^{15}N Nuclear Polarisation in Nitration and Related Reactions. Part 1. Mesitylene

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The nitration of mesitylene by nitric acid in trifluoroacetic acid has been followed by ^1H and ^{15}N n.m.r. spectroscopy using $H^{15}NO_3$ (95—99% ^{15}N). With concentrations of mesitylene > 0.5 mol dm^{-3}, the direct nitration by the nitronium ion is accompanied by an autocatalytic reaction involving nitrous acid. The nitrous acid-catalysed process is inhibited by azide ions and can be made to predominate by the addition of nitrous acid. Nitration by the nitronium ion gives no nuclear polarisation in the product but the nitrous acid-catalysed reaction gives marked ^{15}N nuclear polarisation: the ^{15}N n.m.r. spectrum of nitromesitylene during reaction then appears in emission with a degree of enhancement that can exceed a factor of 200. This nuclear polarisation is attributed to the formation of a radical pair $ArH^{+\cdot}\,{}^{\cdot}NO_2{}^{\cdot}$ by the diffusion together of the components. The side-products formed in the nitrous acid-catalysed process are consistent with reactions through $ArH^{+\cdot}$. The direct nitration of mesitylene by the nitronium ion does not appear to involve this cation radical.

Over the last three years, a number of examples of ^{15}N nuclear polarisation have been observed in nitration and related reactions. These include the nitrous acid-catalysed nitration of amines[1] and aromatic hydrocarbons,[2] nitrous acid-catalysed *ipso*-attack in aromatic amines,[3] nitro-group exchange reactions,[4] the nitramine rearrangement,[5] and one rearrangement following *ipso*-attack at a C-NO_2 position.[6] Some of these reactions have given rise to emission spectra[1, 4] and others to enhanced absorption.[4, 6] The present series is intended to deal with the analysis of these results in mechanistic terms and it is convenient to start with one of the simplest of the reactions, the nitration of mesitylene with ^{15}N-labelled nitric acid in trifluoroacetic acid. Complications arising from *ipso*-attack and initial reaction at a side-chain are absent with this substrate.

The nitration of mesitylene by nitric acid has been studied previously by a number of workers using a wide range of reaction media.[7] In the absence of nitrous acid catalysis, the reaction goes cleanly to mononitromesitylene: a recent g.l.c. analysis of the reaction mixture from the nitration of mesitylene by nitric acid in acetonitrile found no other product.[8] There is clear evidence from relative reactivities that the reaction of mesitylene with the nitronium ion occurs on encounter.[7] In some aqueous media, the kinetics of nitration are first order with respect to the aromatic substrate and the rate coefficient accords with a diffusion-controlled process. If the nitrating medium has a low water content or if high concentrations of mesitylene are used, the reaction of the nitronium ion with mesitylene becomes faster than the back reaction to reform nitric acid: the rate-determining step then shifts to the formation of the nitronium ion and the order with respect to the aromatic substrate approaches zero.[7] There is also a nitrous acid-catalysed mechanism which leads to essentially complete mononitration (with some unidentified side-products).[9] The catalysed mechanism has been considered to involve nitrosation followed by oxidation.[9]

Kinetic Studies by ^1H N.m.r. Spectroscopy.—Our procedure has been to determine the kinetics of reaction from the changes in the height of the ^1H n.m.r. peaks of the aromatic protons or methyl groups and to use these results to determine the most suitable conditions for studies with ^{15}N-labelled nitric acid. Trifluoroacetic acid [containing 10% (w/w) of water] was used as the reaction medium because of the need to combine a high concentration of substrate with a fast reaction rate.

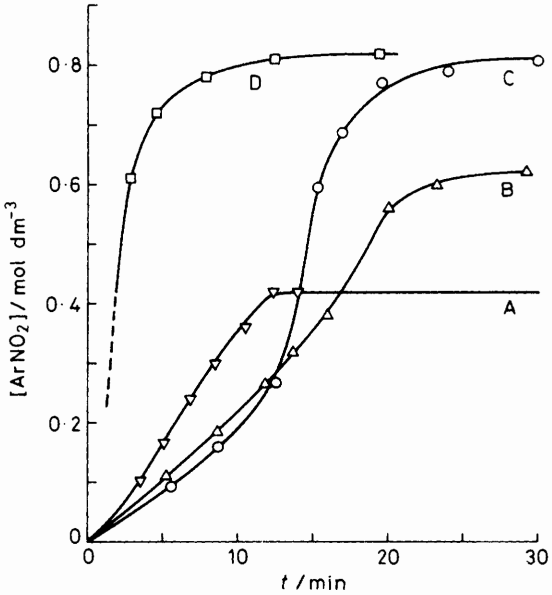


Figure 1. Nitration of mesitylene with nitric acid (2.1 mol dm^{-3}) in aqueous trifluoroacetic acid at 24 ± 0.5 °C. Initial concentrations of mesitylene 0.42 (A); 0.56 (B); 0.84 (C); 0.84 mol dm^{-3} (D). Run D was carried out in the presence of sodium nitrite (0.048 mol dm^{-3}). Nitrobenzene (0.42 mol dm^{-3}) was present in all runs

Some previous work has been done on the nitration of mesitylene in this solvent;[10] the kinetics observed were consistent with reaction through the nitronium ion and the work indicates that under our conditions the rate of formation of the nitronium ion should be rate determining.[10]

In the present work, the concentrations of mesitylene (0.42—0.84 mol dm^{-3}) have been greater than those used previously. A group of such kinetic runs is shown in Figure 1: the results for run A ([ArH] 0.42 mol dm^{-3}) have the expected kinetic form for the rate-determining formation of the nitronium ion and the corresponding rate-coefficient [k_1, equation (1)] is 3.3×10^{-4} s^{-1} at 24 °C. This value cannot be compared directly with those reported previously[10] because of differences in the conditions of reaction. It is however within the range of values for this rate coefficient (2.9×10^{-4}—4.5×10^{-4} s^{-1}) obtained previously from the nitration of toluene ([ArH] 0.3 mol dm^{-3}) in trifluoroacetic acid containing 0.1—0.8 mol dm^{-3} of water at 25 °C. Our solutions are more aqueous (10% by weight of water) but the acidity function of trifluoroacetic acid is not very sensitive to the concentration of water over the range 90—100% acid.[11]

$$\text{Rate} = k_1[HNO_3] \qquad (1)$$

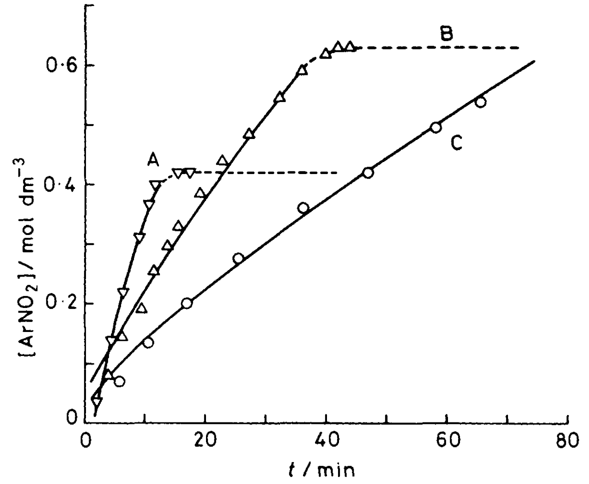


Figure 2. Nitration of mesitylene in the presence of sodium azide (0.084 mol dm^{-3}). The conditions of reaction are otherwise as described for runs A—C in Figure 1

Table 1. First-order rate coefficients [k_1, equation (1)] for the nitration of mesitylene by nitric acid (2.1 mol dm^{-3}) in trifluoroacetic acid containing 10% w/w of water at 24 ± 0.5 °C. Nitrobenzene (0.42 mol dm^{-3}) was also present

[ArH]	[NaN$_3$]	[NaOAc]	10^4k_1
mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	s^{-1}
0.42			3.3
0.42	0.08		3.4
0.63	0.08		1.4
0.84	0.08		0.71
0.42	0.05	0.45	0.74
0.42	0.1	0.4	0.81
0.42	0.2	0.3	0.84

Runs B and C in Figure 1 show how the kinetic form changes as the concentration of mesitylene is increased: the initial reaction rate decreases but the reaction shows autocatalysis. The decrease in the initial reaction rate is almost certainly a further example of the medium effect reported previously[10,12] and the autocatalysis appears to derive from a nitrous acid-catalysed process. The evidence for this comes partly from the strong catalysis of the reaction by low concentrations of nitrous acid (Figure 1, run D) and partly from the absence of the autocatalysis in the presence of azide ions (an effective trap for nitrous acid).[13] The relevant runs are shown in Figure 2. The solid lines in Figure 2 correspond to calculated curves according to equation (1) and the resulting values of k_1 are given in Table 1. This Table also includes rate coefficients for runs in which the concentration of azide ions is varied while the total base concentration ([N_3^-] + [OAc^-]) is held constant: the results show that increasing the concentration of azide ions above 0.05 mol dm^{-3} does not lead to a further reduction in the reaction rate.

These results indicate that, for nitration in these relatively concentrated solutions, we have to consider two reaction paths, the classical reaction through the nitronium ion and a nitrous acid-catalysed reaction that can give rise to autocatalysis. The first can be isolated by the addition of a low concentration of azide ions, and the second can be made to predominate by the addition of a low concentration of nitrous acid. No sign of nuclear polarisation was observed in the ^1H n.m.r. spectra.

Kinetic Studies by ^{15}N N.m.r. Spectroscopy.—These runs were carried out using $H^{15}NO_3$ (95 or 99% ^{15}N) in trifluoroacetic acid containing 10% (w/w) of water. Nitrobenzene labelled with ^{15}N was used as an internal standard for the intensity measurements and the chemical shifts. It is convenient to consider first the runs carried out in the presence of azide ions and relating therefore to nitration by the nitronium ion. Some sulphuric acid was added to these solutions to bring the half-life of the reaction into the region where nuclear polarisation might be readily observed.

The ^{15}N n.m.r. absorption of $H^{15}NO_3$ in this medium appears initially as a sharp peak 31 p.p.m. to high field of nitrobenzene; this peak moves downfield by *ca.* 2 p.p.m. in the course of reaction. During reaction this peak varies in height in a somewhat irregular manner and a new peak for nitromesitylene appears 9.1 p.p.m. to low field of nitrobenzene. The changes in the spectra are shown for one kinetic run in Figure 3 and the corresponding intensities are given in Table 2. The final columns of this Table show the extent of reaction calculated from the intensity of the ^{15}N n.m.r. absorption of nitro-

Table 2. Intensities of the ^{15}N n.m.r. signals in the uncatalysed nitration of mesitylene (ArH) (0.84 mol dm^{-3}) with $H^{15}NO_3$ (2.10 mol dm^{-3}) in trifluoroacetic acid at 25 °C in the presence of $Ph^{15}NO_2$ (0.42 mol dm^{-3}), sulphuric acid (0.166 mol dm^{-3}), and sodium azide (0.084 mol dm^{-3}). Number of pulses, 4; delay time, 30 s

	Recorded intensities			Corrected intensities[a]		Reaction (%)	
t/min	$Ar^{15}NO_2$	$Ph^{15}NO_2$	$H^{15}NO_3$	$Ar^{15}NO_2$	$H^{15}NO_3$	^{15}N	^1H[b]
4—6	3.1	6.8	27.7	0.22	1.00	22	29
7—9	5.3	5.0	29.6	0.51	1.45	51	39
11—13	7.4	6.2	34.6	0.57	1.36	57	48
18—20	9.0	7.3	32.5	0.59	1.09	59	62
26—28	12.3	5.3	29.3	1.12	1.35	(112)	71
35—37	12.4	6.3	30.7	0.95	1.19	95	84
46—48	12.0	6.2	24.4	0.93	0.97	93	93
55—57	14.0	6.6	29.3	1.02	1.09		
73—134[c]	9.7	4.7	17.3	1.00	0.90		

[a] Relative to absorption of $Ph^{15}NO_2$ and then adjusted to give a final value of unity for $Ar^{15}NO_2$ and an initial value of unity for $H^{15}NO_3$. [b] Calculated by interpolation at the mean times from a run with identical concentrations followed by ^1H n.m.r. spectroscopy at 24 °C. [c] Using 123 pulses.

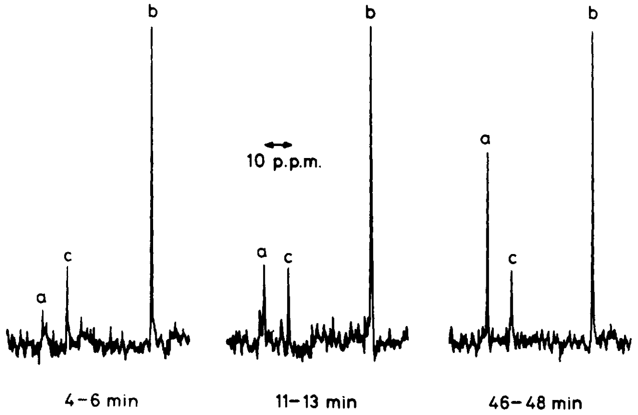


Figure 3. ^{15}N N.m.r. spectra during the catalysed nitration of mesitylene (ArH) under the conditions described in Table 2. a, $Ar^{15}NO_2$; b, $H^{15}NO_3$; c, $Ph^{15}NO_2$

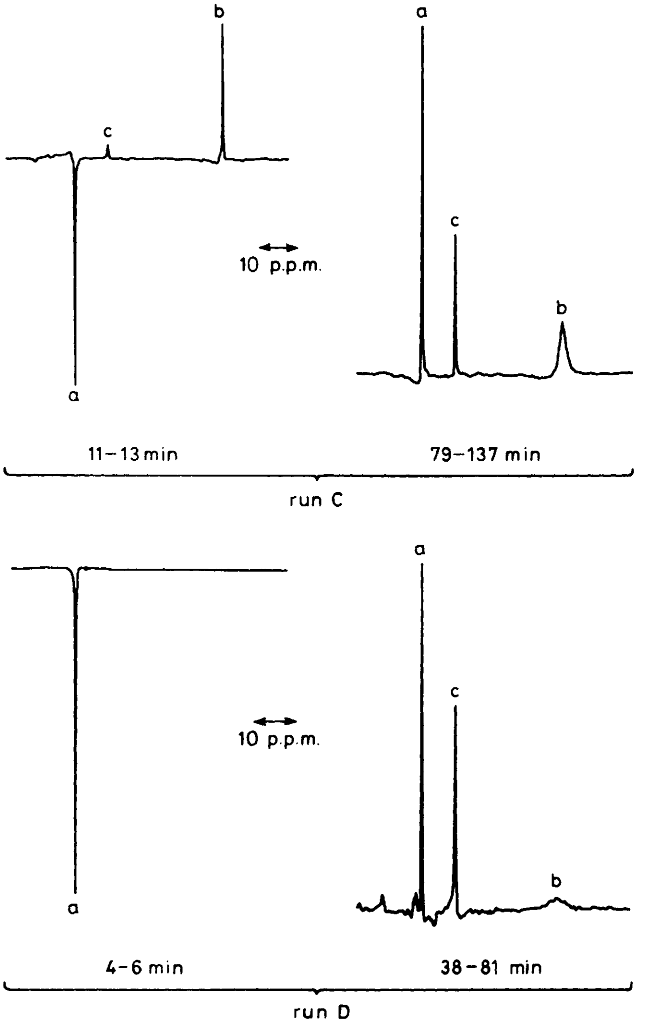


Figure 4. ^{15}N N.m.r. spectra during the nitrous acid-catalysed nitration of mesitylene (ArH) under the conditions described in Tables 3 (run C) and 4 (run D). The labelling of the peaks follows that in Figure 3

Table 3. Intensities of the ^{15}N n.m.r. signals in the autocatalysed nitration of mesitylene (ArH) under the conditions listed in Table 2 but without the sulphuric acid and sodium azide. Sodium acetate (0.084 mol dm^{-3}) was also present

	Recorded intensities			Corrected intensities[a]	
t/min	$Ar^{15}NO_2$	$Ph^{15}NO_2$	$H^{15}NO_3$	$Ar^{15}NO_2$	$H^{15}NO_3$
1—3	−4.7	3.9	27.7	−0.49	1.00
4—6	−20.3	5.8	37.7	−1.42	0.92
7—9	−40.6	6.6	38.6	−2.51	0.83
11—13	−71.3	7.4	44.7	−3.91	0.85
15—17	−105.0	7.0	45.1	−6.10	0.91
19—21	−173.0	8.1	41.9	−8.71	0.73
22—24	−244.9	8.6	40.2	−11.58	0.66
26—28	−257.9	8.0	33.7	−13.07	0.59
30—32	−168.4	7.7	28.1	−8.89	0.51
34—36	−32.1	8.1	9.7	−1.61	0.17
38—40	6.3	7.3	5.9	0.35	0.11
42—44	13.5	7.1	*b*	0.66	*b*
57—59	14.4	6.9	*b*	0.85	*b*
70—72	16.0	8.2	*b*	0.79	*b*
143—145	16.0	6.5	*b*	1.00	*b*

[a] See footnote *a*, Table 2. [b] Very broad peak.

mesitylene and that calculated from the ^1H n.m.r. spectra of a run under almost identical conditions. The comparison of these columns shows that the extents of reaction as calculated from the ^{15}N n.m.r. spectra are scattered about the line defined by the ^1H n.m.r. spectra. The results from ^{15}N n.m.r. spectroscopy are clearly less accurate but give no evidence for anomalous intensities arising from nuclear polarisation.

A very different result is obtained when the azide ions are replaced by acetate ions. The nitromesitylene peak in the initial ^{15}N n.m.r. spectra then appears in emission and the intensity of this emission increases until it is 13 times greater than the absorption at the end of reaction. The characteristics of the spectra are illustrated in Figure 4, run C, and the intensities before and after correction with respect to nitrobenzene are shown in Table 3. The marked increase in the intensity of the emission is a little later than the time of maximum autocatalysis shown in an identical run followed by ^1H n.m.r. spectroscopy (Figure 1C).

Two less obvious characteristics of these reactions are the increase in the intensity of absorption of the nitrobenzene by a factor of about two during the run and the marked broadening and decrease in height of the peak for $H^{15}NO_3$ (Table 3). Both presumably derive from the nitrous species produced in the autocatalytic process. Since some of these species should be radicals, the resulting local magnetic fields should lead to a general reduction in the relaxation time of ^{15}N nuclei in the solution and hence under our conditions (see Experimental section) to an increase in the intensity of absorption. Some exchange could also occur between the N^{III} and N^{V} states leading to broadening of the $H^{15}NO_3$ absorption.

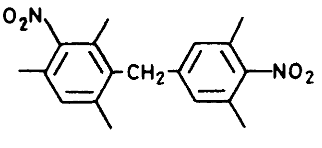
If nitrous acid is initially present in the nitrating mixture, the emission peak of nitromesitylene is initially very intense: for the run listed in Table 4, the intensity of the first peak exceeds that of the final absorption by a factor of 220 (Table 4). When such spectra are plotted on a suitable scale, this marked enhancement of one peak causes the absorption of the nitrobenzene standard and the nitric acid to be lost (Figure 4D). Normal absorption spectra are observed at the end of reaction but the peak for the excess of nitric acid is even broader than that when no initial nitrous acid is present (compare Figure 4, runs C and D). This is in marked contrast to the spectra of the excess of nitric acid when azide ions are present (Figure 3).

Products. Analysis of the reaction products by h.p.l.c. has confirmed earlier reports that the nitration of mesitylene by the nitronium ion mechanism gives no significant amount of side-

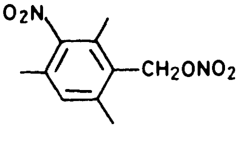
Table 4. Intensities of the ^{15}N n.m.r. signals in the nitrous acid-catalysed nitration of mesitylene (ArH) under the conditions given in Table 3 but with sodium nitrite (0.048 mol dm^{-3}) in the place of the sodium acetate.

	Recorded intensities		Corrected intensities^a
t/min	$\mathrm{Ar^{15}NO_2}$	$\mathrm{Ph^{15}NO_2}$	$\mathrm{Ar^{15}NO_2}$
1—3	−1 800		−220.6
4—6	−1 000		−122.6
7—9	−121		−14.8
11—13	−12.6	5.1	−7.9
15—17		5.1	
22—24	3.0	4.5	0.4
32—34	6.2	5.1	0.8
38—81	6.9	4.2	1.0

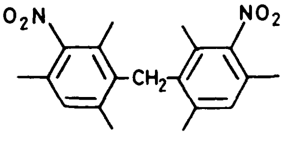
^{a} See footnote a, Table 2. The great intensity of the peak for nitromesitylene in the early stages of this run prevented detection of the nitrobenzene peak; the figure of 5.1 was used for the nitrobenzene intensity in this region.



(1) 0·07 %



(2) 0·36 %



(3) 2·01 %

products.[7,8] The products from a run carried out in the presence of nitrous acid under the conditions defined in Table 4 gave on analysis by h.p.l.c. 94.15% nitromesitylene and more than 15 other products. Three of these have been identified by a combination of m.s. and ^{1}H n.m.r. spectroscopy and are shown above together with the yields found. The remaining products proved difficult to separate and analyse; these unidentified products amount to 3.4% of the total yield.

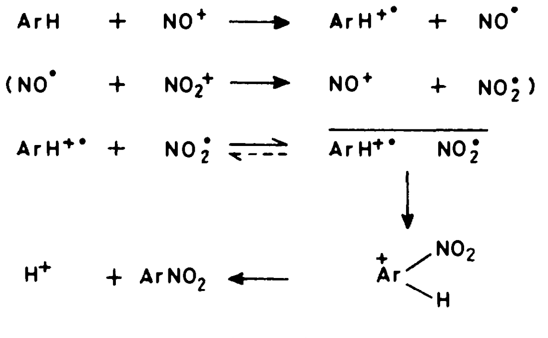
When structure (3) was first identified as one of the major side-products, it seemed possible that it might be derived from some isodurene present as an impurity in the mesitylene used. The analysis was therefore repeated using mesitylene that had been rigorously purified by g.l.c.: the result was unchanged.

Discussion

The above results show that the emission signal in the ^{15}N n.m.r. spectrum of nitromesitylene is observed only when nitrous acid catalysis is present and that the intensity of the emission increases with the rate of the catalysed reaction. The intensity of the emission signal exceeds that of the final absorption signal (observed when reaction is effectively complete) by a factor which depends on the conditions and time but which can be > 200 (Table 4). In ^{15}N n.m.r. spectroscopy, an enhanced emission signal can arise from the nuclear Overhauser effect (NOE)[14] because of the negative magnetogyric ratio of ^{15}N but that cannot be the explanation of our results since our experiments were carried out without proton decoupling. The corresponding enhancement factor for an NOE emission signal is also limited to a factor[14] of *ca.* 4. The enhanced emission observed here points clearly to chemically induced dynamic nuclear polarisation and hence to the presence of radical pairs on the reaction path.[15]

$$\mathrm{ArH} + \mathrm{NO^+} \xrightarrow[\text{slow}]{} \mathrm{ArNO} + \mathrm{H^+}$$
$$\mathrm{ArNO} + \mathrm{HNO_3} \xrightarrow[\text{fast}]{} \mathrm{ArNO_2} + \mathrm{HNO_2}$$
$$\mathrm{HNO_2} + \mathrm{H^+} \rightleftharpoons \mathrm{NO^+} + \mathrm{H_2O}$$

Scheme 1.



Scheme 2.

In principle, the nuclear polarisation could be generated through the reaction of the nitric acid with the nitrous species in the solution and then carried over into the nitromesitylene by a conventional electrophilic substitution. A related process accounts for the nuclear polarisation sometimes found in the products of diazo-coupling when this occurs by a direct electrophilic reaction.[16] However, that cannot be the explanation here since there is no evidence for such an emission signal in the ^{15}N n.m.r. absorption of the nitric acid during reaction (Figure 4). The nuclear polarisation must therefore arise from the interaction of the nitrous and nitric species with the aromatic compound.

To consider the possible ways in which this can occur, it is necessary to start with the mechanisms that have been proposed for nitrous acid-catalysed nitration. The classical mechanism[9] (Scheme 1) involves initial nitrosation followed by an oxidation step that regenerates the nitrous acid. More recently,[17] a different mechanism has been suggested involving an initial electron transfer as shown in the first line of Scheme 2. This second mechanism was originally proposed to explain certain special features of the nitration of *NN*-dimethylaniline[17] but there is evidence that it may apply also to other systems.[18]

In order to distinguish between the reaction paths in Schemes 1 and 2, some work has been carried out in trifluoroacetic acid as solvent on the reaction of nitrous acid with mesitylene and on the reactions of nitrosomesitylene (see Experimental section). When nitrous acid (0.02—0.84 mol dm^{-3}) is added to a solution of mesitylene (0.84 mol dm^{-3}) in trifluoroacetic acid at 24 °C, there is no evidence from the ^{1}H n.m.r. spectra of any formation of nitrosomesitylene over a period of 2.5 h but the n.m.r. signals for the ArH and $\mathrm{CH_3}$ protons are shifted to low field to an extent that depends on the amount of nitrous acid present. This accords with the fast formation of an equilibrium concentration of a π-complex.[19] Nitrosomesitylene has been prepared in other ways; it is sufficiently stable in trifluoroacetic acid for the ^{1}H n.m.r. spectrum to be determined but decomposes over a period of *ca.* 1 h to yield nitromesitylene and a number of other unidentified products. When nitric acid is present in the reaction mixture, the reactions of nitrosomesitylene are far more rapid but again a variety of products are formed with *ca.* 30% nitromesitylene.

The absence of any fast formation of the nitroso compound from mesitylene and nitrous acid under our conditions together with the complexity of the product composition in the oxidation of nitrosomesitylene points against the mechanism presented in Scheme 1. To check whether the oxidation of a nitroso-compound could give rise to the observed CIDNP effect, ^{15}N labelled nitrosomesitylene has been prepared and oxidised under the conditions used for the nitrous acid-catalysed nitration. No such effect was observed when the oxidation was carried out immediately after the solution of the nitroso compound in trifluoroacetic acid. A small emission signal for the formation of the nitro compound was observed when the rate of oxidation was decreased by the addition of azide ions and also when the nitrosomesitylene was permitted to remain for some time in the solvent before the addition of the nitric acid. The formation and reactions of nitrosomesitylene are being investigated further but it does not seem that reaction through the nitroso compound as outlined in Scheme 1 is a likely explanation of our results, or that it contributes significantly to the overall reaction.

Before considering the results in terms of the reactions in Scheme 2, it is helpful to look at the application of Kaptein's rule[20] for the phase of net polarisation to a radical pair from an aromatic cation radical ($ArH^{+\cdot}$) and a ^{15}N-labelled nitrogen radical $R^{\cdot}$. When ^{15}N n.m.r. spectroscopy is used, this rule has the form of equation (2).

$$\Gamma = -\mu\varepsilon a_N(g_{R\cdot} - g_{ArH^{+\cdot}}) \qquad (2)$$

In this equation, the sign of Γ is positive for absorption and negative for emission. The initial negative sign on the right hand side was not present in the original formulation[20] but is necessary[21] because of the negative magnetogyric ratio of ^{15}N. The sign of μ is positive when the radical pair is formed by the diffusion together of free radicals and negative when the radical pair is formed from a singlet precursor, *e.g.*, by electron transfer from ArH to R^+. The sign of ε is positive for recombination products and negative if the products derive from radicals that have escaped from the cage. The values of the hyperfine coupling constant (a_N) for the ^{15}N nucleus in the radicals $NO^{\cdot}$ and $NO_2^{\cdot}$ should be negative because of the negative magnetogyric ratio.*

The sign of the term ($g_{R\cdot} - g_{ArH^{+\cdot}}$) requires more careful consideration. The *g* values[23] for a number of aromatic radical cations lie in the range 2.002 49—2.002 55. The reported *g* values for nitrogen dioxide extend on both sides of this range[24] but this variation appears to come, at least in part, from the ease with which nitrogen dioxide forms complexes with other molecules, especially dinitrogen tetraoxide.[25] The most recent value[22] (*g* 2.0000) appears to be the most reliable because the corresponding e.s.r. spectrum and the hyperfine coupling constant (a_N 50 G for $^{14}NO_2$) are then as expected; the *g* value also accords with results for related radicals.[26] The reported *g* values for nitric oxide[27] are in the range 1.909—1.983. Thus for R = NO and NO_2, the sign of ($g_{R\cdot} - g_{ArH^{+\cdot}}$) should be negative.

There is therefore sufficient information to permit the phase of nuclear polarisation to be used as a mechanistic criterion in nitration and related reactions. If the nitration of an aromatic compound occurred by electron transfer from ArH to $^{15}NO_2^+$ followed by the essentially complete combination of the radicals formed, the ^{15}N n.m.r. spectrum of the product could show enhanced absorption but not emission. The corresponding formation of $Ar^{15}NO$ from ArH and $^{15}NO^+$ following electron transfer should give the same result and so if nitromesitylene were formed by that route followed by oxidation the product could show enhanced absorption. However, the application of Kaptein's rules to the reactions in Scheme 2 shows that this reaction path could give rise to the observed emission signal for $Ar^{15}NO_2$ because the radical pair is formed by diffusion.

This emission signal can also be rationalised in the following, somewhat oversimplified, way. When the radicals $ArH^{+\cdot}$ and $^{15}NO_2^{\cdot}$ diffuse together, the resulting radical pair can be in either a singlet or a triplet state. If the radical pair is in a singlet state, there need be no barrier to combination. If the radical pair is in a triplet state, combination cannot occur unless a triplet ⟶ singlet conversion occurs before the radicals finally separate. It follows from the electron–nuclear spin coupling[15b] that for the radical pair considered here the triplet singlet interconversion is faster when the ^{15}N nucleus ($I = \frac{1}{2}$) is in the upper of the two permitted states. The product should therefore contain initially an excess of nuclei in this state and hence give rise to an emission signal. A more complete account should stress the possibility of triplet ⟶ singlet conversions occurring between successive encounters of the same radical pair.[28]

The interpretation of the nuclear polarisation in terms of the partition of the $\overline{ArH^{+\cdot}NO_2^{\cdot}}$ radical pair between combination and dissociation receives support from studies in which this type of radical pair is generated in other ways. In some related work on the nitramine rearrangement[5] of amines $ArNR^{15}NO_2$ and on a rearrangement following *ipso*-attack[6] by $^{14}NO_2^{\cdot}$ on $C\text{-}^{15}NO_2$, the same type of radical pair has been generated and ^{15}N nuclear polarisation has been found in the product. In these studies, the reactions of the $\overline{ArH^{+\cdot}NO_2^{\cdot}}$ radical pair give rise to enhanced absorption but that is exactly as expected from equation (2) since here the radical pair is being generated from a singlet precursor. We have also looked for nuclear polarisation in the ^{13}C and ^{1}H n.m.r. spectra of nitromesitylene but this has not been found probably because of the lower coupling constants in the aromatic radical, shorter relaxation times of these nuclei, and (with the ^{13}C spectra) because isotopically enriched material was not available.

We propose therefore that the nuclear polarisation observed in the nitrous acid-catalysed nitration of mesitylene arises from the partition of the radical pair $\overline{ArH^{+\cdot}NO_2^{\cdot}}$ between combination and dissociation as shown in Scheme 2. The earlier stages of the reaction are represented in a simplified way in this Scheme: thus, the complex formation between the aromatic compound and the nitrous species is omitted and the oxidation of nitric oxide to the nitrosonium ion cannot be limited to the reaction with the nitronium ion for the rate of the nitrous acid-catalysed nitration greatly exceeds the rate of formation of nitronium ions in the medium. The second line of Scheme 2 should therefore be taken to indicate the overall stoicheiometry of the oxidation, not the mechanism.

The probable mechanism of formation of the side-products (**1**)—(**3**) from the radical cation is shown in Scheme 3.† The formation of the nitro product (**3**) was most unexpected but the corresponding hydrocarbon (**4**) is among the minor products formed when mesitylene is oxidised in trifluoroacetic acid with cobalt(III) and manganese(III) trifluoroacetates;[29] these reactions are also considered to involve the mesitylene radical cation.

The stoicheiometry of the side-reactions implies a reduction

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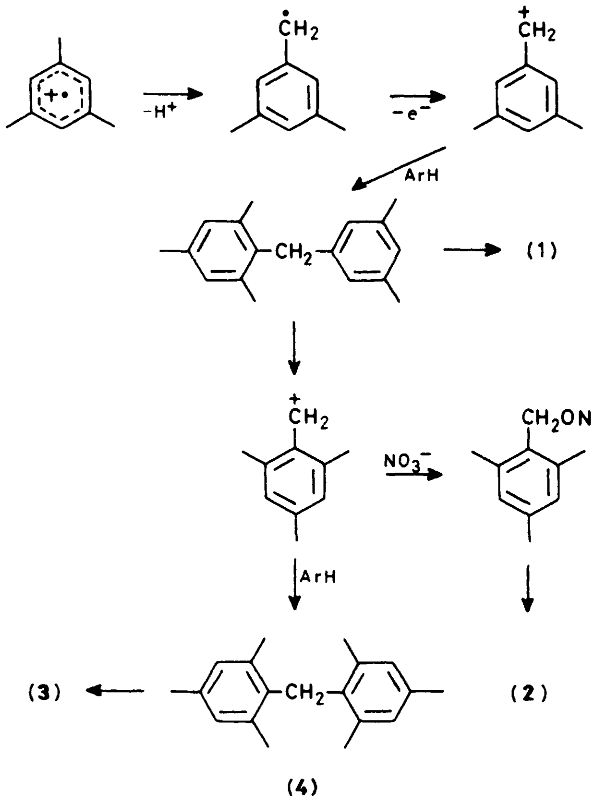
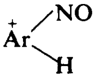
* This argument assumes a positive spin density in the 2*s* orbital of the nitrogen atom (*cf.* ref. 22).

† Another mechanism for nitrous acid-catalysed nitration and for the formation of such side-products has been suggested in the literature[19] but we have not discussed it in detail since it does not appear to offer an explanation of the nuclear polarisation.



Scheme 3.

of nitric acid to nitrous acid and thus explains the autocatalysis observed (Figure 1). This autocatalysis is the probable explanation of one curious result in the literature[10] in which the relative reactivity of mesitylene to toluene is recorded as 4.0 when determined by competition experiments and as 2.8 when determined by direct kinetic studies. The concentrations used in competition experiments were much greater and would thus favour a contribution from the autocatalysed reaction path. Since the autocatalysis derives from the oxidation of the substrate it should be much less important for toluene.

The remaining problems include the mechanism of the initial steps in the nitrous acid-catalysed reaction. These have been written in Scheme 3 in terms of NO$^+$ but the equilibria involving nitrous acid have not been studied in detail* in trifluoroacetic acid and this may be an oversimplification. The initial formation of the aromatic cation radical could involve the formation of the Wheland intermediate  $\overset{+}{\mathrm{Ar}}\genfrac{}{}{0pt}{}{\diagup \mathrm{NO}}{\diagdown \mathrm{H}}$ followed by homolytic dissociation of the C–N bond. Other problems concern the mechanism of oxidation of nitric oxide and the proportions of side-products, especially the presence of a relatively large amount of the nitro product (3).

One clear result from this work is the absence of any nuclear polarisation in the direct attack by the nitronium ion on mesitylene. If formation of the radical pair ArH$^{+\cdot}$NO$_2^{\cdot}$ had occurred in this reaction, some nuclear polarisation would have been expected since such polarisation has been observed when analogous singlet radical pairs have been formed in other ways.[5,6] We conclude therefore that the reaction of mesitylene with the nitronium ion goes directly to the Wheland intermediate.

Experimental

Materials.—Mesitylene was distilled before use and some was further purified by g.l.c. using a 20 ft × $\frac{3}{8}$ in O.D. column packed with 20% Carbowax 20M on Supasorb 60—80 at 120 °C. Trifluoroacetic acid was distilled at least three times before use. Trifluoroacetic anhydride was distilled once. Nitric acid (95—99% ^{15}N) was obtained as a 40% solution from B.O.C. Prochem and was used without purification. The nitrating solutions were prepared by adding trifluoroacetic anhydride (3.3 ml) to the aqueous $H^{15}NO_3$ solution (1.47 g) at 0 °C and diluting with trifluoroacetic acid. Sodium nitrate (95% ^{15}N) was obtained from Goss Chemicals.

For the preparation of [^{15}N]nitrosomesitylene, a solution of sodium [^{15}N]nitrate (1.0 g) in trifluoroacetic acid (35 ml) and water (3 ml) was kept over sodium azide (19.5 mg) for *ca.* 1 min and then added to mesitylene (0.96 g) in trifluoroacetic acid (2 ml). After 6 h in the dark at room temperature, the mixture was quenched with water (75 ml) and extracted with methylene dichloride (3 × 40 ml). The extract was dried and evaporated to give [^{15}N]nitromesitylene (1.1 g). This was dissolved in ethanol and reduced (Sn–HCl) to give the corresponding amine (0.876 g). A solution of *m*-chloroperbenzoic acid (2.05 g) in chloroform (25 ml) was added to a solution of the amine in chloroform (30 ml); the mixture was stirred for 2.5 h at 0 °C and left to come to room temperature overnight. After washing with aqueous sodium sulphite (2%), aqueous sodium carbonate (5%), and water, the organic layer was evaporated to give [^{15}N]nitrosomesitylene (0.97 g) which, after recrystallisation from ethanol, had m.p. 121—121.5 °C (lit.,[30] 119 °C).

Kinetic Runs.—The reactions followed by ^{1}H n.m.r. spectroscopy were carried out at 24 ± 0.5 °C using a Varian HA-100 spectrometer. The extent of reaction was normally calculated from the relative heights of the signals for the aromatic protons in mesitylene and nitromesitylene, since these are well separated singlets. However, towards the end of the runs involving autocatalysis, the signal for the aromatic protons in mesitylene moves to lower field and overlaps with that of nitromesitylene (a consequence of complex formation, see Discussion section); the extent of reaction was then calculated from the relative heights of the signals for the methyl protons. When sodium nitrite (0.84 mol dm^{-3}) is added to a solution of mesitylene (0.84 mol dm^{-3}) in trifluoroacetic acid containing 10% w/w water, the aromatic signal moves 0.24 p.p.m. downfield and the methyl signal moves 0.03 p.p.m. downfield; these shifts were measured using tetramethylammonium chloride as an internal standard.

The studies involving ^{15}N n.m.r. spectroscopy were carried out at 25 ± 0.5 °C using a Varian XL-200 Fourier transform spectrometer. The concentrations of reagents were the same as those used in the corresponding runs followed by ^{1}H n.m.r. spectroscopy but both the nitric acid and the nitrobenzene were labelled with ^{15}N (95—99%). The spectra were measured using a pulse angle of 25° and those taken during reaction involved either four pulses with a delay of 30 s or eight pulses with a delay of 15 s.

The oxidation of [^{15}N]nitrosomesitylene by nitric acid was studied using equal concentrations of reactants (0.28 mol dm^{-3}) under the conditions used in the studies of nitration. The reaction was too fast for quantitative study but, with freshly prepared solutions, no evidence of nuclear polarisation was seen.

Products.—A solution of nitric acid in trifluoroacetic acid (6 ml, 2.1 mol dm^{-3}) containing sodium nitrite (20 mg) was added to a mixture of mesitylene (0.6 g; purified by g.l.c.) and trifluoroacetic acid (0.2 ml). After 24 min, the mixture

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* Our preliminary studies by u.v. spectroscopy suggest that molecular nitrous acid is not a major component of this equilibrium.

was quenched with water and extracted with chloroform. Evaporation of the solvent gave a dark orange product (687.2 mg) which was analysed by h.p.l.c. using 2 × 25 cm × 4.5 mm ID Partisil 5 silica gel columns, a refractive index detector, and elution with 25% methylene dichloride—petroleum spirit +0.0125% methanol. The products separated in this way included nitromesitylene (647.0 mg) and three minor products identified by ^{1}H n.m.r. and m.s. studies as structures (**1**)—(**3**). These were not fully characterised because of the small amounts available. One (2.5 mg) gave δ ($CDCl_3$) 2.27 (3 H, s), 2.30 (3 H, s), 2.42 (3 H, s), 5.53 (2 H, s), and 7.03 (1 H, s); *M*, 240.0742. The substituted benzyl nitrate (**2**) ($C_{10}H_{12}N_2O_5$) requires *M* 240.0746. Another product (0.5 mg) had δ ($CDCl_3$) 2.12 (3 H, s), 2.24 (3 H, s), 2.25 (6 H, s), 2.28 (3 H, s), 4.01 (2 H, s), 6.71 (2 H, s), and 7.02 (1 H, s); *M* 328.1455. The dinitro product (**1**) ($C_{18}H_{20}N_2O_4$) requires *M* 328.1423. The third product (13.8 mg), m.p. 147.5—148 °C, had δ ($CDCl_3$) 2.10 (3 H, s), 2.22 (3 H, s), 2.30 (3 H, s), 4.14 (1 H, s), and 6.96 (1 H, s); *M* 342.1589. The dinitro compound (**3**) ($C_{19}H_{22}N_2O_4$) requires *M* 342.1579. The products from the oxidation of nitrosomesitylene were not separated and the estimate of *ca.* 30% nitromesitylene is based upon the ^{1}H n.m.r. spectra of the extracted reaction mixture before and after the addition of a known amount of nitromesitylene.

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