^{15}N Nuclear Polarisation in Nitration and Related Reactions. Part 5.[1] The Borderline between the Classical and the Electron Transfer Mechanisms in Nitration by the Nitronium Ion

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

The nitration of *p*-xylene, mesitylene, naphthalene, [$^2H_8$]naphthalene, durene and some related compounds has been followed by ^{15}N NMR spectroscopy in a mixture of trifluoroacetic acid and nitromethane containing sufficient sodium azide to inhibit nitrous acid catalysed nitration. Significant ^{15}N nuclear polarisation occurs with durene and the naphthalenes and has been analysed by comparison with theoretical curves leading to the calculation of enhancement coefficients. The results indicate that a small part of the reaction of naphthalene with nitronium ions under these conditions involves direct electron transfer between the reactants before the formation of the Wheland intermediate. The extent of this electron transfer is much greater than expected from Marcus theory calculations based on an outer-sphere electron transfer (ET) reaction: the discrepancy is discussed in terms of the initial interaction between the reactants and the solvent effects on the equilibrium constant for the electron transfer.

The previous papers in this series[2] have provided compelling evidence for the involvement of radical reactions in nitrous acid catalysed nitration; this evidence, in conjuction with kinetic studies,[3–5] has led to a mechanism which explains most of the features of these processes. Electron transfer from the aromatic compound now appears to be the initial step on the predominant reaction path in these nitrous acid catalysed reactions.

The importance of electron transfer in nitration by the nitronium ion is less clear. Electrochemical calculations of the rate coefficients suggest that it is unimportant for all common substrates[6] and, in agreement with this, no evidence of ^{15}N nuclear polarisation was found in our previous study of the nitration of mesitylene by nitronium ions.[2a] However, some ^{15}N nuclear polarisation consistent with electron transfer to the nitronium ion was found in the corresponding nitration of durene (1,2,4,5-tetramethylbenzene)[1] and in our preliminary study of the nitration of naphthalene.[7]

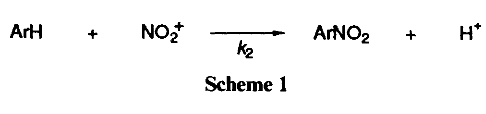
The present work was intended to provide more quantitative evidence on this mechanistic borderline. A series of compounds, including mesitylene and compounds more easily oxidised than mesitylene, has been nitrated under conditions particularly favourable to the detection of ^{15}N nuclear polarisation and the observed variation of the nuclear polarisation with time has been compared with theoretical curves and used to calculate enhancement coefficients. The conditions required the nitration of relatively high concentrations of the aromatic compounds (*ca.* 0.3 mol kg^{-1}) with a half-life of *ca.* 10 min. It was also essential to prevent any contribution from the nitrous acid catalysed mechanism of nitration since this process gives rise to strong ^{15}N nuclear polarisation of the opposite phase to that expected from any electron transfer from the aromatic compound to the nitronium ion.[1,2a]

The last condition proved to be the most difficult to satisfy, particularly when naphthalene was the substrate. This is probably because the nitrous acid catalysed nitration of naphthalene contains a term that is second order with respect to the substrate[8] and so this reaction path is much more intrusive under the above conditions than with the low concentrations of naphthalene used previously in kinetic studies by UV spectroscopy.[9] Eventually, a solvent containing trifluoroacetic acid (49%), nitromethane (50%) and water (1%) (all w/w) was found to be suitable but it was also necessary to include the solutes sodium azide (0.3 mol kg^{-1}) and methanesulphonic acid (0.92 mol kg^{-1}). The sodium azide is needed to stop the nitrous acid catalysed nitration and the methanesulphonic acid to bring the reaction rate to the required value. Nitrobenzene (0.3 mol kg^{-1}) was also added since ^{15}N-labelled nitrobenzene was used as a standard in the ^{15}N NMR studies. For runs followed by ^{1}H NMR spectroscopy using the Varian XL-200 NMR spectrometer, a deuteriated solvent mixture (CD_3NO_2, CF_3CO_2D, D_2O) of the same percentage composition was used instead and many of the runs followed by ^{15}N NMR spectroscopy were carried out in this solvent mixture. The use of the mixed solvent and above solutes at 29 °C will be referred to as the standard conditions for reaction and whether or not the solvent is deuteriated will be specified for each run.

Under these conditions, the nitrations of *p*-xylene, mesitylene, naphthalene, [$^2H_8$]naphthalene, 2-methylnaphthalene and durene (*ca.* 0.3 mol kg^{-1}) with nitric acid (*ca* 0.3 mol kg^{-1}) were found to proceed smoothly without any evidence of nitrous acid catalysis.

Results

Kinetics.—A kinetic study of the nitration of naphthalene and mesitylene was carried out using ^{1}H NMR spectroscopy to obtain the rate coefficients required in the construction of the theoretical curves. From previous studies,[2a] it was known that the nitration of mesitylene (0.28 mol kg^{-1}) with excess nitric acid in trifluoroacetic acid containing 10% water gave zero-order kinetics with respect to the aromatic compound over the greater part of the reaction. This corresponds to the condition $k_2[ArH] \gg k_{-1}[H_2O]$ in Scheme 1. The reactions considered here were therefore expected to be zero-order with respect to the aromatic compound and first-order with respect to the nitric



$$HNO_3 + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2^+ + H_2O$$

$$ArH + NO_2^+ \xrightarrow[k_2]{} ArNO_2 + H^+$$

Scheme 1

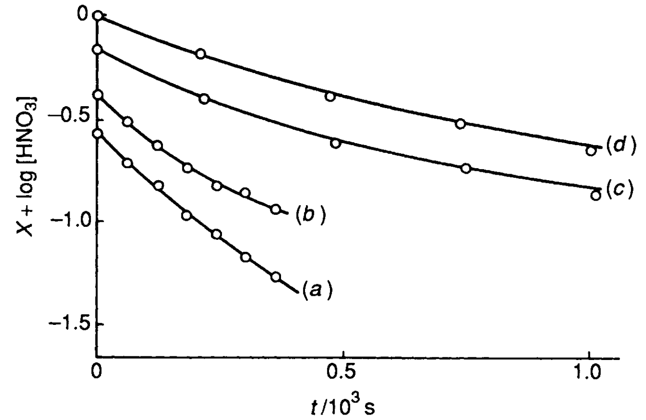


Fig. 1 Logarithmic plots of the concentration of nitric acid in the nitration of mesitylene and naphthalene under the standard conditions. For clarity, they are displaced by 0.2 units. Run (*a*): [mesitylene] = 0.411 mol kg^{-1}, [HNO_3] = 0.279 mol kg^{-1}, normal solvent, X = 0. Run (*b*): [mesitylene] = 0.276 mol kg^{-1}, [HNO_3] = 0.274 mol kg^{-1}, normal solvent, X = 0.2. Run (*c*): [mesitylene] = 0.243 mol kg^{-1}, [HNO_3] = 0.254 mol kg^{-1}, deuteriated solvent, X = 0.4. Run (*d*): [naphthalene] = 0.259 mol kg^{-1}, [HNO_3] = 0.282 mol kg^{-1}, deuteriated solvent, X = 0.6.

Table 1 Values of k_1 and k_2/k_{-1} used in the calculated curves shown in Fig. 1

Run	Substrate	Solvent	$k_1/10^{-3}$ s^{-1}	k_2/k_{-1}
(*a*)	Mesitylene	Undeuteriated	6.7	6.25
(*b*)	Mesitylene	Undeuteriated	6.82	5.6
(*c*)	Mesitylene	Deuteriated	3.02	5.6
(*d*)	Naphthalene	Deuteriated	3.76	5.4

acid, giving overall first-order kinetics. Unfortunately, this simple kinetic form was not obtained, as shown by the curvature of the first-order plots for the nitration of mesitylene and naphthalene in Fig. 1.

The reactions still appear to be zero-order with respect to the aromatic compounds, at least over the initial part of the reaction, for the initial slopes of the logarithmic plots are independent of the concentration of the aromatic compounds. This is illustrated for the nitration of mesitylene in Fig. 1 where the initial slopes of plots (*a*) and (*b*) are almost identical although the two concentrations of mesitylene differ by a factor of 1.5. This accords with the rate-determining formation of the nitronium ion. The runs (*c*) and (*d*) in the deuteriated solvent are slower by about a factor of two: this suggests that the stretching frequencies of the relevant O–H bonds during the heterolysis of the nitric acidium ion are lower than those in the molecular acids present. The solvent isotope effect is in the opposite direction to that expected in aqueous solutions but, in our solutions, the acidic species are mainly present as molecular acids not as hydroxonium ions.

The deviation from first-order kinetics probably comes in part from a decrease in the effective acidity of the medium during the reaction since the amount of water generated during the reaction is a significant fraction of the concentration of methanesulphonic acid present. Some of the curvature should also derive from the change in the ratio [ArH]/[H_2O] during the reaction for this should cause the water to compete more effectively with the aromatic compound for the nitronium ions.

For our purposes, it is unnecessary to determine the relative importance of these factors: it is sufficient to provide a model to reproduce the variation of the rate of nitration with time. A number of complex models have been tried[10] but, for simplicity, we have chosen to use only the second of the above factors and have analysed the kinetics in terms of the values of k_1, and the ratios of k_2/k_{-1} (Scheme 1). This model leads to eqn. (1). The values of the variables have been obtained from the computer program KINETIC[11] which carries out the numerical integration of a set of kinetic equations and optimisation of the parameters. When applied to eqn. (1), this program leads to the results in Table 1 and the plots in Fig. 1.

$$-\mathrm{d}[\mathrm{HNO_3}]/\mathrm{d}t = k_1[\mathrm{HNO_3}][\mathrm{ArH}]/\{[\mathrm{ArH}] + (k_{-1}/k_2)[\mathrm{H_2O}]\} \quad (1)$$

The results in Fig. 1 show that this approach provides a satisfactory fit to the experimental data. As expected, the values of k_1 are very similar for runs (*a*) and (*b*), and although there is some difference between the values of k_1 for runs (*c*) and (*d*), this is probably within the greater experimental error of the run with naphthalene (see Experimental). The values of k_2/k_{-1} are also similar in the different runs. However, in spite of this agreement, no physical significance should be attached to the values of k_2/k_{-1}, partly because this is an oversimplified approach and partly because of the uncertainty over the initial amount of 'unprotonated' water in the medium (here taken to be 0.56 mol kg^{-1} in the undeuteriated solvent and 0.5 mol kg^{-1} in the deuteriated solvent).

A number of kinetic runs have been carried out on the nitration of naphthalene involving variation of the concentrations of naphthalene, nitric acid and sodium azide.[10] The results accord with the above conclusions and show also that changing the concentration of sodium azide from 0.277 to 0.525 mol kg^{-1} approximately halves the rate of reaction, presumably from the change in the acidity of the medium.

Studies of ^{15}N *Nuclear Polarisation*.—A number of kinetic runs have been carried out using 99% ^{15}N labelled nitric acid and have been followed by ^{15}N NMR spectroscopy. In the initial studies on naphthalene, carried out in the absence of sodium azide, no nuclear polarisation was seen, probably because the reaction was so strongly catalysed by nitrous acid that it was effectively complete by the time the NMR measurements could be taken. In the presence of low concentrations of sodium azide, the initial spectra show a strong emission signal for 1-nitronaphthalene [Fig. 2, spectrum (*a*)], as expected for the nitrous acid catalysed mechanism.[2a] However, when the concentration of sodium azide is raised to *ca.* 0.3 mol kg^{-1}, this emission signal is replaced by an enhanced absorption signal; this is illustrated by the relative heights of the signals for the product and the standard ($Ph^{15}NO_2$) in Fig. 2, spectra (*c*) and (*d*).

A number of compounds have now been studied under the standard conditions (see above) for which the nitrous acid catalysed reaction path appears to be eliminated. In each spectrum, the height of the signal for the product has been measured relative to that of the standard and the resulting ratios (h_t) have been divided by the value of the ratio at the end of the run (h_∞). The variation in the values of h_t/h_∞ with time is shown in Figs. 3 and 4. The runs illustrated were all carried out in the deuteriated solvent but the reactions of mesitylene, naphthalene, [$^2H_8$]naphthalene and 2-methylnaphthalene were also studied in the undeuteriated solvent with essentially the same results.

The substrates studied fall into three groups. For *p*-xylene and mesitylene (Fig. 3), the values of h_t/h_∞ during the run are below unity and hence give no evidence for any enhanced absorption. For naphthalene and [$^2H_8$]naphthalene (Fig. 3), the initial values of h_t/h_∞ are *ca.* 2 even though these initial values correspond to only *ca.* 33% reaction. The enhancement of these signals is relatively small but reproducible. The presence of the remaining nitric acid at this stage is shown by the strong

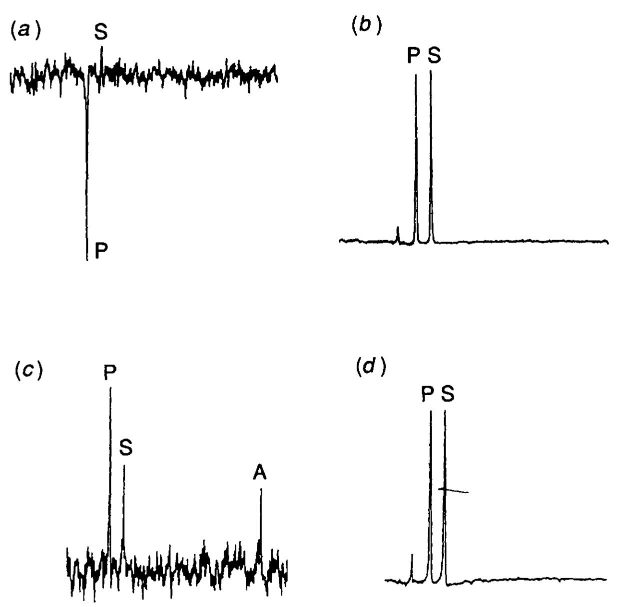


Fig. 2 Initial and final ^{15}N NMR spectra during the nitration of naphthalene under the standard conditions. Spectra (*a*) and (*b*) refer to the nitrous acid catalysed reaction: $[ArH] = 0.258$ mol kg^{-1}, $[HNO_3] = 0.337$ mol kg^{-1}, $[NaN_3] = 0.079$ mol kg^{-1}. Spectra (*c*) and (*d*) refer to the reaction with nitronium ions: $[ArH] = 0.252$ mol kg^{-1}, $[HNO_3] = 0.326$ mol kg^{-1}, $[NaN_3] = 0.272$ mol kg^{-1}. Signals: P, 1-nitronaphthalene; S, standard (nitrobenzene); A, nitric acid. The unidentified peak in each of the final spectra comes from the natural abundance of ^{15}N nuclei in the solvent. For chemical shifts, see Experimental. (*a*) $t = 178$ s; (*b*) $t = \infty$; (*c*) $t = 220$ s; (*d*) $t = \infty$.

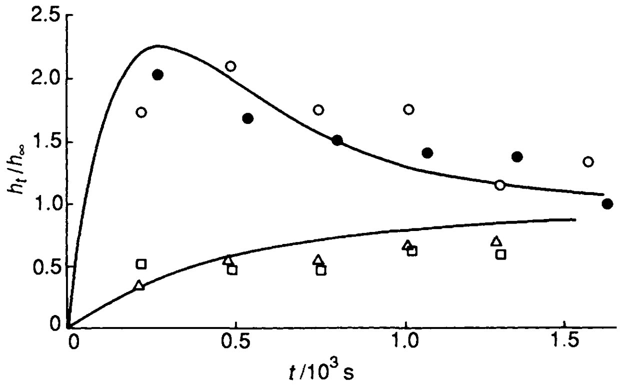


Fig. 3 The variation in the height of the ^{15}N signals during the nitration of the substrates giving unpolarised or weakly polarised products under standard conditions in the deuteriated solvent. *p*-Xylene (□): $[ArH] = 0.269$ mol kg^{-1}, $[HNO_3] = 0.299$ mol kg^{-1}, $[NaN_3] = 0.273$ mol kg^{-1}. Mesitylene (△): $[ArH] = 0.249$ mol kg^{-1}, $[HNO_3] = 0.267$ mol kg^{-1}, $[NaN_3] = 0.274$ mol kg^{-1}. Naphthalene (○): see Fig. 2, spectra (*c*) and (*d*). [$^2H_8$]Naphthalene (●): $[ArH] = 0.26$ mol kg^{-1}, $[HNO_3] = 0.317$ mol kg^{-1}, $[NaN_3] = 0.261$ mol kg^{-1}. The theoretical curves for the first and last pairs of substrates are so similar that each pair of curves has been replaced by a single line.

signal for $H^{15}NO_3$ in Fig. 2, spectrum (*c*). For durene and the 1-nitration of 2-methylnaphthalene (Fig. 4), the initial values of h_t/h_∞ are 17 and 5, respectively, corresponding to a large and unambiguous enhancement.

A few other compounds have been studied.[10] Mesitylene and 2,4,6-[$^2H_3$]mesitylene have been compared by nitration in the undeuteriated solvent and give similar values of h_t/h_∞. The 4-nitration of 1-methylnaphthalene gives similar results to those for the 1-nitration of 2-methylnaphthalene. One kinetic run was carried out on the nitration of 1,2,4-trimethylbenzene: the ^{15}N signals for the 5-nitro and 6-nitro products gave slight evidence for enhanced absorption but any such enhancement is less than that observed with naphthalene and could be within the experimental error of the measurements.

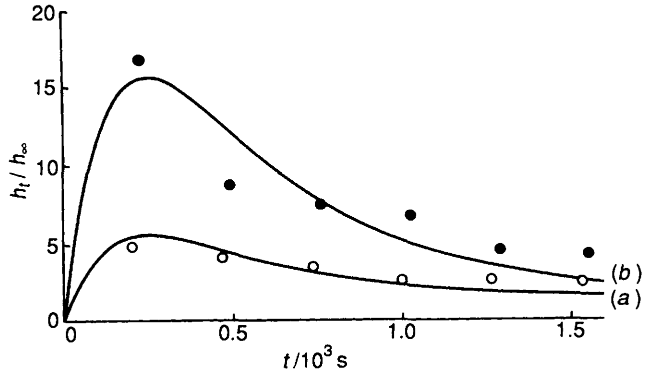
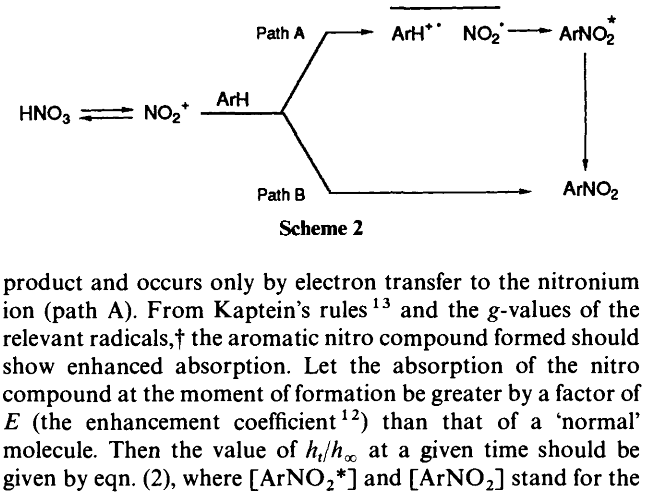


Fig. 4 The variation in the height of the ^{15}N signals during the nitration of the substrates giving strongly polarised products under standard conditions in the deuteriated solvent. 2-Methylnaphthalene (*a*): $[ArH] = 0.265$ mol kg^{-1}, $[HNO_3] = 0.29$ mol kg^{-1}, $[NaN_3] = 0.275$ mol kg^{-1} (nitration in 1-position). Durene (*b*): $[ArH] = 0.265$ mol kg^{-1}, $[HNO_3] = 0.275$ mol kg^{-1}, $[NaN_3] = 0.276$ mol kg^{-1}.

Calculation of the Theoretical Curves.—The variation of nuclear polarisation with time has been discussed for a number of simple kinetic forms[12] but not for the more complex reaction path required by the present observations and shown in Scheme 2. Consider first that the reaction gives only a single product and occurs only by electron transfer to the nitronium ion (path A). From Kaptein's rules[13] and the *g*-values of the relevant radicals,† the aromatic nitro compound formed should show enhanced absorption. Let the absorption of the nitro compound at the moment of formation be greater by a factor of *E* (the enhancement coefficient[12]) than that of a 'normal' molecule. Then the value of h_t/h_∞ at a given time should be given by eqn. (2), where $[ArNO_2^*]$ and $[ArNO_2]$ stand for the concentrations of the polarised and normal products.



Scheme 2

$$h_t/h_\infty = (E[ArNO_2^*]/[ArNO_2]_{t=\infty}) + ([ArNO_2]/[ArNO_2]_{t=\infty}) \quad (2)$$

Since we are assuming that all of the reaction occurs by path A, the rate of change of $[ArNO_2^*]$ is simply the difference between the rate of formation of $ArNO_2^*$ [given by eqn. (1)] and its rate of relaxation to form the normal product. This leads to eqns. (3) and (4), where β is the reciprocal of the relaxation time (T_1) of the ^{15}N nucleus in the nitro group.

$$d[ArNO_2^*]/dt = k_1[HNO_3][ArH]/\{[ArH] + (k_{-1}/k_2)[H_2O]\} - \beta[ArNO_2^*] \quad (3)$$

$$d[ArNO_2]/dt = \beta[ArNO_2^*] \quad (4)$$

---

† For a discussion of the application of Kaptein's rules to this radical pair, see ref. 2(*a*).

Table 2 Comparison of the enhancement factors[a] (E) with the standard potentials (E°) of the redox systems ($ArH^{+\bullet} + e^- = ArH$)

Substrate	E	E°/V (solvent)
Mesitylene	0.67	2.35 (trifluoroacetic acid)[b,c]
p-Xylene	0.72	2.30 (trifluoroacetic acid)[b,c]
[$^2H_8$]Naphthalene	8.21	
Naphthalene	8.76	2.08 (acetonitrile)[d]
2-Methylnaphthalene	25.1	
Durene	76	2.07 (acetonitrile)[c]

[a] For reaction under the standard conditions in the deuteriated solvent. [b] Containing also 7% trifluoroacetic anhydride. [c] Ref. 15. [d] Ref. 16.

The value of k_1 must obviously be independent of the substrate and, in principle, this should also be true for the ratio k_2/k_{-1} since all of the substrates considered here react with the nitronium ion at or near the rate of encounter.[14] The relevant values from Table 1 ($k_1 = 3 \times 10^{-3}$ mol kg^{-1}, $k_2/k_{-1} = 5.6$) and the relaxation time of the ^{15}N nucleus (180 s) have therefore been used to calculate the variation of [$ArNO_2$*] and [$ArNO_2$] with time by the numerical integration of eqns. (3) and (4). The KINETIC program[11] has then been used to select the best value of E for each substrate from eqn. (2).

The possible formation of more than one product is not a significant complication provided that the products are formed concurrently and that the product ratio is not a function of time. From eqn. (2), the values of h_t/h_∞ are unchanged if the terms [$ArNO_2$*], [$ArNO_2$] and $[ArNO_2]_{t=\infty}$ are reduced by a given factor. The consequences for the theoretical curves of concurrent reaction by the electron transfer and classical routes (Scheme 2, paths A and B) are less obvious but a more detailed analysis[10] shows that a contribution from the classical path merely moves the apparent value of the enhancement coefficient E towards unity.

The values of E obtained from the KINETIC program[11] are given in Table 2 and have been used to construct the theoretical curves shown in Figs. 3 and 4.

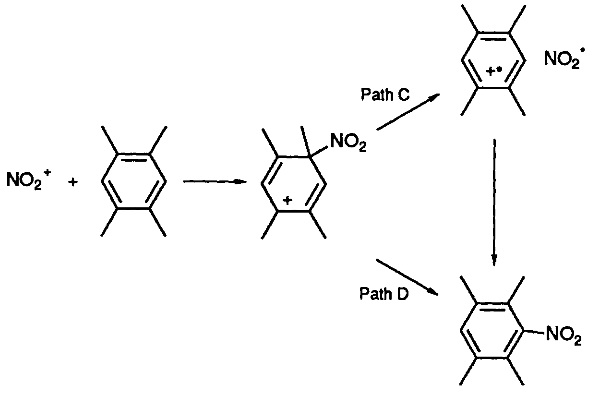
Discussion

In view of the complexity of the reaction mixture, it is necessary to demonstrate first that the ^{15}N nuclear polarisation observed derives from the nitration reaction and is not generated in some other process and merely carried over into the nitro products (as happens, for example, in the diazocoupling of phenols[17]). On this subject, three pieces of evidence point in the same direction. Firstly, the nuclear polarisation is observed in some, but not all, of the substrates used: it must therefore depend on some reaction of the substrate. Secondly, there is no obvious nuclear polarisation generated in the nitric acid. Thirdly, the variation of the nuclear polarisation with time accords reasonably well with the theoretical curves. The agreement is most marked with the curves for 2-methylnaphthalene and durene (Fig. 4) and it is with these compounds that the signals are strongest and the experimental error least. We believe therefore that the nuclear polarisation derives from the process of nitration.

The principle advantage of the comparison with theoretical curves comes from the derivation of the enhancement coefficient (E), for this provides a measure of the extent of polarisation in a form that should be independent of the rate of reaction. This facilitates comparison with results obtained under other conditions although such comparisons need to be treated with caution because of the complexity of the factors determining the extent of nuclear polarisation.[18]

With mesitylene and *p*-xylene, the absence of any enhanced absorption in the ^{15}N signals is consistent with the direct formation of the nitro compound (Scheme 2, path B). This accords with the previous studies on mesitylene[2a] and the only unexpected feature is that the corresponding enhancement coefficients are below unity (Table 2). This could derive from a trace of reaction by the nitrous acid catalysed mechanism but is more likely to result from experimental error. Where there is no enhanced absorption, the signal to noise ratio is low and the experimental error is correspondingly increased.

With durene, the enhancement of the ^{15}N signals ($h_t/h_\infty > 15$, Fig. 4) is much greater than that observed previously ($h_t/h_\infty = 2$),[1] a measure of the greater effectiveness of the present conditions in generating nuclear polarisation. The previous interpretation of this polarisation involved homolysis following *ipso*-attack (Scheme 3) and in view of the much greater enhancement coefficient found with durene (76) compared with naphthalene (8.76) [a compound with a very similar standard potential (Table 2)], this interpretation is still very plausible. However, the results do not imply that the rearrangement of this *ipso*-intermediate occurs only by homolysis followed by recombination, for the enhancement coefficient found with durene is still very low compared with the values found in the homolytic 1,3-rearrangement of 4-methyl-4-nitrocyclohexa-2,5-dienone to 4-methyl-2-nitrophenol ($E \approx 1000$).[19] It seems likely therefore that the homolytic reaction in the nitration of durene is a minor component of the overall reaction path. *ipso*-Attack should also be important in the nitration of *p*-xylene, but here there is no evidence of any homolytic reaction path, presumably because this compound is less easily oxidised (Table 2).



Scheme 3

The most interesting of the present results concerns the nitration of naphthalene for, in this compound, the observed polarisation cannot arise from *ipso*-attack followed by homolysis. The possibility that homolysis might follow the formation of a Wheland intermediate is disproved by the very similar degree of polarisation observed in naphthalene and [$^2H_8$]naphthalene. Thus, if the homolysis of the C–N bond in a Wheland intermediate were in direct competition with the loss of the proton, the replacement of the protons by deuterons would necessarily lead to a greater proportion of homolysis and hence to a greater degree of nuclear polarisation.

The possibility that homolysis might follow attack at the bridgehead positions has been investigated by MO calculations using the MNDO and MINDO/3 methods.[21] The fully optimised results for the energies of the intermediates deriving from attack at the 1-, 2- and 9-positions are given in Table 3 and full details of the calculated structures of the intermediates are available elsewhere.[10] If, to allow for solvent effects, the energy differences for attack at the 1- and 2-positions are scaled down to correspond to the observed 1-/2- ratio of 12 (see Experimental), then the ratio for attack at the 1- and 9-positions becomes a factor of 3.4×10^6 (MNDO) or 5.1×10^6 (MINDO/3). These magnitudes imply that any polarisation arising from attack at the bridgehead positions can be ignored.

Table 3 Calculations by MNDO and MINDO/3 methods of the heats of formation (ΔH_f) of the intermediates produced by the addition of a nitronium ion to the 1-, 2- and 9-positions of naphthalene

	MNDO		MINDO/3	
Position	ΔH_f kJ mol^{-1}	$\delta\Delta H_f$/ kJ mol^{-1}	ΔH_f/ kJ mol^{-1}	$\delta\Delta H_f$/ kJ mol^{-1}
1	1031		921	
		19		14
2	1050		935	
		96		73
9	1146		1008	

It follows, therefore, that the nuclear polarisation observed with naphthalene, and presumably also with 2-methylnaphthalene, derives from a stage before the formation of the Wheland intermediate and hence corresponds to the direct electron transfer shown in Scheme 2, path A. The very low value of the enhancement coefficient in comparison with that for the rearrangement of 4-methyl-4-nitrocyclohexa-2,5-dienone (*vide supra*) suggests that only a very small proportion of the reaction occurs by the electron transfer route and this accords with the different α-/β- ratios found in the nitronium ion reaction and in nitrous acid catalysed nitration (see Experimental). However, even if the contribution of the electron transfer path is as little as 1%, the corresponding second-order rate coefficient must be *ca.* 10^7 dm^3 mol^{-1} s^{-1} since naphthalene reacts with nitronium ions at about the rate of encounter.[14] The rate coefficient for the electron transfer is therefore far greater than that expected from Marcus theory calculations[6] (1.3×10^{-6} dm^3 mol^{-1} s^{-1}).

One reason for this may come from the preliminary interaction between the nitronium ion and the aromatic compound, for the Marcus theory calculations[6] are based on an outer sphere electron transfer in which any such interaction is ignored. Any partial electron transfer should cause slight bending of the nitronium ion and thus bring the geometry of the ion closer to that of the nitrogen dioxide radical. Evidence for initial interaction with related nitrating agents comes from the electronic spectra of the complexes formed.[21] However, a more significant factor could be the marked solvent dependence of the standard potentials for the $NO_2^{\bullet}/NO_2^+$ equilibrium.[22] The Marcus theory calculations have been based on the standard potential for the above equilibrium in acetonitrile[6] but recent electrochemical calculations[22] of log *K* for eqn. (5) have given the following values in different solvents: acetonitrile, −8.67; sulpholane, 0.8; nitromethane, 6.75. These results imply that the boundary between the classical and the electron transfer mechanisms of nitration is likely to be very dependent on the solvent used, with nitromethane favouring the electron transfer process.

$$NO_2^+ + \text{NaphtH} = NO_2^{\bullet} + \text{NaphtH}^{+\bullet} \qquad (5)$$

$$\text{NaphtH} = \text{naphthalene}$$

The high proportion of nitromethane used in the solvent for the present work may therefore have been a fortunate choice for observing the electron transfer processes. For nitration under the above conditions, our conclusions are that the borderline for the detection of the direct electron transfer process (electron transfer before the formation of the Wheland intermediate) should lie with substrates whose standard electrode potentials (Table 2) are between those of mesitylene and naphthalene. For the formation of radical pairs following *ipso*-attack (Scheme 3, path C), the corresponding borderline should lie with substrates whose standard electrode potentials are between those of *p*-xylene and durene (a very similar region, Table 2). However, the electron transfer path is unlikely to be the predominant one for any of the substrates studied since all of the enhancement coefficients are much less than those observed for the known radical pair rearrangements of the 4-nitrocyclohexadienones.[19]

The ready formation of radical cation dimers [$(ArH)_2^{+\bullet}$] from some aromatic molecules, including naphthalene,[23] has not been considered in the above discussion since we have no evidence on whether or not this facilitates the electron transfer to nitronium ions. Reaction through this dimer does, however, provide a separate kinetic term in the nitrous acid catalysed nitration of naphthalene[8] and such reactions may therefore contribute to the nuclear polarisation observed above.

Experimental

Materials.—Nitrobenzene, [$^2H_5$]nitrobenzene, naphthalene, [$^2H_8$]naphthalene, *p*-xylene, mesitylene, 1,2,4-trimethylbenzene, durene and the methylnaphthalenes were obtained from the Aldrich Chemical Co. in grades of the highest purity available and were used without further purification. [^{15}N]Nitrobenzene was prepared by the addition of a solution of [^{15}N]nitric acid (2.5 g, 40% aq.) in acetic acid (5 cm^3) to a solution of benzene (1.2 g) in acetic anhydride (25 cm^3) at 0 °C. Sulphuric acid (98%, 1 cm^3) was then added and the solution was stirred for 3 h. The reaction mixture was then poured into ice-water, extracted (CH_2Cl_2), and dried ($MgSO_4$). Evaporation of the solvent gave [^{15}N]nitrobenzene (1.8 g, 95% yield). 1,3,5-[$^2H_3$]Mesitylene was prepared by leaving mesitylene (1 g) in a mixture of deuterium oxide (1.66 g) and trifluoroacetic anhydride (8.3 g) for 25 days at room temperature. The reaction mixture was then diluted with more deuterium oxide (30 cm^3), poured into ice-water, extracted (CH_2Cl_2), and dried ($MgSO_4$). Evaporation of the solvent gave 1,3,5-[$^2H_3$]mesitylene (0.97 g, 96% yield). The 100 MHz ^1H NMR spectrum indicated 85% deuteriation of the aromatic protons.

Nitric acid (100%) was prepared by the distillation at 0 °C under reduced pressure (1 mmHg) of a mixture of fuming nitric acid (100 cm^3) and sulphuric acid (98%, 100 cm^3); it was then stored at −25 °C. [^{15}N]Nitric acid (100%) was prepared in a similar way except that, since it was supplied as a 40% aqueous solution by MSD Isotopes, the relative volume of sulphuric acid used was increased by a factor of five. Nitromethane, [$^2H_3$]nitromethane and [^2H]trifluoroacetic acid were obtained from the Aldrich Chemical Co. in grades of the highest purity available and were used without further purification. The trifluoroacetic acid and trifluoroacetic anhydride were distilled from phosphorus pentoxide before use. The methanesulphonic acid was a BDH Organics reagent and was used as supplied.

Kinetic Runs.—The aromatic compound and the standard (nitrobenzene) were initially dissolved in a mixture (*ca.* 2 cm^3) of nitromethane (81.7%) and trifluoroacetic acid (18.3%). The nitric acid was initially dissolved in aqueous trifluoroacetic acid (*ca.* 1 cm^3, 97.3%) containing the required amount of sodium azide. After 15 min at 29 °C, the two solutions were mixed and the combined solution was added to the weighed amount of methanesulphonic acid. Because the reaction mixtures were prepared by weighing out the various components, the compositions were not quite uniform, with standard deviations of ±1.32% for the trifluoroacetic acid and ±0.026 mol kg^{-1} for the methanesulphonic acid. The exact composition by weight of each kinetic run is available[10] but we do not believe that these variations effect the validity of the arguments used in this paper.

For mesitylene, the kinetic runs followed by ^1H NMR spectroscopy were based on the ratio of the integrals of the signals for the aromatic protons in nitromesitylene to the sum of the integrals for these protons in mesitylene and nitromesitylene. For naphthalene, these calculations were based on the ratio of

Table 4 Chemical shifts,[a] relative to nitrobenzene, of the ^{15}N signals in the reaction products

Compound	δ/ppm
Nitric acid	35.5
1-Nitronaphthalene	−3.7
1-Methyl-4-nitronaphthalene	−4.0
2-Methyl-8-nitronaphthalene	−4.0
5-Nitropseudocumene	−5.0
2-Nitro-*p*-xylene	−5.4
2-Methyl-1-nitronaphthalene	−6.2
1-Methyl-8-nitronaphthalene	−7.3
Dinitrodurene	−7.7
Nitromethane	−8.2
6-Nitropseudocumene	−8.3
Nitromesitylene	−8.8
Nitrodurene	−12.0

[a] Low field values negative.

the integral for the low-field doublet in 1-nitronaphthalene to the integral of the methyl signal of the methanesulphonic acid. These measurements were somewhat less accurate since the low-field doublet in 1-nitronaphthalene corresponds to only a single proton.

The 100 MHz ^1H NMR spectra were taken on a JEOL JNM-PS-100 CW spectrometer. The 200 MHz ^1H NMR spectra were taken on a Varian XL-200 FM spectrometer using the deuteriated solvent and 64 pulses each of 20 μs followed by a 2 s acquisition time and a 2 s delay. An outer NMR tube containing D_2O was used to provide the lock signal.

The runs followed by ^{15}N NMR spectroscopy were carried out on the Varian XL-200 instrument. Labelled nitric acid (99% ^{15}N) was used and the spectra involved 24 pulses, each of 20 μs with an acquisition time of 0.8 s and a 10 s delay. The other conditions were exactly the same as those of the corresponding ^1H NMR studies. At the end of each kinetic run, a further spectrum using 3000–5000 pulses was obtained. The ^{15}N chemical shifts observed for the products are given in Table 4.

Products.—At the conclusion of the kinetic runs, the ^1H NMR spectra of the reaction mixtures were shown to accord with the NMR spectra of the expected products. For naphthalene, the product ratio was calculated using the integrals of the low field doublets in 1-nitronapthalene and 2-nitronaphthalene. For the pure components, the ratios of the integrals of these doublets to the total integrals are 0.137 and 0.129, respectively. From the relative values of these integrals in the reaction mixtures, the ratio of 1-nitronaphthalene to 2-nitronaphthalene under the above conditions is 12.3 for reaction with the nitronium ion and 23.4 for reaction by nitrous acid catalysed nitration. The former value accords well with the value of 10 reported for the nitration of naphthalene at 25 °C in a nitric acid/sulphuric acid mixture in the presence of urea.[9] The higher value for the nitrous acid catalysed reaction is consistent with the greater selectivity reported for the reaction of naphthalene radical cations with nitrogen dioxide in CH_2Cl_2 where a 1-/2- ratio of 65 has been reported[6] for the much lower temperature of −45 °C.

Calculations.—The calculations involving the KINETIC program[11] were carried out on a VAX 6000-430 computer at Royal Holloway and Bedford New College. At an earlier stage of this work,[10] the KINETIC program was used to calculate both the rate coefficients and the enhancement factors for each kinetic run but the present approach appears to give a more consistent set of conclusions. The semi-empirical molecular orbital calculations were carried out on a Cray 1S/2200 computer at the University of London Computer Centre.

Acknowledgements

One of us (J. F. J.) thanks the SERC for a studentship.

References

1 Part 4, A. H. Clemens, J. H. Ridd and J. P. B. Sandall, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1227.
2 A. H. Clemens, J. H. Ridd and J. P. B. Sandall, *J. Chem. Soc., Perkin Trans. 2*, (*a*) 1984, 1659; (*b*) 1984, 1667; (*c*) A. H. Clemens, P. Helsby, J. H. Ridd, F. Al-Omran and J. P. B. Sandall, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1217.
3 J. C. Giffney and J. H. Ridd, *J. Chem. Soc., Perkin Trans. 2*, 1979, 618.
4 U. Al-Obaidi and R. B. Moodie, *J. Chem. Soc., Perkin Trans. 2*, 1985, 467.
5 M. Ali and J. H. Ridd, *J. Chem. Soc., Perkin Trans. 2*, 1986, 327.
6 L. Eberson and F. Radner, *Acc. Chem. Res.*, 1987, **20**, 53.
7 J. F. Johnston, J. H. Ridd and J. P. B. Sandall, *J. Chem. Soc., Chem. Commun.*, 1989, 244.
8 J. R. Leis, M. E. Peña and J. H. Ridd, *Can. J. Chem.*, 1989, **67**, 1677.
9 R. G. Coombes, R. B. Moodie and K. Schofield, *J. Chem. Soc., Perkin Trans. 2*, 1968, 800.
10 J. F. Johnston, Ph.D. Thesis, University of London, 1989.
11 D. B. Hibbert and J. P. B. Sandall, *J. Chemometrics*, 1989, **3**, 569.
12 A. L. Buchachenko and Sh. A. Markarian, *Int. J. Chem. Kinet.*, 1972, **4**, 513.
13 R. Kaptein, *J. Chem. Soc., Chem. Commun.*, 1971, 732.
14 K. Schofield, *Aromatic Nitration*, Cambridge University Press, 1980, ch. 4.
15 C. J. Schlesener, C. Amatore and J. L. Kochi, *J. Am. Chem. Soc.*, 1984, **106**, 3567.
16 V. D. Parker, *J. Am. Chem. Soc.*, 1976, **98**, 98.
17 E. Lippmaa, T. Pehk, T. Saluvere and M. Magi, *Org. Magn. Reson.*, 1973, **5**, 441.
18 C. Richard and P. Granger, *Chemically Induced Dynamic Nuclear and Electron Polarisations—CIDNP and CIDEP* (vol. 8 of the series *NMR Basic Principles and Progress*, eds. P. Diehl, E. Fluck and R. Kosfeld), Springer-Verlag, Berlin, 1974, ch. 2.
19 S. M. Trevellick, Ph.D. Thesis, University of London, 1989.
20 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899; R. C. Bingham, M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc.*, 1975, **97**, 1285.
21 J. K. Kochi, *Acta Chem. Scand.*, 1990, **44**, 409.
22 A. Boughriet and M. Wartel, *J. Chem. Soc., Chem. Commun.*, 1989, 809.
23 M. A. J. Rodgers, *J. Chem. Soc., Faraday Trans. 1*, 1972, **68**, 1278.

Paper 0/05631F
Received 14*th December* 1990
Accepted 3*rd January* 1991