^{15}N Nuclear Polarisation in Nitration and Related Reactions. Part 4.[1] Durene and Nitrodurene

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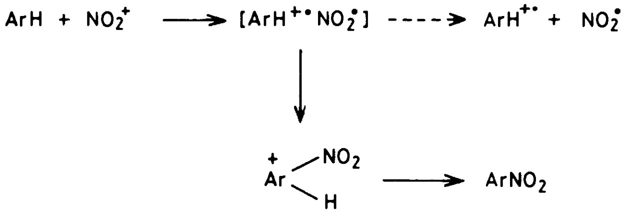
As expected from studies on mesitylene, the nitrous acid-catalysed nitration of durene by $H^{15}NO_3$ in aqueous trifluoroacetic acid gives a strong emission signal during reaction for nitrodurene in the ^{15}N n.m.r. spectrum. However, unlike the corresponding reactions of mesitylene, nuclear polarisation is also found when the nitration of durene under these conditions is carried out by nitronium ions: the ^{15}N n.m.r. signal for nitrodurene during reaction then shows enhanced absorption. The nitration of nitrodurene does not give rise to nuclear polarisation when carried out separately but an emission signal is seen for dinitrodurene in the ^{15}N n.m.r. spectrum during the nitration of durene by nitronium ions. All these results can be understood in terms of nuclear polarisation deriving from the partition of the radical pair $[ArH^{+\bullet}\ NO_2^{\bullet}]$ between dissociation and recombination. In the nitration of durene by nitronium ions, this radical pair is considered to result from *ipso*-attack followed by homolysis of the C–N bond.

The previous papers in this series have been concerned mainly with the formation of radicals during nitrous acid-catalysed nitration, related rearrangements, and nitro-group exchange reactions. The only evidence for radical formation during nitration by nitronium ions has come from some experiments on the nitration of *p*-nitrophenol in the presence of sodium azide,[2] a reagent that inhibits nitrous acid-catalysed nitration. ^{15}N Nuclear polarisation was then observed in the 2,4-dinitrophenol formed but with the opposite phase to that expected from the nitrous acid-catalysed reaction. This result was attributed[2] to the intermediate formation and rearrangement of *p*-nitrophenyl nitrate.

There has, however, always been considerable interest in the possibility of radical formation by direct electron transfer during the attack of the nitronium ion on the aromatic substrate. This possibility was first suggested by Kenner,[3] and the idea has since been developed by a number of authors,[4] most recently Perrin.[5] He has suggested that the reaction of the nitronium ion with those aromatic compounds that are more reactive than toluene occurs through a preliminary electron transfer to form the radical pair $[ArH^{+\bullet}\ NO_2^{\bullet}]$, followed by radical-pair collapse without any activation barrier. This mechanism, with the added possibility of radical-pair separation, is shown in Scheme 1.

Both the experimental and theoretical arguments produced by Perrin have been criticised,[6] and the most recent analysis by Eberson[6c] suggests that the mechanism in Scheme 1 should not apply to nitration until the reactivity of the aromatic substrate greatly exceeds that of toluene. This accords with the absence of nuclear polarisation in the nitration of mesitylene by nitronium ions.[7] We have therefore been studying the more reactive aromatic systems by ^{15}N n.m.r. spectroscopy and, with durene (1,2,4,5-tetramethylbenzene) (**1**), have found evidence for nuclear polarisation that does not derive from the nitrous acid-catalysed reaction path.

A number of studies have been made on the nitration of durene under various conditions. For the nitronium ion reaction, the principal difference between mesitylene and durene comes from the predominance of *ipso*-attack in the nitration of durene,[8] a consequence of the additivity of the substituent effects of the methyl groups. The *ipso*-intermediate (**2**) can rearrange to give nitrodurene, or can be captured by a nucleophile. For nitration in 86.7% sulphuric acid, rearrangement predominates giving initially nitrodurene (97.5%):[9] for reaction in 55.2% sulphuric acid, the *ipso*-intermediate appears to be captured by water and only 12.1% of nitrodurene is formed.[9] The several studies on the nitration of durene in acetic anhydride give widely varying results for the yield of nitrodurene:[10] the other products include 2,3,5-trimethylbenzyl nitrate.[10a] Durene also undergoes nitrous acid-catalysed nitration and forms a coloured π-complex with nitrosonium hexafluorophosphate in acetonitrile or nitromethane.[11]



Scheme 1.

The present paper is also concerned with the nitration of nitrodurene because of the evidence for the formation of some dinitrodurene during the nitration of durene. The reactivity of durene relative to nitrodurene is unusually low (a factor of 19 for second-order nitration in aqueous sulphuric acid),[12] essentially because the rate of nitration of durene is limited by diffusion control: like mesitylene, durene is believed to react on encounter with nitronium ions.[12],† A detailed study has been made of the effect of macroscopic diffusion control on the relative amounts of nitrodurene and dinitrodurene formed during the mixing of solutions of durene with solutions containing preformed nitronium ions:[13] dinitrodurene can then be the major nitro product[11a] even with equal concentrations of reactants. However, in the present work, the rate of formation of nitronium ions is the rate-determining stage of nitration and, under these conditions, the extent of dinitration is small.

Preliminary Studies.—Our preliminary experiments involved ^{1}H n.m.r. spectroscopy to establish suitable conditions for the

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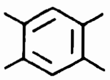
† This implies that the relative reactivity of durene and nitrodurene should be very sensitive to the experimental conditions including, particularly, the viscosity of the medium.



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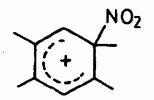

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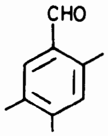

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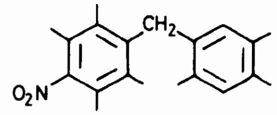

(4)

detection of ^{15}N nuclear polarisation. The solvent system used for the work on mesitylene[7] [trifluoroacetic acid containing 10% (w/w) of water] was again used because of the need to combine a relatively high concentration of the substrate with a fast reaction.

These studies indicated that durene is much more susceptible than mesitylene to the nitrous acid-catalysed mechanism of nitration. Thus the ^1H n.m.r. spectra of a reaction mixture at 24 °C containing durene (0.29 mol dm^{-3}), nitric acid (0.29 mol dm^{-3}), and sodium acetate (0.07 mol dm^{-3})* in the aforementioned solvent show that a great deal of reaction has occurred in the first minute, and that reaction is effectively complete in *ca.* 5 min. This reaction is much faster than the expected formation of nitronium ions.[7] The ^1H n.m.r. spectrum then accords with the formation of nitrodurene but an additional weak peak is present in the methyl region. The position of this peak is not very reproducible and it can overlap with the low-field methyl peak of nitrodurene: both the position and the intensity of this additional peak also change with time and after *ca.* 4 days the additional peak has disappeared. We attribute this peak to a π-complex formed by a mobile equilibrium between durene and nitrosonium ions; the disappearance of the peak can be explained by the slow oxidation of nitrous acid or the complex to give nitrodurene. These observations are in general accord with those of Zollinger and his co-workers.[11]

Of the material isolated by h.p.l.c. for reaction under these conditions, 85.9% was nitrodurene, 4.0% was unchanged durene, 1.7% was the aldehyde (**3**), and 0.8% was the nitrated dimer (**4**). At least six other compounds were present in the remaining 7.6% but were not identified. The formation of products (**3**) and (**4**) can be understood in terms of the reaction path proposed for the nitrous acid-catalysed nitration of mesitylene.[7]

The nitration of durene has also been studied under these conditions in the presence of sodium nitrite and sodium azide. The reaction of durene (0.29 mol dm^{-3}) with nitric acid (0.29 mol dm^{-3}) in the presence of sodium nitrite (0.05 mol dm^{-3}) at 24 °C appeared from the ^1H n.m.r. spectrum to be complete by the time the first spectrum was taken (53 s). The corresponding reaction in the presence of sodium azide (0.07 mol dm^{-3}) was initially much slower but after about 40 min went rapidly to completion (Figure 1). Nitrobenzene (0.58 mol dm^{-3}) was also present in this run to match the conditions used in the later runs followed by ^{15}N n.m.r. spectroscopy. The initial points (up to 29 min) accord with a first-order plot with k_1 3.5 × 10^{-4} s^{-1} (*r* 0.998). This is very similar to the rate coefficient (3.3 × 10^{-4} s^{-1}) found for the rate-determining formation of the nitronium ion in the nitration of mesitylene (0.42 mol dm^{-3}) in this solvent. It appears therefore that the sodium azide initially inhibits the nitrous acid-catalysed mechanism of nitration and that, as expected, the formation of the nitronium ion then becomes rate-determining. However, with durene (but not with mesitylene) the inhibition is limited to the first part of the reaction and, after that, the nitrous acid-catalysed reaction path becomes predominant.

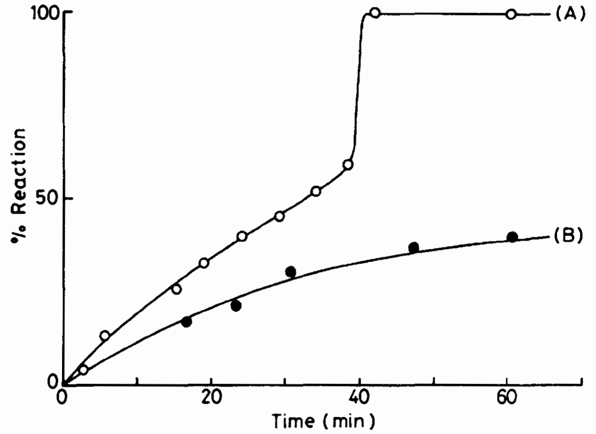

Figure 1. The nitration of durene (A) and nitrodurene (B) in aqueous trifluoroacetic acid at 24 °C in the presence of sodium azide; [ArH] = 0.29 mol dm^{-3}, [HNO_3] = 0.29 mol dm^{-3}, [NaN_3] = 0.07 mol dm^{-3}. The solutions also contained nitrobenzene (0.58 mol dm^{-3})

The nitration of nitrodurene has been followed under the same conditions (Figure 1) using the relative heights of the methyl n.m.r. peaks due to nitrodurene and dinitrodurene; the reaction is only a little slower than the nitration of durene. This is not in conflict with earlier observations[12] that the second-order rate coefficients for the nitration of durene and nitrodurene differ by a factor of 19 for, under the conditions of Figure 1, the rate of formation of nitronium ions is rate-determining in the nitration of durene. All aromatic compounds whose bulk reactivity exceeds that of the water in the solvent should then react at essentially the same rate. Related studies with and without sodium nitrite showed no evidence for catalysis by nitrous acid in the nitration of nitrodurene.

^{15}N *N.m.r. Studies.*—The ^{15}N n.m.r. spectra taken during the nitration of durene by $H^{15}NO_3$ in aqueous trifluoroacetic acid confirm the immediate incursion of the nitrous acid-catalysed mechanism of nitration: the peak for nitrodurene appears initially in emission and remains in emission until reaction is complete (Figure 2). In this Figure the vertical scale is increased by a factor of 8 for the final spectrum. The enhancement of the emission signal has a maximum value of *ca.* 100. In the final spectrum, the only product seen is nitrodurene (12.6 p.p.m. to low field of the standard). Nitration reactions carried out in the presence of sodium nitrite gave very similar results except that the maximum emission signal was seen in the first spectrum.

The ^{15}N n.m.r. spectra taken during the nitration of durene in aqueous trifluoroacetic acid in the presence of sodium azide show two new features. One is that the peak for nitrodurene appears initially in enhanced absorption. Thus, in the first spectrum in Figure 3, this peak is of similar height to that of the standard and has about twice the height observed at the end of reaction, despite the fact that at the relevant time only about 20% reaction has occurred (compared with Figure 1). The other new feature is an emission signal at the position corresponding to dinitrodurene (6.4 p.p.m. to low field of the standard). This must be strongly enhanced for no signal for dinitrodurene is found in the spectrum at the end of reaction (Figure 3, 65—121

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* Added as an 'inert' base to facilitate comparison with kinetic runs carried out in the presence of sodium nitrite and sodium azide.

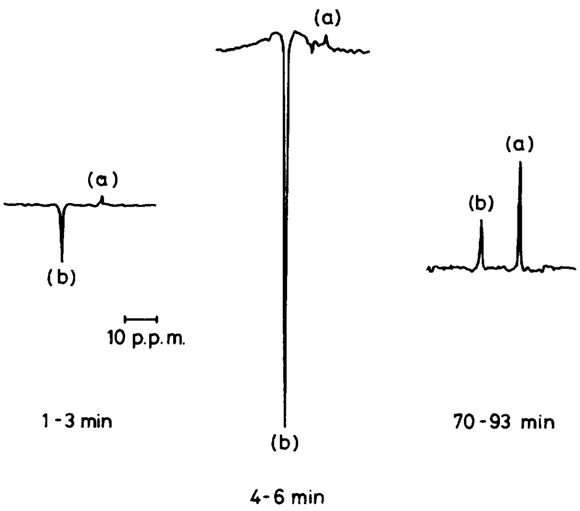


Figure 2. ^{15}N N.m.r. spectra during nitration of durene (0.29 mol dm^{-3}) with H^{15}NO$_3$ (0.29 mol dm^{-3}) in aqueous trifluoroacetic acid at 25 °C in the presence of sodium acetate (0.07 mol dm^{-3}) and Ph^{15}NO$_2$ (0.58 mol dm^{-3}): peak (a), Ph^{15}NO$_2$; peak (b), nitrodurene. The first two spectra had 8 pulses; the last had 89 pulses; pulse repetition time 15 s; pulse angle 25°

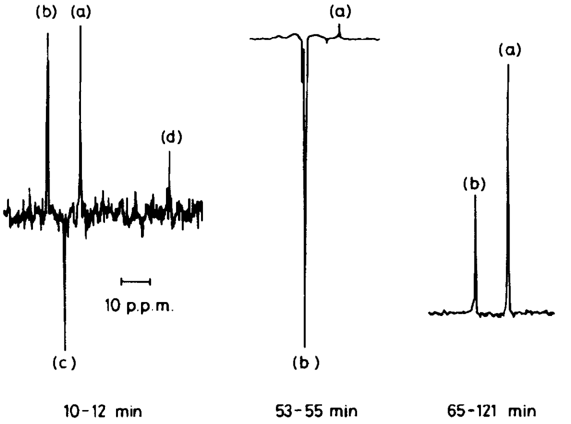


Figure 3. ^{15}N N.m.r. spectra during the nitration of durene under the conditions used for the run in Figure 2 but with sodium azide in the place of sodium acetate: peak (a), Ph^{15}NO$_2$; peak (b), nitrodurene; peak (c), dinitrodurene; peak (d), H^{15}NO$_3$. The first two spectra had 8 pulses; the last had 206 pulses. Pulse repetition time 15 s; pulse angle 25°

min). In the second spectrum in Figure 3, taken towards the end of the reaction, the peak for nitrodurene shows the emission signal characteristic of nitrous acid-catalysed nitration as expected from the kinetic study shown in Figure 1. The source of the accompanying emission signal (0.9 p.p.m.) to low field of this is unknown.

The nitration of nitrodurene was also studied by ^{15}N n.m.r. spectroscopy under the same conditions with and without the addition of sodium azide, but no evidence for CIDNP was found.

Discussion

The nuclear polarisation and the side-products found in the nitrous acid-catalysed nitration of durene are as expected for the reaction path proposed previously[7] and hence this aspect of the work will not be discussed further.

Table. The relative intensity[a] and enhancement[b] of the signal for nitrodurene (ND) in the ^{15}N n.m.r. spectra of the reaction mixture during the nitration of durene (0.29 mol dm^{-3}) with H^{15}NO$_3$ (0.29 mol dm^{-3}) in aqueous trifluoroacetic acid at 24 °C. Sodium azide (0.07 mol dm^{-3}) and (^{15}N)nitrobenzene (0.58 mol dm^{-3}) were also present

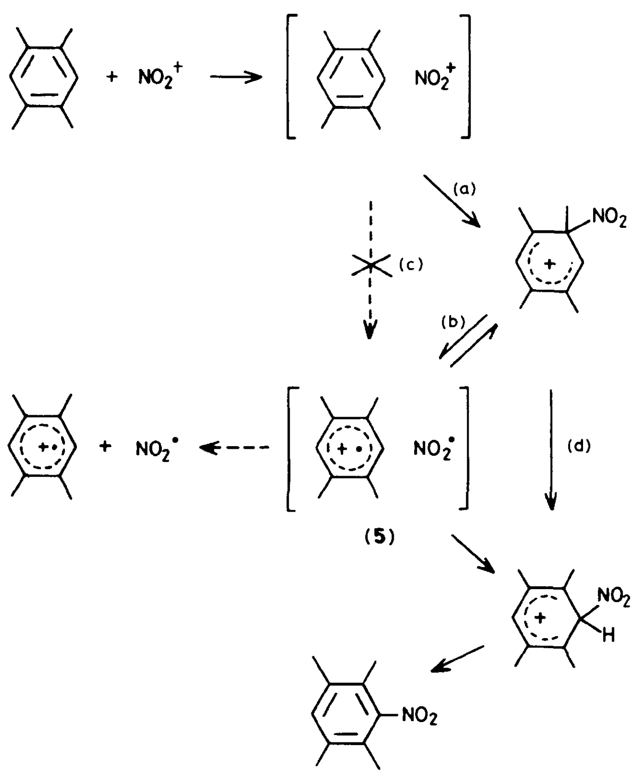
Time (min)	Relative intensity[a]	10^2[ND]/mol dm^{-3} [c]	Enhancement[b]
4—6	78.3	2.9	15.7
7—9	100.4	4.5	12.9
10—12	96.1	6.0	9.5
13—15	77.3	7.4	6.1
16—18	76.0	8.7	5.1
18—20	78.9	9.5	4.8
22—24	72.8	11.1	3.8
25—27	73.4	12.2	3.5
29—31	71.4	13.6	3.0
33—35	80.5	14.8	3.1
36—38	61.4	15.7	2.3
40—42	79.5	16.7	2.8
50—52	−915	29.0	−18.3
53—55	−2154	29.0	−43.0
65—121	50.1	29.0	1.0

[a] Relative to the absorption of the standard (Ph^{15}NO$_2$) as 100. [b] Calculated from the change in the relative intensity of the signal for nitrodurene during reaction and the concentrations given in column 3. [c] Calculated from the kinetic studies carried out using ^{1}H n.m.r. spectroscopy.

The principle interest of the present work comes from the enhanced absorption found in nitrodurene produced during the initial stage of nitration in the presence of sodium azide (Figure 3). The magnitude of this enhancement is shown by the figures in the fourth column of the Table. The initial enhancement is by a factor of *ca.* 10 and is hence much greater than the experimental error. This degree of enhancement was found in a number of runs carried out under similar conditions.

All the examples of nuclear polarisation found so far[1,2,7] can be understood in terms of the partition of the radical pair $[\mathrm{ArH}^{+\bullet}\ \mathrm{NO}_2^{\bullet}]$ between combination and dissociation. When the present results are interpreted in that way, using the arguments presented previously,[7] it follows that the radical pair $[\mathrm{ArH}^{+\bullet}\ \mathrm{NO}_2^{\bullet}]$ must be formed from a singlet precursor in order to yield a product showing enhanced absorption. There are two obvious ways in which this could occur. One involves preliminary electron transfer from the aromatic compound to the nitronium ion (Scheme 1). The other involves the direct formation of the *ipso*-intermediate followed by homolytic fission of the C–N bond (Scheme 2). The work in Part 3[1] has provided evidence for homolytic fission following *ipso*-attack, and such homolytic fission can of course provide a pathway for the migration of the nitro group to an unsubstituted site.

We do not know of any arguments that permit a clear decision between these two interpretations but there are two pieces of evidence that favour the second. One comes from the comparison of durene and naphthalene. The standard electrode potentials (in acetonitrile) and ionisation potentials for these substrates are similar[14] (durene: E° = 2.03 V, I.P. = 8.025 eV; naphthalene; E° = 2.08 V, I.P. = 8.12 eV) but our preliminary studies have not detected such enhanced absorption during the nitration of naphthalene under identical conditions. This would be expected if direct electron transfer occurred from the substrate. The other is the fact that the most recent Marcus Theory calculations[6c] for the rates of electron-transfer reactions to the nitronium ion suggest that such electron transfer should not occur at a diffusion-controlled rate until the standard electrode potential of the substrate drops below 0.17 V. One



Scheme 2.

important term leading to this conclusion comes from the high reorganisation energy (140 kcal mol^{-1}) required for the electron transfer because of the differences in the geometries of the nitronium ion (linear) and the nitrogen dioxide radical (bent). Because of these results, we prefer the interpretation in Scheme 2.

On this interpretation, the change in the geometry of the nitronium ion occurs at the same time as the formation of the C–N bond, and so the energy terms involved in bond formation help to lower the energy of the transition state. The subsequent homolysis of the C–N bond does not require so great a reorganisation energy because the O–N–O system is bent in both reactants and products. Eberson and Radner[6c] have suggested that even apparent electron-transfer reactions involving the nitronium ion and a number of easily oxidisable substrate (*e.g.* ferrocene) involve the formation and subsequent homolysis of Wheland intermediates. The energy barriers corresponding to the stage (a), (b), and (c) in Scheme 2 are shown diagrammatically in Figure 4.

On this interpretation, the barrier (a) must be negligible since reaction occurs on encounter: the energy of the *ipso*-intermediate cannot therefore be significantly higher than that of the encounter pair [ArH NO_2^+] and we have chosen to show it somewhat below this energy. The barrier (b) must also be small in order that homolytic dissociation of the *ipso*-intermediate can compete with the normal 1,2-rearrangement of the nitro group. It follows therefore that the energy of the radical pair [$ArH^{+\bullet}$ $NO_2^\bullet$] cannot be much greater than that of the *ipso*-intermediate.

There is one difficulty with this interpretation. From the standard electrode potentials in acetonitrile for the oxidation of durene (E° = 2.03 V)[14] and nitrogen dioxide (E° = 1.56 V),[15] it appears that the radical pair [$ArH^{+\bullet}$ $NO_2^\bullet$] should be of significantly higher energy than that of the encounter pair [ArH NO_2^+]; it is not obvious therefore why the radical pair should be formed readily from the *ipso*-intermediate. The same difficulty would also arise if the radical pair were considered to be formed by direct electron transfer from the aromatic compound to the nitronium ion. It may be significant that the standard electrode potential in acetonitrile for NO^+/NO (E° = 1.51 V)[15] is very similar to that for NO_2^+/NO_2, and that there is evidence also for electron transfer from durene to the nitrosonium ion in the nitrous acid-catalysed nitration of durene (see before); the electron transfer must occur easily but not necessarily on encounter. For $X^\bullet$ = $NO^\bullet$ or $NO_2^\bullet$, the energy of the radical pairs [$ArH^{+\bullet}$ $X^\bullet$] in trifluoroacetic acid appears less than would be expected from the standard electrode potentials in acetonitrile. This is possibly because of stabilisation of the neutral nitrogen radicals by hydrogen bonding.*

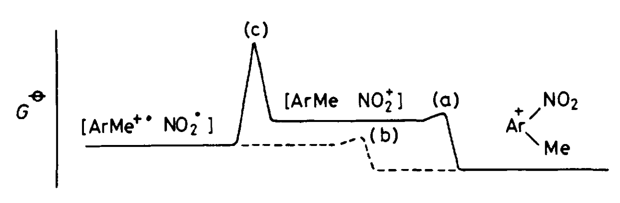


Figure 4. Diagrammatic representation of the energy levels and energy barriers consistent with the first reactions in Scheme 2

We do not wish to imply that the rearrangement of the *ipso*-intermediate (2) occurs necessarily by the radical pathway, since nuclear polarisation developed in the *ipso*-intermediate by the homolytic dissociation (b) could be transferred to the rearranged product by a concerted process [represented in Scheme 2 by the line (d)]. The incursion of the radical process in this reaction presumably derives from the relatively low ionisation potential of the substrate. In this connection, it is probably significant that our preliminary experiments on the nitration of *p*-xylene (which should also undergo considerable *ipso*-attack) have not given evidence for such enhanced absorption in the ^{15}N n.m.r. spectrum.

An emission signal is observed for dinitrodurene (Figure 3, first spectrum) during that part of the reaction when an enhanced absorption signal is seen for nitrodurene. This emission signal can however be understood as a consequence of the polarisation created during the mononitration stage if the polarised NO_2 radicals which escape from the radical pair (5) are rapidly oxidised to nitronium ions by electron transfer with nitronium ions or by related reactions. The polarisation thereby transferred to the 'pool' of nitronium ions would be of the correct sign to give rise to an emission signal for dinitrodurene when the latter is formed by a conventional nitronium ion nitration.†

We have attempted a semi-quantitative calculation to check the validity of the foregoing interpretation, but the number of uncertain quantities is too great to make this of much value. It is clear, however, that the enhancement of the signal for dinitrodurene must be very large, for no signal for dinitrodurene is seen in the final spectrum.

In conclusion, the foregoing work provides evidence that the formation of radical intermediates in the nitration of aromatic hydrocarbons is not limited to nitrous acid-catalysed reactions. We consider it probable however that these radicals arise from *ipso*-attack by the nitronium ion followed by homolysis of the C–N bond, not by direct electron transfer to the nitronium ion.

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* *Cf.* the evidence for the hydrogen bonding and protonation of nitroxides.[16]

† The molecular nitric acid does not give an emission signal under these conditions (Figure 3). This is understandable since there is no equilibrium between the nitronium ions and the nitric acid. The rate of formation of nitronium ions is the rate-determining stage of the overall reaction.

Experimental

Materials.—The reagents and solvents were purified as described previously.[7] Nitrodurene was prepared by the addition of nitric acid in aq. trifluoroacetic acid (10% w/w water) to an equivalent amount of durene in the same solvent at *ca.* 20 °C. The final reactant concentrations were 0.16 mol dm^{-3}, and sodium azide (0.08 mol dm^{-3}) was also present. After 50 min the product was isolated in the usual way and purified by repeated recrystallisation from ethanol [m.p. 108—111 °C (lit.,[17] 113—114 °C)] and gave the expected n.m.r. spectrum with evidence of slight contamination with dinitrodurene.

Kinetics.—The kinetic studies on the nitration of durene were based on the relative heights of the ^{1}H n.m.r. signals for the aromatic protons of durene and the protons of nitrobenzene present as a standard. The instruments and other procedures for these runs and those involving ^{15}N n.m.r. spectroscopy were as described previously.[7] The kinetic studies on the nitration of nitrodurene were based on the relative heights of the ^{1}H n.m.r. signals for the methyl groups in nitrodurene and dinitrodurene. The runs carried out to check on possible ^{15}N polarisation in the nitration of nitrodurene and the analogous runs followed by ^{1}H n.m.r. spectroscopy used the concentrations showed in Figure 1 but with the addition of sulphuric acid (0.2 mol dm^{-3}) to reduce the half-life to *ca.* 3.5 min. No such polarisation was detected with or without the addition of sodium azide. The addition of sodium nitrite slightly decreased the reaction rate.

Products.—A solution of nitric acid in 10% aqueous trifluoroacetic acid (0.8 cm^3; 2.1 mol dm^{-3}) was added to a solution of durene in the same solvent (5 cm^3; 0.34 mol dm^{-3}). After 4 h the solution was quenched in water, extracted with methylene dichloride, and analysed by h.p.l.c. (25 cm × 4.5 mm ID Partisil 5 silica gel column). For the first elution 50% methylene dichloride–light petroleum was used; the main peak was then reanalysed with 10% methylene dichloride–light petroleum. The products separated in this way include nitrodurene (85.9%), durene (4%), and at least six others. One (1.7%) was a yellow oil, δ($CDCl_3$) 2.05 (6 H, s), 2.4 (3 H, s), 6.85 (1 H, s), 7.35 (1 H, s), and 10.1 (1 H, s); M^+, 148.0893 [calc. for the substituted aldehyde (**3**) ($C_{10}H_{20}O$) 148.0888]. Another (0.8%) was a white solid, δ($CDCl_3$) 2.07 (3 H, s), 2.10 (6 H, s), 2.19 (9 H, s), 2.35 (3 H, s), 3.88 (2 H, s), 6.20 (1 H, s), and 6.99 (1 H, s); M^+ 311.1875 [calc. for the nitrated dimer (**4**) ($C_{20}H_{25}NO_2$) 311.1885].

Acknowledgements

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