

The Polar Mechanism for the Nitration of Benzene with Nitronium Ion: Ab Initio Structures of Intermediates and Transition States

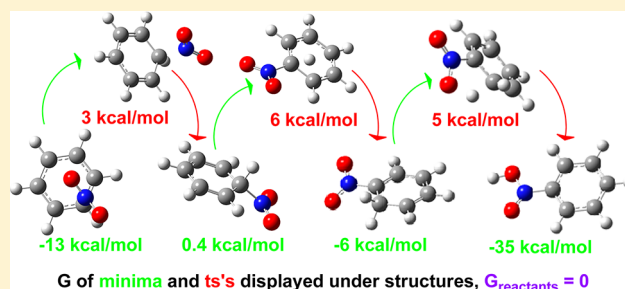
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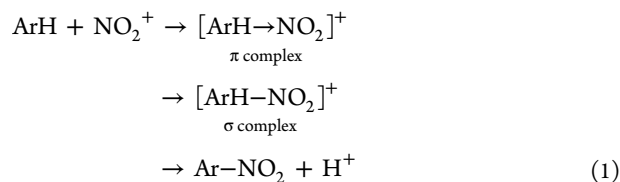
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S Supporting Information

ABSTRACT: The nitration of benzene by nitronium ion in the gas phase has been re-examined. New features have been revealed; in particular, three transition states have been detected along the reaction coordinate. These have been shown by IRC analysis to connect an initially formed π complex (pi1) to a σ complex (sig1) (via ts1), sig1 to sig2 (via ts2), and finally sig2 to the product (via ts3). Sig2 also connects to another isomeric σ complex sig3 (via sig23ts), which connects to sig4 (via sig34ts).



The long-held formulation of electrophilic nitration of benzene and other arenes (ArH) by nitronium ions can be described in terms of the successive formation of a π complex from the reactants and its direct transformation into a covalently bound σ complex, followed by proton transfer to yield the substitution product (the so-called polar mechanism; eq 1).¹ On the basis of experimental spectroscopic and kinetic studies, with computational support, the polar mechanism has been challenged in recent years by a mechanism in which electron transfer (ET) between the aromatic and the electrophile takes place.^{2–4} Originally envisaged as an outer-sphere electron transfer,⁵ this ET is now thought to occur within the initially formed π complex, giving an $\text{ArH}^{\bullet+}/\bullet\text{NO}_2$ pair, collapse of which affords the σ complex. Such a reaction pathway is to be expected particularly in the case of aromatic compounds of low ionization potential⁶ and in the gas phase.



Ab initio configuration interaction computations of the nitration of benzene and toluene led to a development of the ET mechanism in which an initially formed ground-state charge-transfer complex is transformed into an excited singlet state by passage through a conical intersection of the ground- and excited-state potential energy surfaces (PESs).⁷ The excited singlet represents a contact radical cation/radical pair $\text{PhH}^{\bullet+}/\bullet\text{NO}_2$ that relaxes and can collapse to the σ complex or dissociate. The role of excited-state structures, formed by crossover between the ground and excited PESs, in electrophilic aromatic substitution reactions has recently been further

refined;⁸ it is suggested, however, that nitration of benzene takes place entirely on the ground-state PES, with an avoided crossing to the excited state. A related reaction, bromination of arenes by Br_2 (an overall electrically neutral system) has been shown computationally to take place by competitive addition and substitution mechanisms not involving the traditional σ complexes.⁹

Despite the enormous effort put into the study of the reaction, there remain some doubts about the relative importance of the polar and single-ET mechanisms of aromatic nitration, in particular the roles of the intermediates involved and the part they play in mediating the electron transfer, whether outer-sphere or inner-sphere. What further attracted our attention to the nitration reaction is the possibility that other reactions that pass through non-covalently bonded complexes might also involve ET steps. Work over the past 15 years by one of us¹⁰ suggests that many bimolecular reactions take place by a mechanism involving kinetically significant reactant complexes. These observations might even suggest the generalization that bimolecular reactions take place by ET mechanisms, a point of view held by many in the 1970s.¹¹ If correct, the latter would require a change in paradigm in the understanding of organic reaction mechanisms.

We now show, on the basis of high level computations, that nitration of benzene by nitronium ion in the gas phase follows a polar route rather than the ET pathway from reactants to the intermediate σ complex and thence to the final product (see eq 2). Collapse of the $\text{ArH}^{\bullet+}/\bullet\text{NO}_2$ pair results in a σ complex with C–O rather than C–N bonding.



Received: August 13, 2013

Published: August 23, 2013

Our initial computations were carried out using the Gaussian 09 package at the MP2/6-311++G(d,p) level in the gas phase.¹² This was followed by single-point calculations at higher levels ranging from CCSD(T) to MP4SDTQ. All of the calculations employed the 6-311++G(d,p) basis set, and energies (E) are expressed in kcal/mol relative to sig1.¹³ The reaction coordinate diagram for the polar mechanism is illustrated in Figure 1.

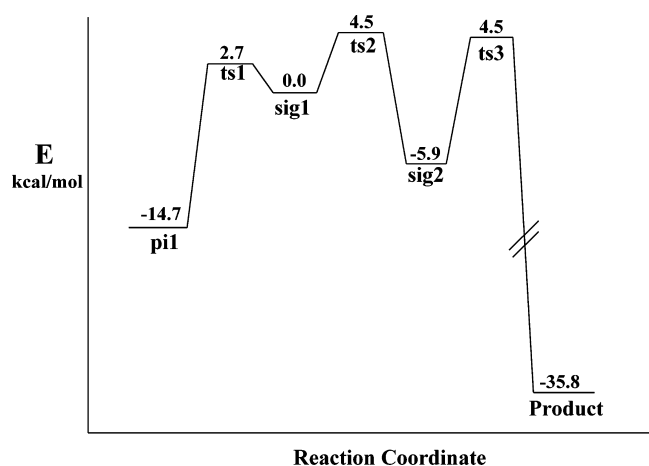


Figure 1. Reaction coordinate for the polar mechanism of nitration of benzene by nitronium ion in the gas phase. The // on the line leading from ts3 to Product indicates a break in the E scale. Computations were performed at the MP2/6-311++G(d,p) level.

Our computations revealed a number of intermediates and transition states¹⁴ for the benzene/nitronium ion reactions that have not been reported in previous studies.^{2–4} The formulation of the ET mechanism by Kochi² applies to the formation of a σ complex (sig1) via a π complex (pi1). The initial product of nitration in the gas phase is nitrobenzene protonated on an oxygen atom (this is the product shown by computation). Not knowing how the latter is formed from sig1 makes the reported mechanism incomplete. Structures involved in nitration are gathered in Scheme 1.

The identification of three transition states suggests the sequence of reactions shown in Figure 1. The sequence can be

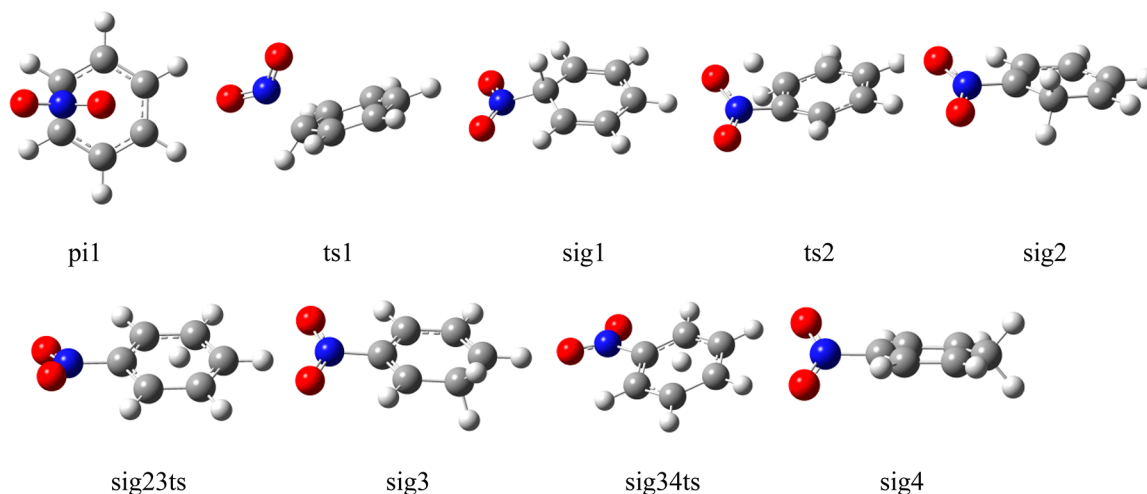
verified by an intrinsic reaction coordinate (IRC) analysis that begins at a transition-state saddle point and proceeds downward in both directions.¹⁵ A successful analysis results in connecting the reaction pathway from one minimum through a transition state to another minimum on the PES and applies to all transition states believed to be included in the mechanism.

The results of IRC analyses beginning with ts1, ts2, and ts3 are illustrated in Figure 2. The structures of the labeled points were optimized at the MP2/6-311++G(d,p) level, completing the formal verification of the reaction coordinate diagram shown in Figure 1.

Two isomers that do not take part directly in the nitration reaction (sig3 and sig4) approach equilibrium with sig2, as shown in Scheme 2. The E values of the σ complexes are 0.0 (sig1), -6.3 (sig2), -4.3 (sig3) and -6.2 (sig4) kcal/mol. The latter indicates that sig1, reported earlier,¹ is present in somewhat lower concentration than the other three σ complexes. The order of the E values (MP2) of the σ complexes is not what we expected, since on conventional formulations of electrophilic substitutions sig3 should be the most stable. The results of higher-level CCSD(T) and MP4SDTQ calculations, shown in Table S1 in the Supporting Information (SI), verify that the differences between the E values of the σ complexes are small and that those from sig2, sig3, and sig4 are most likely within the error limits of the methods. Our MP2 computations show that sig1 is considerably less stable than pi1 (-15 kcal/mol), contrary to CCSD(T) E values reported earlier.² However, a similar discrepancy between CCSD(T) and MP2 values was reported in ref 2 (see the SI for that paper).

The highest-level methods used to obtain E values in Table S1 are CCSD(T) and MP4SDTQ. In fact, CCSD(T), when fully optimized with a larger basis set, has recently been described as the “gold standard” of quantum chemistry methods.¹⁶ This description, when used for single-point calculations on the geometry optimized at a lower level, is not generally accepted by computational chemists since another viewpoint is that no one method is best for all systems. It can be seen that the CCSD(T) results, as expected from the earlier report,¹ show that sig1 is more stable than pi1. However, the MP4SDTQ results in Table S1 regarding the relative pi1 and

Scheme 1. Structures of Intermediates and Transition States during the Polar Reaction of Benzene with Nitronium Ion in the Gas Phase



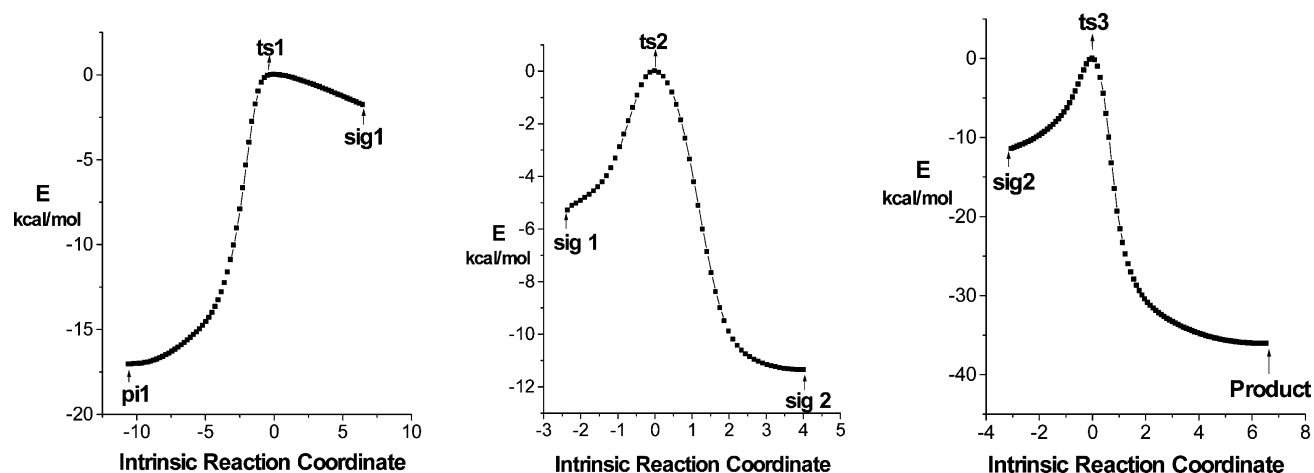
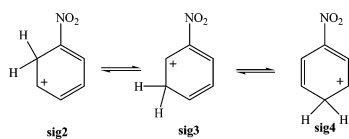


Figure 2. Intrinsic reaction coordinates for the conversions of pi1 to sig1, sig1 to sig2, and sig2 to the product in the reaction of benzene with nitronium ion in the gas phase. Analysis began at the transition state in each case.

Scheme 2. Equilibria Corresponding to 1,2-Hydrogen Migrations of Nitro-Substituted Hexadienyl Cations



sig1 *E* values are nearly identical to the relative MP2 values. An observation supporting the contention that the MP2 values for these relative energies may be more reliable is evident from the *E* differences between the higher-level methods and MP2 can be found in Table 1. For all structures, with the exception of the

Table 1. CCSD(T) and MP4SDTQ Energies Relative to Those Obtained from MP2/6-311++G(d,p)

structure	ΔE (kcal/mol)		
	CCSD(T)	MP2	MP4SDTQ
pi1	-45.1	0.00	-69.0
sig1	-60.8	0.00	-71.1
sig2	-59.3	0.00	-70.3
sig3	-61.6	0.00	-71.2
sig4	-59.0	0.00	-70.4
ts1	-61.7	0.00	-72.3
ts2	-56.3	0.00	-68.3
ts3	-56.2	0.00	-68.3
sig12ts	-56.3	0.00	-68.3
sig23ts	-57.1	0.00	-68.0
sig34ts	-56.7	0.00	-19.4

final entry, the difference in *E* between that computed by MP4SDTQ and by MP2 fell in the range from -68 to -72 kcal/mol. The same comparison for CCSD(T) and MP2 results, where the relative *E* values, with the exception of the entry for pi1, fell in the range from -56 to -62 kcal/mol. These comparisons suggest that the CCSD(T) values for pi1 as well as the MP4SDTQ value for sig34ts may be suspect. Although these observations cannot be considered to be strong evidence for the greater stability of pi1 relative to sig1, they do suggest that there is no valid reason for choosing the CCSD(T) result over that of MP4SDTQ. In any event, since the most important aspect of our work is the polar mechanism for the

nitration of benzene by nitronium ion, the absolute difference in *E* values has little bearing on our conclusions.

The IRC procedure¹⁵ illustrated in Figure 2 verifies the sequence shown in the equilibria (Scheme 2) through transition states sig23ts and sig34ts. The latter were optimized before use as the anchor points on the reaction pathway between sig2 and sig4.

The computations by Peluso and Del Re⁷ on the reactions of benzene and toluene with nitronium ion in the gas phase revealed the existence of a conical intersection between the ground state and the first excited charge-transfer singlet, leading to electron transfer from the aromatic substrate to the nitronium ion to generate the radical cation/radical pair. They proposed that the barrier to ET is no more than 13 kcal/mol. Xu, Zilberg, and Haas⁸ more recently proposed that a barrierless conical intersection between the ground-state benzene/ NO_2^+ complex and the radical cation/radical pair may be involved in the reaction of benzene with nitronium ion. We have no argument to counter this proposition, but we believe that it refers to a competing pathway. The $\text{PhH}^{\bullet+}/\bullet\text{NO}_2$ pair gives rise to an oxygenated product rather than to nitration (see the next paragraph).

Esteves⁴ rationalized mass spectrometric data in terms of a $\text{PhH}^{\bullet+}/\bullet\text{NO}_2$ pair generated from the reaction of benzene with nitronium ion that could partition between C–N and C–O products. Since the C–O distance in the $\text{PhH}^{\bullet+}/\bullet\text{NO}_2$ pair is considerably shorter than the C–N distance, it is not clear that the partition between products is expected. In fact, our attempts to identify this pathway for the C–N-bonded product failed. The polar mechanism proposed here appears to be a likely alternative for the nitration reaction, i.e., formation of the C–N product. There appears to be no question that the C–O product is derived from the ET pathway.

In summary, the nitration of benzene by nitronium ion in the gas phase was revisited computationally and found to be completely consistent with a polar mechanism. Three transition states that were not observed in previous studies^{2–4} were found on the reaction coordinate. We failed to find nitration products derived from the $\text{PhH}^{\bullet+}/\bullet\text{NO}_2$ pair in attempts to obtain evidence for the ET mechanism. IRC analyses resulted in direct connections of pi1 with sig1, of sig1 with sig2, and of sig2 with product by way of ts1, ts2, and ts3, respectively. These connections provide unequivocal evidence of the feasibility of

the polar mechanism. We have no evidence that the formation of the $\text{PhH}^{\bullet+}/\bullet\text{NO}_2$ pair results in nitration of benzene.

■ ASSOCIATED CONTENT

■ Supporting Information

Structures, energies, and coordinates of all compounds and complexes discussed in this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the National Science Foundation under Grant CHE-090317ARR is gratefully acknowledged. Unfettered computer access (V.D.P.) from the Center for High Performance Computing at Utah State University is greatly appreciated.

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(14) The reason that the transition states and other intermediates found here were not previously observed is most likely because they were not looked for. Computations can only be carried out on structures that are provided as “best guesses”. Single-point MP2/6-311++G(d,p) computations at the geometry of pi1 indicate that the singlet–triplet gap is equal to about 58 kcal/mol.

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