

An Experimentally Established Key Intermediate in Benzene Nitration with Mixed Acid

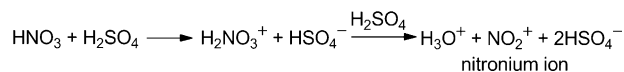
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In memory of Paul von Rague Schleyer

Abstract: Experimental evidence is reported for the first intermediate in the classic S_EAr reaction of benzene nitration with mixed acid. The UV/Vis spectroscopic investigation of the reaction showed an intense absorption at 320 nm (appearing as a band shoulder) arising from a reaction intermediate. Our theoretical modeling shows that the interaction between the two principal reactants with solvent (H_2SO_4) molecules significantly affects the structure of the initial complex. In this complex, a larger distance between the aromatic ring and nitronium ion precludes the possibility for electronic charge transfer from the benzene π -system to the electrophile. The computational modeling of the potential energy surface reveals that the reaction favors a stepwise mechanism with intermediate formation of π - and σ - (arenium ion) complexes.

The electrophilic aromatic nitration reaction and its mechanism under various conditions have been investigated extensively, both experimentally and theoretically, for decades.^[1–31] The nitration of aromatic compounds is an essential route to numerous important nitro products and process intermediates. Many nitration reagents are effective, but nitric and sulfuric acid mixtures (“mixed acid”), dilute aqueous nitric acid, nitric acid in polar organic solvents, and stable nitronium salts in polar organic solvents, have been employed most commonly to nitrate aromatic compounds.^[1–31] Sulfuric acid acts as a catalyst in mixed acid conditions. Euler’s 1903 suggestion^[8] that NO_2^+ was the nitrating agent was established by the subsequent kinetic and spectroscopic studies of the mechanism of aromatic nitration by Bennett, Brand, and Williams,^[9] by Westheimer and Kharasch,^[10] as well as by Ingold and Hughes.^[11,12]

Nitration of benzene by mixtures of nitric acid and sulfuric acid is typically conducted at 50 °C.^[1–7] Nitronium cation formation is depicted in Scheme 1.



Scheme 1. Representation of nitronium ion formation in mixed acid solution.

According to the classic Ingold–Hughes nitration mechanism,^[1–7,11,12] the first stage of benzene nitration (commonly described as rate-controlling) involves attack of NO_2^+ , resulting in the formation of a σ -complex (arenium ion or Pfeiffer–Witzinger–Wheland intermediate).^[13–15] The reaction then gives nitrobenzene by removal of the *ipso* proton from $ArHNO_2^+$ by either the sulfuric acid or the bisulfate anion, HSO_4^- , which both act as a base. A single electron transfer (SET) mechanism, widely considered as an alternative reaction path, involves the transfer of an electron from the aromatic ring to the nitronium ion; recombination of the resulting radical pair produces the same Wheland intermediate ($ArHNO_2^+$).^[18–23] Early model gas-phase computations by Peluso and Del Re^[21] on the interaction of benzene and NO_2^+ established the possibility of a conical intersection between the ground and the first excited singlet state, accompanied by charge-transfer, thereby supporting the SET mechanism for the reaction. In 2010, Xu, Zilberg, and Haas^[23] employed CASSCF computations with the cc-pVDZ basic set to investigate the interactions of benzene with several positively charged electrophiles, including NO_2^+ . The results suggested that benzene and the charged electrophile are in an electronically excited state in the gas phase initially, whereas the rate-controlling step lies on the ground state potential energy surface. The transition from excited to ground state is achieved by a conical intersection. These studies^[21–23] only considered the interactions between isolated reactants in the gas phase. Indeed, other theoretical investigations of the mechanism of nitration with nitronium cation NO_2^+ rarely have involved the specific role of the medium.^[28,31] Rosokha and Kochi^[29] conducted a theoretical investigation of charge-transfer complexes of various aromatic donors with typical electron acceptors, such as Br_2 , NO^+ , and NO_2^+ , as precursors to electrophilic aromatic substitutions. The charge-transfer mechanism calculated by Kochi^[30] for the electrophilic aromatic nitration at the coupled-cluster CCSD(T)/6-31G** level found that the bimolecular interaction of aromatic compounds with NO_2^+ leads to π -complexes by concurrent electron transfer. Such π -complexes transform rapidly into the σ -complex. The theoretical investigation of the mechanism of electrophilic aromatic substitution by Esteves^[31] suggested that the nitration reaction involves three intermediates. An electron donor–acceptor complex (an un-oriented π -complex) forms first through a charge-transfer

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interaction between the NO_2^+ ion and the π -aromatic system. The second intermediate, a SET complex (an oriented π -complex), a radical cation-molecule pair, $\text{C}_6\text{H}_6^{+\bullet}/\text{NO}_2$, indicates that a single-electron transfer from the aromatic π -system to NO_2^+ has occurred. A σ -complex is the final intermediate.

Herein, we report clear experimental evidence for the formation of a π -complex intermediate between benzene and nitronium ion in mixed acid solution. In contrast to previous assumptions, both experimental data and theoretical computations show that a single electron transfer does not take place at the stage of π -complex formation in mixed acid medium.

The computations used the Gaussian09^[32] and MOLPRO^[33,34] programs. The DFT M06-2X^[35] functional was combined with the 6-311 + G(2d,2p) and 6-311++G(2df,2p) basis sets.^[36] Equation-of-motion (EOM) CCSD/aug-cc-pVDZ computations^[37] were performed for the DFT-optimized structures of the π -complexes between the reactants in the gas phase. Computed harmonic vibrational frequencies of all optimized structures verified that they were either minima or transition states. Intrinsic reaction coordinate (IRC) computations validated the connections between reactants, transition states (first-order saddle points), and products.^[38] The conductor-like polarizable continuum model (CPCM)^[39,40] was used to simulate bulk solvent effects theoretically. The geometries and energies of all optimized compounds can be found in the Supporting Information (Tables S1–S8).

We also conducted natural bond orbital (NBO)^[41,42] and Hirshfeld^[43] analyses for the charge shifts during the formation of the intermediate π -complex. The single electron transfer (SET) $\text{S}_\text{E}\text{Ar}$ reaction mechanism^[18,19] is based on the assumption that considerable electron donation from the aromatic species to the attacking electrophile takes place during π -complex formation.

UV/Vis spectroscopic experiments were conducted to verify the possible intermediate formation of a π -complex during benzene nitration by mixed acid (mixture of nitric acid and sulfuric acid).

We considered the complex nature of the reaction media when modeling the nitration with mixed acid. HNO_3 acts as a Brønsted base in equilibrium with sulfuric acid (Scheme 1); both the bisulfate ion (HSO_4^-), NO_2^+ , and the H_2SO_4 solvent may participate as reacting species. In the presence of the strong electrophile NO_2^+ , the nitric acid cannot be an electrophilic reactant. Both the sulfuric acid and the bisulfate anion can act as proton-removing agents. However, the H_2SO_4 solvent is much more abundant than the HSO_4^- ion. Thus the entropy barrier is expected to be much higher for the process involving HSO_4^- . Therefore, a fuller description of the reaction mechanism needs to account for the effects of H_2SO_4 on the course of the reaction, both as a medium and as a reactant. As mentioned, solvent effects were modeled by the CPCM approach. Furthermore, the influence of an explicit solvent molecule on the reaction route was considered. The energies of saddle-point structures along the reaction pathway as obtained from M06-2X computations are presented in Table 1. The IRC procedure beginning from TS1 clearly leads to a σ -complex intermediate.

Table 1: Relative energies ($\Delta E = E + \text{ZPE}$)^[a] of the critical structures along the reaction paths for the nitration of benzene by mixed acid by a stepwise mechanism in simulated highly polar solvent ($\epsilon = 109$) at M06-2X.

Species	6-311+G(2d,2p)	6-311++G(2df,2p)
π -complex	−5.0	−5.3
TS1	−2.1	−1.2
σ -complex	−17.2	−14.6
TS2	−17.9	−15.5
product-complex	−47.0	−45.2

[a] Energies (in kcal mol^{-1}) are relative to benzene, and $\text{NO}_2^+\text{H}_2\text{SO}_4$.

Figure 1a shows the optimized structures of the π -complex, σ -complex, and transition states, as well as their important bond lengths and bond angles. The energies (ΔE) of benzene nitration in simulated highly polar ($\epsilon = 109$) media, and the results of the IRC computations on the transition states are compared in Table 1. Formamide was chosen as a model solvent because its dielectric constant ($\epsilon = 108.94$) is close to that of sulfuric acid ($\epsilon \approx 100$), the usual medium for nitration with mixed acid.

We also conducted analogous computations employing dimethylsulfoxide as a model solvent, which is structurally more similar to sulfuric acid though less polar ($\epsilon = 46.8$; Supporting Information, Table S9). The obtained energies of the critical structure along the potential energy surface are quite analogous to those with formamide as the model solvent (Table 1).

The ΔE values (Table 1) indicate low barriers, consistent with the mild experimental reaction conditions. Comprehensive IRC computations reveal a smooth transition from the TS1 to the σ -complex (Figure 2). Employing the larger 6-311++G(2df,2p) basis set with the M06-2X functional led to analogous results for the reaction mechanism (Table 1), and confirmed the stepwise character of the process. The computed energy of the σ -complex is slightly higher than the energy of TS2. The optimization procedure applied followed the changes in electronic energy. The purely electronic energy of the σ -complex intermediate is lower than the TS2 energy (see the Supporting Information, Tables S1–S4). The vibrational corrections applied result in a reversed ratio of total energies. The very small energy difference between the two structures shows that the existence of the intermediate is only fleeting. To further verify these results, we conducted MP2 computations^[44] combined with the 6-311 + G(d,p) basis set for the σ -complex and TS2. The data obtained showed that the total energy of the σ -complex is $1.1 \text{ kcal mol}^{-1}$ higher than the TS2 energy (Supporting Information, Table S10). Application of the B3LYP-D3 method^[45,46] with the 6-311 + G(2d,2p) basis set in evaluating the energies of the PES critical structures also confirmed the results from the computations employing the M06-2X functional (Supporting Information, Table S11).

An intriguing problem associated with aromatic nitration is the possibility of charge transfers accompanying the formation of critical structures along the reaction pathway. A number of theoretical studies^[29–31] have reported that a considerable transfer of electronic charge from the aromatic ring to the nitronium unit takes place at the stage of π -

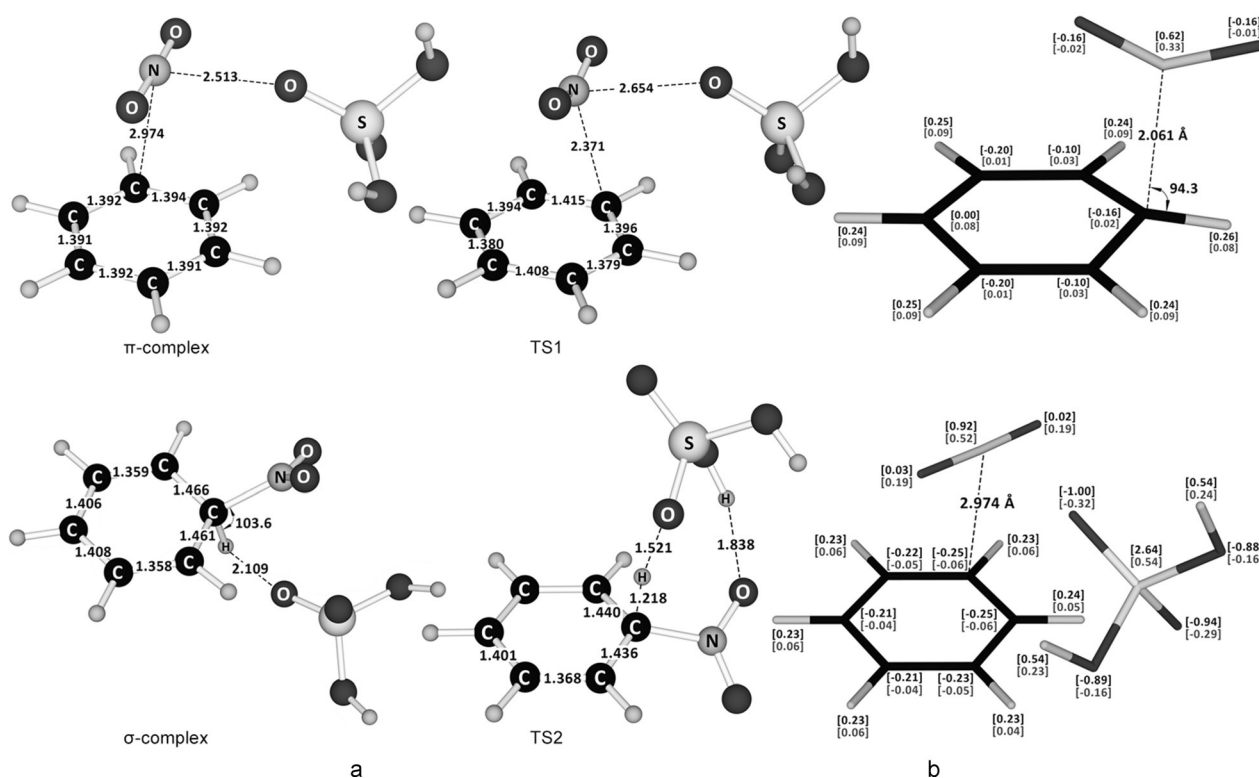


Figure 1. a) Fully optimized structures along the reaction path for nitration of benzene with NO_2^+ in the presence of H_2SO_4 by a stepwise mechanism in simulated highly polar solvent ($\epsilon = 109$) at M06-2X/6-311 + G(2d,2p). b) NBO (top, black) and Hirshfeld (bottom, gray) charges in the π -complex formed in benzene nitration with NO_2^+ in isolation (gas phase) at B3LYP/6-311 + (2d,2p) (top figure); and in benzene nitration with NO_2^+ associated with one explicit H_2SO_4 molecule (bottom figure) by a stepwise mechanism in simulated highly polar solvent ($\epsilon = 109$) at M06-2X/6-311 + (2d,2p).

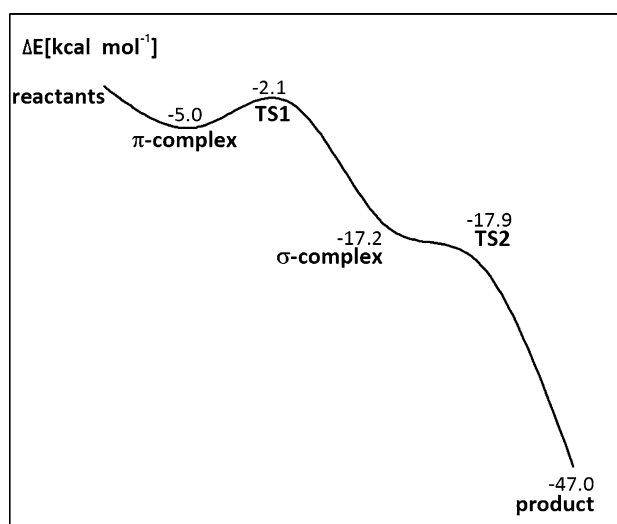


Figure 2. Representation of the potential energy surfaces for benzene nitration with NO_2^+ in the presence of H_2SO_4 by a stepwise mechanism in simulated highly polar solvent ($\epsilon = 109$) at M06-2X/6-311 + G(2d,2p).

complex formation. The SET mechanism of nitration is a well-established concept.^[18–23] We estimated the electron transfer from the aromatic π -system to the nitronium unit by applying two alternative population analysis methods. Figure 1b compares computed atomic charges for the π -complex

intermediates in isolation (gas phase), computed at B3LYP/6-311 + G(2d,2p) and within the stepwise route in mixed acid conditions. Both the NBO method^[41,42] and Hirshfeld population analysis^[43] predict a roughly 0.70 e charge transfer from the aromatic ring to the NO_2^+ ion for the complex in isolation. However, when analyzing the mechanism of the reaction in mixed acid, considering both bulk solvent effect and the explicit association of the electrophile with H_2SO_4 , M06-2X computations do not reveal any appreciable charge transfer between the reactants owing to π -complex formation (Figure 1b). Moreover, the π -complex structures resulting from these computations are quite different from that of the complex in gas phase. The nearly 3 Å distance (Figure 1b) between the *ipso* ring carbon and the nitronium unit hampers any significant charge transfer. The association between NO_2^+ and H_2SO_4 largely precludes the competitive interaction of the nitronium ion with the benzene π -system, resulting in a larger distance between the nitronium nitrogen atom and the *ipso* carbon atom, compared to the complex in isolation (2.061 Å, Figure 1b). Therefore, the present computations do not support the idea that a SET mechanism operates in the nitration of benzene by mixed acid.

To verify our theoretical findings, we conducted UV/Vis spectroscopic studies of the nitration of benzene in mixed acid. The most characteristic spectroscopic feature for complex formation is the appearance of new bands in the UV/Vis spectrum.^[47,48] A literature survey revealed that no UV/Vis spectroscopic data exist for π -complex formation in studies of

benzene nitration by mixed acid. Such bands, however, have been observed for processes in which alternative nitrating agents were applied.^[49–57]

Concentrated H_2SO_4 and HNO_3 in the usual ratio of 2:1, as well as 1:1, were mixed and left to cool to a room temperature (around 25°C). The sulfuric acid was initially heated until fuming to remove possible SO_2 content. The UV spectra of these mixtures (2:1 and 1:1) show strong absorbance below 300 nm from HNO_3 , and the baseline for the subsequent experiments (Supporting Information, Figures S2a,b) reveals a good compensation after 320 nm. As a second step, we recorded the UV spectrum of nitrobenzene at molar concentration 0.02 mol L^{-1} in mixed acid medium (Figure 3). A shoulder of the most intense band of nitrobenzene produces absorbance of 0.49 at 320 nm.

The spectrum of 1:1 ($\text{H}_2\text{SO}_4/\text{HNO}_3$) reaction mixture containing 0.02 M benzene, recorded shortly (4 min) after mixing the reactants, is shown in Figure 3. An intensity signal at 320 nm was clearly observed (absorbance of 0.98). Benzene does not absorb at these wavelengths. The absorbance of the nitrobenzene product at the same molar concentration has much lower intensity. This result clearly indicates that a new band with a maximum below 300 nm has appeared in the reaction mixture spectrum. Further strong evidence for the formation of a reaction intermediate came from analyzing the

dynamics of spectral changes with time. Figure 3 (top) illustrates the shifts of spectral intensity at 320 nm with time for the reaction conducted at 25°C (1:1 mixture of sulfuric and nitric acids). The intensity of the 320 nm band shoulder gradually reduces and reaches a minimum after 60 min. No further changes are observed, and it should be assumed that the 60 min spectrum arises from the nitrobenzene reaction product. Comparison with the nitrobenzene spectrum in the same medium (Figure 3) confirms this conclusion. The spectrum of reaction mixture with 2:1 $\text{H}_2\text{SO}_4/\text{HNO}_3$ ratio, recorded 4 min after introducing the reactants, shows only absorbance corresponding to the final nitrobenzene product (Supporting Information, Figure S2). Under these conditions, the reaction is too fast and the intermediate is not observed.

To shed more light on the possible source of the increased absorption at 320 nm, we conducted EOM CCSD/aug-cc-pVDZ computations for the optimized structure (at B3LYP/6-311+G(2d,2p)) of the π -complex between benzene and NO_2^+ in isolation (gas phase). The following results for the lowest energy excitations belonging to the A' and A'' symmetry classes of this complex (C_s symmetry) were obtained: $A' = 306 \text{ nm}$ (oscillator strength $f = 0.459$), and $A'' = 429 \text{ nm}$ (oscillator strength $f = 0.019$). The computations suggest the presence of a strong band over 300 nm and a low intensity band over 400 nm. No such bands are observed in the spectrum of the reaction mixtures studied. The experimental spectrum of the reaction mixture in the 200–600 nm region is shown in the Supporting Information (Figure S1).

We also conducted computations at the same level of theory (EOM CCSD/aug-cc-pVDZ) for the π -complex (Figure 1a) obtained from our theoretical modeling of the reaction pathway. The following results for the lowest energy excitations of this complex (C_1 symmetry) were obtained: $\lambda_{\text{max}}(1) = 315 \text{ nm}$ ($f = 0.0126$), $\lambda_{\text{max}}(2) = 311 \text{ nm}$ ($f = 0.0122$), and $\lambda_{\text{max}}(3) = 309 \text{ nm}$ ($f = 0.0050$). The theory predicts that such a complex will not have any strong absorption over 320 nm and no absorption near 400 nm. Overall, the theoretically evaluated spectroscopic properties are in good agreement with the π -complex structure shown in Figure 1a. As emphasized, such a structure of the π -complex does not allow a charge transfer from the aromatic ring to the nitronium unit.

Our broader theoretical modelling of benzene nitration with nitronium ion in simulated nitric and sulfuric acid (“mixed acid”) media, which includes explicit consideration of the role of the sulfuric acid, reveals that the reaction favors a stepwise mechanism with the formation of a σ complex (arenium ion) intermediate. The existence of this arenium ion (Pfeifer–Witzinger–Wheland intermediate) only is fleeting. NBO and Hirshfeld population analyses show that no charge transfer from the benzene π -electron system to the nitronium ion occurs at the stage of π -complex formation, when the association of the NO_2^+ ion with the solvent (H_2SO_4) is explicitly considered. UV/Vis spectroscopic experiments revealed the formation of a band, exhibiting an intense shoulder at 320 nm. The UV study of the reaction kinetics at 25°C showed that this absorption is associated with a reaction intermediate. Our EOM CCSD/aug-cc-pVDZ computations revealed that the observed absorption does not arise from the

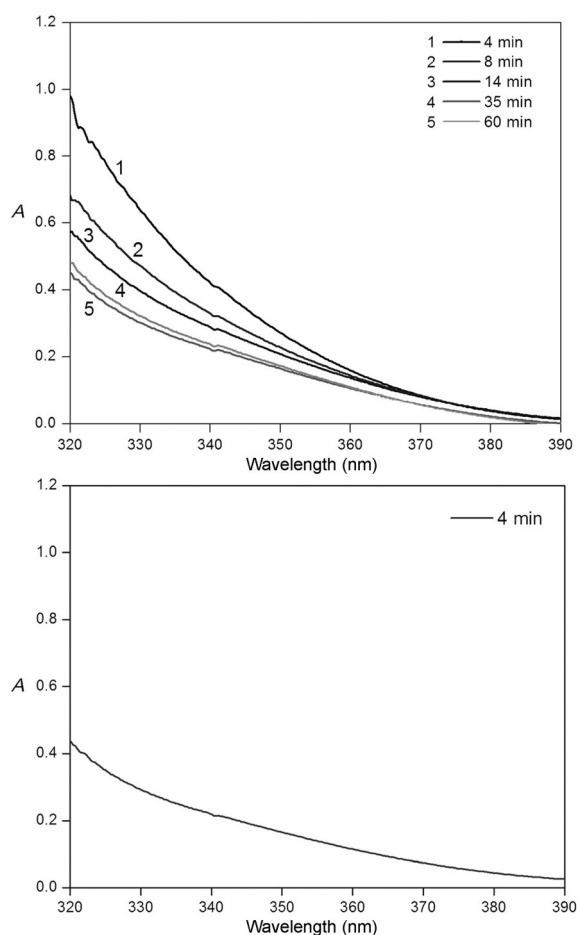


Figure 3. Kinetics of nitration of benzene (at 25°C) with mixed acid in 1:1 $\text{HNO}_3:\text{H}_2\text{SO}_4$ as followed by UV/Vis spectroscopy (top) and spectrum of neat nitrobenzene (bottom) in 1:1 mixed acid medium.

accepted structure of the π -complex intermediate in aromatic nitration processes consisting of interacting benzene and NO_2^+ ion. Instead, the computations suggest that the π -complex is strongly influenced by interaction of the two principal reactants with an explicit solvent (H_2SO_4) molecule. The computational predictions are in harmony with the experimental spectroscopic observations. The present results provide clear experimental evidence for the first intermediate in the benzene nitration by mixed acid, long sought in studies of this key $\text{S}_\text{E}\text{Ar}$ reaction.

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