The Mechanism of Aromatic Nitration in Solution: Marcus Theory and Semi-empirical Molecular Orbital Calculations on NO_2^+ and NO^+ as One-electron Oxidants

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Marcus theory calculations of rates of electron transfer (ET) have been carried out for attack by NO^+ and NO_2^+ on various reactive aromatic substrates including alkylbenzenes and naphthalene. While reasonable agreement between calculation and experiment is obtained for nitrous acid catalysed nitration, the calculated rate of electron transfer in the nitration of naphthalene by nitronium ion is too low by between nine and fifteen orders of magnitude. Possible reasons for this discrepancy are discussed and it is suggested that $H_2NO_3^+$ may be the ET agent responsible for the previously observed CIDNP effects in this system. Semi-empirical molecular orbital calculations have been carried out on relevant species, including reaction coordinates for the nitration of naphthalene in the 1- and 2-positions. Transition state energies suggest that attack in the 1-position is very much favoured by the ET process.

Recently we have demonstrated experimentally[1,2] the borderline between classical electrophilic attack and the electron-transfer process (ET) for nitration by nitronium ion in solution using ^{15}N NMR CIDNP studies. ET followed by radical-pair separation makes a small but significant contribution to the nitration of naphthalene but not apparently to less reactive substrates such as the xylenes and mesitylene. A series of investigations[3] of nitrous acid catalysed nitration on substrates ranging in reactivity from benzene to polyalkylbenzenes and naphthalene has demonstrated that, for NO^+ as oxidant, ET is significant for all substrates more reactive than toluene. The mechanism for this latter process which best fits all the experimental results is that the aromatic radical cation, resulting from oxidation by NO^+, encounters a NO_2 molecule forming a radical pair which collapses to give the product. It is important for our subsequent discussion to notice[3d] that the experimental results imply that this radical pair is sufficiently long-lived, even with the less reactive substrates such as the xylenes, for some escape from it to occur. This whole aspect has recently been comprehensively reviewed.[4]

Sankaraman and Kochi[5] and Kim, Lee and Kochi[6] have examined the nitration of various arenes with a series of *N*-nitropyridinium cations with which they form electron donor–acceptor complexes. The rates of nitration were shown to be correlated with the HOMO–LUMO gap in the $[ArH,XPy\text{-}NO_2^+]$ complex and it is suggested that the mechanism is best visualised in terms of a stepwise process in which substrate selectivity is governed by the charge-transfer process forming $[ArH^{+\bullet},XPyNO_2^{\bullet}]$ and the product ratios depend on the relative stabilities of the Wheland intermediates generated from the collapse of the $[ArH^{+\bullet},NO_2^{\bullet}]$ radical pair formed as the XPy molecule escapes. They further suggest that since nitration with *N*-nitropyridinium cations and a very wide range of other nitrating agents give similar product ratios with both naphthalene and toluene, then this radical mechanism should be applied generally.

In contrast to the varied views on the mechanism of nitration in solution, in the gas phase one-electron oxidation by NO_2^+ followed by substitution is the rule rather than the exception, even for benzene.[7] This work confirmed the earlier theoretical studies[8] based on gas-phase ionisation potentials. On the other hand, NO^+ ion reactions in the gas-phase, while certainly resulting in the formation of a wide range of aromatic radical cations,[7] give stable radical cation-NO complexes rather than substitution.

Two different theoretical approaches have attempted to overcome the problem of applying calculation methods to nitration reactions in solution. Eberson and Radner[9] applied Marcus theory for outer-sphere ET[10] to the reactions of both NO_2^+ and NO^+ with a series of aromatic hydrocarbons in acetonitrile. Rate constants (k) were calculated giving values of log k -5.9 and -0.4 for NO_2^+ and NO^+ attack, respectively, on naphthalene. In the case of NO_2^+ this is at least 14 orders of magnitude too slow;[1] for NO^+ actual rate coefficients for the ET step have not yet been calculated from experimental measurements. Eberson and Radner suggested that the inefficiency of NO_2^+ compared to NO^+ as an oxidising agent arises from the large bond reorganisation energy for the former.

A different method has been utilised by Feng, Zheng and Zerner[11] who carried out MNDO SCF calculations on benzene, toluene, the xylenes and nitrobenzene, investigating attack by NO_2^+ to generate radical pairs, π-complexes and σ-complexes. Energetics, electron-densities and spin densities all suggested that nitration by NO_2^+ proceeds through the radical pair for benzene and the alkylbenzenes in the gas phase and also indeed in solution for substrates more reactive than toluene. This latter observation depends on a calculation of the effect of dielectric strength of the solvent on ionisation potential.

Clearly there are discrepancies between the calculations and the experimental studies, the chief of which is the failure of the Marcus outer-sphere approach for nitration with NO_2^+. Also, the implication of the MNDO calculations, that radical pairs lie on the reaction path for NO_2^+ attack on the xylenes, seems to be at odds with experiment for, as pointed out earlier, if this is the case then the radical pair thus generated should undergo some separation and hence an enhanced absorption ^{15}N NMR signal will result in an appropriate CIDNP experiment. Despite careful investigation,[3d] such signals have never been observed even with the more easily oxidised mesitylene. This difficulty also applies to the interpretation of aromatic nitration by Kochi and co-workers[5,6] who suggest that the collapse of this same radical pair is responsible for observed isomer ratios, which in turn implies that this pair lies on the reaction coordinate for nitration of a wide range of arenes with many reagents.

Since these sets of calculations were carried out, new data has become available[12,13] on standard electrode potentials in

Table 1 Standard electrode potentials (E^0/V) for relevant species in various solvents relative to SHE

	CH_3CN	$(CH_2)_4SO_2$	CH_3NO_2	CF_3CO_2H
NO_2^+	1.56,[a] 1.59[h]	2.05[b]	1.53,[a] 2.32[c]	
NO^+	1.51,[e] 1.55[h]		1.58,[c] 1.60[h]	
Naphthalene	2.08[e]			
Durene	2.07[f]			
Mesitylene				2.35[f]
1,3-Xylene				2.38[f]
Toluene	2.61[g]			
Benzene	3.03[e]			

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Table 2 Bond and solvent reorganisation energies (kJ mol^{-1}) for relevant species in acetonitrile[a]

	λ_i[b]	λ_o[c]	λ_o[d]	λ[e]
NO_2^+/NO_2	435	150		585
NO^+/NO	88	205	92[f]	293
$ArH/ArH^{+\bullet}$				42,[g] 120[h]

[a] L. Eberson and F. Radner, *Acta Chem. Scand., Ser. B*, 1984, **38**, 861. [b] Bond reorganisation energy. [c] Solvent reorganisation energy. [d] Aqueous solution. [e] Total reorganisation energy, $\lambda = \lambda_i + \lambda_o$. [f] See text. [g] All organic self-exchange reactions assumed to have same total reorganisation energy.[a] [h] L. Eberson, *New J. Chem.*, 1992, **16**, 151.

nitromethane (the major solvent actually used in the experimental work on naphthalene) which are required for the Marcus calculation, and the AM1 Hamiltonian[14] has now generally replaced MNDO for reaction-path calculations. In any case it would be interesting to extend the application of semi-empirical methods to the investigation of the critical borderline molecule, naphthalene.

Results and Discussion

Marcus Theory Calculation.—The Marcus treatment depends on a knowledge of the appropriate values for the standard electrode potentials for the reagents and also the bond and solvent reorganisation energies. Experimental values of the necessary standard potentials are given in Table 1. Examination of those for the NO_2^+/NO_2 couple shows that there is a large variation between values in the same solvent. Clearly there must be systematic errors in the case of nitronium ion and a simple average cannot be used. For nitrosonium ion an average value of 1.54 V seems appropriate—the variation with organic solvent seems minimal. In aqueous solution, however, it is necessary to consider the free energy of transfer of the ion from the organic solvent to water. Selected values (ΔG°, water to acetonitrile) for various unipositive ions are tabulated by Marcus.[15] These vary from *ca.* 25 kJ mol^{-1} for Li^+ to -23.2 kJ mol^{-1} for Ag^+, clearly very dependent on specific interactions of the ion with the solvent. An approximate value for NO^+ has been found using MOPAC 6 calculations, computing the free energy difference between the gas-phase ion complexed with one molecule of water and then with one molecule of acetonitrile from the corresponding calculated standard enthalpy and entropy changes. This gives a value of -11 kJ mol^{-1} (water to acetonitrile), resulting in an increase in E° of 0.11 V in water giving a final value of 1.65 V.

Some of the bond and solvent reorganisation energies required have been estimated by Eberson and Radner[9a] and are given in Table 2. The only further values we need are solvent reorganisation energies in the mainly aqueous/acid solvents that have been used for the investigation of nitrous acid catalysed nitration. The required total reorganisation energies for self-exchange reactions of organic species in essentially aqueous solution are difficult to deduce since most organic molecule ET processes have been carried out in non-aqueous systems. However, Kowert, Marcoux and Bard[16] have shown that for *N,N,N′,N′*-tetramethyl-4-phenylenediamine generating its radical cation, the experimental total reorganisation energy increases from 45 to 150 kJ mol^{-1} on going from acetonitrile to deuterium oxide. Layloff *et al.*[17] give increases of *ca.* 30 kJ mol^{-1} on addition of 10% water to DMF for radical anion formation with both benzoquinone and nitrobenzene resulting in final values of 75 and 125 kJ mol^{-1}, respectively. On the other hand, Meisel and Fessendon,[18] for the benzoquinone/benzoquinone anion reaction in a mainly aqueous solvent, give a value of 75 kJ mol^{-1}, very close to the DMF–water figure of Layloff *et al.* Very recently, Eberson[19] has obtained a value for the naphthalene reorganisation energy of 120 kJ mol^{-1} in acetonitrile for a system considered to be a true outer-sphere process. He suggests that many organic molecule self-exchange processes are affected by an inner-sphere component, which in turn leads to the lower values of reorganisation energies previously obtained.

For the nitrous acid catalysed nitration of naphthalene in sulfuric acid (54%) containing some acetic acid (4.8%), Leis, Peña and Ridd[3j] obtained a pseudo-first-order rate coefficient of 1.63×10^{-3} s^{-1} under conditions where the stoicheiometric concentration of nitrous acid was 1.15×10^{-4} mol dm^{-3} and the rate-determining step was the oxidation of naphthalene by NO^+. When their pseudo-first-order rate coefficient is converted to a second-order rate coefficient and corrected[20] for the extent of ionisation of nitrous acid to NO^+, the resulting rate constant for ET from naphthalene to NO^+ becomes 52.2 dm^3 mol^{-1} s^{-1}. Using the E^0 value for naphthalene of 2.08 V (electrochemical potentials for organic species do not differ much from solvent to solvent),[9b] E^0 for NO^+ 1.65 V (the figure for acetonitrile corrected for aqueous solution), the reorganisation energies listed in Table 2 for NO^+ and the figure of 120 kJ mol^{-1} for naphthalene (above) give a second-order rate constant for ET of 0.2 dm^3 mol^{-1} s^{-1}. In view of the assumptions involved, particularly the change in solvent, this probably represents reasonable agreement between theory and experiment. There is no doubt that the reaction takes place by ET, with a large outer-sphere component.

Alternatively, we may use the measured rate constant and outer-sphere Marcus theory to calculate the total reorganisation energy for the system and hence a new value for the reorganisation energy of the NO^+ ion in this particular solvent. This gives a value of 92 kJ mol^{-1} which is rather low.

Using the appropriate figures from Tables 1 and 2 we can now calculate second-order rate constants for the ET step for nitrous acid catalysed nitration of a range of aromatic hydrocarbons. The outcome is given in Table 3 and fits in rather well with the CIDNP results in that ET only becomes of significance with the xylenes and then only in the presence of large quantities of nitrous acid. Also, the results are consistent with the active oxidising species being NO^+ rather than molecular nitrous acid. Recent kinetic studies[21] confirm the earlier suggestion[3] that significant diffusion apart of the $ArH^{+\bullet}$, NO radical pair can take place after its formation by ET.

Turning our attention to NO_2^+ as an ET reagent, the first task is to arrive at a suitable value of E^0 for the nitronium ion. The difference between what appears to be the most reliable

Table 3 Calculated rate constants for ET (ArH/NO^+) in aqueous and non-aqueous solvents

	$k_2/dm^3\ mol^{-1}\ s^{-1}$	
ArH	Aqueous	Non-aqueous
Naphthalene	48	0.8
Durene	61	1.0
Mesitylene	29	0.47
1,3-Xylene	3.8×10^{-2}	2.2×10^{-4}
Toluene	1.7×10^{-5}	2.1×10^{-7}
Benzene	1.1×10^{-11}	1.4×10^{-13}

Table 4 Reaction coordinate for loss of H_2O from $H_2O{\cdot}NO_2^+$

N–O Bond length/Å	E/kJ mol^{-1}
2.64 (van der Waals' complex)	615.3
2.10	636.6
1.70	709.9
1.60	740.0
1.50	768.4
1.40	799.8
1.33 (N–OH length in nitric acid)	836.8
1.30	864.7

values in acetonitrile (1.56 V,[9b] 1.59 V)[13] and in nitromethane (2.32 V)[12a] is presumably due to experimental error, since a more recent value[13] in nitromethane confirms the lower figure. For naphthalene the E^0 value of 2.08 V gave good results for the nitrous acid catalysed nitration and therefore will be used. The necessary bond reorganisation energies are given in Table 2 for acetonitrile solution—there should be no great variation in these for nitromethane as solvent, nor for the solvent reorganisation energies. Using these values we obtain a figure for k_2 of *ca.* 2×10^{-8} dm^3 mol^{-1} s^{-1} for both naphthalene and mesitylene. Since the experimental figure for naphthalene is of the order of 1.0×10^8 dm^3 mol^{-1} s^{-1} the calculated rate constant is too low by a factor of the order of 10^{15} as pointed out earlier.[1,2] Using the highest possible value (2.32 V) for nitronium ion, this discrepancy is reduced to an order of 10^9.

One possible source of error is the fact that the NO_2 molecule may dimerise thereby decreasing its activity. This effect may be roughly quantified by application of the Nernst equation to the redox reaction (1).

$$NO_2^+ + ArH \longrightarrow ArH^{+\bullet} + NO_2 \qquad (1)$$

If we assume that the activities of the two cations cancel and that the activity of naphthalene is unity then the electrode potential for the reaction can be calculated for any given activity of NO_2. Taking this to be as low as 0.01 increases the potential for the reaction from the standard value of 0.24 to 0.36 V, corresponding to an increase in the second-order rate constant by a factor of *ca.* 20, clearly insufficient to account for the observed error.

One other possible reason has previously been suggested[2,9c] for the large deviation between the result of the Marcus theory calculations and the experimental value of k_2 for nitronium ion attack on naphthalene: that the process of nitronium ion attack to produce a radical pair by ET is not a true outer-sphere process. If we assume the measured rate coefficient for ET in naphthalene to be accurate, we can then calculate using Marcus theory the actual bond reorganisation energy for nitronium ion required to give the experimental rate constant for electron transfer. Even taking the highest possible oxidising potential (2.32 V), gives a value of *ca.* 0 kJ mol^{-1} as opposed to the value calculated for an outer-sphere process of 435 kJ mol^{-1} suggesting that complete binding of the nitronium ion has already taken place before ET, the driving force for this being the interaction of the ion with the π-cloud of the naphthalene molecule. This would appear to imply significant bond formation before the electron transfer takes place and hence preclude the possibility of subsequent partial escape of the NO_2 molecule as required by the CIDNP observations. The possibility of an 'inner-sphere' process[9c] arising from dissociation of the Wheland intermediate has been shown to be unlikely[2] since perdeuteriation of the naphthalene substrate gave no significant increase in the extent of the observed CIDNP effect. Recent proposals by Shaik[22] that a transition state for an inner-sphere process may be distinguished from the transition state for a polar mechanism appear to be limited to odd electron systems and are not relevant for either NO^+ or NO_2^+ attack on aromatic substrates. Investigation of the reaction coordinate for NO_2^+ attack on naphthalene using semi-empirical MO methods (UHF, vide infra) gives an O–N–O angle in the transition state very close to that of NO_2 itself. In outer-sphere Marcus calculations of course the assumption is made that the transition state approximates to a structure containing a NO_2 grouping which has an angle halfway between the ion and the molecule. The π-complex calculated previously[11] has a linear ONO structure *ca.* 4 Å distant from the aromatic species, and presumably therefore even if this structure is correct, it does not play a significant part in the reaction. This structure may be contrasted with the experimental results[13c] for arene–NO^+ complexes where large structural changes were observed.

This somewhat contradictory state of affairs may be circumvented by the assumption that the nitric acidium ion is sufficiently long lived[23] in the predominantly organic solvent to be the effective oxidising agent. Nguyen and Hegarty[24] have carried out *ab initio* calculations on the two possible structural isomers (both hydrogen atoms on the same oxygen atom or on different oxygen atoms) and shown the former to be more stable by *ca.* 35 kJ mol^{-1}. This structure, however, is a molecular complex of an almost linear nitronium ion and a water molecule with a N–O (H_2O) bond of length 2.23 Å and hence cannot be the effective ET agent. These results have recently been confirmed at a higher level of theory[25] and both structures have been detected spectroscopically in the gas phase.[26] These latter workers also showed, using $H_2{}^{18}O$, that ^{18}O scrambling could occur *via* a four-coordinate nitrogen structure formed from $(HO)_2NO^+$ and $H_2{}^{18}O$ without isomerisation to the $H_2ONO_2^+$ structure, despite the much greater stability of the latter. We have carried out a reaction coordinate calculation (MOPAC 6, Table 4) showing that the structure protonated on OH oxygen ($H_2ONO_2^+$) is much *less* stable when *initially* formed from a proton and nitric acid (836.8 kJ mol^{-1}) than the structure obtained by protonation of the more negatively charged multiply bonded oxygen atoms of the acid [$(HO_2)NO^+$, 714.4 kJ mol^{-1}]. As long as ET to this latter species is faster than proton transfer (diffusion controlled) to the oxygen already bearing hydrogen then this intermediate could play a significant role. The calculated ionisation potential of the radical H_2NO_3 (Table 5) is even higher than that of nitrogen dioxide, suggesting that the E^0 value for the corresponding cation might be at least the same magnitude as that of nitronium ion. The bond reorganisation energy would be eliminated as far as the NO_2 structure is concerned as this part of the molecule has already the correct angle. Calculation shows that loss of water from the H_2NO_3 radical is even more exothermic than loss of water from $H_2NO_3^+$ (−300 kJ mol^{-1} *cf.* −222 kJ mol^{-1}).

Some parameters for NO, NO_2, H_2NO_3, NO^+, NO_2^+ and $H_2NO_3^+$ calculated using the MNDO,[27] AM1[14] and PM3[28] Hamiltonians are given in Table 5. As can be seen, while there is

Table 5 Calculated[a] and experimental ionisation potentials (E_i) and structures for NO, NO_2 and H_2NO_3 using the MNDO, AM1 and PM3 Hamiltonians

		NO[a]	NO_2[a]	H_2NO_3[b]
E_i/eV	MNDO	10.02	10.70	11.14
	AM1	9.85	10.31	10.67
	PM3	9.69	9.11	9.83
	Experiment	9.25	9.79	—
Bond length/Å	MNDO	1.122	1.174	
	AM1	1.115	1.159	
	PM3	1.126	1.181	
	Experiment	1.12	1.20	
Bond angle/°	MNDO		113.4	
	AM1		111.8	
	PM3		111.2	
	Experiment		113.0	

[a] Vertical ionisation potentials calculated as ΔE (SCF) for the corresponding cations (NO^+ and NO_2^+). [b] Calculated using Koopman's Theorem.

Table 6 Standard heats of formation (MOPAC 6) for relevant species and reaction coordinate for nitronium ion attack on naphthalene at the 1- and 2-positions

	1-Substitution[a]	2-Substitution[b]
C–N length/Å	E/kJ mol^{-1}	E/kJ mol^{-1}
1.553 (σ-complex)	993.2	1009.3
1.65	1002.1	1018.7
1.75	1020.5	1037.4
1.85	1032.5	1047.0
1.90	1030.6	1043.4
1.95	1024.2	1035.4
2.00	1015.5	1025.2
2.05	1005.5	1013.5
2.15	982.4	988.6
2.25	961.0	965.0
2.35	942.1	945.0

[a] Naphthalene, 162.2 kJ mol^{-1}; NO_2^+, 921.2 kJ mol^{-1}. [b] Naphthalene radical cation, 954.1 kJ mol^{-1}; NO_2, −69.4 kJ mol^{-1}.

reasonable agreement between the results for all three methods and the experimental values as far as the structures of the oxides are concerned, the same does not apply to the ionisation potentials. The values obtained using Koopman's theorem are generally slightly too high; calculation of the energy differences of the neutral and positively charged species is better. However, the use of the AM1 Hamiltonian does not give rise to parameters which would significantly alter the conclusions of Feng, Zheng and Zerner.[11] It seems clear that the semi-empirical MNDO methods, even when corrected for the presence of solvent, over emphasise the extent of electron transfer.

A reaction coordinate calculation (AM1, UHF) has been carried out for the nitration of naphthalene by nitronium ion in both the 1- and 2-positions by stretching the C–N bond of the appropriate Wheland intermediate. As expected for a gas phase calculation, the dissociation is homolytic; the results are reported in Table 6. It is noteworthy that the difference between the activation energies for 1- and 2-substitution suggest a ratio of *ca.* 300:1 for rates of attack at these two positions. This confirms the observation of Eberson and Radner[9b] that attack of NO_2 on the naphthalene radical cation is more, not less, selective than the attack of NO_2^+ on naphthalene, i.e. >50:1 compared with *ca.* 10:1 for the electrophilic process. However, the situation remains somewhat unclear; for instance, the nitrous acid catalysed nitration of naphthalene, the product forming stage of which takes place through the NO_2–naphthalene cation radical pair, normally results in a ratio of *ca.* 20:1 for attack at the two positions. On the other hand, the suggestion[5] that the charge-transfer nitration of naphthalene by *N*-nitropyridinium cation under irradiation must take place *via* this same radical pair seems unlikely in view of the isomer ratio of 6:1 which is even lower than the typical value of 10:1 reported for nitronium ion attack.[29]

We have previously reported[2] the standard heats of formation of the Wheland intermediates arising from attack at these positions; the AM1 results are intermediate between the MNDO and MINDO/3 values. The energy difference in the transition states for 1- and 2-attack is *ca.* 10% smaller than that of the corresponding energy difference for the Wheland intermediates. As far as the structures of the transition states are concerned, the ONO angle remains close to that of the NO_2 molecule even at distances where the energies of the two transition states are identical.

One possible complication in the semi-empirical MO calculations is the ready stabilisation of the naphthalene radical cation by a second molecule of naphthalene.[30] Since if naphthalene itself were to dimerise significantly it would presumably be in an 'edge-face' situation,[31] the resulting increase in the level of complexity of the calculations would make it not worthwhile to carry them out; especially since the ease of oxidation of naphthalene in solution is already overestimated.

In conclusion, we suggest that the experimentally observed ET during the nitration of naphthalene possibly arises from the presence of nitric acidium ion as the oxidising agent, rather than nitronium ion, since the measured standard electrode potential for the latter species would have to be greatly in error or it would have to bond covalently to the aromatic substrate to a significant extent before ET took place. The results of the Marcus theoretical calculations, however, do confirm the role of NO^+ as the outer-sphere ET agent in nitrous acid catalysed nitration.

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