Review Article

Some Unconventional Pathways in Aromatic Nitration

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Dedicated to Professor Lennart Eberson on the occasion of his 65th birthday

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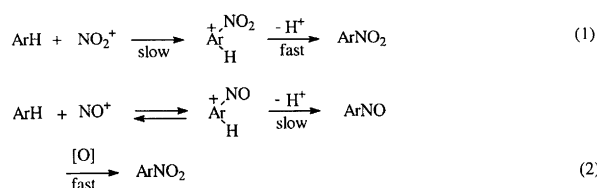
This review deals with a group of reaction paths for nitration in homogeneous solution associated particularly with the species NO^+, $NO_2^.$, $NO_3^.$ and N_2O_5. Studies on the properties of these and some related nitrogen compounds are considered first, with special reference to the interaction of these species with aromatic compounds. Evidence on the electron transfer mechanism of nitrous acid catalysed nitration, on nitration by nitrogen dioxide in organic solvents, on nitration by preformed dinitrogen pentoxide, and on ozone mediated nitration by nitrogen dioxide is then considered. The emphasis is on the mechanisms of these reactions when carried out using thermal rather than photochemical processes. Some interesting features of these mechanisms are then examined, with particular reference to the oxidation of aromatic substrates by $NO_3^.$ and possibilities for further work.

1. Introduction

In this review, the conventional pathways for nitration have been taken to be the main two mechanisms put forward by Hughes, Ingold and coworkers[1] and summarised in Scheme 1. The first of these involves the direct attack of the nitronium ion on the aromatic substrate followed by a fast proton loss [eqn. (1)]; the second involves the nitrosation of the aromatic substrate followed by the fast oxidation of the nitrosocompound [eqn. (2)]. The slow proton loss shown in the nitrosation stage was not recognised in the original formulation. The first of these pathways is still recognised as a valid model of nitration over a wide range of conditions[2,3] and the second certainly operates under some conditions.[4] However, in recent years a number of other reaction paths have been recognised, some corresponding to important new synthetic methods of nitration.[5] This review is concerned with a group of such pathways

involving thermal reactions in homogeneous solution and associated particularly with the species NO^+, $NO_2^.$, $NO_3^.$ and N_2O_5. The fact that these pathways involve rather closely related radical reactions makes it convenient to consider them together. The emphasis is on the mechanisms involved rather than the synthetic implications.

To avoid overlap with other recent or current reviews, two aspects of recent work are dealt with very briefly. One involves the reaction of nitrogen dioxide with phenols, for this is being covered in a separate review by Hartshorn[6] in this journal. The other concerns the possibility of initial electron transfer in the reaction of nitronium ions with aromatic compounds. Much of the original interest in this area stemmed from the suggestion of Perrin[7] that all aromatic compounds more reactive than toluene undergo nitration by initial electron transfer from the aromatic compound to the nitronium ion followed by reaction between the resulting aromatic radical cation and the nitrogen dioxide formed. The interest in this type of reaction path was further stimulated by the work of Kochi and coworkers[8] on the photochemical generation of aromatic radical cations and nitrogen dioxide within an encounter complex. However, Eberson et al.[2,3] have shown that the interpretation of the photochemical studies is much less straightforward than originally thought and that, even

$$\text{ArH} + \text{NO}_2^+ \xrightarrow[\text{slow}]{} \overset{+}{\underset{\text{H}}{\text{Ar}}}{\overset{\text{NO}_2}{}} \xrightarrow[\text{fast}]{-\text{H}^+} \text{ArNO}_2 \qquad (1)$$

$$\text{ArH} + \text{NO}^+ \rightleftharpoons \overset{+}{\underset{\text{H}}{\text{Ar}}}{\overset{\text{NO}}{}} \xrightarrow[\text{slow}]{-\text{H}^+} \text{ArNO}$$

$$\xrightarrow[\text{fast}]{[\text{O}]} \text{ArNO}_2 \qquad (2)$$

*Scheme 1.* The conventional reaction paths for nitration.

with compounds as reactive as naphthalene, the main reaction with the nitronium ion occurs without the involvement of a radical cation intermediate. This conclusion is in agreement with the results of chemically induced dynamic nuclear polarisation using ^{15}N-labelled nitronium ions;[9] the detailed arguments will be found in the quoted reviews.[2,3,9] There are, however, still some problems in this area concerning particularly thermal and photochemical nitration by N-nitropyridinium ions.[8a]

Before considering the new pathways for nitration, it is useful to look at some of the background information available on the relevant nitrogen compounds and their interaction with aromatic systems, for this helps in assessing the plausibility of some of the new reaction paths.

2. Interaction of the relevant nitrogen compounds with aromatic systems

2.1. Nitric oxide.
Nitric oxide is considered to be unreactive to non-activated arenes,[10] although a complex reaction occurs with some alkenes in the presence of a trace of nitrogen dioxide.[11] Its relevance here comes from its ready reaction with paramagnetic species, especially oxygen, to form more reactive intermediates.

2.2. Nitrosonium ion.
The nitrosonium ion interacts with aromatic compounds to give a variety of products depending on the substrate and the conditions (Scheme 2).* At low temperatures, in sulfur dioxide as solvent, the reaction of naphthalene and its methyl
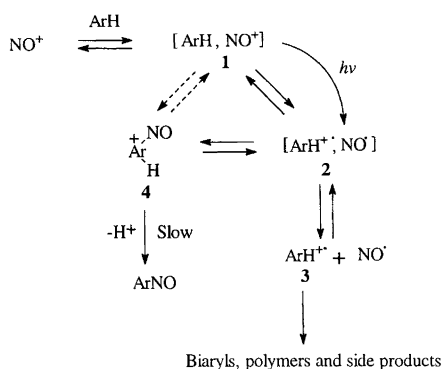
Scheme 2. The reactions of the nitrosonium ion with aromatic systems.

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* In Scheme 2 the reverse electron transfer is shown as occurring only via the radical pair complex 2 (an inner-sphere mechanism) in accord with the arguments of Kochi.[12] This complex is also shown as the source of the Wheland intermediate 4, although the possibility of the direct formation of this intermediate from the initial charge transfer complex 1 is indicated by the broken arrows. The presence of the broken arrows permits the complex 2 to be arise by homolysis of the Wheland intermediate as suggested by Radner.[13]

derivatives with $NO^+ \ AlCl_4^-$ stops at the π-complex stage 1, and the ^{1}H, ^{13}C and ^{15}N NMR spectra of these complexes have been determined.[14] Studies on the reactions of mesitylene, durene, pentamethylbenzene, and hexamethylbenzene with $NO^+ \ PF_6^-$ in dichloromethane[15] have led to the isolation of similar complexes as solid salts with the composition $(ArH, NO^+ \ PF_6^-)$, and X-ray crystallography on the mesitylene complex shows that the nitrosonium ion is positioned over the centre of the ring.[8a,12] These structures are clearly charge-transfer complexes and have characteristic colours.[12] Anisole forms a similar complex with $NO^+ \ AlCl_4^-$ in a sulfur dioxide–dichloromethane solvent at $-70\,^\circ C$, but under these conditions thioanisole forms an n-complex with the nitrosonium ion at the sulfur atom.[16]

At higher temperatures, and with the more activated aromatic compounds, an electron transfer is considered to occur to form a complex 2 containing the aromatic radical cation and nitric oxide. The electron transfer can be photoinduced by laser pulse excitation of the charge-transfer bands,[12] and this has permitted Kochi and coworkers to carry out a study of the rate coefficients of the various steps involved.[12] Dissociation of the complex 2 competes with the reverse electron transfer and typical reactions of the free radical cation 3 are then observed; thus naphthalene gives a complex mixture of hydrocarbons through partial polymerisation,[14] but with other substrates (e.g. 1,2,4-trimethoxybenzene) and in the presence of air, good yields of the corresponding biaryl can be obtained.[17]

With some easily oxidised substrates the radical cation 3 is the final product; thus it has been known for many years that the reaction of some heteroaromatic compounds (e.g. phenothiazine) with $NO^+BF_4^-$ in acetonitrile in the presence of a stream of nitrogen is a good way of obtaining the solid tetrafluoroborate salts of the corresponding radical cations.[18] Again, some further reactions can occur; thus carbazole reacts under these conditions to give 3,3'-dicarbazolyl tetrafluoborate.[18]

With some polymethylbenzenes and anisoles, the reaction with nitrosonium ions can be taken beyond the radical cation stage; the Wheland intermediate 4 is apparently formed, and the corresponding nitrosocompounds can be obtained in good yield using $NO^+BF_4^-$ in acetonitrile at room temperature.[19] The rate of this nitrosation reaction depends in a curious way on the structure of the substrate; thus m-xylene and mesitylene are far more reactive than durene or pentamethylbenzene. Aqueous nitrosation reactions have long been known to have a deuterium isotope effect,[20] and the extra methyl groups in durene and pentamethylbenzene have been considered to retard the overall reaction by stabilising the Wheland intermediate and thus decreasing the rate of the final proton transfer.[19] As might be expected, competitive nitrosations using $NO^+BF_4^-$ on deuterated and undeuterated mesitylene show[19] a k_H/k_D ratio of 3.5–4.0.

2.3. Molecular nitrogen dioxide.

2.3. Molecular nitrogen dioxide.† Under almost all conditions, molecular nitrogen dioxide can be considered to be in equilibrium with the predominant form of the dimer: the planar and symmetrical structure **5**. Since the equilibrium constant at 25 °C for the dissociation of the dimer[21] is ca. 10^{-4} mol dm^{-3} in such solvents as cyclohexane or carbon tetrachloride, this dimer is the predominant form under preparative conditions. However, small amounts of *anti* nitrosyl nitrate (**6**) and *syn* nitrosyl nitrate (**7**) have been detected[22] and have been the subject of several recent calculations;[23] these species are less stable than **5** but have been considered as possible intermediates[23a,24] in nitrosation and nitration by nitrogen dioxide. Nitrosyl peroxonitrite **8** is probably too unstable to play a part in the reactions considered here,[23] with the exception of the reaction of nitric oxide with oxygen.[23b]

5   **6**   **7**   **8**
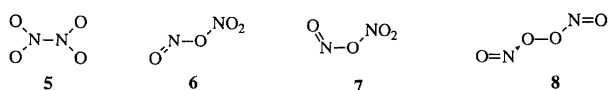
The reaction of molecular nitrogen dioxide with alkenes is known to involve an initial addition of one nitrogen dioxide molecule to the double bond, followed by the reaction of the resulting nitroalkyl radical with a second nitrogen dioxide molecule.[25] The first reaction is invariably on the nitrogen atom, but in the second reaction the nitrogen dioxide molecule reacts at either the nitrogen atom or at one of the oxygen atoms to give a mixture of dinitrocompounds and nitronitrites in the final product. Either can predominate, depending on the substrate and the conditions.[23a]

In the reactions of nitrogen dioxide, it is not always easy to distinguish between those involving the monomer and those involving the dimers in equilibrium with it (see Section 2.4). However, there are two pathways considered to derive from reaction with molecular nitrogen dioxide. One, observed in non-polar solvents such as benzene, cyclohexane or carbon tetrachloride, involves the addition of a nitrogen dioxide molecule to the aromatic system in a way analogous to the reaction with alkenes; this reaction is normally followed by the addition of a further nitrogen dioxide molecule to the nitro-aromatic radical.[26,27] The other reaction path is observed with phenols and has, as its initial stage, the abstraction of the phenolic hydrogen atom by molecular nitrogen dioxide;[28] this is followed by the reaction of the phenoxy radical thereby formed with a further nitrogen dioxide molecule to form the σ-complex **9** and a final prototropic shift form the nitrophenol. The kinetic studies of Coombes *et al.*[28] have shown that the rate-determining step can be either the initial loss of the phenolic hydrogen atom or the proton loss from the σ-complex **9**.

† In the remainder of this review, the term 'nitrogen dioxide' without the qualification 'molecular' will be used to refer both to this species and the various forms of the dimer in equilibrium with it.


9   **14**   **15**

2.4. Dimers of nitrogen dioxide.
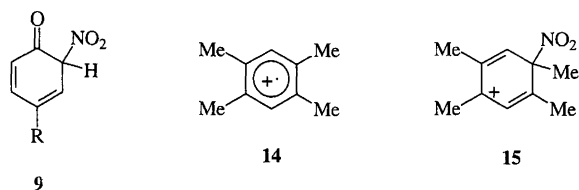
2.4. Dimers of nitrogen dioxide. As outlined above, we have to consider the symmetrical dimer **5** (the bulk component of the equilibrium under most conditions) and the two less stable nitrosyl nitrate dimers **6** and **7**.

Kinetic studies have indicated that one of the dimers of nitrogen dioxide (presumably the symmetrical structure **5**) is involved in the addition of nitrogen dioxide to alkenes,[29,30] and that this reaction path can be of comparable magnitude to that involving molecular nitrogen dioxide. The reaction has been considered[29] as a substrate catalysed homolysis of **5** and leads to the same products as the reaction through molecular nitrogen dioxide.[30] There is some evidence[31] for the related involvement of one of the dimeric forms in addition to aromatic systems (Section 4).

There is also evidence for the involvement of these dimers in electron transfer reactions leading to aromatic radical cations. The rate of nitration of aromatic compounds by nitrogen dioxide in polar solvents such as dichloromethane is very sensitive to the structure of the substrate, and, from this and the product compositions, Pryor deduced[32] that an electron transfer process was involved.

One major problem is the identity of the electron acceptor. Pryor's original suggestion that the electron was transferred to nitrogen dioxide to form a nitrite ion[32] was criticised by Eberson and Radner[33] partly on the basis of theoretical calculations involving the Marcus equation and partly because experimental studies showed that the reaction of nitrite ions with the radical cations of naphthalene[34a] and perylene[34b] showed a rapid and quantitative electron transfer in the reverse direction. Their calculations also suggested that the nitrosonium ion would be an inadequate electron acceptor and were led to consider nitrosated dinitrogen tetroxide ($N_2O_4NO^+$) as the effective electrophile.[33]

Bosch and Kochi[24] studied the nitration of a series of polymethylbenzenes with nitrogen dioxide in dichloromethane and were able to show that the colours initially present in the solutions were those of the charge-transfer complexes of the aromatic compounds with the nitrosonium ion. These complexes were considered to arise from the substrate promoted ionisation of the nitrosyl nitrate dimers of nitrogen dioxide as shown in Scheme 3. As with the complexes produced from other nitrosonium salts[12] (Section 2.2), photochemical electron transfer can be observed at low temperatures converting the charge-transfer complexes **10** into radical pairs containing aromatic radical cations and nitric oxide **11**. Separation of these radical pairs then gives the free radical cations **12**
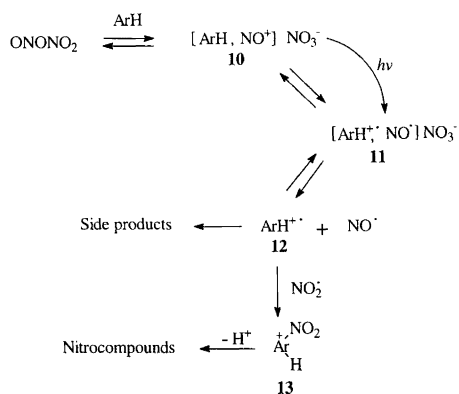
Scheme 3. The mechanism of nitration attributed to nitrosyl nitrate.

which can either add nitrogen dioxide to form the normal Wheland intermediates 13 or undergo sidechain substitution to form benzyl nitrates or derivatives of phenylnitromethane.

There are sufficient similarities in the pattern of substitution between the thermal reactions at 25 °C and the photochemical reactions at −78 °C to suggest[24] that these thermal reactions of nitrogen dioxide also follow the radical cation pathway in Scheme 3. The apparent discrepancy between the Marcus theory calculations[33] and the required rate of electron transfer to the nitrosonium ion does not appear to be a problem if the thermal electron transfer in the complex 10 is treated as an inner sphere reaction because of the strength of the charge transfer interaction involved.[3,12] Bosch and Kochi have shown[24b] that, when ArH is hexamethylbenzene, the complexation of the nitrosonium ion in 1 (with BF_4^- as the counter-ion) can stabilise the system by as much as 25 kJ mol^{-1}.

In the reaction of 1,4-dimethoxy-2,3-dimethylbenzene with nitrogen dioxide in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP), the radical cation ($ArH^{+\cdot}$) is formed in high concentration and can be detected spectroscopically.[35] Eberson and his coworkers have shown that HFP is an exceptionally useful solvent for observing radical cations.[35]

2.5. Nitronium ion. For benzene or compounds less reactive than benzene, the conventional mechanism of reaction with nitronium ions (Scheme 4, path A) has always been accepted. However, for compounds more reactive than
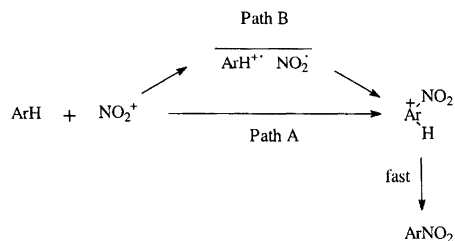
Scheme 4. The possible electron transfer mechanism for nitration by the nitronium ion.

toluene, there has recently been an intense debate on the possible role of the electron transfer mechanism (Scheme 4, path B). The subject has recently been reviewed[2,3] and it now appears that the formation of the radical cation is relatively unimportant when the initial attack occurs at an unsubstituted position. The key evidence comes from the fact that, even for compounds as reactive as napthalene or anisole, the direct reaction with the nitronium ion gives a product distribution that is different from that obtained by the reaction of nitrogen dioxide with the preformed radical cation. This conclusion is supported by studies of CIDNP effects,[9] although these do suggest that a few percent of the reaction of naphthalene with the nitronium ion occurs through the radical cation pathway.[36] Some authors still stress the evidence for the similarity of the classical and electron transfer paths.[8]

Where much of the the initial attack occurs at a substituted position as in durene, the CIDNP studies[37] show that a significant part of the overall reaction can involve the corresponding radical cation 14; this is presumably formed by homolysis of the ipso-intermediate 15. It is reasonable that the radical cation 14 should be formed in the rearrangement stage rather than in the initial substitution for the different geometries of the nitrogen dioxide molecule (bent) and the nitronium ion (linear) lead to a high reorganisation energy for electron transfer to the nitronium ion.[3,38] Since the O–N–O bond in the nitro group is bent, the change in geometry is less when the nitrogen dioxide molecule is formed by homolysis of a $C–NO_2$ bond. Of course, the direct reaction (Scheme 4, path A) also involves a major change in the geometry of the O–N–O group but the energy terms involved in bond formation should then stabilise the transition state. Homolytic rearrangements of nitro groups are well known in the reactions of nitrocyclohexadienones[39] but in the general rearrangements of ipso-intermediates there is also strong evidence for direct 1,2-shifts,[40] and so this may still be the main pathway in the overall reaction.

2.6. Nitrogen trioxide. The structure of nitrogen trioxide is not well defined for the vibrational spectra do not accord with the expected threefold symmetry. The results of theoretical calculations depend on the level of approximation but favour a structure with one long and two short NO bonds.[41] Some authors have suggested that the structure depends on the medium and that this is related to medium effects on the reactivity.[42]

The interaction of nitrogen trioxide with aromatic systems seems to take one of three paths: electron transfer, hydrogen abstraction or addition to the ring (Table 1). With p-xylene and a number of more alkylated compounds in acetonitrile at 20 °C, electron transfer occurs leading to the corresponding aromatic radical cations; these undergo subsequent deprotonation.[43] With toluene and with m- and o-xylene under the same conditions, complex formation initially occurs followed by the

Table 1. Second-order rate coefficients (k_2) for the reaction of nitrogen trioxide with aromatic compounds in acetonitrile. The temperature was 20 °C unless stated otherwise.

Compound	$10^{-6}\, k_2/\text{s}^{-1}$ $\text{mol}^{-1}\,\text{dm}^3$	Type of reaction	Ref.
Benzene	1.0	Addition to ring[a]	42
Benzaldehyde	24	Hydrogen transfer	42
Toluene	100	Hydrogen transfer	43
Durene	13 000	Electron transfer[b]	43

[a]This is the interpretation sugested by the authors; other workers[44] have considered that an electron transfer mechanism may be involved. [b]At room temperature.

transfer of a hydrogen atom to form benzyl radicals. An analysis of structural and isotope effects suggests that the reaction is an electron transfer concerted with the deprotonation of the incipient radical cation.[43] Aromatic aldehydes undergo loss of the aldehyde hydrogen atom.[42]

In a systematic study of the rates of reaction of a series of aromatic compounds with nitrogen trioxide in acetonitrile, the plots of $\log k_2$ vs. the ionisation energy generated three correlation lines:[45] one, with slope close to zero, for substituted anisoles which are oxidised to the radical cations in an encounter reaction with nitrogen trioxide; one with slope of -2.5 for substituted toluenes with ionisation potentials of 8.45–8.80 eV; and one with slope of -1.8 for benzene, substituted benzenes and toluenes with deactivating substituents (ionisation potentials >8.8 eV). The reactions corresponding to the last two lines are considered to be the loss of a hydrogen atom from a methyl group and the addition of nitrogen trioxide to the aromatic ring.[45] Such addition reactions are clearly seen in the nitration of strongly deactivated aromatic compounds[46] (Section 3.3).

Nitrogen trioxide is a very electrophilic radical: the ρ-value for hydrogen atom abstraction from aromatic aldehydes[42] is -1.3 (for comparison, the corresponding ρ-value for the trichloromethyl radical[47] is -0.74). It is also very reactive, as shown by the absolute rate coefficients listed in Table 1. This presumably explains why, in spite of its electrophilicity, it will still add rapidly to deactivated aromatic systems.

2.7. The peroxonitrite radical.

This species (ONOO˙) is isomeric with nitrogen trioxide and should exist in *cis* and *trans* forms; it has been considered to be an intermediate in the reaction of nitric oxide with oxygen.[48] The evidence for it and the results of a number of theoretical calculations have been summarised by McKee.[23b] The most recent calculations suggest that this radical is too exothermic to play a part in the reaction and that a weakly bound complex of nitric oxide and oxygen is involved instead.[23b]

2.8. Dinitrogen pentoxide.

This oxide crystallises as ionic nitronium nitrate[49] but it is covalent in the vapour phase and in solution in organic solvents. In the vapour phase, the electron diffraction data[50] shows that it has the structure O_2NONO_2 and an NON angle of 111.8°. The covalent molecule will also dissociate into nitrogen trioxide and nitrogen dioxide [eqn. (3)].[51]

$$NO_2^+ + NO_3^- = O_2NONO_2 = NO_2^{\cdot} + NO_3^{\cdot} \qquad (3)$$
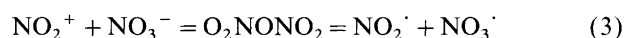
Nitrogen trioxide and nitrogen dioxide also react together in a much slower step via interaction between two oxygen atoms; this reaction has been studied in detail and leads to the formation of nitrogen dioxide, nitric oxide and oxygen.[52]
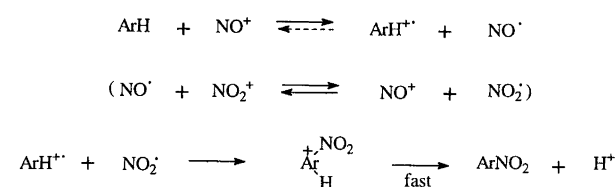
When dissolved in a large excess of a strongly acidic medium (e.g. sulfuric acid), dinitrogen pentoxide acts primarily* as a source of nitronium ions as expected from eqn. (4) but, when dissolved in an organic solvent, there is evidence for nitration through the covalent oxide.[53]

$$N_2O_5 + 3H_2SO_4 = 2NO_2^+ + H_3O^+ + 3HSO_4^- \qquad (4)$$
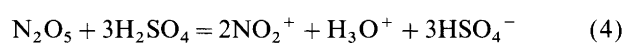
3. New pathways for nitration

3.1. The electron transfer mechanism for nitrous acid catalysis.

This pathway appears to be initiated by an electron transfer from the aromatic compound to the nitrosonium ion (Scheme 5). It was first recognised in the nitrous acid catalysed nitration of N,N-dimethylaniline,[54] and was then shown to be more general.[55] Probably the clearest evidence for this mechanism comes from the characteristic ^{15}N nuclear polarisation generated by the $ArH^{+\cdot}\,NO_2^{\cdot}$ radical pair for this leads to a strong emission signal in the ^{15}N NMR spectrum for the nitro group in the product.[56] If this radical pair had been generated by electron transfer from an aromatic compound to a nitronium ion, the corresponding signal for the nitro group would show enhanced absorption.[56b]

The first reaction in Scheme 5 accords with the results in Section 2.2 for the interaction of aromatic compounds with nitrosonium ions. The nitrogen dioxide formed in the second reaction apparently captures the aromatic radical cations before the typical side reactions of these species become important. In Scheme 5 the second reaction is enclosed in parentheses to indicate that this reaction shows the stoichiometry of this stage, not the mechanism. The mechanism of this stage must be more complex, for the rate of nitrous acid catalysed nitration can greatly exceed the rate of nitronium ion formation

$$ArH + NO^+ \rightleftharpoons ArH^{+\cdot} + NO^{\cdot}$$

$$(NO^{\cdot} + NO_2^+ \rightleftharpoons NO^+ + NO_2^{\cdot})$$

$$ArH^{+\cdot} + NO_2^{\cdot} \longrightarrow Ar{\underset{H}{\overset{+NO_2}{|}}} \xrightarrow{\text{fast}} ArNO_2 + H^+$$

Scheme 5. The electron-transfer mechanism for nitrous acid catalysed nitration.

* The observed results in nitric acid as solvent are more complex; see section 3.3.

in the medium as measured by the limiting zeroth-order rate of nitration.[56b]

This mechanism has not been observed with toluene,[56e] but it has been detected in the nitration of the xylenes and in a number of more reactive aromatic compounds.[9,56f]

The balance between this mechanism and the classical mechanism for nitrous acid catalysed nitration [Scheme 1, eqn. (2)] should depend on the reaction conditions. In the classical mechanism, the final proton loss is rate-determining, and so the electron-transfer mechanism (Scheme 5) is favoured by an increase in the acidity of the medium. Thus, the classical mechanism of nitrous acid catalysed nitration has been found to provide the major pathway in the nitration of anisole in 43–47% sulfuric acid although at higher acidities the electron transfer mechanism becomes predominant.[4b] Another factor is the concentration of nitrous acid for, with high concentrations of nitrous acid, the combination of the $ArH^{+\cdot}$ and $NO_2^{\cdot}$ radicals can apparently become rate-determining; this leads to a kinetic form that is independent of the concentration of nitrous acid.[57] The classical mechanism remains first-order in nitrous acid, and so high concentrations of nitrous acid can therefore favour the classical mechanism. The widespread observation of nuclear polarisation in nitrous acid catalysed nitration[9,56] suggests that this reaction normally occurs by the electron-transfer mechanism, although a contribution from the classical mechanism may be present when the reaction occurs with relatively high concentrations of nitrous acid in relatively low acidities.

The classical and electron-transfer mechanisms of nitrous acid catalysis can give different product compositions for, in the first, the product composition is that corresponding to nitrosation and, in the second, the product composition derives from the radical recombination stage. Also, in the classical mechanism, the intermediate nitroso compound can undergo side reactions; thus, in the nitrous acid catalysed nitration of anisole in 43–47% sulfuric acid,[4b] the intermediate p-nitrosoanisole undergoes demethylation to give p-nitrophenol as the predominant product.

3.2. Nitration by nitrogen dioxide in organic solvents. The use of nitrogen dioxide in strongly acidic solvents or in the presence of high concentrations of Lewis acids provides merely another way of carrying out conventional nitronium ion nitrations or nitrous acid catalysed nitrations: these reactions have been reviewed elsewhere.[58,59]

As outlined in Section 2.3, molecular nitrogen dioxide in nonpolar organic solvents will attack some organic systems by adding to one of the double bonds. For this reaction to occur, it is helpful if the double bond is to some extent localised or part of a polycyclic system as in the work of Pryor and coworkers on naphthalene,[60] anthracene[26] and fluoranthrene.[27] Thus, the reaction of anthracene with dry nitrogen dioxide in carefully purified carbon tetrachloride gives a mixture of cis- and trans-

9,10-dinitro-9,10-dihydroanthracenes.[26] Careful purification of the reagents and solvent is necessary because water and acidic species favour the ionic pathway (see below). Elimination of nitrous acid from the initial dinitro compound can give unexpected mononitro compounds: the conventional nitration of fluoranthrene with nitric acid gives a mixture of the 3-nitroisomer and the 8-nitroisomer but the addition–elimination reaction with nitrogen dioxide gives mainly 2-nitrofluoranthrene[27] (Scheme 6). Related addition elimination reactions have been used to explain the unexpected formation of 1,3- and 2,3-dinitronaphthalenes as the major products in the reaction of naphthalene with nitrogen dioxide in carbon tetrachloride.[60]

In the specified reactions of naphthalene, anthracene, and fluoranthrene[26,27,60] there seems no evidence for the formation of nitronitrites. However, in the reaction of phenanthrene with nitrogen dioxide in benzene as solvent,[31] the trans nitronitrate can be the major product (Scheme 7). The product composition is very sensitive to the reaction conditions and with higher concentrations of phenanthrene significant amounts of a dimeric nitronitrate are formed. The nitronitrates are considered to be formed by oxidation of the intermediate nitronitrites.[31] The products from the nitration of 2,3,4-trimethyl-biphenyl with nitrogen dioxide in benzene include small amounts of biphenylmethyl nitrates; this is attributed to hydrogen abstraction from the methyl groups of the intermediate nitroaromatic radicals.[61]

When the medium is changed from benzene or carbon tetrachloride to a polar solvent such as dichloromethane or acetonitrile, the homolytic addition of molecular nitrogen dioxide appears to be replaced by the electron transfer reaction illustrated in Scheme 3 and probably derived from an initial reaction with nitrosyl nitrate. This leads to the smooth nitration of those polycyclic benzen-
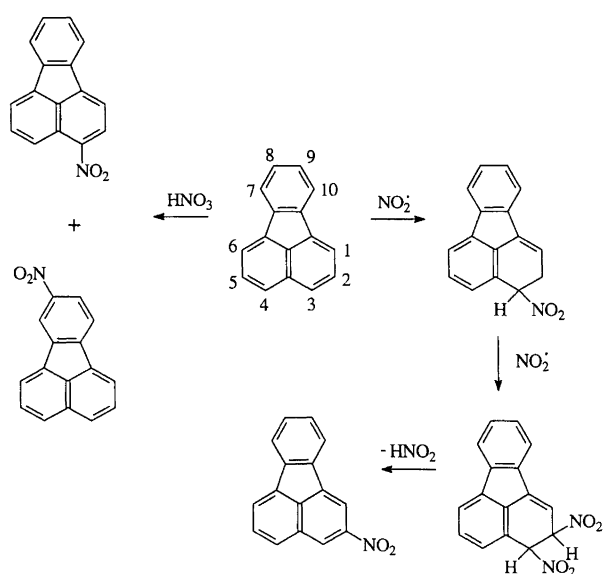
Scheme 6. The reactions of fluoranthrene with nitric acid and with nitrogen dioxide.
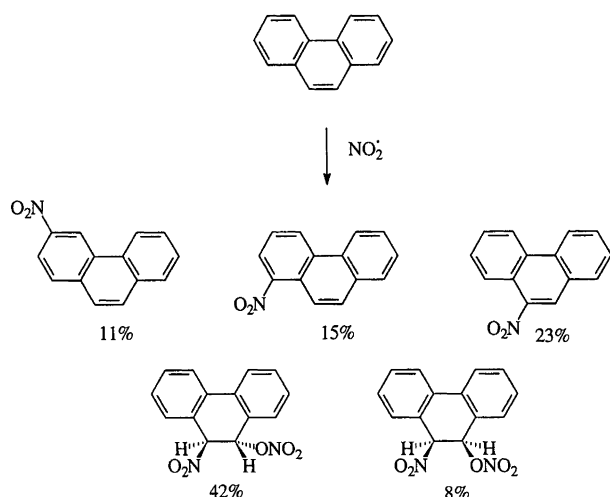
Scheme 7. Product composition from the nitration of phenanthrene (0.056 mol dm^{-3}) with excess nitrogen dioxide in benzene at 5 °C.

oid compounds whose reactivity is equal or greater than that of mesitylene[33,62] although, for some of these substrates, it is helpful to add a little acid (e.g. methanesulfonic acid) as a catalyst. The results for a number of aromatic substrates show that the product composition found is similar to that for the electron transfer mechanism of nitrous acid catalysed nitration discussed above and to that for other conditions where the aromatic radical cation is allowed to react with molecular nitrogen dioxide.[2,3] As an example, the 2-/3-ratio for the nitration of dibenzofuran is 0.17 for reaction with nitrogen dioxide in dichloromethane and 0.11–0.15 for nitrous acid catalysed nitration.[63] For nitration with nitronium ions, the corresponding ratio[63] is 1.5.

Relative rates[32] for the reaction of a range of polycyclic aromatic hydrocarbons with nitrogen dioxide in dichloromethane have been determined at 25 °C and the wide range of reactivity observed (perylene is more reactive than benzene by a factor of 10^4) is consistent with the intermediate formation of the radical cation. It is, however, surprising that the authors found it possible to include benzene in this series since this substrate does not normally show nitrous acid catalysis in nitration.

3.3. Nitration with preformed dinitrogen pentoxide. The early work on nitration by dinitrogen pentoxide in carbon tetrachloride and other nonpolar solvents[53] has been well summarised.[5b,64] An analysis of the overall kinetics indicates that there is an uncatalysed reaction attributed to attack by molecular dinitrogen pentoxide accompanied by an autocatalysed reaction attributed to attack by the nitronium ion. The autocatalysis is considered to derive from the nitric acid formed during reaction [eqn. (5)] for this should facilitate the ionisation of the dinitrogen pentoxide.[53]

$$N_2O_5 + ArH \rightarrow ArNO_2 + HNO_3 \qquad (5)$$

In view of later work (Section 3.4) it is interesting that the two reactions are said to give different ratios of mononitro compounds[53] and that, for chlorobenzene, the uncatalysed reaction gives a smaller percentage of the *p*-isomer. Unfortunately, no detailed product compositions are given.[53]

The recent mechanistic studies by Moodie and his coworkers[46,65] provide evidence for additional reaction paths. In this work, kinetic studies and product analyses are combined with studies of ^{15}N nuclear polarisation.

The nitration of a number of deactivated substrates in solutions of nitric acid containing dinitrogen pentoxide has been compared with the corresponding nitration reactions in solutions of nitric acid containing nitronium salts.[46,65] The nitration of some of the substrates in the presence of dinitrogen pentoxide is accompanied by the formation of dienes, and the reactions of 1,2,4-trichloro-5-nitrobenzene (16a) (Scheme 8) have been studied in detail. The yield of the nitrated product 17a drops from 96% to 58% as the concentration of dinitrogen pentoxide is increased over the range 0–5.1 mol dm^{-3}, and two dienes are formed with NMR spectra consistent with the two stereoisomers of structure 19a (or 20a). The initially formed dienes showed strong ^{15}N nuclear polarisation and the phase is consistent the reaction path shown in Scheme 8; other transitory ^{15}N signals point to the presence of further, apparently unstable, dienes. The evidence for the reversible reaction with nitrogen trioxide to form the radical 18a comes from the absence of any variation of the reaction rate and product composition in the presence of added nitrogen dioxide.*

The formation of the nitro compound 17a is not accompanied by ^{15}N nuclear polarisation;[46] this indicates that nitration occurs by path A and that path B (Scheme 8) is unimportant. However, in the corresponding formation of 1,2-dichloro-4,6-dinitrobenzene 17b from 1,2-dichloro-4-nitrobenzene 16b, the product does show the ^{15}N nuclear polarisation expected for some reaction via a diene intermediate (e.g. path B). The
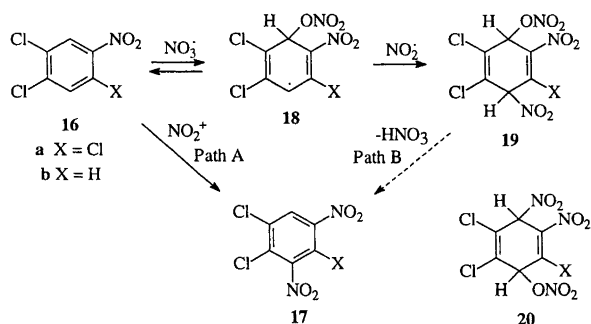
Scheme 8. Pathways for reaction with dinitrogen pentoxide in nitric acid.

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* The added nitrogen dioxide should decrease the equilibrium concentration of nitrogen trioxide [eqn. (3)], and therefore also that of the radical 18 but it should increase the rate of the subsequent stage leading to the formation of the adduct by the same factor.

relevant diene was not identified and may not be **19b**. Studies of the product composition with and without added dinitrogen pentoxide suggest that reaction via the diene is of minor importance,[46] but the reaction is of interest partly because it corresponds to one of the reaction paths originally proposed by Titov[66] and partly because this type of reaction path appears again in ozone mediated nitration with nitrogen dioxide (Section 3.4).

For concentrations of dinitrogen pentoxide up to $1.5-2.0 \, \text{mol dm}^{-3}$, the rates of these nitration reactions in nitric acid correspond well to the concentration of nitronium ions present, but with higher concentrations of dinitrogen pentoxide, there is a significant rate enhancement and this is present whether or not the reaction shows evidence of diene formation.[65a] The rate enhancement has been provisionally attributed to a medium effect.[65a]

3.4. Ozone mediated nitration with nitrogen dioxide.

In 1991, Suzuki et al.[67] showed that a mixture of nitrogen dioxide and ozone in dichloromethane was very effective in nitrating a range of aromatic compounds and appeared to be a better nitrating agent than the dinitrogen pentoxide that might have been formed from it. The application of this procedure, known as *Kyodai* nitration from the name of Kyoto University, was rapidly developed by Suzuki, and the work has been summarised in a recent review.[5a] A large number of compounds have been studied and the following comments deal only with some key structures. A small amount of a catalyst (methanesulfonic acid or borontrifluoride–diethyl ether) is sometimes added to the reaction mixture.

Before considering the unusual features of these Kyodai nitrations, it is helpful to look at the several reaction mechanisms considered[5a] to be involved (Scheme 9). Ozone and nitrogen dioxide are known to

react together to form nitrogen trioxide [eqn. (6)], and

$$NO_2^{\cdot} + O_3 \rightarrow NO_3^{\cdot} + O_2 \tag{6}$$

this is capable of both oxidising aromatic systems and adding to the aromatic ring (Section 2.6); nitrogen trioxide can also add to nitrogen dioxide to form dinitrogen pentoxide (Section 2.8). The product resulting from addition of nitrogen trioxide to the aromatic ring is itself a radical and can be expected to add nitrogen dioxide (Scheme 9, path A); the adduct formed could then lose nitric acid, to give a nitro compound.[68] Another possible pathway involves the oxidation of the aromatic compound to a radical cation followed by the reaction of this radical cation with nitrogen dioxide to give nitro products (Scheme 9, path B). A third pathway involves nitration by dinitrogen pentoxide or by the nitronium ions formed from the ionisation of dinitrogen pentoxide (Scheme 9, path C). Because of the complex equilibria in these systems, the authors recognise that still other species (e.g. NO^+, N_2O_3) could be involved.[69]

The mechanistic analysis of Kyodai nitration is complicated by the change in the conditions during reaction for, in the absence of additional catalysts, the stoichiometry of these nitrations[5a] corresponds to eqn. (7). The

$$ArH + 2NO_2 + O_3 = ArNO_2 + HNO_3 + O_2 \tag{7}$$
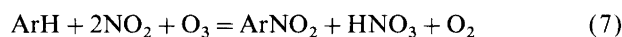
medium therefore becomes increasingly acidic during the reaction. It is therefore difficult to study the product composition under conditions where the mechanism is controlled.

The evidence for path A (Scheme 9) comes from the fact that, under some experimental conditions, the major product from toluene, anisole and chlorobenzene at the start of reaction is the *meta* nitrocompound.[68] After a few percent of reaction, the orientation changes to the predominating *ortho/para* substitution expected for these substrates. The reaction giving *meta* substitution is facilitated by the addition of pyridine to the reaction mixture and inhibited by the use of acidic catalysts ($MeSO_3H$ or HNO_3).[68] The authors suggest that, in the presence of an acidic medium, the nitrate ion is removed from the radical cation–anion pair **21** by protonation and that the radical cation is then trapped by nitrogen dioxide (Scheme 9, path B). A similar separation of a radical cation–anion pair by protonation occurs in the photochemical reaction of aromatic compounds with tetranitromethane.[2]

With some substrates, the product composition gives evidence for the involvement of the aromatic radical cation. Nitration through the naphthalene radical cation is recognised[70] to give α/β ratios of ca. 50 in contrast to the ratios of ca. 15 with nitration by nitronium ions.[2] Under Kyodai nitration, naphthalene[71] gives an α/β ratios of 23–70 with a curious dependence of the ratio on the exact experimental conditions. The authors suggest that this derives from the reaction of naphthalene through both the monomeric and dimeric radical cations
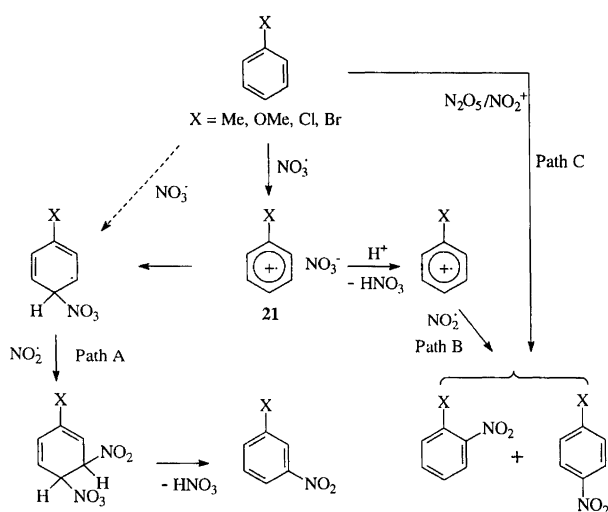

Scheme 9. Some of the reaction paths believed to be involved in Kyodai nitration. For the significance of the dotted line see Section 4.

and that it is the dimeric radical cation **22** which favours α-substitution.[71]

22 **23** **24**
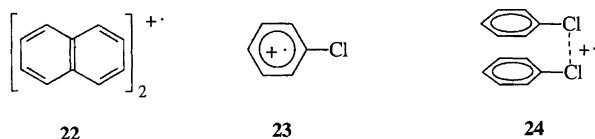
Similar evidence comes from studies on bicumene **25** for the corresponding radical cation is known to undergo cleavage readily[24a] and when dilute solutions of bicumene are subjected to Kyodai nitration only the products of cleavage are found[72] (Scheme 10). This is in marked contrast to the results of nitration by nitronium salts[72] which gives only nuclear substitution (Scheme 10). Unfortunately, this apparently clear distinction between the results of conventional and Kyodai nitration is blurred when higher temperatures and more concentrated solutions of the reagents are used; thus the Kyodai nitration of bicumene at 0 °C can give up to 41% of substitution in the aromatic ring.[72] The proportions of aromatic nitro compounds then formed (o, 20; m, 15; p, 67%)* show that the Kyodai nitration of bicumene gives more *ortho* substitution than nitration by a nitronium salt[72] (compare with the percentages in Scheme 10).

An unexpected feature of these reactions is that the *ortho/para* ratio in the nitration of chlorobenzene and bromobenzene depends on the initial concentration of the substrate. Thus, for the Kyodai nitration of chlorobenzene in dichloromethane at 0 °C, the product composition ($o:m:p$) changes from (52.4:0:47.6) with a dilute solution of chlorobenzene to (30.0:3.0:67.0) for reaction with neat chlorobenzene.[73] The second set of values are close to those observed (29.6:0.9:69.5) in the nitration of chlorobenzene in acetic anhydride.[74] The change in the product composition corresponds to a change from 1.10 to 0.45 in the *ortho/para* ratio. An even lower *ortho/para* ratio (0.25) is obtained from Kyodai nitration in carbon tetrachloride.[73] The authors attribute[73] this variation in the *ortho/para* ratio to reaction through both the monomeric (**23**) and dimeric forms[75] (**24**) of the aromatic radical cation. Calculated frontier

o, 8%; m, 24%; p, 68%
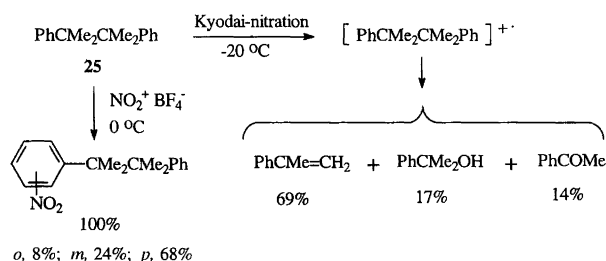
Scheme 10. Comparison of Kyodai nitration (with low reactant concentrations) and nitration with nitronium ions.

* There appear to be some typing errors in Ref. 80 for these percentages add up to 102%, and the maximum concentration of the aromatic compound is given as 100 mol L^{-1}. This should presumably be 100 mmol L^{-1}.

electron densities using the PM3 method provide some support for the greater extent of *para* substitution in the dimeric radical cation.[73]

The initial oxidation of the substrate to the radical cation is central to the authors' interpretation of these results on the halogenobenzenes and the same interpretation has been applied to the Kyodai nitration of the alkyl benzenes.[69] However, for the alkylbenzenes, the results (Table 2) are very similar to those for nitration by nitric acid in acetic anhydride, and this similarity extends to the partial rate factors. Thus, for toluene, the partial rate factors* for Kyodai nitration[69] are: $f_o = 57$; $f_m = 3$; $f_p = 71$; for nitration in acetic anhydride, the corresponding values are $f_o = 47$; $f_m = 3$; $f_p = 62$.[76]

With some of the other substrates listed in Table 2, the differences between the two methods of nitration are more marked, most obviously in the increased amount of *ortho* substitution with acetophenone and benzoic acid. The more deactivated aromatic compounds (acetophenone, benzoic acid and nitrobenzene) are believed to react directly with dinitrogen pentoxide or with the nitronium ions derived from it (Scheme 9, path C).[77] In the Kyodai nitration of acetophenone, there is an induction period attributed to the build up of a complex involving the substrate and dinitrogen pentoxide.[77]

Some work has been carried out on a form of Kyodai nitration using a mixture of nitric oxide, nitrogen dioxide and oxygen.[10] This mixture is more effective than a mixture of nitrogen dioxide and oxygen presumably because of the formation of nitrogen trioxide from nitric oxide and oxygen; however, the slow reaction with chlorobenzene suggests that this mixture is less effective than the original use of nitrogen dioxide and ozone.[10]

Table 2. Comparison of the product comparison (%) from Kyodai nitration in dichloromethane at −10 °C with that (in parentheses) for conventional nitration by nitric acid in acetic anhydride at 0 °C (unless otherwise noted).

Compound	ortho	meta	para	Ref.
Toluene	57 (58.1)	2 (3.7)	41 (38.2)	5a (76)
Ethylbenzene	44 (45.9)	3 (3.3)	53 (50.8)	5a (78)
iso-Propyl-benzene	23 (28.0)	4 (4.5)	73 (67.5)	5a (78)
tert-Butyl-benzene	13 (10.0)	6 (6.8)	81 (83.2)	5a (78)
Acetophenone	52 (26.4)[a]	48 (71.6[a])	0 (0–2)[a]	5a (79)
Benzoic acid	27[b] (17[c])	72[b] (82)[c]	1[b] (1)[c]	5a (80)
Nitrobenzene	8[d] (4.7)[e]	91[d] (93.9)[e]	1[d] (1.4)[e]	5a (81)
Acetanilide	78 (77)[f]	0 (0)[f]	22 (23)[f]	5a (82)

[a] In 80.3% sulfuric acid at 25 °C. [b] At 0 °C in dichloroethane. [c] In nitric acid at 0 °C. [d] In the presence of methanesulfonic acid. [e] In concentrated sulfuric acid at 0 °C. [f] In acetic anhydride at 25 °C.

* These partial rate factors have to be obtained by competition since the Kyodai nitration of the alkylbenzenes is zeroth-order with respect to the substrate[69] presumably because of the rate-determining formation of nitrogen trioxide.

Table 3. Standard electrode potentials ($E°$/V) vs. NHE for the relevant nitrogen oxides. The values[a] are taken from Ref. 83 unless otherwise indicated.

Solvent	Donor no.[b]	NO⁺/NO	NO₂/NO₂⁻	NO₂⁺/NO₂	NO₃/NO₃⁻
Dichloromethane	—	1.72		1.75	
Nitromethane	2.7	1.57		1.57, 2.21[c]	
Acetonitrile	14.1	1.52	0.7[d] 0.25[e]	1.56	
Sulfolane	14.8	1.41		1.42, 2.00[f]	
Ethyl acetate	17.1	1.57		1.53	
Dimethyl formamide	26.6	1.30			
Water	33		1.0[g]		2.3[g]
					2.2–2.7[h]

[a]After addition of the value of $E°$ for the calomel electrode (SCE, 0.2412 V) to the values of $E_{1/2}$ listed Ref. 83. [b]The Gutmann donor number; see Ref. 84. [c]Ref. 85a, see also Ref. 3. [d]Ref. 86. [e]Ref. 33. [f]Ref. 85b, see also Ref. 3. [g]An indirect estimation based on calculated free energies of hydration (Ref. 87). [h]An indirect estimation based on chemical reactivity (Ref. 88).

4. Mechanistic aspects deserving further study

There are two curious features in the addition reactions of nitrogen dioxide with aromatic systems. The reactions of naphthalene,[60] anthracene[26] and fluoranthrene[27] with nitrogen dioxide in non-polar solvents appear to involve the successive addition of two nitrogen dioxide molecules but it is strange that nitronitrites or their oxidation products (e.g. nitronitrates) are not reported. The reaction of molecular nitrogen dioxide with nitroalkyl radicals occurs to a rather similar extent at nitrogen and oxygen centres[23a] and the analogous reaction of phenanthrene with nitrogen dioxide in benzene[31] can give the *trans* nitronitrate as the major product (Scheme 7). Secondly, in this reaction of phenanthrene, the concentrations of the *cis* and *trans* nitronitrates vary in different ways with the initial reaction conditions and the authors suggest[31] that the *cis* isomer may be formed by the attack of molecular dinitrogen tetroxide or by a substrate catalysed homolysis of this molecule. It would be interesting to use ¹⁵N CIDNP effects to look for evidence for such a substrate-catalysed homolysis since, by analogy with the arguments used for alkenes,[56g] the phase of the polarisation should be opposite to that for the separate addition of the two nitrogen dioxide molecules.

Table 4. Standard electrode potentials ($E°$/V) vs. NHE for the oxidation of aromatic compounds. For sources see Ref. 89.

Compound	Solvent	$E°$/V
Benzene	MeCN	3.03
Toluene	MeCN	2.61
m-Xylene	CF₃CO₂H	2.38
o-Xylene	CF₃CO₂H	2.37
Mesitylene	CF₃CO₂H	2.35
Bicumene	CH₂Cl₂	(2.32)[a]
p-Xylene	CF₃CO₂H	2.30
Naphthalene	MeCN	2.08
Durene	MeCN	2.07
Anthracene	MeCN	1.61
Pyrene	MeCN	1.60
Perylene	MeCN	1.30

[a]An irreversible oxidation wave. See Ref. 72.

The plausibility of the various electron transfer steps proposed in Section 3 is of course dependent on the redox potentials involved. A selection of relevant standard electrode potentials are given in Tables 3 and 4 taken mainly from the more recent literature. For the NO/NO⁺ and NO₂/NO₂⁺ equilibria, these electrode potentials clearly depend on the solvent and one group of results[83] has shown a clear correlation with the Lewis base properties of the solvent as measured by the Gutmann donor number.[84] Unfortunately, for NO₂/NO₂⁺, the results in Table 3 show that there is significant disagreement between the values of the electrode potential given in the literature, even for a given solvent.

For electron transfer to NO⁺, the range of the proposed electron transfer mechanisms and the CIDNP effects are consistent with the electrode potentials[90] and, in general, the same is true for electron transfer to NO₂⁺ given the present uncertainty in this electrode potential.[2,3] However, for electron transfer to nitrogen trioxide the evidence is less clear because of the uncertainty over the relevant electrode potential in organic solvents. By analogy with nitrogen dioxide (Table 3) the electrode potential for nitrogen trioxide should be lower in organic solvents than in water and then the proposed oxidation of benzene and the alkylbenzenes in Kyodai nitration may be open to question. Indeed, more direct studies of the reaction of nitrogen trioxide with benzene and toluene suggest that, at least in acetonitrile, the former reacts by addition of nitrogen trioxide to the aromatic ring and the latter by a concerted loss of an electron and a hydrogen ion (Section 2.6).

There is also the curious fact that the Kyodai nitration of the alkylbenzenes yields essentially the same product compositions and partial rate factors as nitration by conventional means (Table 2, Section 3.4). This is in contrast with the clay-catalysed nitration of toluene (a reaction considered[91] to occur through the radical cation) for this gives a significantly lower *ortho/para* ratio[91] (*ortho*, 43; *meta*, 2; *para*, 55%) from that found in Kyodai or conventional nitration (Table 2).

The results with strongly deactivated compounds

(Section 3.3, Scheme 8) show that the radical cation is not a necessary intermediate in the addition of nitrogen trioxide to an aromatic ring. This direct addition of nitrogen trioxide to an aromatic ring is shown as a dotted line in Scheme 9. The initial *meta*-substitution observed in the Kyodai nitration of toluene and chlorobenzene does not therefore necessarily require the intermediate formation of the radical cation. The transition from the initial pathway through the diene (Scheme 9, path A) to conventional attack by the nitronium ion (Scheme 9, path C) could arise as a result of the known[53] nitric acid catalysed ionisation of dinitrogen pentoxide.

The above arguments do not, of course, cast doubt on the evidence (Section 3.4) for radical cation formation in the Kyodai nitration of naphthalene and bicumene but these substrates are more easily oxidised (Table 4). The arguments do, however, suggest that it would be useful to have further evidence on the range of radical cation reactions in Kyodai nitration and in nitration by preformed dinitrogen pentoxide in organic solvents. It would be particularly helpful if the studies with dinitrogen pentoxide could combine kinetics, product analyses and ^{15}N CIDNP effects. Since the electron transfer mechanism of nitrous acid catalysed nitration (Section 3.1) would not be expected to occur with toluene and chlorobenzene, the presence of emission signals[9] in the ^{15}N NMR spectra of the *ortho* and *para* nitro products from these substrates would then point to initial oxidation by nitrogen trioxide followed by the reaction of the aromatic radical cation with nitrogen dioxide.

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