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Electron Transfer Reactions in Organic Chemistry. VI.* Possible Role of Electron Transfer in Aromatic Nitration by Nitrosonium and Nitronium Ion

LENNART EBERSON ** and FINN RADNER

Division of Organic Chemistry 3, Chemical Center, University of Lund, P. O. Box 740,
S-220 07 Lund, Sweden

The feasibility of non-bonding (outer-sphere) electron transfer (ET) between aromatic/heteroaromatic compounds and nitrosonium or nitronium ion has been assessed in terms of the Marcus theory. Although the $E°$ values of these two reagents are almost identical, a large difference in ET oxidizing ability is predicted to arise from an extraordinarily large difference in estimated reorganization energies (70 kcal mol^{-1} for the NO^+/NO and 140 kcal mol^{-1} for the NO_2^+/NO_2 self-exchange reaction). This causes a ratio of 10^5-10^6 between the calculated rate constants for ET from a common substrate to NO^+ or NO_2^+, respectively.

Thus, while the nitrosonium ion is predicted to be an effective non-bonding ET oxidant, the nitronium ion should undergo non-bonding ET from extremely easily oxidizable substrates only (with $E°<$*ca.* 0.2 V *vs.* NHE). It is postulated that actually observed cases of ET from aromatic/heteroaromatic compounds to NO_2^+ proceed *via* a mechanism involving direct bond formation to give the Wheland intermediate, followed by homolytic cleavage of the latter to $ArH^{+\cdot}$ and NO_2.

The timely revival in 1977 of earlier suggestions[1–4] of electron transfer (ET) mediated aromatic substitution mechanisms by Perrin[5] has given rise to considerable activity in this area. Thus it now seems unavoidable that radical cation mechanisms must be taken into account in an increasing number of cases of what are formally electrophilic aromatic substitutions, especially nitrations.[6–9] Moreover, this type of mechanism is nowadays not only of academic interest, since it probably plays an important role in the formation of nitro derivatives of polycyclic aromatic hydrocarbons in exhausts from combustion engines and in airborne matter.[10]

Perrin[5] suggested that the nitronium ion mediated nitration of all aromatic substrates with an oxidation potential lower than that of toluene, should follow the mechanism given in eqn. (1) and provided some experimental evidence for the case of naphthalene

$$ArH + NO_2^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArH^{\cdot+}NO_2 \xrightarrow{k_2} \overset{+}{Ar}(H)NO_2 \qquad (1)$$

nitration by NO_2^+ in acetonitrile. While this evidence turned out to be inconclusive on closer scrutiny,[11,12] it nevertheless remains that the mechanism of eqn. (1) has many attractive features, especially in connection with explaining a number of possible side-reactions in aromatic nitration.[13] These are often of the oxidative substitution type and resemble very much the spectrum of radical cation mediated reactions that can be realized upon anodic[14] or metal ion oxidation[15] of aromatic, and especially alkylaromatic compounds [eqns. (2) and (3)].

$$ArH \xrightarrow{NO_2^+} \begin{array}{l} \text{Quinone} \\ Ar'(OH)NO_2 \textit{ via } ArONO_2 \\ Ar-Ar \end{array} \qquad (2)$$

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[**] Author to whom correspondence should be addressed.

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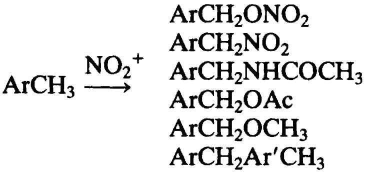


$$ArCH_3 \xrightarrow{NO_2^+} \begin{array}{l} ArCH_2ONO_2 \\ ArCH_2NO_2 \\ ArCH_2NHCOCH_3 \\ ArCH_2OAc \\ ArCH_2OCH_3 \\ ArCH_2Ar'CH_3 \end{array} \qquad (3)$$

Thus there is a strong need for further work in this area, and especially to find simple guidelines for defining suitable model systems for experimentation. As already pointed out,[11] the naphthalene system in all probability follows the normal aromatic nitration mechanism, but can we find others with greater chance of displaying ET behaviour?

A modification of the mechanism of eqn. (1) has been suggested by Ridd *et al.*[8] for the nitrous acid catalyzed nitration by NO_2^+ (in trifluoroacetic acid) and involves as the crucial electron transfer step eqn. (4), which is then followed by (5) and (6).

$$ArH+NO^+ \rightleftharpoons NO+ArH^{+\cdot} \qquad (4)$$

$$NO^{\cdot}+NO_2^+ \rightleftharpoons NO^+ + NO_2 \qquad (5)$$

$$NO_2+ArH^{+\cdot} \rightarrow \overset{+}{Ar}(H)NO_2 \qquad (6)$$

This interpretation was strongly supported by the observation of C.I.D.N.P. effects when $H^{15}NO_3$ was used.[7] Further support for this view can be found in a number of cases of radical cation formation by one-electron oxidation of aromatic and hetero-aromatic compounds by nitrosonium salts.[16-19]

Recently, an attempt was made to estimate the ET rate constant k_1 of eqn. (1) with ArH=naphthalene by use of the Marcus treatment.[20,21] The preliminary result, an estimated k_1 value of the order of 10^2 M^{-1} s^{-1}, was taken to indicate that ET is not competitive with the normal mechanism (experimental rate constant *ca* 10^{10} M^{-1} s^{-1}) in this particular case. We now report a full discussion of this problem, concluding that nitronium ion should be an ineffective ET oxidant due to the very high reorganization energy of the NO_2^+/NO_2 self-exchange reaction. Such an effect does not influence the ET oxidizing properties of nitrosonium ion.

RESULTS

The Marcus treatment. The feasibility of ET steps of the types shown in eqns. (1) and (4) can in principle be assessed by the Marcus theory for non-bonded (a term that for organic systems[22] replaces the term "outer-sphere" of inorganic chemistry) electron transfer.[23] According to this treatment, $\Delta G^{\neq}$ for electron transfer between the two species ArH and NO_2^+ (or NO^+) is given by eqn (7).

$$\Delta G^{\neq}=(\lambda/4)(1+\Delta G^{\circ}/\lambda)^2 \qquad (7)$$

Here λ is the *reorganization energy* (see below) and ΔG° the free energy change for ET. The underlying physical model in the simplest case is that of two spherical species, embedded in a continuous medium of dielectric constant D, which diffuse together and form a collision complex. This is sometimes called the precursor complex within which an electron is exchanged when the transition state has been reached. For the transition state to be reached from the initial collision complex, the two reacting species must undergo bond reorganization, bond and/or angle deformations, with a bond reorganization energy of λ_i. In addition, the immediately surrounding solvent molecules must undergo solvent reorganization (with a solvent reorganization energy of λ_o) to accommodate electrostatic changes in the transition state upon ET. The reorganization energy of eqn. (7), λ, is then the sum of λ_i and λ_o. The need for bond/solvent reorganization to occur before reaching the transition state is a consequence of the Franck-Condon principle, which requires that the transfer of an electron must take place on a time-scale (*ca.* 10^{-16} s) which is much faster than that of nuclear movements (*ca.* 10^{-13} s).

For any electron transfer reaction, Marcus' theory demands that λ can be expressed as the mean value of the λ values of the two corresponding self-exchange reactions. For the ET process of eqn. (1), the self-exchange reactions are shown in eqns. (8) and (9).

$$ArH^{\cdot +}+ArH \rightleftharpoons ArH+ArH^{\cdot +} \qquad (8)$$

$$NO_2^+ + NO_2 \rightleftharpoons NO_2 + NO_2^+ \qquad (9)$$

Values of λ for self-exchange reactions can be experimentally determined (for a list, see Ref. 20) or calculated (see below).

Application of the Marcus treatment to reactions of NO_2^+ and NO^+. In order to estimate ΔG° of eqns (1) and (4), we need E° of NO_2^+/NO_2, NO^+/NO and $ArH^{\cdot+}/ArH$. The former values (1.56 and 1.51 V, respectively, *vs.* the normal hydrogen electrode; all potentials given in this paper are referred to this standard) were obtained from Bontempelli *et al.*[24] whereas E° values for the oxidation of aromatic hydrocarbons have been determined by Parker.[25]

Turning to ways of estimating λ values for the pertinent self-exchange reactions, one can first note that only a few experimental λ values for $ArH^{\cdot+}/ArH$ are known from the literature[26] and that these mostly refer to heteroaromatic systems (dibenzo-*p*-dioxin, phenoxazine, phenoxathiin and phenothiazine in acetonitrile; 9,10-diphenylanthracene in dichloromethane is the only truly aromatic system). They are all low (<10 kcal mol^{-1}) and it appears reasonable to assume that $ArH^{\cdot+}/ArH$ systems of the type treated here have similar λ values. A determination of the heterogeneous ET rate constant for the perylene$^{\cdot+}$/perylene electrode reaction (0.7 cm s^{-1}) supports this assumption.[27] For $ArH/ArH^{\cdot-}$ systems far more λ values are known, among them that of naphthalene/(naphthalene)$^{\cdot-}$, and they are similarly low, provided the radical anion is not ion-paired (*e.g.*, for naphthalene, anthracene, pyrene, tetracene, perylene and dibenzofuran λ is <10 kcal mol^{-1}). Thus the value of 10 kcal mol^{-1} was assigned to λ of $ArH^{\cdot+}/ArH$.

The λ_i value of NO^+/NO was calculated using the classical Marcus expression which in this particular case simplifies to eqn. (10).

$$\lambda_i(NO^+/NO)=2\frac{k^R_{str}\,k^P_{str}}{k^R_{str}+k^P_{str}}\,(r^R-r^P)^2 \qquad (10)$$

Here k_{str} and r are the stretching force constant and equilibrium bond length of the N–O bond in the reactants (R) and products (P), respectively. For the NO_2^+/NO_2 couple it was assumed that only the N–O stretch and O–N–O bending modes are involved and the transition state is symmetrical, with all N–O bonds equal in length and the two O–N–O angles identical. The same assumptions underlie a calculation of $\lambda(NO_2/NO_2^-)$.[28] With these approximations, $\lambda_i(NO_2^+/NO_2)$ is given by eqn. (11), in which k_{bend} and v are bending force constants and bond angles, respectively (see Table 2).

$$\lambda_i(NO_2^+/NO_2)=4\frac{k^R_{str}\,k^P_{str}}{k^R_{str}+k^P_{str}}\,(r^R-r^P)^2+ 2\frac{k^R_{bend}\,k^P_{bend}}{k^R_{bend}+k^P_{bend}}\,(v^R-v^P)^2 \qquad (11)$$

The parameters required for the application of eqns. (10) and (11) are given in Table 1, and the resulting λ_i in Table 2 (for details, see Ref. 20). To obtain λ_o, Kharkats'[34] model was calibrated against the λ_o of NO_2/NO_2^-. The rate constant for self-exchange between NO_2 and NO_2^- is known[35] (10^{-2} M^{-1} s^{-1}, corresponding to $\lambda=71$ kcal mol^{-1}) and thus λ_o can be estimated as $\lambda-\lambda_i=71-35=36$ kcal mol^{-1}.

Starting from Kharkats' ellipsoidal model of two identical, triaxial ellipsoids with semiaxes *a*, *b*, and *c* (*a*>*b*>*c*) and with the *c* axes and *ac* planes coinciding, λ_o can be calculated as a function of $r^{\ddagger}$, the distance between the centers of the ellipsoids, for which *a*, *b*, and *c* were

Table 1. Molecular parameters for nitrogen-oxygen species of interest.

Species	N–O length/Å	O–N–O angle/deg	Force constant NO-stretch/ mdyn $Å^{-1}$	O–N–O bend/ mdyn Å rad^{-2}
NO^a	1.1503	—	15.9	—
NO^{+b}	1.0619	—	23.9	—
NO_2^{-c}	1.236	115.4	7.50	2.55
NO_2^d	1.197	134.3	11.04	2.28
NO_2^{+e}	1.154	180.0	17.45	0.688

[a] Ref. 29. [b] Force constant (k) calculated from the stretching frequency of NO^+ ($\nu=2340$ cm^{-1}) by the formula $\nu=1307\,(k/\mu)^{\frac{1}{2}}$ where μ is the reduced mass.[30] [c] Ref. 31. [d] Ref. 32. [e] Ref. 33.

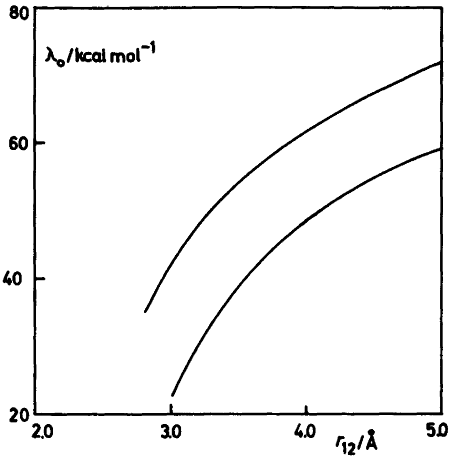


Fig. 1. Solvent reorganization energy (λ_o) as a function of $r^{\ddagger}$ according to Kharkats' model. Lower curve for NO_2/NO_2^- (and NO_2^+/NO_2), upper one for NO^+/NO.

estimated to be 2.56, 1.55 and 1.50 Å, in the transition state (see Fig. 1). The λ_o value of $NO_2^{\cdot}/NO_2^-$ is then used to estimate $r^{\ddagger}$ which comes out at 3.40 Å, slightly longer than the distance between the centra of the ellipsoids at contact, $2c$=3.00 Å. Such an "expanded" transition state was found[20] to be a consequence of Kharkats' model in a large number of cases, and in fact the percentage expansion, expressed as 100 $(r^{\ddagger}-2c)/c$, lies slightly outside the range found (63±21 %, to be compared with that of the NO_2/NO_2^- transition state, 27 %).

By assuming that the NO_2^+/NO_2 transition state has the same expansion factor as that of NO_2/NO_2^-, $\lambda_o(NO_2^+/NO_2)$ becomes available. The possible errors inherent in this assumption are rather small. If the expansion factor is taken to be, *e.g.* 0 and 54 %, log *k* (see Table 3) would change by ±(0.6−0.7) in the endergonic region. Similarly, with $r^{\ddagger}$=3.29 Å, corresponding to an

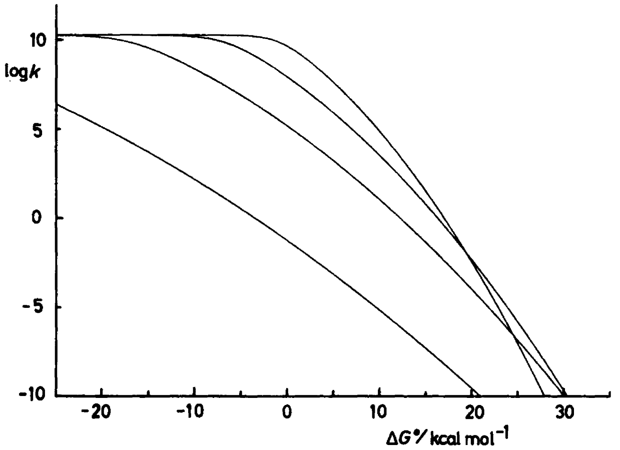


Fig. 2. Plots of log *k* *vs.* $\Delta G°$ according to eqn. (13) with λ=15(1) 25(2), 40(3) and 75(4) kcal mol^{-1}. The latter two curves correspond to ET oxidation by NO^+ and NO_2^+, respectively.

Table 2. Calculated λ_i, λ_o and λ values of NO_2^-/NO_2, NO_2^+/NO_2 and NO^+/NO in acetonitrile.[a]

Self-exchange process	λ_i[b]/kcal mol^{-1}	λ_o[c]/kcal mol^{-1}	λ[d]/kcal mol^{-1}
NO_2/NO_2^-	35	36[e]	71.0[f]
NO_2^+/NO_2	104	36	140
NO^+/NO	21	49	70

[a] n_D^{25}=1.3441, D=36.2. [b] Calculated according to eqn. (10) or (11), using the molecular parameters of Table 1. [c] Calculated by Kharkats' equation, assuming that the expansion of the transition state is 27 %. [d] $\lambda=\lambda_i+\lambda_o$. [e] Obtained as the difference between the experimental λ value and λ_i. [f] Experimental value (Ref. 35).

Table 3. Calculated log k ($M^{-1}\ s^{-1}$) for ET reactions between ArH and $NO^+(NO_2^+)$ in acetonitrile at 25 °C.

Compound ($E°$/V)[a]	$\Delta G°$/kcal mol^{-1} [b]	log k ($M^{-1}\ s^{-1}$) for reaction with NO^+ $\lambda=15$	25	40 kcal mol^{-1}	log k ($M^{-1}\ s^{-1}$) for reaction with NO_2^+ $\lambda=15$	25	75 kcal mol^{-1}
Benzene (3.03)	35.0, 33.8	−18.0	−13.9	−13.3	−16.6	−12.8	−16.4
Toluene (2.61)	25.4, 24.1	−7.4	−6.1	−7.1	−6.3	−5.2	−11.5
Mesitylene (2.43)	21.2, 20.9	−3.5	−3.1	−4.7	−2.5	−2.3	−9.5
Naphthalene (2.08)	13.1, 11.9	2.9	1.9	−0.4	3.7	2.5	−5.9
Hexamethylbenzene (1.85)	7.8, 6.6	6.1	4.6	2.0	6.8	5.2	−3.8
Dibenzo-1,4-dioxine (1.63)	2.8, 1.6	8.6	6.8	4.1	9.1	7.3	−1.5
Anthracene (1.61)	2.3, 1.1	8.8	7.0	4.3	9.3	7.5	−1.7
Perylene (1.30)	−4.8, −6.0	10.3	9.4	6.8	10.3	9.7	0.9
Zn(II)TPP (0.95)	−12.9, −14.1	10.3	10.3	9.1	10.3	10.3	3.4
Phenothiazine (0.71)	−18.4, −19.6	10.3	10.3	10.0	10.3	10.3	5.0
Ferrocene (0.60)	−21.0, −22.2	10.3	10.3	10.2	10.3	10.3	5.7

[a] $E°$ values were taken from Refs. 20, 25 and 36. [b] The first value refers to the NO^+ reaction, the second one to the NO_2^+ reaction.

expansion of the transition state by 27 %, $\lambda_o(NO^+/NO)$ (*a*, *b*, and *c* equal to 2.00, 1.45, and 1.45 Å) comes out at 49 kcal mol^{-1}. The last column of Table 2 then gives the λ values for the NO_2^+/NO_2 and NO^+/NO self-exchange reactions.

The calculated λ values of NO_2^+/NO_2 and NO^+/NO were then used for $\Delta G^{\neq}$ calculations according to eqn. (7). The λ values of eqns. (1) and (4) thus are $0.5(10+140)=75$ and $0.5\times(10+70)=40$ kcal mol^{-1}. For comparison, calculations were also performed for eqn. (1) with $\lambda=15$ and 25 kcal mol^{-1}, corresponding to $\lambda=20$ and 40 kcal mol^{-1} for the NO_2^+/NO_2 or NO^+/NO self-exchange reactions, respectively.

Calculations were performed for a series of compounds covering a $\Delta G°$ interval between 35 and −22 kcal mol^{-1} (Fig. 2 and Table 3). Instead of reporting $\Delta G^{\neq}$ according to eqn. (7), log k values were estimated for the kinetic scheme of eqn. (12) (kinetically equivalent to eqn. (1)), in which k_d and k_{-d}

$$ArH+NO_2^+ \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} [ArH\ NO_2^+] \xrightarrow{k_{el}} \overline{ArH^{\cdot +}\ NO_2} \qquad (12)$$

are the rate constants for formation and dissociation of the collision complex and k_{el} is the monomolecular rate constant for ET within the complex. Application of the steady state approximation to this situation and expressing k_{el} according to the Eyring equation eventually gives k in the form of eqn. (13). Values of k_d and k_{-d} were taken to be $2\times10^{10}\ M^{-1}\ s^{-1}$ and $6.3\times10^{10}\ s^{-1}$, respectively, and Z to be $10^{13}\ s^{-1}$.

$$k=\frac{k_d}{1+\frac{k_{-d}}{Z}\exp\left[\frac{\lambda}{4}\left(1+\frac{\Delta G°}{\lambda}\right)^2/RT\right]} \qquad (13)$$

Nitrosonium ion as a one-electron oxidant. In view of the fact that nitrosonium ion appears to be a good one-electron oxidant toward different types of compounds,[16–19] experiments were carried out to qualitatively assess its behaviour with respect to the borderline region between oxidizable and "non-oxidizable" substrates (Table 4).

Table 4. Properties of NO$^+$ as a one-electron transfer oxidant toward organic molecules.

Substrate	E° or $E_{\frac{1}{2}}$/V	Result[a]	Ref.
Dibenzodioxine	1.63	RC formed in solution	16
Phenoxathiine	1.50	RC formed in solution	16
Thianthrene	1.52	RC formed in solution	16
Phenothiazine	0.71	RC salt isolated	16
10-Methylphenothiazine	0.94	RC salt isolated	16
5,10-Dimethyl-5,10-dihydrophenazine	0.35	RC salt isolated	16
RC of 5,10-dimethyl-5,10-dihydrophenazine	1.07	Dication salt isolated	16
Perylene	1.30	RC formed in solution and as solid	This work, 16
9,10-Diphenylanthracene	1.44	RC formed in solution	This work
9,10-Dimethylanthracene	1.11	RC formed in solution	This work
9-Phenylanthracene	1.34	RC formed in solution	This work
Pyrene	1.60	RC formed in solution[b]	This work
Anthracene	1.61	RC formed in solution[b]	This work
Chrysene	1.88	Less than 1 % of RC formed at equilibrium[b]	This work
Triphenylene	2.12	No reaction	This work
Naphthalene	2.08	No reaction	This work
Ferrocene	0.60	RC formed in solution	This work
1,5-Dithiacyclooctane	0.88	RC formed in solution	17
RC of 1,5-dithiacyclooctane		Dication salt isolated	17
N,*N*,*N'*,*N'*-Tetramethylphenylenediamine	0.26	RC formed in solution	18

[a] RC=radical cation. [b] The RC solution was not stable upon standing.

Since the reduced form of the NO$^+$/NO couple is a gas and thus can escape from the solution and drive the equilibrium to the right, this region can only be approximately established unless precautions are taken to perform measurements in a closed system. Another source of uncertainty resides in the chemical reactivity of radical cations of systems displaying borderline behaviour, leading to relatively rapid radical cation decay.

With due notice of these difficulties, Table 4 demonstrates that radical cations are formed in high concentrations by NO$^+$ oxidation of compounds with E° values up to *ca* 1.6 V. Even chrysene with E°=1.88 V is converted to its radical cation, but here the effects of an unfavorable equilibrium position and unstable radical cation are clearly visible. Moreover, the combined results of Table 4 are in good agreement with the experimentally determined E° of NO$^+$/NO, 1.51 V.[24]

DISCUSSION

Before we embark on a discussion of the calculations reported in Table 3, it is important to pinpoint the nature of the problem at hand. We know empirically that nitration by NO$_2^+$ of all substrates more reactive than toluene – and this is the case of interest here – proceeds at a diffusion controlled rate, *i.e.*, with a rate constant of the order of 10^{10} M^{-1} s^{-1}.[37]

Thus the main philosophy of our treatment must rest on the assumption that the Marcus theory can "forbid" ET in specific cases. In other words, if a calculated rate constant for a certain ET process is of a much lower magnitude than the experimentally observed one, we should conclude that ET is not feasible in this particular case and that another mechanism must be valid. On the other hand, agreement between a calculated and experimental rate constant only tells us that ET *might* take place. In order to establish this as a reliable fact, extensive experimentation might be necessary. And yet, as certainly the case of nitration ET mechanisms bears witness of, a definitive answer might not be easily obtainable due to either methodological or interpretational difficulties.[20]

Thus we actually want to use the Marcus theory as a sorting device to find out which type of compound(s) might be the best choice for experimental studies of ET mediated nitration. From what was said above, it is evident that only reactions with very high predicted ET rate constants can be acceptable candidates, and from the outset we therefore fix a lower limit of this value at $\geqq 10^8$ M^{-1} s^{-1}. If an ET reaction with this rate constant competes with a polar alternative proceeding at diffusion controlled rate ($\sim 10^{10}$ M^{-1} s^{-1}), there is a reasonable chance that the one percent of ET can be detected experimentally.

Since the application of the Marcus theory gives room for a fair amount of ambiguity in the choice of parameters for eqn. (13), it is important to discuss why and how these values were chosen, and how these choices can influence the calculated log k values.

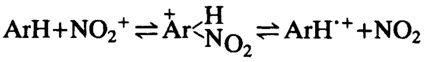
One suitable principle in a case of the type treated here, is obviously to slant the parameters toward values that exclude as few reactions as possible. This is equivalent to saying that we want to find the highest possible $E°$ of a substrate for which electron transfer is feasible, using the self-imposed rate constant limit given above, 10^8 M^{-1} s^{-1}. Judging from eqn. (13) one can see that this requirement leads to choices of the highest possible values of k_d and Z and the lowest possible ones of k_{-d} and λ.

It is easy first to dispose of k_d, k_{-d} and Z. The value of the diffusion controlled rate constant for the charge situation $Z_1Z_2=0$ in acetonitrile is 2×10^{10} M^{-1} s^{-1}, and this is in the majority of cases higher than the corresponding ones for solvents commonly used in aromatic nitration. For Z the value of a first-order process, 10^{13} s^{-1}, was chosen in view of the fact that we are dealing with an "intramolecular" electron transfer within a collision complex. The Z value can in principle be smaller, perhaps down to 10^{11} s^{-1}, *but not larger.*

For k_{-d}, the charge situation $Z_1Z_2=0$ in water demands a value of 6.3×10^{10} s^{-1} which was deemed a suitable solvent for defining a "minimum" of this rate constant.[23e]

The main difficulty resides in the choice of λ. In the Results Section we have used what are judged to be the best possible methods for the calculation of $\lambda(NO_2/NO_2^+)$ and $\lambda(NO/NO^+)$ and found one very high value (140 kcal mol^{-1}) and a more reasonable one (70 kcal mol^{-1}), respectively. As a consequence, *not even the most easily oxidizable substrate of Table 3, ferrocene* (see also Fig. 2), would be a candidate for ET to NO_2^+ with our current constraints! Yet we know – or think we know – that ferrocene is oxidized to ferricinium ion by NO_2^+ in a very fast reaction.

The way out of this dilemma is either to find reasons for selecting a lower value of $\lambda(NO_2^+/NO_2)$ or to accept that ET is not feasible even in the case of such an extreme substrate as ferrocene. For this conclusion to be compatible with the experimental outcome, we have to postulate an alternative mechanism to outer-sphere ET. Then polar association/homolytic dissociation according to eqn. (14) is a logical choice. The thermodynamics of this pathway are governed by exactly the same factors as that of ET.


$$ArH+NO_2^+ \rightleftharpoons \overset{+}{Ar}{<}^{H}_{NO_2} \rightleftharpoons ArH^{\cdot+}+NO_2 \qquad (14)$$

It should not be impossible to derive consequences of this mechanism that are amenable to experimental testing. This mechanistic possibility is discussed in more detail below.

To return to our main track, let us first consider the properties of NO^+ as an ET oxidant. Nitrosonium salts, *e.g.* the tetrafluoroborate or perchlorate, have been successfully used to achieve one-electron oxidations, as in the preparation of radical cation salts of heteroaromatic compounds (Table 4). It is also known to act as a hydride transfer oxidant,[38] but this involves aliphatic and cycloaliphatic substrates of very high oxidation potentials, far outside the range within which ET is feasible.

Among the compounds capable of undergoing ET to NO^+ with high degree of conversion (Table 4), pyrene, anthracene and dibenzodioxine have the highest standard potentials, 1.60, 1.61 and 1.63 V, respectively. The predicted log k values for these reactions (Table 3), using the calculated λ value of 40 kcal mol^{-1}, is *ca.* 4. This would then represent the lower rate limit for this class of compounds. Obviously, this λ value is in reasonable agreement with the qualitative studies reported in Table 4. It would be of great interest to determine the actual rate constants to establish if the agreement is quantitative.

Finally, the calculations of Table 3 on NO^+ oxidation of aromatics indicate that such ET steps for the more difficultly oxidizable compounds, like mesitylene, are predicted to be too slow to be compatible with experimentally found rates (half-lives of 5–10 min under conditions allowing for the study of ^{15}N C.I.D.N.P.)[39] One way out of this difficulty is to assume – and this can of course be tested experimentally – that the acidic media used (trifluoroacetic acid, sulfuric acid) enhance the $E°$ of NO^+/NO.

A substantially more complex problem is posed by the calculations of ET rates for reaction of NO_2^+. There is ample experimental evidence that easily oxidizable compounds (*e.g.* dibenzodioxine,[40] phenothiazine,[41] perylene[42] and ferrocene[43]) undergo formal one-electron oxidation by NO_2^+ to give solutions of the corresponding radical cations, and that recombination of NO_2 and $ArH^{\cdot+}$ can take place to give the Wheland intermediate and ultimately the nitro derivative after proton abstraction.[11b] Yet ET between NO_2^+ and even such an extremely favorable ET reductant as ferrocene ($\Delta G° < -22$ kcal mol^{-1}) is predicted to be far slower than the limiting value, 10^8 M^{-1} s^{-1}. In order to reach the latter value, $\Delta G°$ must be < -32 kcal mol^{-1} ($E° < 0.17$ V).

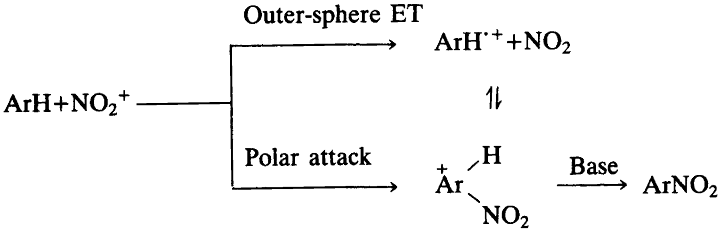
As already indicated, one logical way out of this difficulty is to look at the full range of possible reactions in the encounter between NO_2^+ and ArH (Scheme 1).

With the assumption that non-bonded ET between NO_2^+ and ArH is "forbidden" except for extremely easily oxidizable ArH, a second mechanism leading to the radical cation would be polar attack to give $Ar^+(H)NO_2$, followed by homolytic dissociation of this species to give NO_2 (and ultimately N_2O_4, which is the thermodynamically favored form of this equilibrium[44]) and $ArH^{\cdot+}$. With a suitable balance between the two E° values involved, the radical cation will predominate at equilibrium and formation of $ArNO_2$ will be dependent upon the nature of the base available for proton abstraction from the Wheland intermediate. In a coming paper,[42] it will be shown that the nitration of perylene under different conditions can be interpreted only with recourse to Scheme 1. The impossibility of nitrating ferrocene (FcH) with NO_2^+ is now easily understood; the equilibrium between $FcH^{\cdot+}$ and NO_2 (N_2O_4) to give the Wheland intermediate is so far to the $FcH^{\cdot+}/NO_2$ side that even addition of a base like 2,6-di-tert-butyl-4-methylpyridine will not drive the reaction toward formation of $FcNO_2$. We are convinced that NO_2^+ or, in general N(V) species, are not suitable for the nitration of easily oxidizable aromatics because of the complications inherent in Scheme 1. Instead, N_2O_4 in dichloromethane should be the preferred reagent.[45]

Qualitatively, we can understand why NO_2^+ is such an unfavorable ET oxidant in terms of the structure of the transition state leading to either ET or direct bond formation (Scheme 1). To reach the transition state for ET, considerable bending of the linear NO_2^+ ion must occur, as reflected in the very high λ_i value of 104 kcal mol^{-1}, whereas for bond formation the bond energy gain from the incipient C–N bond compensates at least partially for the O–N–O bending energy expended.

EXPERIMENTAL

Materials. The aromatic substrates were of the highest commercial quality available and used without further purification. Dichloromethane (Merck, zur Rückstandanalyse) was dried and stored over 3 Å molecular sieves. Sulfolane was distilled and passed through a column packed with neutral alumina and molecular sieves, and stored over molecular sieves. Solutions of nitrosonium tetrafluoroborate (ca 0.4 M) were prepared by dissolving $NOBF_4$ (Merck) in sulfolane at 40 °C.



Scheme 1.

Reactions with nitrosonium tetrafluoroborate. Solutions of the aromatic compounds (20 mM, 20 ml) in dichloromethane were flushed with argon for 3 min, 1.0 ml of 0.4 M $NOBF_4$ was added, and the mixture flushed by argon for 10 min. For the more easily oxidizable substrates, an intense coloration immediately appeared and in some cases precipitation of the radical cation tetrafluoroborate occurred. In the case of perylene quantitative isolation of the salt was possible (filtration). The visible spectrum of this solid in dichloromethane showed λ_{max} at 540 nm. For the less easily oxidizable substrates precipitation of $NOBF_4$ instead occurred. Thus naphthalene showed no coloration and white crystals of $NOBF_4$ immediately separated, while in the case of chrysene the solution turned green but most of the $NOBF_4$ precipitated.

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