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Theoretical Study of Ipso Attack in Aromatic Nitration

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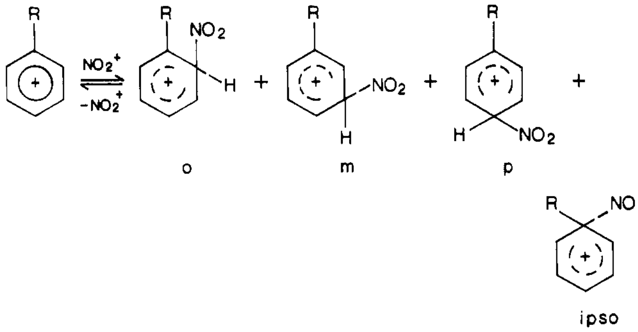
We examine the nitration of benzene, toluene, the xylenes, and nitrobenzene in the context of two possible mechanisms: classical electrophilic substitution and radical pair recombination. Various geometric structures in the reaction are examined by using the MNDO self-consistent field (SCF) method. More detailed information on these structures are obtained by using INDO-SCF and SCF-CI calculations. We present and characterize different radical pairs and π and σ complexes that result in these reactions, concluding that classical electrophilic substitution may be the mechanism for the nitration of benzene but that radical pair recombination may also be the mechanism. For toluene and the xylenes, radical pair recombination is suggested by the calculations, and only this mechanism can successfully predict the correct product distribution. The nitration of nitrobenzene is the only case in this study that appears to proceed through the classical electrophilic mechanism. Substituents on an aromatic that deactivate the system toward nitration may do so by raising the ionization potential of the aromatic above that of NO_2, thus inhibiting the one-electron transfer required for radical pair formation.

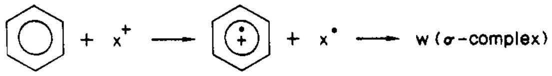
I. Introduction

Nitration is one of the most studied and best understood of organic reactions.[1,2] But the mechanism of aromatic nitration continues to be a subject of active research,[3-7] and there still exists some controversy, especially with respect to ipso attack; i.e.,



Ipso attack is not easily explained by the usual theory of aromatic electrophilic substitution. According to this theory the electrophilic reagent, in this case the nitronium ion, NO_2^+, should attack preferentially the position with the largest electron density. Most calculations, however, indicate that the ipso position is seldom the position with the largest electron density.[8] For example, in *p*-xylene, the net charge density and the π populations from our calculations are given in Figure 1. The ipso position is not negative. Ab-initio calculations[8] in these systems give the same trends as do these INDO[9] calculations. However, ipso attack accounts for 75% of the product.[10]

As early as 1945, Kenner[11] proposed that one-electron charge transfer may play an important role in the mechanism of nitronium ion nitration. In 1954, Nagakura and Tanaka[12] using molecular orbital theory proposed a mechanism involving single-electron transfer, but no sufficient attention was paid to this suggesting at that time. R. D. Brown gave the idea theoretical support and clearly postulated charge-transfer complexes as stable intermediates.[13] Pedersen, Petersen, Tossell, and Lawesson[14] represented electrophilic substitution as



and found a linear relationship between the logarithm of the relative rate constants for nitrations in acetic anhydride of polynuclear aromatics and the ionization potentials of the aromatics.

These ideas have not been widely adopted but appear from time to time in the literature.[15] The proposal of initial *one-electron transfer* between the nitronium ion and the aromatic substrate was reemphasized by Perrin[16] where he demonstrated that only radical-ion recombination could successfully predict the product distribution.

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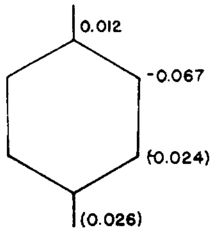

Figure 1. Net and (net π) charge densities from deorthogonalized INDO calculations for *p*-xylene.

Table I. Total Energies from MNDO Calculations (eV)

compd	energy	compd	energy
NO_2^+	−837.94	*o*-xylene	−1164.58
benzene	−851.49	*m*-xylene	−1164.69
nitrobenzene	−1684.95	*p*-xylene	−1164.69
toluene	−1008.11		

Table II. Total Energies for the Radicals of This Study from MNDO Calculations (eV)

compd	energy	compd	energy
NO_2	−847.22	*o*-xylene$^+$	−1155.88
benzene$^+$	−842.44	*m*-xylene$^+$	−1155.98
nitrobenzene$^+$	−1675.15	*p*-xylene$^+$	−1156.00
toluene$^+$	−999.29		

According to the radial-ion recombination mechanism, nitration occurs according to

$$NO_2^+ + ArH \rightarrow [NO_2, ArH^+] \rightarrow HArNO_2^+$$

The product distribution is determined by the unpaired spin density on the ArH^+ radical. Often this is completely determined by the highest occupied molecular orbital (rather than the net, or total π electron population) as it is this "orbital" that loses the electron.

In 1981 Schmitt, Roos, and Buttrill[17] reported the first direct evidence for the reaction between aromatic radical cations and NO_2 leading to the formation of σ-bonded intermediates.

In this work we re-examine this old question and compare the π-complex, σ-complex mechanism proposed by Olah and Dewar[18,19] with that of radical cation recombination following a one-electron transfer. We examine nitration of benzene, toluene, the xylenes, and nitrobenzene. Geometric structures are obtained by using the MOPAC-MNDO extrapolation procedure of Dewar and collaborators.[20-22] At these optimized structures, wave functions and charge and spin distributions are obtained by using the INDO/S model.[9] These model studies explain the observed results of aromatic nitration quite satisfactorily.

II. Results

A. The geometries that we obtain for the molecules of this study using the MNDO method are presented in Figure 2, calculated net electronic populations are presented in Figure 3, and the spin populations of the corresponding radicals are given in Figure 4. Slight breaks in symmetry have to do with the use of valence bond coordinates during the geometry optimization and are removed only slowly by continuing the optimizations. Calculated total energies are presented in Tables I and II for the closed shell and open shell species, respectively. The geometries used for the calculation of the radicals are the same as those optimized for the parent closed shell systems. Since one-electron transfer, at least in the gas phase, is related to the ionization potentials, I, of ArH and NO_2, we compare our calculated values obtained from ΔE(SCF), viz.

$$I = E^+ - E^0 = \Delta E(\mathrm{SCF}) \qquad (1)$$

where E^+ and E^0 are the energies of the positive and neutral molecules, respectively, with experimental values[23] in Table III. With the possible exception of NO_2, the results we obtain are quite good. The order is preserved, however; only nitrobenzene among the molecules we studied has an ionization potential higher than that of NO_2. *In the gas phase, to which all of these calculations relate, one-electron transfer should occur in all of the cases we studied except in the nitration of nitrobenzene.* This is summarized in Table IV where we present

$$E_s = E(\mathrm{ArH}) + E(NO_2^+) \qquad (2)$$

$$E_f = E(\mathrm{ArH}^+) + E(NO_2) \qquad (3)$$

and

$$\Delta E_R = E_f - E_s \qquad (4)$$

ΔE_R, the energy of this electron transfer, is negative except in those compounds which have electron-withdrawing substituents that tend to stabilize the aromatic neutral and, experimentally, are known to inhibit nitration. In those cases in which one-electron transfer occurs (at least in the gas phase), complexation could still lead to state

Table III. Ionization Potentials (eV) from ΔE(SCF) Calculations (See Text)

molecules	calcd value	lit.[a] value
NO_2	9.28	9.79
benzene	9.05	9.24
nitrobenzene	9.80	9.92
toluene	8.82	8.82 ± 0.01
o-xylene	8.70	
m-xylene	8.71	
p-xylene	8.69	8.44

[a] From ref 23 and other references cited therein.

Table IV. Energies (eV) of $ArH + NO_2^+ \rightarrow ArH^{\cdot+} + NO_2^{\cdot}$, $E_f - E_s = \Delta E_R$ (See Text)

molecules	E_s	E_f	ΔE_R
nitrobenzene	−2522.88	−2522.37	0.52
benzene	−1689.42	−1689.66	−0.23
toluene	−1846.05	−1846.51	−0.46
o-xylene	−2002.52	−2003.10	−0.58
m-xylene	−2002.62	−2003.19	−0.57
p-xylene	−2002.63	−2003.22	−0.59

Table V. Energies of the π-Complexes, E_π, and Their Stability Relative to the Isolated Closed Shell Molecules, ΔE_π, from MNDO Calculations

π-complex	E_π (eV)	ΔE_π (eV)
nitrobenzene–NO_2^+	−2523.21	−0.32
benzene–NO_2^+	−1689.55	−0.13
toluene–NO_2^+	−1846.15	−0.10
o-xylene–NO_2^+	−2002.61	−0.09

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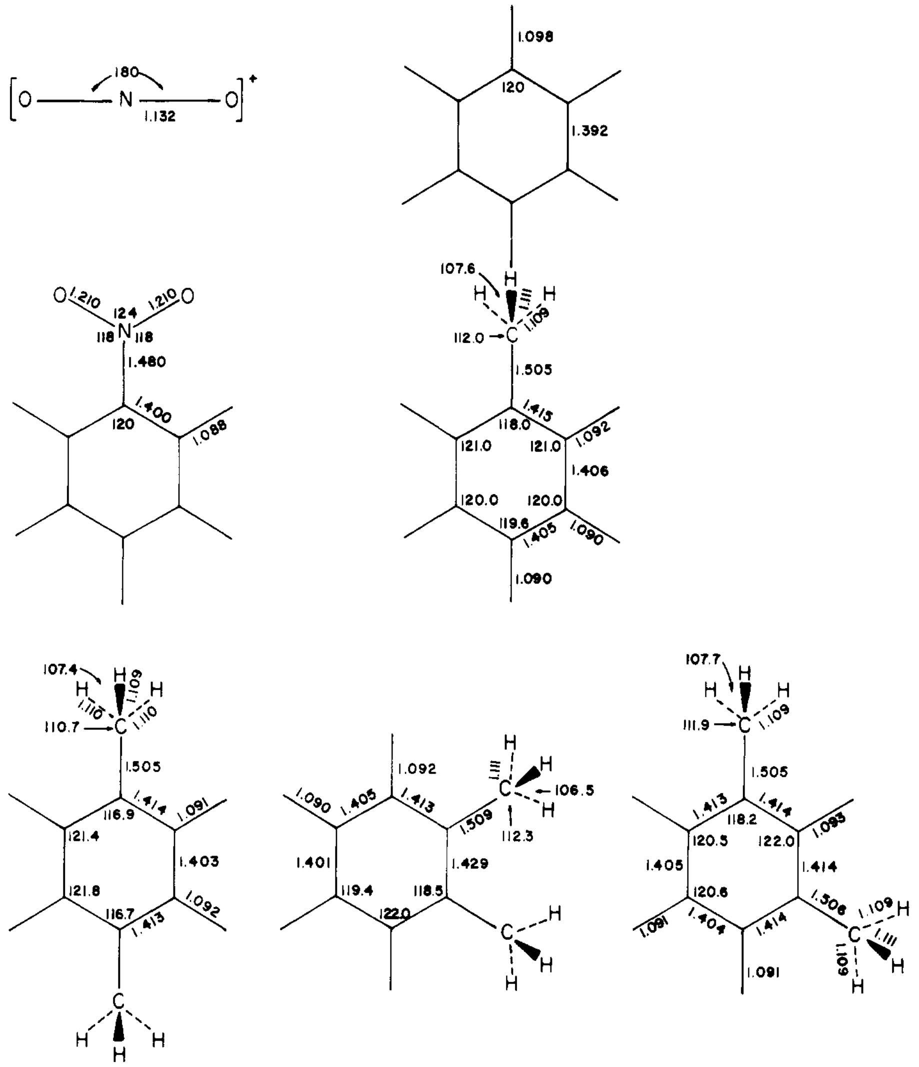


Figure 2. Calculated structures of the closed shell systems of this study. Bond lengths are in angstroms.

crossing, restoring the π-complex, σ-complex scheme.

B. π-Complexes. We examine four π-complexes. The optimized geometries are given in Figure 5 and the energies in Table V. The geometries we obtain for benzene–NO_2^+ and toluene–NO_2^+, are similar to those obtained by Politzer, Jayasuriya, Sjoberg, and Laurence.[8] The NO_2^+ to aromatic distance that they obtain from ab initio STO-3G calculations is about an angstrom shorter than that which we obtain from these MNDO calculations. The potential energy, however, is quite soft to this interplanar displacement: movement of ±0.5 Å from the calculated equilibrium position costs less than 3 kcal/mol.

ΔE_π, defined as the stabilization energy of the π-complex (eq 5) suggests that only in the nitrobenzene case is the

$$\Delta E_\pi = E_\pi - E_s \tag{5}$$

π-complex favored over the radical-pair. A comparison of Table IV, ΔE_R, and Table V, ΔE_π, suggests that the situation in benzene might be close; the difference is calculated to be but 0.10 eV $\simeq$ 2.3 kcal/mol, and this might be reduced or reversed by the rather severe reaction conditions in most nitration experiments that would tend to preferentially stabilize NO_2^+ rather than ArH^+.

Using the geometries of Figure 5, we obtain the charge distributions for the π-complexes given in Figure 6 and Table VI. These results seem to indicate a considerable range of charge transfer from the aromatic to NO_2^+, from 0.05 electron to 0.22 electron. The trend in charge is as expected considering the ionization potentials of the aromatics.

Table VI. Net Electronic Populations of the NO_2 Moiety in the π-Complexes

	N	total NO_2
free ion	+0.957	+1.000
nitrobenzene–NO_2^+ π	+0.948	+0.955
benene–NO_2^+ π	+0.930	+0.924
toluene–NO_2^+ π	+0.891	+0.820
o-xylene–NO_2^+ π	+0.876	+0.783

Politzer et al.[8] have also estimated the stability of the π-complex of benzene and toluene and obtained a value of about 0.26 eV, a value twice as large as that which we report. Comparing this value with those of Table IV in the radical-pair formation suggests that benzene might nitrate through the π-complex but that toluene probably does not.

Technically, we are able to calculate π-complexes from restricted Hartree–Fock (RHF) calculations, in spite of the fact that the radical-pair system lies lower in energy, as this latter situation is related to the former by a single electron excitation from aromatic to NO_2^+. The RHF calculation is stable relative to this "de-excitation" through Brillouin's Theorem, a fact we later confirm through configuration interaction (CI) calculations in which all calculated states are upper bounds to the states they are supposed to represent.

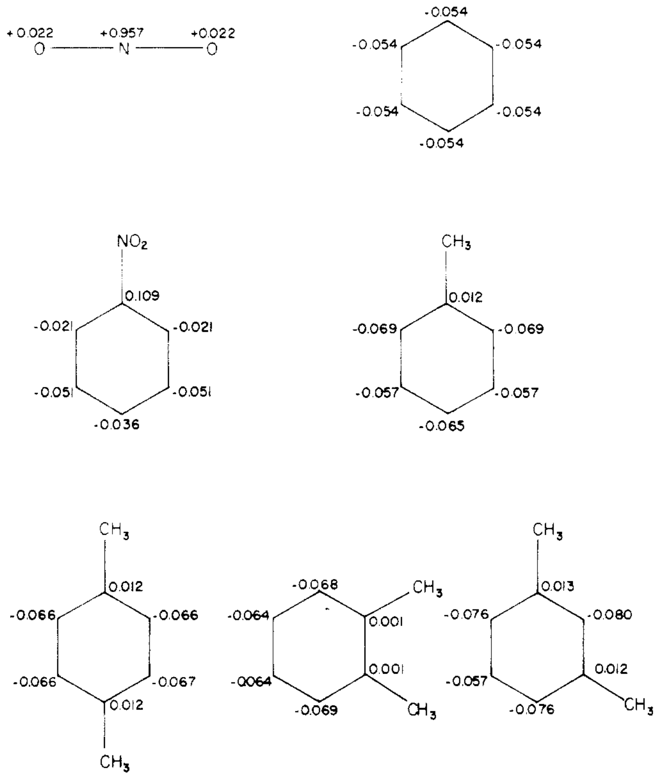


Figure 3. Calculated net populations of the closed shell systems of this study from a Mulliken population analysis using the deorthogonalized INDO wave function.

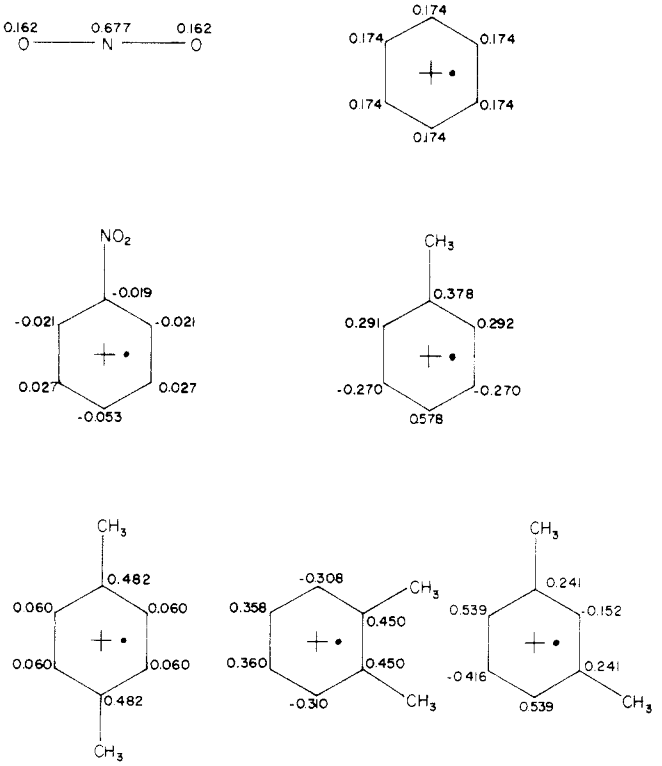


Figure 4. Calculated spin densities in the radical systems of this study, from a Mulliken population analysis.

C. σ-Complexes. The geometries we obtain for the σ-complexes are given in Figure 7. Guided by the spin density of the cation, as discussed later, and the experimental observations, we examine *p*-toluene-NO_2^+, and ipso attack on *o*-xylene. We examine the meta position of nitrobenzene, as this is the position suggested as most electron rich from the study of the π-complex.

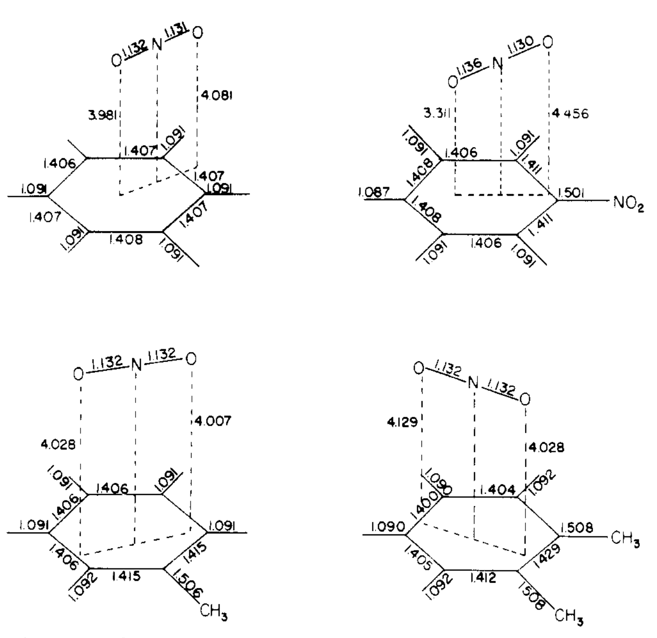


Figure 5. Calculated structures of the π-complexes. Distances are in angstroms.

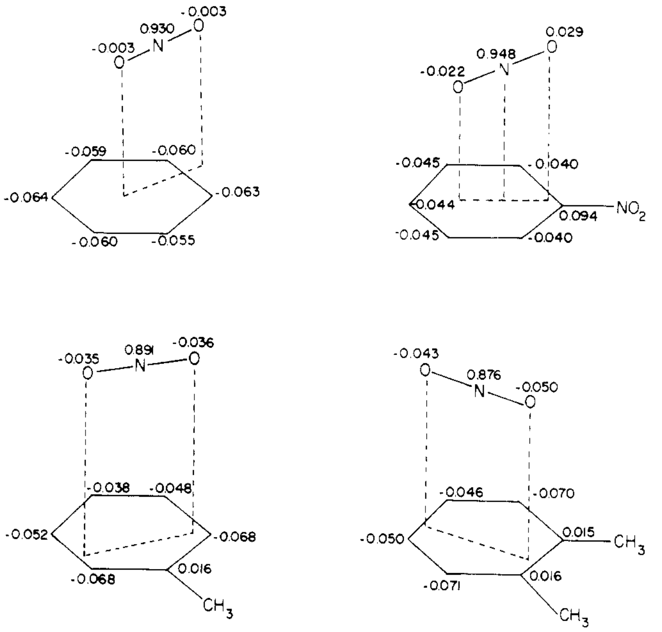


Figure 6. Net electronic populations calculated for the π-complexes.

Table VII. Stabilization Energy (eV) of the σ Complexes from MNDO Calculations

σ-complex	E_σ	ΔE_σ
benzene-NO_2^+	−1690.12	−0.69
toluene-NO_2^+	−1840.84	−0.79
o-xylene-NO_2^+	−2003.69	−1.17
nitrobenzene-NO_2^+	−2523.55	−0.66

The energies of the σ-complexes, E_σ, and the stability

$$\Delta E_\sigma = E_\sigma - E_s \qquad (6)$$

energy are given in Table VII. These structures have lower energy than the π-complexes or than the separated radical-cation pairs and represent the products or the final precursors to the products.

III. Discussion

In this work we have re-examined two possible mecha-

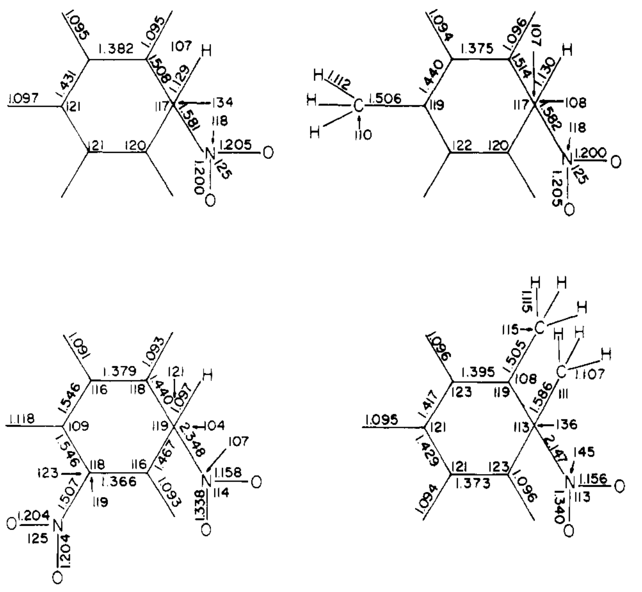
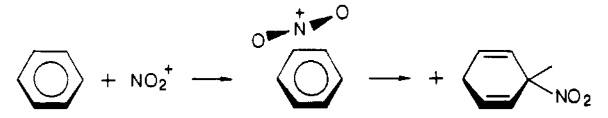
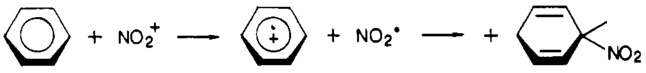


Figure 7. Calculated structures of the σ-complexes. Distances are in angstroms.

nisms for the nitration of aromatics: (i) electrophilic addition



and (ii) radical pair recombination



and have used for our examples benzene, toluene, the xylenes, and nitrobenzene. The initial formation of a radical pair is favored for all but nitrobenzene. This is suggested, at least in the gas phase, from the experimental ionization potentials of the aromatics and NO_2 and from the calculated ΔE_R values of Table IV. To further check this conclusion, CI calculations of the INDO/S type[9] were performed on benzene–NO_2^+, toluene–NO_2^+, and *p*-xylene–NO_2^+ supermolecules separated by 15 Å. De-excitations were observed from the reference closed shell case representing aromatic-π to NO_2^+–π^* charge transfer at about –0.23 eV, –0.65 eV, and –0.99 eV in the benzene, toluene, and *p*-xylene cases, respectively. For benzene this value is in remarkable agreement with the values obtained from the MNDO calculations of ionization potential differences, Table III, and ΔE_R, Table IV. The experimental difference of ionization potentials, 9.79–9.24 = 0.55 eV, is larger. The values we obtain from the CI calculations for the toluene and *p*-xylene cases are again larger than those obtained by the MNDO method, 0.46 eV and 0.59 eV, respectively, but are in better accord with those values suggested from experimental ionization potentials, 0.77 eV and 1.35 eV. Experiment, the MNDO calculations, and the INDO/S-CI calculations all favor electron transfer and radical-pair formation in benzene, toluene, and the xylenes. The π orbital of benzene and the π^* orbital of NO_2^+ involved in this electron transfer are shown in Figure 8. Electron transfer is not favored by these considerations in the nitrobenzene case. These calculations are summarized in Figure 9.

Although radical-pair formation may occur, it is still possible that a π-complex is formed of lower energy as the reaction proceeds. For nitrobenzene this π-complex is quite stable, Table V. For benzene the radical pair is predicted to be only about 2 kcal/mol more stable than the π-complex, suggesting that either may occur, and, if these calculations are accurate, different reaction conditions might force a different mechanism. The observations of Schmitt et al.[17], however, seem to indicate a radical-pair mechanism in the gas phase, as suggested here. This calculation clearly suggests that toluene and xylene use a radical-pair recombination mechanism. A π-like complex might also occur in this case between these *radicals*, but we have not examined this question here.

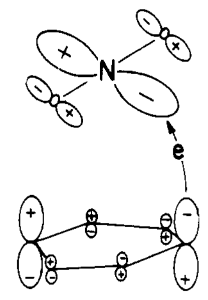


Figure 8. Orbitals of benzene and NO_2^+ involved in the one-electron transfer. At 15 Å, there are four degenerate transitions between the degenerate $e_g(\pi)$ of benzene and the degenerate π^* of NO_2^+.

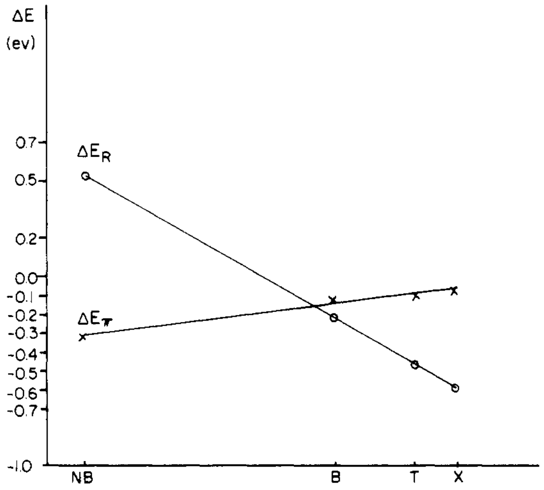


Figure 9. Energy of radical ion-pair formation, ΔE_R, and π-complex formation, ΔE_π, represented as a function of the aromatic. Values plotted are those obtained from the MNDO calculations. (NB = nitrobenzene, B = benzene, T = toluene, and X = *o*-xylene).

Although a continuum may exist between the classical electrophilic mechanism and the radical-pair recombination mechanism,[15] we have no evidence for this in our limited investigation of points along the reaction path. In the radical-pair reaction a single electron is transferred with resulting spin density appropriate for each species. On the classical surface, for example, at the geometry of the π-complex, charge is transferred from the aromatic to NO_2^+. As expected the amount of this charge is increased with decreased ionization potential of the aromatic (Figure 6), but the amount of charge is not greater than 0.25 electron for the cases we have examined, and no unpaired spin density can be developed on the reactants through the self-consistent field calculation alone. A subsequent configuration interaction calculation does not mix the classical closed shell description of the π-complex with any open shell single excitation, including that representing the singlet-coupled combination of the two doublet radicals. Direct coupling is not allowed, as a consequence of Brillouin's Theorem, but indirect coupling could, but does not, occur through the inclusion of higher excitations in

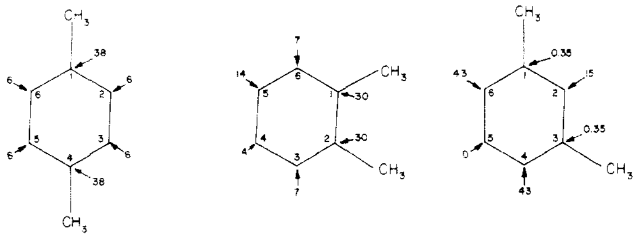


Figure 10. Product distribution, in percent of product, from the nitration of the xylenes. Distribution has been symmetrized: i.e., 75% of the product in *p*-xylene is ipso, etc.

the CI treatment. These two potential energy surfaces, the "classical" surface and the "radical pair" surface, may cross during the course of the reaction, and their intersection might by described as a mixture of both, but throughout most of the reaction we believe one or the other mechanism pertains.

The product distribution can also be used to confirm these conclusions. A radical-pair mechanism favors attack at positions where the greatest unpaired spin density is found. Classical electrophilic substitution favors attack on the most electron rich regions of the system.

In toluene, the observed product distribution is somewhat sensitive to experimental conditions, but ipso attack seems to account for less than 3% of the product.[24] Under ordinary reaction conditions 56% of the product is reported to be *o*-nitrotoluene and 40% *p*-nitrotoluene.[25] Considering the fact that there are two ortho positions and one para, this gives a clear preference for para attack, and, indeed, under special conditions, 95% of the product obtained is para.[26] Considering the net populations of Figure 3, and the spin densities of Figure 4, better agreement with these observations is, perhaps, obtained by invoking the radical-pair mechanism, in agreement with our conclusions based on energetics.

The product distribution for nitration of the xylenes is summarized in Figure 10.[9] Ipso attack is favored 6 to 1 in *p*-xylene, in accord with the spin densities of the aromatic cation, but not the net populations of the neutral. The order of product formation and spin density is again in agreement for the case of *o*-xylene nitration; the net electronic population is not.

Although both *p*-xylene and *o*-xylene cations have their greatest calculated spin densities in the ipso position, *m*-xylene does not. For *m*-xylene, again, nitration occurs principally at the atoms of greatest spin density,[9] Figure 4.

Nitrobenzene nitrates 90% on the meta position.[27] This product is suggested by the net population reported for nitrobenzene in Figure 3, but not with the calculated spin density of the cation of Figure 4 (most of this spin density is on the NO_2 group). This suggests the classical π-complex mechanism may be operative, as do the energetics previously discussed. In the π-complex of Figure 6 the positive nitrogen atom of NO_2^+ seems idealy situated to attack the most negative meta carbon atoms.

Since quantum mechanical calculations usually refer to gas-phase conditions, we have been careful to stress these conditions throughout this discussion. In order to estimate the effect of a solvent, however, we have performed exploratory calculations using a self-consistant reaction field technique within the INDO/CI methodology.[28,29] Assuming a solvent dielectric strength of 78.5 (as in water), the calculated ionization potential of NO_2 is reduced by more than that of either benzene or toluene.[30] The electron-transfer process from aromatic to NO_2^+ is made endothermic by 0.7 eV for both systems, a consequence of the fact that the NO_2^+ ion is preferentially stabilized in a dielectric media. Applying this correction to the *experimental* ionization potentials, however, leaves the benzene to NO_2^+ transfer endothermic by 0.5 eV, and that for toluene to NO_2^+ endothermic by only 0.2 eV. Reaction conditions are thus predicted to be quite important in selecting which mechanism is operative.

An estimate of the effect of a solvent of dielectric strength D (dimensionless) on the ionization potential, IP, of a species of charge q can be made via

$$\mathrm{IP}(D) = \mathrm{IP} + 7.2\,(1 - 1/D)(q^2/R - (q + 1)^2/R')\ [\mathrm{eV}]$$

where R and R' are the cavity radius (in angstroms) of the parent and ion, respectively. In general, $R \simeq R'$, and R (or R') can be estimated in a variety of ways.[28,29] This equation is the leading team in a multipole expansion and does not take into account charge assymmetries and the solvent reaction to such assymmetries. Nevertheless, it can be used with some reliability in estimating under what conditions one-electron charge transfer is likely if the gas-phase IP's of the reactant are known experimentally, or through calculations such as these.

This study suggests that the radical-pair recombination mechanism will be favored for nitration whenever the ionization potential of the aromatic is much less than that of NO_2. Substituents or reaction conditions that raise the ionization potential of the aromatic to a value higher than that of NO_2 prevent this radical-pair formation by preventing the one-electron transfer and force the classical electrophilic mechanism. These substituents are those usually associated with deactivation, and it is tempting to suggest that this deactivation is a consequence of forcing the slower π-complex, σ-complex mechanism.

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Registry No. NO_2^+, 14522-82-8; NO_2, 10102-44-0; nitrobenzene–NO_2^+ π complex, 104642-38-8; benzene–NO_2^+ π complex, 104642-39-9; toluene–NO_2^+ π complex, 104642-40-2; *o*-xylene–NO_2^+ π complex, 104642-41-3; benzene–NO_2^+ σ complex, 65963-62-4; toluene–NO_2^+ σ complex, 65963-65-7; *o*-xylene–NO_2^+ σ complex, 104642-42-4; nitrobenzene–NO_2^+ σ complex, 104642-43-5; benzene$^{\bullet+}$, 34504-50-2; nitrobenzene$^{\bullet+}$, 61116-96-9; toluene$^{\bullet+}$, 34504-47-7; *o*-xylene$^{\bullet+}$, 34510-20-8; *m*-xylene$^{\bullet+}$, 34510-21-9; *p*-xylene$^{\bullet+}$, 34510-22-0; benzene, 71-43-2; toluene, 108-88-3; xylene, 1330-20-7; nitrobenzene, 98-95-3; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3.

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