the concentrations of these species is presumably too low for the resulting reaction to contribute significantly to the overall rate of substitution. In both the direct nitration and the nitrous acid-catalysed reaction, the only product observed was 2,4-dinitrophenol.[2,5]

Kinetic Studies by ^{1}H *N.m.r. Spectroscopy.*—As with mesitylene, we have had to choose somewhat different conditions from those used previously for the nitration of *p*-nitrophenol in order to obtain the necessary concentrations and reaction rates for the studies of nuclear polarisation. Aqueous trifluoroacetic acid (10% w/w water) has again been used as the solvent, and the concentrations of reactants were as shown in Figure 1.

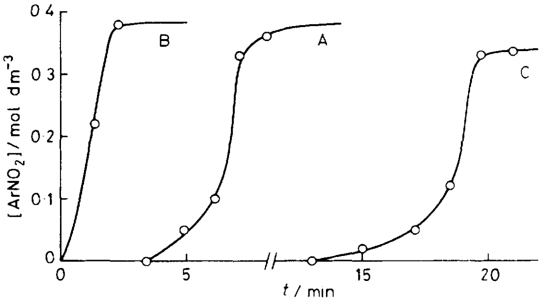

Figure 1. Nitration of *p*-nitrophenol (0.38 mol dm^{-3}) with nitric acid (0.38 mol dm^{-3}) in aqueous trifluoroacetic acid at 24 ± 0.5 °C. Additives: run A, sodium acetate (0.09 mol dm^{-3}); run B, sodium nitrite (0.02 mol dm^{-3}); run C, sodium azide (0.09 mol dm^{-3}). All reaction mixtures also contained nitrobenzene (0.83 mol dm^{-3})

Some typical kinetic runs followed by ^{1}H n.m.r. spectroscopy are shown in Figure 1. The obvious induction period seen in run A suggests that direct nitration by the nitronium ion is insignificant and this is reasonable in view of the much lower reactivity of *p*-nitrophenol compared with mesitylene.† The reaction has the characteristics of an autocatalysed nitration and the comparison of runs A and B shows that nitrous acid is the catalyst. The presence of the autocatalysis is a little surprising since it was not found in the earlier work in acetic acid as solvent but in those experiments the sensitivity of the reaction to nitrous acid catalysis was much less and the concentration of nitrous acid used greatly exceeded the concentration of the substrate; the formation of nitrous acid through side-reactions involving the substrate would therefore have been less important.

The nitration of *p*-nitrophenol in trifluoroacetic acid differs markedly from that of mesitylene in the effect of azide ions. With mesitylene as substrate, a concentration of azide ions of 0.08 mol dm^{-3} is sufficient to prevent the onset of the autocatalytic reaction:[1] with *p*-nitrophenol as substrate, a similar concentration of azide ions merely postpones the onset of the autocatalytic reaction by *ca.* 10 min (Figure 1, run C). When the initial concentrations of nitric acid and *p*-nitrophenol

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† Sodium acetate was added to this reaction mixture to facilitate the comparison of runs A and C, and in particular to distinguish between the effect of sodium azide as a base and as a scavenger for nitrous acid.

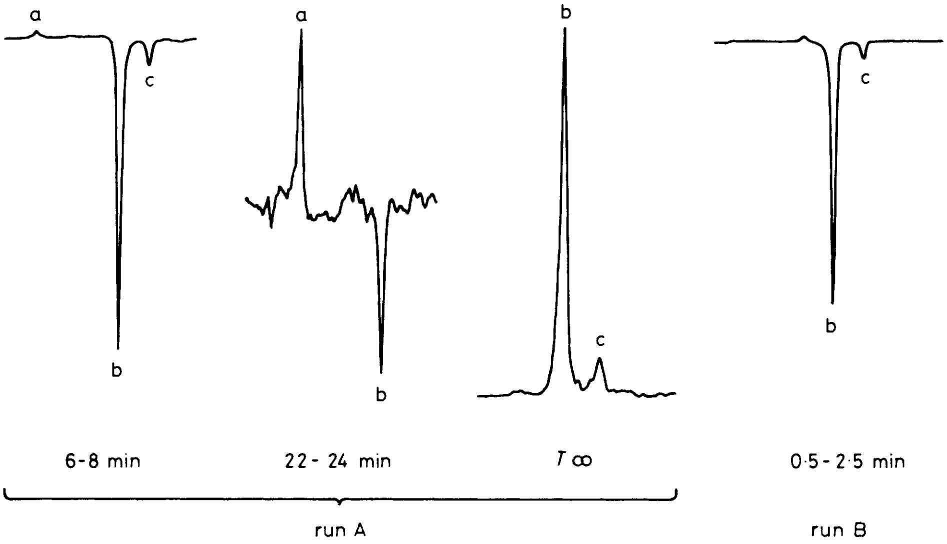


Figure 2. ^{15}N N.m.r. spectra during the reaction of *p*-nitrophenol with $H^{15}NO_3$ to give 2,4-dinitrophenol under the conditions described for runs A and B in Figure 1 but at 25 °C. a, $Ph^{15}NO_2$; b, 2-$^{15}NO_2$ group in product; c, 4-$^{15}NO_2$ group in product.

are equal, the effect of azide ions is to reduce the final concentration of 2,4-dinitrophenol in the solution below that expected for complete reaction. A reaction between azide ions and nitric acid is known[6] but we have checked that, in the absence of *p*-nitrophenol, it is far too slow under our conditions to explain these results.

The nitration of *p*-nitroanisole was also studied under these conditions. It is then much less reactive than *p*-nitrophenol and the reaction shows no autocatalysis or catalysis by nitrous acid. Thus, under the conditions of run A (Figure 1), the half-life for the nitration of *p*-nitroanisole was *ca.* 70 h, increasing to *ca.* 250 h in the presence of sodium nitrite (0.03 mol dm $^{-3}$). The retardation by added nitrous acid is as expected for nitration by the nitronium ion[5] and the absence of nitrous acid catalysis accords with other evidence[5] that this reaction of *p*-nitrophenol requires the breaking of the O–H bond.

Kinetic Studies by ^{15}N *N.m.r. Spectroscopy.*—These runs were carried out under essentially the same conditions as those followed by ^{1}H n.m.r. spectroscopy. Consider first the run carried out using unlabelled *p*-nitrophenol and $H^{15}NO_3$, with the standard ($Ph^{15}NO_2$) and sodium acetate present (Figure 2, run A). Initially the nitric acid absorbs at *ca.* 34 p.p.m. to high field of the nitrobenzene but, after *ca.* 5 min, this peak disappears and two strong emission signals appear, the main one corresponding to 2,4-dinitrophenol labelled with ^{15}N in the *ortho*-position and the minor peak (of *ca.* 1/10 the intensity) corresponding to the same compound labelled with ^{15}N in the *para*-position. Both are to high field of the standard with chemical shifts 5.4 and 7.3 p.p.m. respectively and both are strongly enhanced, the intensity of the main peak being greater than its final value by a factor of *ca.* 140. The second spectrum in Figure 2 shows the stage when the emission signal is weaker and comparable in intensity with the standard. The third spectrum shows the two absorption signals obtained at the end of the run. The presence of these two signals shows that substitution occurs at both the 2- and 4-position.

When nitrous acid is present at the start of reaction (Figure 2, run B) the pattern of results is very similar except that no induction period is seen and the enhancement of the signal is increased to a factor of 660 for the 2-nitro group. With this degree of enhancement, the peak for the $^{15}NO_2$-labelled nitrobenzene is not seen [the weak signal to low field of the main absorption (Figure 2) was not identified]. The results with ^{1}H n.m.r. spectroscopy suggest that the reaction is effectively complete in *ca.* 2.5 min under these conditions and so the fall-off in the intensity of the emission with time[7] has been used to calculate the T_1 relaxation time of the 2-^{15}N nucleus in 2,4-dinitrophenol: the result (see Experimental section) gives T_1 125 s. A conventional determination of this relaxation time for a solution of 2,4-dinitrophenol in [$^{2}H_6$]acetone gave a value of 182 s. The difference probably derives from the presence of radicals in solution during the kinetic run. The corresponding relaxation time for the $^{15}NO_2$ group in nitrobenzene[8] is 170 s.

The emission signals observed in these nitrations of *p*-nitrophenol are similar to those seen in the nitrous acid-catalysed nitration of mesitylene under the same conditions. However, a new feature is seen in the nitration of *p*-nitrophenol in the presence of hydrazoic acid. From the studies by ^{1}H n.m.r. spectroscopy, it appears that hydrazoic acid (0.09 mol dm^{-3}) causes a prolonged induction period (Figure 1C); during this period, the ^{15}N n.m.r. spectrum would be expected therefore to show merely the signals for the labelled nitric acid and the labelled nitrobenzene standard. The observed spectrum includes however a strongly enhanced absorption signal for the 2-$^{15}NO_2$ group in 2,4-dinitrophenol accompanied (in some spectra) by a weak signal for the corresponding 4-$^{15}NO_2$ group. Over 4—6 min, the intensity of the signal for the 2-$^{15}NO_2$ group is greater than that of the standard nitrobenzene by a factor of 5 despite the negligible extent of reaction as judged from the ^{1}H n.m.r. spectra; at the end of reaction the corresponding factor is 0.5 (Figure 3). After *ca.* 18 min, the enhanced absorption signal decreases to zero and then reappears (together with that for the 4-$^{15}NO_2$ group) as an emission signal (Figure 3, second spectrum). This change corresponds to the start of the 'normal' nitrous acid-catalysed reaction when followed by ^{1}H n.m.r spectroscopy (Figure 1, run C). Finally, at the end of reaction, the normal weak absorption signals are seen.

A number of runs have been carried out with ^{15}N-labelled *p*-nitrophenol and unlabelled nitric acid under the conditions used for run A (Figure 1) but without added sodium acetate. The direct nitration at the *ortho*-position is not then observed by ^{15}N n.m.r. spectroscopy and only reactions involving the 4-nitro group are seen. The ^{15}N n.m.r. spectrum shows clearly that the conversion of *p*-nitrophenol into 2,4-dinitrophenol is accompanied by the partial migration of the original nitro group from the 4-position to the 2-position since the peak for the 2-$^{15}NO_2$ group of 2,4-dinitrophenol is seen in the product (Figure 4). This migration corresponds to the formation of some of the 4-$^{15}NO_2$-labelled product in the nitration of unlabelled *p*-nitrophenol with ^{15}N-labelled nitric acid (see above). The most interesting feature of these results is the strong temporary enhancement of the ^{15}N n.m.r. signal of the group that has migrated to the 2-position: thus over 7—9 min the absorption of this group is about twice that of the standard nitrobenzene whereas, at the end of reaction, the ratio is only 0.07. The time of maximum enhancement of the migrating group is approximately the same as the time of the maximum emission signal in the nitration of unlabelled *p*-nitrophenol with labelled nitric acid.

These results point clearly to a radical mechanism for the migration. The rearrangement of the nitro group appears to be essentially intramolecular since a two-fold increase in the concentration of nitric acid does not lead to an observable drop in the extent of labelling at the 2-position; such a drop should occur if the ^{15}N label were diluted by mixing with the excess of nitric acid. A small fraction of the migrating groups appear however to escape since an emission signal for the 2-$^{15}NO_2$ group is seen for a brief period at the end of the reaction; this can be understood as a 'normal' nitrous acid-catalysed substitution at the 2-position involving labelled nitric acid that has been formed in the solution.

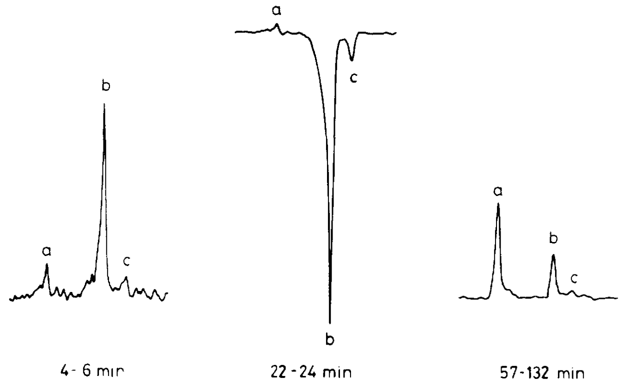


Figure 3. ^{15}N N.m.r. spectra during the nitration of *p*-nitrophenol (0.39 mol dm^{-3}) with $H^{15}NO_3$ (0.39 mol dm^{-3}) in aqueous trifluoroacetic acid at 25 °C in the presence of sodium azide (0.1 mol dm^{-3}) and nitrobenzene (0.61 mol dm^{-3}). The labelling of the peaks is as in Figure 2

The evidence for the partial 1,3-migration of the original nitro group during the nitration of *p*-nitrophenol comes from the experiments with labelled nitric acid and those with labelled *p*-nitrophenol; both sets of results point to 11 ± 2% migration when calculated by integration of the final spectra (using 300—2 000 pulses). Estimates based on the relative heights of the two peaks are *ca.* 2% lower. The scatter in the values seems to be mainly experimental error but one result obtained from a run containing added sulphuric acid (0.76 mol dm^{-3}) was significantly lower (5% migration). Product analyses by mass spectrometry show that essentially all the 2,4-dinitrophenol has one ^{15}N atom.

Some experiments were carried out on the nitration of *p*-nitroanisole with $H^{15}NO_3$ using the reactant concentrations given in Figure 1, run A but with addition of sulphuric acid (0.91 mol dm^{-3}) to facilitate the reaction. The half-life of the reaction as determined from ^1H n.m.r. spectroscopy was then < 1 min but no sign of nuclear polarisation was found. It was impossible to determine from the ^{15}N n.m.r. spectrum of the product whether any migration of the original nitro group had occurred since, in 2,4-dinitroanisole, the chemical shifts of the 2- and 4-$^{15}NO_2$ groups are very similar. The product was therefore demethylated and the ^{15}N n.m.r. spectrum of the resulting 2,4-dinitrophenol showed that the ^{15}N label was limited to the *ortho*-position.[9]

Discussion

The induction period observed in these nitrations and the extension of this period in the presence of azide ions (Figure 1) makes it clear that nitration by the nitronium ion is much less important for *p*-nitrophenol than it was for the nitration of mesitylene under the same conditions;[1] this is as expected from other evidence of the relatively low reactivity of *p*-nitrophenol towards nitronium ions (see above). The induction period

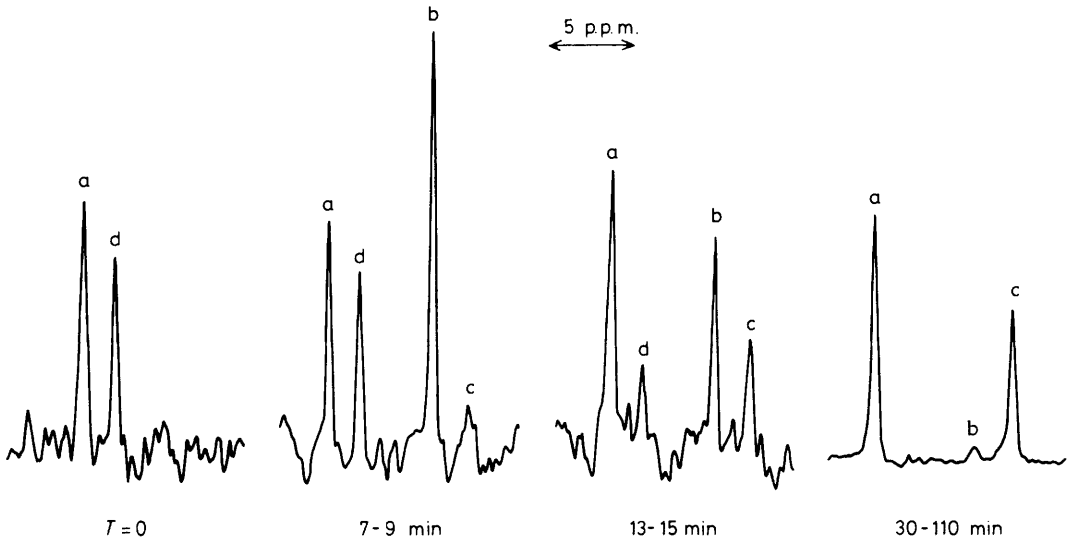
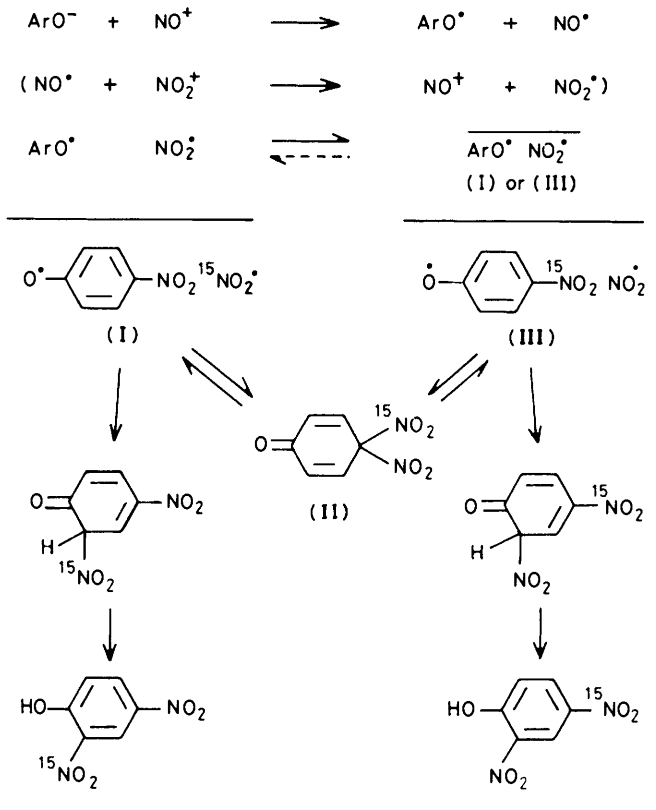


Figure 4. ^{15}N N.m.r. spectra during the nitration of ^{15}N-labelled *p*-nitrophenol with unlabelled nitric acid under the conditions of run A (Figure 2) but with more of the standard [^{15}N]nitrobenzene (0.54 mol dm^{-3}). The labelling of the peaks is as in Figure 2 with the addition of the labelled *p*-nitrophenol, d



Scheme 1.

combined with the catalysis by added sodium nitrite (Figure 1) indicates that the major reaction path involves nitrous acid-catalysed nitration. The absence of this catalysis in the nitration of *p*-nitroanisole suggests that the catalysed reaction involves, at some stage, the breaking of the O–H bond in *p*-nitrophenol as suggested by the rate profile observed previously.[5] It is not clear whether the initial interaction in the nitrous acid-catalysed nitration involves the *p*-nitrophenol molecule or the *p*-nitrophenoxide ion but, for simplicity, the latter will be assumed. The analogy with the nitration of mesitylene[1] then suggests that the initial stages of the reaction can be written as shown in the first three lines of Scheme 1.* In Scheme 1, the second reaction indicates the stoicheiometry involved; the mechanism must be more complex.[1]

No specific isotopic labelling is implied by the reactions shown in the first three lines of Scheme 1 but in the subsequent stages it is necessary to distinguish between the reactions involving labelled nitric acid and those involving labelled *p*-nitrophenol. If the ^{15}N label is initially in the nitric acid, the initial radical pair formed is (**I**) and the nuclear polarisation (Figure 2, run A) is then considered to derive from the partition of this radical pair between dissociation and combination (at either the 2- or 4-position). From the symmetry of the *ipso*-intermediate (**II**) and the fact that 11% substitution occurs at the 4-position, it follows that 22% of the initial attack should occur at this position. This large extent of *ipso*-attack at a C-NO$_2$ group was unexpected but it does accord with the evidence of Tiecco and his co-workers[11] for substantial *ipso*-attack at C-NO$_2$ positions by other radicals. From Kaptein's rules[12] (*cf.* Part 1) and the *g* value for the 4-nitrophenoxyl radical (2.005 4),[13] the nuclear polarisation resulting from the partition of the radical pair (**I**) should lead to emission as observed (Figure 2, run A). Since the reaction is catalysed by nitrous acid, it is reasonable that the nuclear polarisation should be increased when nitrous acid is present initially in the reaction mixture and, on the scale used, the peak of the Ph^{15}NO$_2$ cannot then be seen (Figure 2, run B).

When the ^{15}N label is in the *p*-nitro group, the radical pair (**III**) should be formed first and partitioned between combination and dissociation as outlined above. This should, however, lead to much less polarisation of the ^{15}N nucleus since the ^{14}N hyperfine coupling constant of the *p*-nitrophenoxyl radical at the 4-position (a_N 2.4 G)[13] is much less than that in nitrogen dioxide (a_N 50 G).[14] The main nuclear polarisation should therefore come as before from the partition of the radical pair (**I**), formed by the sequence (**III**)→(**II**)→(**I**). However, since this radical pair is now formed from a singlet precursor, the application of Kaptein's rules[12] indicates that the nuclear polarisation should lead to enhanced absorption, as observed (Figure 4).

Our interpretation of the *ipso*-attack leading to the intermediate (**II**) as a radical reaction is supported by the experiments on *p*-nitroanisole for, with this substrate, no nuclear polarisation was observed and there was no substitution at the 4-position. The mechanism outlined in Scheme 1 explains therefore the main features of the reaction and accords with that put forward for the nitration of mesitylene.[1]

There are two features of this work that cannot be explained by the reactions in Scheme 1. One concerns the strongly enhanced ^{15}N n.m.r. absorption found for the traces of nitro-product formed during the 'inhibition period' in the runs carried out in the presence of azide ions (Figure 3). This presumably comes from the underlying reaction with nitronium ions and would be consistent with the formation of the radical pair ArO$^•$ NO$_2$$^•$ from a singlet precursor.

One obvious way for this radical pair to be formed would be by electron transfer between *p*-nitrophenol and the nitronium ion. However, the absence of any corresponding nuclear polarisation in the nitration of mesitylene[1] by nitronium ions does not support this step. We suggest therefore that an equilibrium concentration of *p*-nitrophenyl nitrate is formed in the solution and that this (or its conjugate acid) slowly breaks by homolytic fission of the N–O bond to give the singlet radical pair $\overline{\mathrm{ArO^• \; NO_2{}^•}}$. By analogy with the other reactions in which this radical pair is formed (see above), the predominant reaction (apart from recombination to the nitrate) should be intramolecular rearrangement but some of the radical pairs should dissociate to generate nitrous acid in the solution. This dissociation would explain the appearance of the nitrous acid-catalysed reaction after the short induction period in the absence of azide ions (Figure 1A).

There is some support in the literature for such a reaction path. Nitration at oxygen is a well established reaction:[15] the *O*-nitration of *p*-nitrobenzyl alcohol by nitric acid in nitromethane gives zeroth-order kinetics indicating reaction through the nitronium ion.[15] The work on mesitylene shows that, under our conditions, the nitronium ion is formed sufficiently rapidly to establish an equilibrium concentration of *p*-nitrophenyl nitrate in the solution. The nuclear polarisation observed would then be analogous to the enhanced absorption found in the nitramine rearrangement.[16]

The other unexpected feature of this work is the curiously brief inhibition of the nitrous acid-catalysed nitration by sodium azide. This appears to derive from a reaction between hydrazoic acid and nitric acid since, when equivalent concen-

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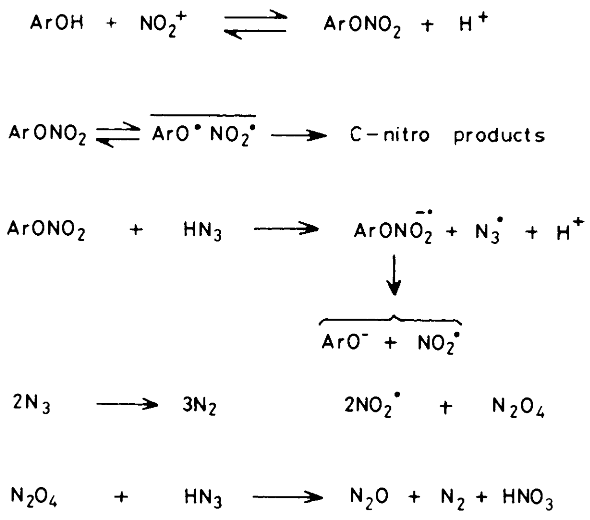
* There is some evidence[10] for the direct formation of phenoxyl radicals by the abstraction of the O–H hydrogen atom of phenols by nitrogen dioxide; we have, however, preferred to retain the mechanism proposed for the nitration of mesitylene because of the similarity in the conditions and rates of these two nitrous acid-catalysed nitrations.



Scheme 2.

trations of *p*-nitrophenol and nitric acid are allowed to react in the presence of sodium azide, the final concentration of 2,4-dinitrophenol is less than expected (Figure 1C) and the ^{1}H n.m.r. spectrum of the unreacted *p*-nitrophenol can be seen at the end of reaction without any obvious side-products. It is clear that *p*-nitrophenol must be involved in this reaction between hydrazoic acid and nitric acid since, in the absence of *p*-nitrophenol, this reaction is far too slow. There is also no sign of an analogous process in the nitration of mesitylene,[1] for sodium azide then appears to provide permanent inhibition of the nitrous acid-catalysed reaction.

These results suggest that hydrazoic acid reacts with an intermediate formed reversibly from nitric acid and *p*-nitrophenol, and it is simplest to suggest that this intermediate is also *p*-nitrophenyl nitrate. The reaction concerned could be an electron transfer analogous to those observed from hydrazoic acid or azide ions to a number of inorganic oxidising agents[17] followed by homolysis of the N–O bond in the aromatic radical formed.[18] The suggested reactions of *p*-nitrophenyl nitrate are shown in Scheme 2. We hope to investigate this aspect of the work in more detail later.

On this interpretation, the oxygen atom of *p*-nitrophenol is the most reactive centre for attack by nitronium ions but the resulting *p*-nitrophenyl nitrate is mainly hydrolysed back to the reactants apart from a small fraction that undergoes a radical rearrangement. This reaction may be accompanied by the direct attack of nitronium ions at the 2-position but such direct substitution does not appear to be significant under our conditions.

Experimental

Materials.—*p*-Nitrophenol was recrystallised from aqueous ethanol; *p*-nitroanisole was purified by vacuum distillation. The other reagents were as described previously.[1]

[^{15}N]-*p*-Nitrophenol was prepared by the nitration of fluorobenzene with $H^{15}NO_3$ followed by the replacement of the fluorine by a hydroxy group. A mixture of aqueous $H^{15}NO_3$ (2.94 g, 40%) and trifluoroacetic anhydride (6.6 cm^3) was added to fluorobenzene (0.96 g) followed by the dropwise addition of sulphuric acid (97%, 0.265 g). After reaction was complete, the reaction mixture was poured into water and extracted with methylene dichloride to give [^{15}N]-*p*-nitrofluorobenzene (1.24 g). A solution of sodium hydroxide (1.11 g) in aqueous dimethyl sulphoxide [27.5 cm^3; 10% (v/v) H_2O] was added to a solution of the [^{15}N]-*p*-nitrofluorobenzene (0.6 g) in dimethyl sulphoxide (6 cm^3) and the mixture kept at 90—95 °C until reaction was complete (20 min). The reaction mixture was then poured into aqueous sulphuric acid and extracted with ether. The [^{15}N]-*p*-nitrophenol formed (0.48 g) was recrystallised from chloroform and had m.p. 114 °C.

Table. The intensities of the signals in the ^{15}N n.m.r. spectrum of the reaction mixture during the nitration of *p*-nitrophenol under the conditions listed in Figure 2, run B

	2,4-Dinitrophenol		
t/min	2-^{15}N	4-^{15}N	[^{15}N]Nitrobenzene[a]
0.5—2.5	−2 113	−155	
3—5	−668	−57	
7—9	−125	−10.3	7.6
11—13	−17.1		5.4
17—19			4.1
25—27	3.2		4.7
53—55	3.89[b]		5.0

[a] Present as standard. [b] Taken as I_∞, see text.

Kinetic Runs.—These were carried out as described previously[1] using trifluoroacetic acid containing 10% w/w water as solvent. For the experiments involving ^{1}H n.m.r. spectroscopy, the extent of reaction was calculated from the relative heights of the signals for the aromatic protons. The ^{15}N n.m.r. spectra taken during reaction had 8 pulses with a delay time of 15 s and a pulse angle of 25°. Up to 2 400 pulses were used in recording the spectra of reaction products.

The variation in the intensity (I) of the signals during the nitration of *p*-nitrophenol under the conditions given for run B, Figure 2, are shown in the Table. A plot of $\log_e|(I - I_\infty)/I_\infty|$ against time[7] gives T_1 for the 2-^{15}N nucleus as 125 s. The determination of the relaxation time of this nucleus in a [$^2H_6$]-acetone solution of 2,4-dinitrophenol was carried out by the fast inversion recovery method[19] using a wait time of *ca.* T_1.

Products.—The nitration of *p*-nitrophenol (0.27 g) with one equivalent of nitric acid under the conditions of run B, Figure 1 gave, after quenching and extraction as described,[1] pure 2,4-dinitrophenol (0.336 g, 94%). Examination by h.p.l.c. gave no evidence of any other product. Examination by mass spectrometry showed that the $M/M + 1$ ratio for the sample was the same as that obtained from the nitration of ^{15}N-labelled *p*-nitrophenol with unlabelled nitric acid and that obtained from unlabelled *p*-nitrophenol. It appears therefore that no detectable amount of doubly labelled products is formed.

The estimation of the ratio of labelling in the 2- and 4-position was based on integration of the ^{15}N n.m.r. signals using 2 400 pulses. The product from the nitration of *p*-nitroanisole with $H^{15}NO_3$ was demethylated before estimation. A solution of sodium hydroxide (0.62 g) in aqueous dimethyl sulphoxide [13.2 cm^3; 10% (v/v) H_2O] was added to a solution of ^{15}N-labelled 2,4-dinitroanisole (0.4 g) in dimethyl sulphoxide (8 cm^3) and brought to 90—95 °C for 50 min. The reaction mixture was then poured into aqueous sulphuric acid and extracted with ether to give ^{15}N-labelled 2,4-dinitrophenol (0.31 g), m.p. 107.5 °C after recrystallisation from methanol. The ^{15}N n.m.r. spectrum gave no evidence of any product with the label at the 4-position.[9]

Acknowledgements

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