# Properties of Some Possible Intermediate Stages in the Nitration of Benzene and Toluene

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**Abstract:** Structures, atomic charges, and stabilization energies have been computed for some possible intermediate stages in the reactions of benzene and toluene with $NO_2^+$. Ab initio minimum basis SCF procedures were used (GAUSSIAN 70 and GAUSSIAN 80). When $NO_2^+$ was allowed to approach the aromatic molecule with both reactants restricted to their equilibrium ground-state geometries, a weakly bound complex was produced ($\Delta E_{stab} \approx -7$ kcal/mol) in which the positive ion is approximately parallel to the aromatic ring and roughly 2.8 Å above it, in a region of negative electrostatic potential. The interaction involving toluene is slightly the stronger of the two, probably reflecting activation of the ring by the methyl substituent. When $NO_2^+$ was permitted to interact with a specific ring carbon and the entire structure optimized, strongly bound $\sigma$ complexes were obtained, with $\Delta E_{stab}$ ranging from $-76$ kcal/mol for benzene–$NO_2^+$ to $-87$ kcal/mol for *p*-toluene–$NO_2^+$. These involve a partial loss of aromatic character since a quasi-tetrahedral carbon is formed, and the positive charge of the system is delocalized over the hydrogens (including those of the methyl group) and the ring carbons that are ortho and para to the site of nitration. An interesting observation is that the methyl group in these systems, including toluene itself, induces a polarization that leads to a more positive charge on the ring carbon to which it is attached. The $^{13}C$ NMR spectra of benzene and toluene are in agreement with this conclusion.

The mechanism of aromatic nitration continues to be a subject of active research and some controversy. Since the classic studies by Ingold and his collaborators,[1] it has been generally accepted that the nitrating agent is usually the nitronium ion, $NO_2^+$, and that the reaction involves an intermediate $\sigma$ complex, such as I in the case of benzene.[1-5] This complex can also be described in terms of the resonance structures II–IV.
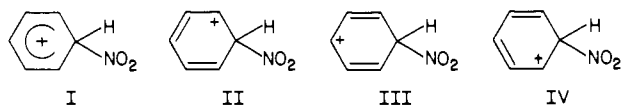


It is now believed that a distinct (although weak) interaction occurs even prior to the formation of the $\sigma$ complex. This initial weakly bound state, the existence of which was postulated in order to explain the observed kinetic data, has been described variously as an encounter pair[2,6,7] (which may or may not involve any significant attractive interaction), a $\pi$ complex,[3,7,8] a charge-transfer complex,[9,10] an outer complex,[8] and a radical ion pair.[11] As has been pointed out, the distinction between some of these descriptions is not a sharp one.[3]

In this paper, we report the results of a computational study of the interaction of the $NO_2^+$ ion with benzene and with toluene. Our aim has been to characterize and gain further insight into the intermediate stages through which these reactions may proceed.

The calculations were in two phases: First, $NO_2^+$ and the aromatic molecule were brought together with each kept in its equilibrium ground-state geometry but with their optimum relative orientations and separations being determined computationally. This was found to produce weakly bound complexes in which the ion is located well above the aromatic ring (Figure 1). Second, we allowed the $NO_2^+$ to interact specifically with one of the ring carbons, and we optimized the geometry of the entire system. Strongly bound complexes were then obtained, which correspond quite closely to I. The properties of both the weakly and the strongly bound systems will be discussed in detail.

## Methods

All geometries, energies, and other properties were computed by using the ab initio self-consistent-field GAUSSIAN 70 and GAUSSIAN 80 procedures.[12] Geometry optimizations were carried out with the STO-3G basis set, which has been shown to be effective for calculating geometries[13] (although we have encountered one difficulty, which is discussed below). A final STO-6G wave function was then computed for each system. All energies, atomic charges, and the electrostatic potential presented in this paper are at the STO-6G level.[14]

We have found that minimum basis sets significantly overestimate the N–O bond lengths in the $NO_2^+$ ion and in the $NO_2$ group. For the ion, for example, the predicted STO-3G and STO-6G values are 1.19 Å, whereas crystallographic determinations of this distance fall in the range between 1.05 and 1.15 Å.[15] However, optimization at the 5-31G level produced a N–O bond length of 1.11 Å, which is within the crystallographic range and also agrees well with the 1.12 Å obtained in a more sophisticated computation that included configuration interaction.[16] We had a similar experience with nitrocyclopropane, for which the optimum STO-6G N–O distance, 1.27 Å, is about 0.05 Å greater than the 5-31G and comparable experimental values.[17]

Since 5-31G optimization of the present benzene and toluene $\sigma$ complexes is not practical, we have set the N–O bond lengths in all these systems at 1.24 Å, a value that appears to be reasonable in light of the available experimental data.[18]

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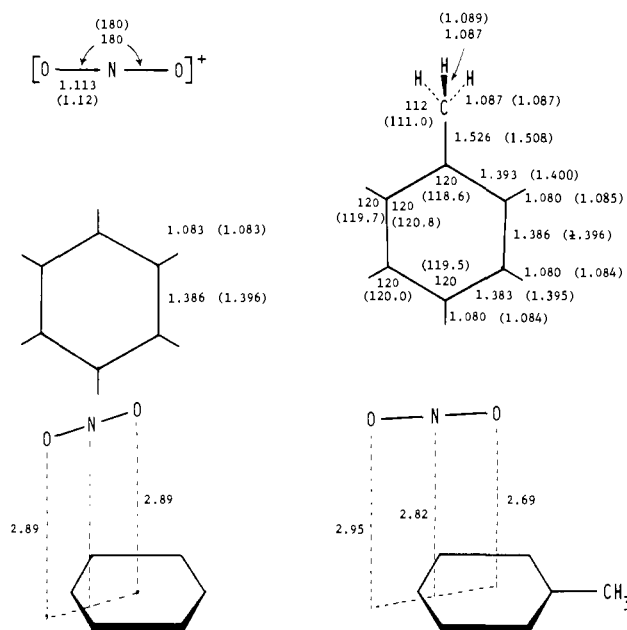
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**Figure 1.** Calculated structures, optimized at STO-3G level. Distances are in angstroms, angles in degrees. Top: $NO_2^+$, benzene, and toluene. Best available literature values are given in parentheses.[29] Bottom: Weakly bound benzene–$NO_2^+$ and toluene–$NO_2^+$ complexes. In the former, the $NO_2^+$ is in a symmetry plane perpendicular to the ring and bisecting two opposite C–C bonds.

## Results and Discussion

**A. Free Molecules.** We computed optimized structures for benzene, toluene, and $NO_2^+$ even though these can be found in the literature, in order to ensure consistency in subsequent comparisons and calculations of energy differences. Our structures, shown in Figure 1, are in good agreement with the best available in the literature.

The atomic charges in these systems, as determined by the population analysis procedure,[19] are given in Figure 2. A particularly interesting feature of these is that the methylated carbon in toluene is more positive, by 0.08 electron units, than in benzene, a conclusion supported by the fact that this carbon is deshielded, relative to benzene, in the $^{13}C$ NMR.[20] Its increased positive nature appears to be due in part to a movement of some of its electronic charge into the remainder of the aromatic ring, perhaps in response to the negatively charged carbon of the methyl group.[21]

**B. Weakly Bound Complexes.** An attractive (although weak) interaction, with a definite stabilization energy, was found to occur between $NO_2^+$ and both benzene and toluene even when they are all restricted to their ground-state geometries. This is consistent with the fact that both benzene and toluene have extensive regions of negative electrostatic potential above and below the aromatic ring, to which a positively charged species would be attracted. This electrostatic potential that is created in the space around a molecule by its nuclei and electrons is expressed rigorously by the formula

$$V(\bar{r}) = \sum_A \frac{Z_A}{|\bar{R}_A - \bar{r}|} - \int \frac{\rho(\bar{r}') \, d\bar{r}'}{|\bar{r}' - \bar{r}|} \qquad (1)$$

The first term on the right-hand side of eq 1 represents the contribution of the nuclei, which is positive; $Z_A$ is the charge on nucleus A, located at $\bar{R}_A$. The second term gives the potential due to the electrons, which is negative; $\rho(\bar{r})$ is the electronic density of the molecule at any point $\bar{r}$, which we obtain from the molecular



**Figure 2.** Calculated atomic charges, in electron units, for all the systems discussed in this paper. Left side, starting at top: $NO_2^+$, benzene, toluene, weakly bound benzene–$NO_2^+$, and weakly bound toluene–$NO_2^+$. Right side, starting at top: benzene–$NO_2^+$ $\sigma$ complex and toluene–$NO_2^+$ $\sigma$ complexes (ortho, meta, and para, respectively).



**Figure 3.** Electrostatic potential of toluene in the symmetry plane perpendicular to the plane of the ring, computed at STO-6G level. Solid contours correspond to positive potentials, dashed contours to negative potentials. Black circles indicate positions of most negative values (potential minima), –11.6 kcal/mol. Starting from the 0.0 contours (shown), the values corresponding to the positive charge are 3.1, 6.3, 12.5, 31.4, 50.2, 62.7, 314, 627, and 3136 kcal/mol. The negative contours are –3.1, –6.3, –7.5, –8.8, –10.0, and –11.3 kcal/mol.

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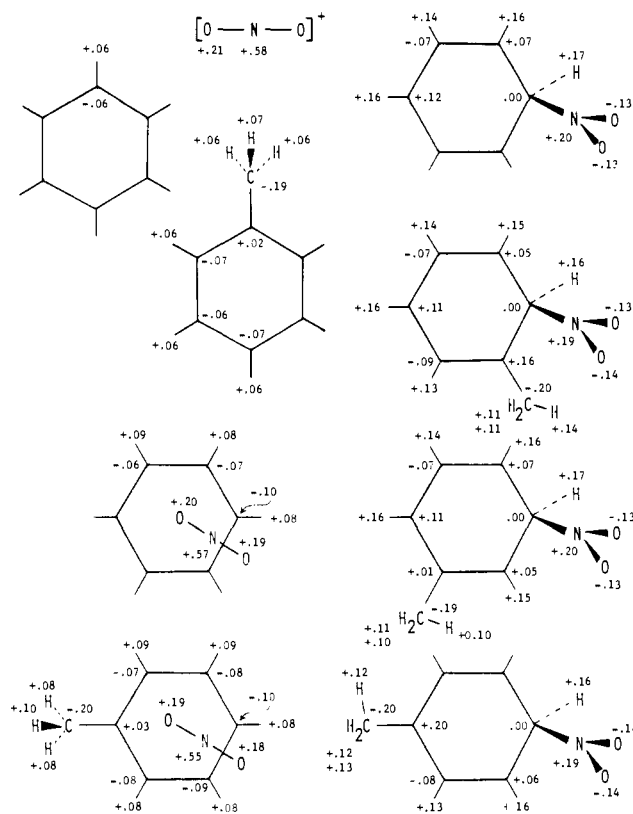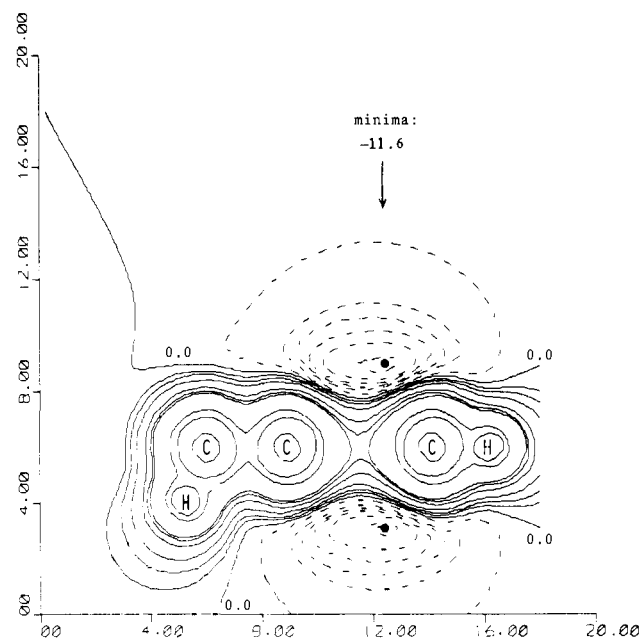
wave function. Thus, a region in which $V(\bar{r})$ is negative is one in which the effect of the electrons predominates and to which an electrophile, such as $NO_2^+$, would be attracted. In recent years,

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**Table I.** Calculated Energies

| system | total energy (STO-6G), hartrees | stabilization energy (STO-6G), kcal/mol |
|---|---|---|
| free molecules | | |
| benzene | −230.1311 | |
| toluene | −269.0909 | |
| $NO_2^+$ | −202.8540 | |
| weakly bound complexes | | |
| benzene–$NO_2^+$ | −432.9945 | −6.0 |
| toluene–$NO_2^+$ | −471.9568 | −7.5 |
| strongly bound complexes | | |
| benzene–$NO_2^+$ | −433.1061 | −76 |
| *o*-toluene–$NO_2^+$ | −472.0759 | −82 |
| *m*-toluene–$NO_2^+$ | −472.0705 | −79 |
| *p*-toluene–$NO_2^+$ | −472.0829 | −87 |

the electrostatic potential has been used with considerable success to interpret and predict molecular reactive behavior.[22-24]

The regions of negative potential above and below the aromatic ring of toluene are shown in Figure 3; those of benzene have been presented earlier.[25] In keeping with the well-established tendency of the methyl group to weakly activate an aromatic ring toward electrophilic attack,[4,26] $V(\vec{r})$ reaches a more negative value in the $\pi$ region of toluene, −11.6 kcal/mol, than it does for benzene, −10.6 kcal/mol.[25] This suggests that the weakly bound toluene–$NO_2^+$ complex may be slightly more stable than its benzene counterpart. This was indeed found to be the case, as will be seen below.

In arriving at our final structures for these weak complexes, we considered a variety of possible relative orientations and separations of the $NO_2^+$ ion and the aromatic molecules, including arrangements in which the axis of the (linear) $NO_2^+$ is perpendicular to the plane of the ring. The energetically optimum structures are shown in Figure 1. These interactions are not highly localized; we found energy barriers of less than 2 kcal/mol for lateral movement anywhere above the ring or vertical shifts of as much as 0.2 Å, and for small displacements the barriers are much less.

The stabilization energies of these complexes, defined as

$$\Delta E_{stab} = E_{complex} - (E_{aromatic\ molecule} + E_{NO_2^+}) \qquad (2)$$

are −6.0 kcal/mol for benzene–$NO_2^+$ and −7.5 kcal/mol for toluene–$NO_2^+$ (Table I). The slightly greater stability of the toluene complex confirms the expectation based on the somewhat more negative electrostatic potential of toluene above and below the ring.

A comparison of the calculated atomic charges for these weak complexes and for the free molecules (Figure 2) reveals some movement of electronic charge from the hydrogens, both of the aromatic ring and of the methyl group, to the carbons in the ring, especially those near the $NO_2^+$. There is a small transfer of electronic charge from the aromatic molecule to the $NO_2^+$: 0.04 electron from benzene and 0.08 from toluene.

**C. Strongly Bound Complexes.** For the strongly bound benzene–$NO_2^+$ and toluene–$NO_2^+$ systems, which it seems appropriate to call $\sigma$ complexes, we started by computing the completely optimized structures of protonated benzene and protonated toluene, including all three isomers of the latter. $H^+$ was then replaced by $NO_2^+$ in each case, and the structural parameters associated with the >$CHNO_2$ portion of the system were optimized (except for the N–O distances, as explained above). Our final structures for the benzene–$NO_2^+$ and the three isomeric tolu-

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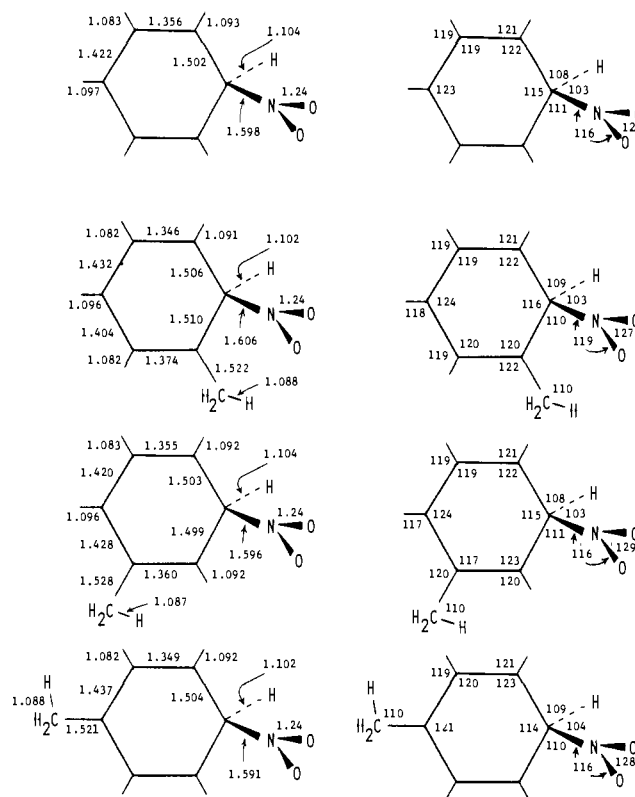


**Figure 4.** Calculated structures of $\sigma$ complexes, optimized at STO-3G level. Distances (left side of figure) are in angstroms; angles (right side) are in degrees. From top to bottom: benzene–$NO_2^+$ and *o*-, *m*-, and *p*-toluene–$NO_2^+$, respectively.

ene–$NO_2^+$ $\sigma$ complexes are shown in Figure 4.

In these strongly bound systems, the $NO_2$ group is localized at a single carbon atom and is no longer linear; the O–N–O angles are between 127° and 129°. The structures of these carbocations reflect the partial loss of aromatic character that accompanies the formation of a $\sigma$ complex, as seen in I. The $NO_2$-bearing carbons are quasi-tetrahedral, and their bond lengths to the adjoining carbons approach the average value for C–C single bonds, 1.54 Å.

The calculated structures and atomic charge distributions in these four $\sigma$ complexes show a remarkably consistent pattern. The benzene complex can be regarded as the prototype upon which the effect of the methyl groups in the other three systems is superposed. The C–C bond lengths given in Figure 4 show that it is invariably the bonds that are one removed from the tetrahedral carbon that approach most closely the typical value for a C=C double bond, 1.34 Å, regardless of the location of the methyl group. This suggests that resonance structures III and V–VII make the strongest contributions to these systems.
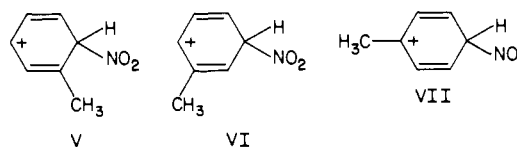


Looking first at benzene–$NO_2^+$, Figure 2 shows positive charges at the positions ortho and para to the tetrahedral carbon, as predicted by structures II–IV. The largest of these, +0.12, is on the para carbon, consistent with III being the major contributor. Essentially the same quantitative pattern of atomic charges is repeated in the three toluene–$NO_2^+$ $\sigma$ complexes, with the added feature that the methyl-bearing carbon in each case has acquired an additional positive charge of about 0.08, above its value in the benzene complex. This is exactly the same situation as was found above for free benzene and toluene.[20] This added positive charge, which can again be interpreted as a reaction to the significantly negative nature of the methyl carbon (approximately −0.20

electron units), may be somewhat surprising, since alkyl substituents are generally regarded as donating electronic charge to carbocations and thereby stabilizing them.[27-29] The results suggest instead that the stabilization may come about from the electrostatic interaction between the negative methyl carbon and the positive ring site. Based on our calculated charges, the magnitude of this effect should then be para > ortho ≫ meta.

The stabilization energies of these σ complexes, calculated with eq 2, are fully in accord with the prediction. (See Table I.) The least stable is the benzene complex, in which no ring activation or alkyl sustituent effect can occur, while the stabilities of the toluene system isomers increase in the expected order, meta < ortho < para. These findings are in complete agreement wht experimental observations of relative reactivities and orientational preferences.[2]

In these σ complexes, there is a very sizable transfer of charge from the aromatic molecule to the $NO_2$ group, amounting to 1.06–1.09 electron units (Figure 2). The original +1 charge of the latter is more than neutralized. (In contrast, for protonated benzene and toluene, we found only about 0.85 electron units to be transferred, and the tetrahedral carbons had negative charges of approximately −0.14, whereas they are 0.00 in Figure 2. This shows the strong electron-withdrawing effect of the $NO_2$ group.) Thus, the $NO_2$ is carrying out its well-known function of deactivating the aromatic system toward electrophilic attack.[4,26] Roughly half of this transferred electronic charge comes from the hydrogens, including those of the methyl groups in the toluene complexes. It is notable that the methyl carbon has virtually the same charge in all the systems shown in Figure 2.

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## Summary

Our intention in this work has not been to try to conclusively settle the controversial points related to the mechanism of aromatic nitration but rather to provide quantitative descriptions and a better understanding of some systems that may be involved in these processes. We have accordingly presented and discussed the structures, atomic charge redistributions, and stabilization energies associated with the formation of both weakly and strongly bound benzene-$NO_2^+$ and toluene-$NO_2^+$ complexes that are possible intermediate stages in the nitration of these aromatic molecules.

Certain interesting and consistent patterns can be seen in our results. One of these is the fact that the same type of resonance structure appears to be the dominant contributor to each of the four σ complexes that have been studied. Another is the picture that has emerged of the two functions performed by the methyl group in toluene and its complexes: First, it induces a rearrangement of charge within the aromatic ring whereby the carbon to which it is attached becomes more positive, by essentially the same increment in each case. The resulting electrostatic interaction,
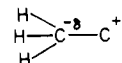


may be responsible for the various stabilization effects in the toluene-$NO_2^+$ σ complexes that result in the well-known ortho, para-directing properties of $CH_3$. Second, the methyl group, under the stimulus of the strong electron-attracting power of the $NO_2$, is a source of electronic charge, which comes from its hydrogens. This is observed in the weakly bound complex as well as the strongly bound ones.

# Factors Favoring an M···H—C Interaction in Metal–Methyl Complexes. An MO Analysis[†]

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**Abstract:** Electron-deficient alkyl complexes of transition metals sometimes exhibit striking structures in which the alkyl group is distorted in such a way that a C–H bond interacts with the metal atom, leading to an electron donation from the C–H bond to the metal and to a weakening of that bond. In particular, this is the case for the octahedral $d^0$ complex **4**. However, in the tetrahedral $d^0$ complex **7**, no significant distortion of the methyl group appears. Model octahedral and tetrahedral complexes, $H_5TiCH_3^{2-}$ and $H_3TiCH_3$, respectively, have been studied by extended Hückel calculations in order to understand the reasons for the different structures of **4** and **7**. It is shown that a distortion of the methyl group is likely to occur only if a strong interaction between the $\sigma_{Ti-C}$ orbital and a low-lying d orbital of proper symmetry develops upon distortion. In both octahedral and tetrahedral complexes such an interaction exists, but it is much larger in the former. The stability of the distorted structure originates more from an electronic reorganization of the M–C bond than from a direct C–H electron donation into the metal. Substituent effects have also been analyzed: π donors disfavor distortion in the plane in which they are lying, while π acceptors have the opposite effect; a ligand trans to the metal–methyl bond favors distortion. Finally, the role of electron number in the complexes and that of the ligand field around the metal were discussed, and comparison with experimental data was made when available.

Current interests in aliphatic C–H bond activation by transition metal arise from the need for homogeneous catalytic systems capable of selectively functionalizing aliphatic hydrocarbons.

Although C–H bonds of a hydrocarbon are considered as chemically inert, numerous reactions involve the insertion of a transition metal into a C–H bond. Intramolecular reactions such as α and β eliminations commonly occur and are responsible for the instability of many alkyl–metal complexes.[1] Examples of insertion