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Electrophilic Aromatic Substitution: The Role of Electronically Excited States

X. F. Xu, S. Zilberg,* and Y. Haas*

*Institute of Chemistry and the Farkas Center for Light Induced Processes,
The Hebrew University of Jerusalem, Jerusalem, Israel*

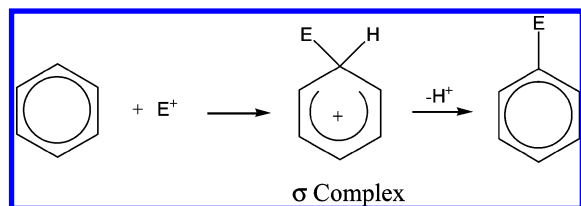
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Electrophilic aromatic substitutions (EAS), one of the most extensively studied organic reactions, can be considered under certain circumstances as a photochemical reaction without light. Thermochemical considerations show that in the gas phase, the reaction system (electrophile plus aromatic neutral) is often found initially in an electronically excited state, whereas the reaction products are formed on the ground state potential energy surface (PES). The crossing to the ground state is usually very rapid, so that the rate-determining steps take place on the ground state surface. It is shown that after the crossing (through a conical intersection (CI)), the system can be found on different parts of the ground state potential surface. In particular, the CI is connected without a barrier to all moieties assumed to be important in the reaction (π complex, radical pair, and σ complex). In some cases, due to a relatively low electron affinity of the electrophile and bond reorganization, the reaction starts on the ground state PES; a conical intersection exists in these cases, but is not accessed by the reactants. The topology of the reaction surface due to the avoided crossing is reminiscent of that in which an actual crossing takes place. The paper provides a comprehensive model for several EAS reactions. The CIs are located computationally, and an energy level diagram is proposed for some representative EAS reactions.

I. Introduction

Electrophilic aromatic substitutions (EAS) are among the most extensively studied organic reactions, and the well-known Ingold–Hughes (or polar two-electron) mechanism of EAS reaction is usually quoted in textbooks (Scheme 1):¹ where the

SCHEME 1: Ingold–Hughes Mechanism of EAS Reaction



Wheland adduct (σ complex, or Ingold–Hughes arenium ion) is referred to as the key intermediate (or transition state²) en route to the final substituted aromatic product. However, for several decades, experimental and theoretical chemists have been debating several important mechanistic details of the EAS process: (1) Is it possible that an electron-transfer (ET) step takes place prior to the formation of the Wheland adduct? (2) Are there other intermediates involved on the reaction potential energy diagram? (3) How to explain the high positional selectivity but the low substrate selectivity?³

A π complex, first proposed by Dewar,⁴ was suggested by Olah and his co-workers as an intermediate prior to the σ complex in a two-step model (path 1 in Scheme 2).⁵ Formation of the π complex in the first step was proposed to account for the low substrate selectivity, whereas the regional selectivity was assigned to the sequential σ complex. X-ray crystallography⁶

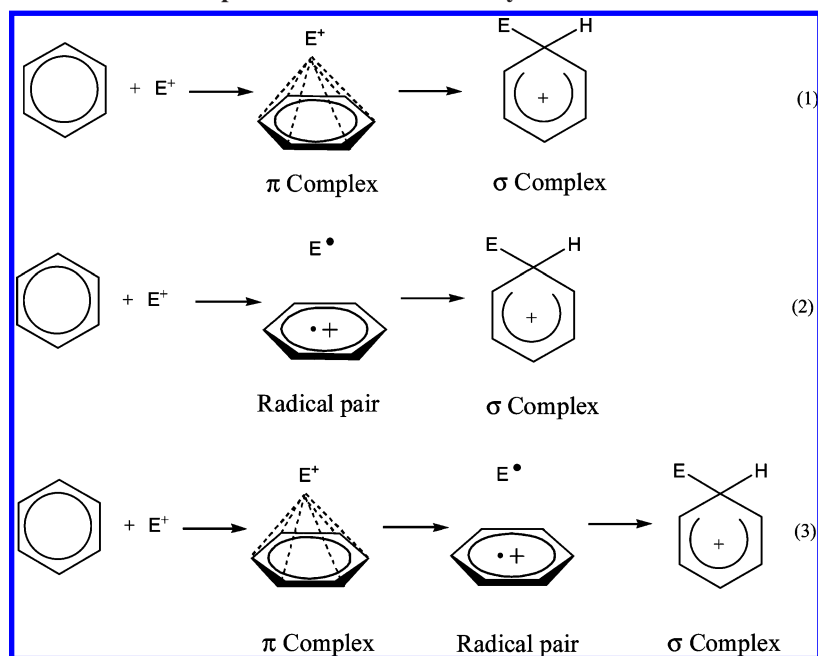
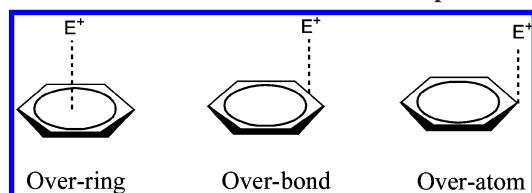
substantiated the formation of a π complex with charge-transfer (CT) character for some EAS reactions, such as bromination of benzene and toluene, and aromatic nitrosation. The π /CT complex has been portrayed either as a centrosymmetric over-riding structure or an unsymmetrical “over-bond” structure⁷ (Scheme 3). The relative stability of the two kinds of π structures is believed to depend both on the nature of the electrophile and the aromatic substrate.⁷ The over-bond structure of π complex not only offers an explanation to the low selectivity of the substrate but also rationalizes the high intramolecular (positional) selectivity. However, it is still controversial whether the π complex is a necessary key intermediate in EAS reaction path.^{2,5,7–9}

For aromatic nitration, the classic example of EAS reaction, Perrin⁹ proposed that “the π complex description is inadequate for a species in which an electron has been transferred from the aromatic moiety to NO_2^{+} ”, and that the positional selectivity could be explained by the formation of a radical ion pair. This alternative mechanism (path 2 in Scheme 2) involves a single-electron transfer (SET)^{9,10} from the aromatic substrate to the electrophile to form a radical ion pair, followed by its collapse to the identical Ingold–Hughes arenium ion (the σ complex). Thus, the substrate selectivity would be absent for all activated aromatics, while the radical ion pair recombination directed by spin density explains the high positional selectivity. The extensive time-resolved spectroscopy study as well as thermal activation of aromatic nitration by Kochi et al.¹¹ provided strong experimental evidence for the SET mechanism, at the same time it suggested the inclusion of a donor–acceptor (EDA) complex (CT complex), preceding the formation of radical pair in the reaction path.

In 2003, on the basis of theoretical studies, Olah and co-workers¹² unified all previous mechanistic proposals and modified their two-step model through involving all three separate intermediates on the potential energy diagram of the electrophilic

* To whom correspondence should be addressed.

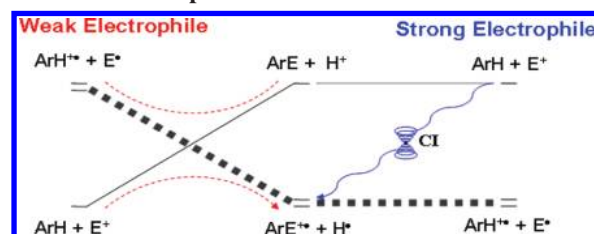
SCHEME 2: Important Intermediates Proposed in EAS Reactions by Previous Studies

SCHEME 3: Possible Structures of π Complex

aromatic nitration, π /CT complex, cation radical pair, and σ complex, as shown in path 3 of Scheme 2. In the same year, by the convergence of molecular-orbital and Marcus–Hush theories with experiments, Gwaltney et al. proposed a CT mechanism² for electrophilic aromatic nitration and nitrosation, in which electron transfer is concurrent with spontaneous rapid complexation of the arene with electrophile. The CT mechanism challenged the role of the classical σ complex as a necessary intermediate in EAS reactions. Recently, Esteves and his co-workers¹³ performed an extensive experimental study of gas phase nitration in a mass spectrometer using naked and monosolvated nitronium ions with several monosubstituted aromatics. They found strong evidence for the SET mechanism and proposed to settle the debate of the SET versus polar mechanisms by considering them as two extremes in a continuum pathway. The occurrence and extent of these two extremes is governed, according to their suggestion, by the ability of the aromatic compound to transfer an electron to the ionized electrophile. Their proposed PES included an avoided crossing as a key ingredient. As we shall show, in many cases the crossing is real and its nature can be rationalized in terms of valence bond theory and verified computationally.

We start our analysis with the case of protonation of aromatics, one of the most fundamental EAS reactions, which has ever served as a benchmark for investigations of the EAS mechanism. Different from the system of the larger “spherical” closed-shell ions (e.g., alkali metals ion) with benzene, in which the formation of a π complex is preferred over the σ complex,¹⁴ a σ complex of benzene with a proton is found as the most stable structure by both theoretical¹⁵ and experimental IR¹⁶ spectrum studies. No π complex was reported, except for a mass spectrometric study¹⁷ in 1995, which led to the conclusion that

CHART 1: Natural State Correlation Diagram for the Gas Phase Electrophilic Aromatic Substitution



the π complex was slightly more stable than the σ complex. However, this inference was questioned by subsequent work.¹⁸ The role of the π complex in the EAS reaction of a proton with benzene is indecisive once again.

To date, most experimental and theoretical studies of the EAS mechanism assumed only a ground-state reaction pathway. This standpoint is reasonable for weak electrophilic reaction systems, just as a natural state correlation diagram (Chart 1) shows: The original reactants state ($ArH + E^+$) for a weak electrophile is lower in energy than the ET state ($ArH^{++} + E^-$), which is naturally correlated to the ground-state product ($ArE^{++} + H^+$); therefore, a ground-state reaction pathway involving a single electron shift in the transition-state region, through an avoided crossing, is exclusively responsible for the EAS mechanism. On the basis of thermochemical considerations, the $ArE + H^+$ product pair lies on an excited state surface. In contrast, when a strong electrophile is reacting, the original reactants state ($ArH + E^+$) is often located on an electronically excited state. The ground-state product ($ArE^{++} + H^+$) can only be attained through a funnel connecting the excited state surface with the ground-state one, which might be a conical intersection. Therefore, an explicit consideration of the involvement of excited states in the study of EAS reactions is called for, in order to better understand their mechanism. The distance between the two reactants at which the crossing takes place may be quite large, as electron transfer could be by a harpoon mechanism,¹⁹ at intermolecular separations much larger than those typical of chemical interactions.

Peluso et al.²⁰ discussed an avoided crossing of electronic PES of the ground state and the first excited state, through ab

initio configuration interaction computations, which strongly supported the SET mechanism. However, their mechanism nevertheless focuses on the formation of a radical pair from a π complex in the ground-state reaction pathway. In this paper, we explicitly explore the consequences of incorporating electronically excited states in the discussion of EAS reactions. Detailed theoretical investigations are presented for gas phase reactions of benzene with several electrophiles (H^+ , Cl^+ , $\text{C}\equiv\text{CH}^+$, CH_3^+ , NO_2^+ , or NO^+). On the basis of the gas phase electron affinity (EA) of electrophiles and ionization potential (IP) of benzene,²¹ ($\text{EA}(\text{H}^+) = 13.60 \text{ eV} > \text{EA}(\text{Cl}^+) = 12.97 \text{ eV} > \text{EA}(\text{C}\equiv\text{CH}^+) = 11.61 \text{ eV} > \text{EA}(\text{CH}_3^+) = 9.84 \text{ eV} > \text{EA}(\text{NO}_2^+) = 9.59 \text{ eV} > \text{EA}(\text{NO}^+) = 9.26 \text{ eV}$ vs $\text{IP}(\text{C}_6\text{H}_6) = 9.24 \text{ eV}$), the six electrophiles show different propensities for extracting an electron from benzene. Moreover, as some of these reactions necessarily start on an excited electronic potential surface, a comparative study of these systems is used to construct a consistent and full mechanistic picture of EAS reactions. In addition, the gas phase nitrosation of aniline ($\text{IP} = 7.72 \text{ eV}$) is investigated as an example of an EAS reaction of a substituted benzene whose IP is smaller than the EA of NO^+ and for discussing the positional selectivity.

II. Computational Details

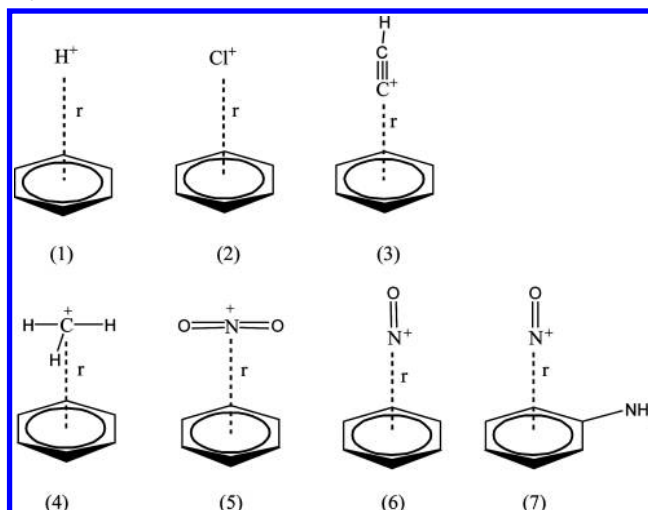
All computations were performed using CASSCF²² methodology implemented in PCGAMES²³ package, with cc-pVDZ basis set. The $[\text{ArE}^+]$ state ($\text{ArH} + \text{E}^+$ in Chart 1) corresponds to a closed-shell configuration and is always a totally symmetric state, while the $[\text{Ar}^+\text{E}]$ state ($\text{ArH}^{++} + \text{E}^-$ in Chart 1) usually results in the two singly occupied orbitals with different symmetry and is of a lower symmetry. Therefore, in calculations, the application of high symmetry helps to completely partition the two kinds of electronic states, allowing a better comprehension of the nature of the EAS mechanism.

For H^+ or Cl^+ with benzene, six π electrons and four high-energy σ electrons of benzene are included in the active space composed of five π orbitals, 2 σ orbitals of benzene, and 1s orbital of hydrogen atom or one long pair p orbital of chlorine, denoted as CAS(10,8). The highest π^* orbital of benzene is not included in the active space. The active space of $\text{C}\equiv\text{CH}^+$ with benzene is CAS(10,10): 10 π electrons are allowed to distribute arbitrarily into 10 orbitals including 9 π orbitals and 1 sp hybrid orbital of the side carbon atom of $\text{C}\equiv\text{CH}^+$. For the study of CH_3^+ with benzene, all π orbitals (three occupied and three unoccupied) of benzene, two high-energy σ occupied orbitals and one p orbital of CH_3^+ constitute the active space of CAS(10,9). Similarly, an active space CAS(10,9) is used in the investigation of nitration or nitrosation of benzene: 10 π electrons are allowed to distribute into 9 π orbitals, of which the 5 π orbitals belong to benzene, and the others belong to NO_2^+ or NO^+ ; the highest π^* orbital of benzene is not involved inside. In the calculations for the nitrosation of aniline, a smaller active space, CAS(6,7), is used, in which six π electrons are distributed into the seven frontier π orbitals. All these active spaces are shown in the Supporting Information (Figure S1).

III. Results

Gas Phase versus Condensed Phase Reactions. In this paper we are primarily interested in gas phase reactions. The products of the overall reaction (Scheme 1) are habitually presented as a substituted benzene plus a proton. In solution, the proton is usually allowed to react with a base B^- to form a neutral BH species. In the gas phase, under collision free conditions (e.g., in a mass-spectrometer), the initial energy of the system is

SCHEME 4: The Proposed Definition of the Reaction Coordinates r for the 7 Investigated EAS Reaction Systems



preserved and must somehow be dissipated. As the reaction can be highly exothermic, the reacting pair, which is charged, usually decomposes along different pathways. In the present analysis, we consider the σ -complex (Scheme 1), which is found to be local minimum for all systems in this study, as the principal reaction product and use its energy as the standard for comparison with other species. Under real experimental conditions this species converts to dissociation products, as briefly discussed in Section IV-5.

1. H^+ , Cl^+ , and $\text{C}\equiv\text{CH}^+$ with Benzene: Locating Conical Intersections. Since the electron affinities of H^+ , Cl^+ , and $\text{C}\equiv\text{CH}^+$ are all considerably greater than the ionization potential of benzene, the system in its initial state (large separation between E^+ and benzene with the charge on the attacking electrophile $[\text{PhHE}^+]_0$) must be located on an excited electronically state. It is well-known that, according to the Jahn–Teller theorem, the benzene cation in its ground state is distorted²⁴ from the doubly degenerate E-state of D_{6h} symmetry and two types of nearly isoenergetic configurations are formed. Thus, we expect that after electron transfer from benzene to electrophile, the adduct (benzene cation plus electrophile, denoted as $[\text{PhH}^+\text{E}]$), will have two types of critical points in the ground state.

We begin our search by assuming that the electrophile line of attack is perpendicular to the ring and directed at the benzene's center, as shown in Scheme 4. During the search the internal coordinates of benzene are kept unchanged, the symmetry group is C_{6v} ; nevertheless, in view of later optimizations, we use the labeling of lower symmetry groups, C_{2v} and C_s , as appropriate. Under C_{2v} symmetry, at large separations, the isoenergetic lower-energy states of the biradical pair formed after electron transfer, $[\text{PhH}^+\text{E}]$, are 1B_1 and 1B_2 and the closed-shell state 1A_1 , $[\text{PhHE}^+]$ is electronically excited. At short separations, however, partial electron transfer takes place to form a CT π complex in which the charge is distributed between the benzene and the electrophile. In this species, the 1A_1 state becomes the ground state due to charge delocalization, and the degenerate pair is electronically excited. The calculated potential energy curves as a function of r ($<3 \text{ \AA}$ for H^+ or $\text{C}\equiv\text{CH}^+$ with benzene, $<3.5 \text{ \AA}$ for Cl^+ with benzene) are shown in Figure 1, panels a–c. In this calculation the internal geometrical parameters of neutral benzene and of $\text{C}\equiv\text{CH}^+$ are conserved along the path, therefore the 1B_1 and 1B_2 states are strictly degenerate.

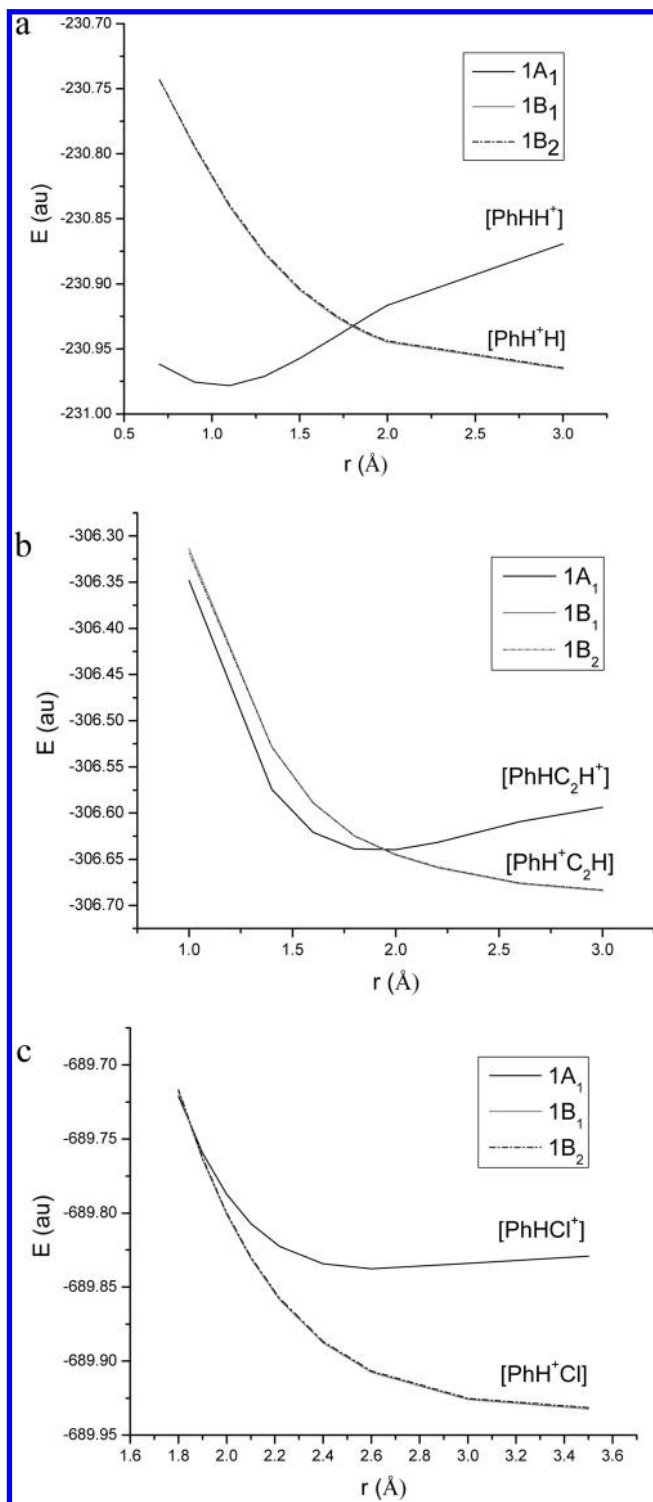


Figure 1. The potential energy curves of the lower-energy electronic states of the two species $[\text{PhH}^+\text{E}]$ and $[\text{PhHE}^+]$ for an approach along the line connecting the centers of mass (CM) of the two reactants as a function of r , the distance between the two reactants. C_{2v} symmetry is assumed, and the internal geometrical parameters of neutral benzene and of $\text{C}\equiv\text{CH}^+$ are conserved along the path. The degenerate 1B_1 and 1B_2 states and the closed-shell state 1A_1 are shown. At large r the $1\text{B}_1/1\text{B}_2$ radical pair is on the ground state, whereas at short distance, the charge is transferred to form the Coulomb-stabilized π/CT complex of 1A_1 symmetry, which becomes the ground state. (a) H^+ with benzene; (b) $\text{C}\equiv\text{CH}^+$ with benzene; (c) Cl^+ with benzene. A crossing is found for all three systems.

Therefore, as expected from the EAs of electrophiles and IP of benzene, at the starting geometry the original reactants state

$[\text{PhHE}^+]_0$ (the positive charge located on the electrophile) is located on an excited state PES for all the three systems, (cf. Chart 1). As the two moieties approach each other to the region of interaction, a crossing of the 1A_1 , 1B_1 , and 1B_2 states is found at $r = 1.8 \text{ \AA}$ for proton with benzene, and at $r = 1.9 \text{ \AA}$ for $\text{C}\equiv\text{CH}^+$ with benzene. We shall refer to this crossing as the center-CI, in view of the geometry of the system. The coordinates that define this CI are the two Jahn–Teller coordinates of the benzene cation radical and the distance between the electrophile and the benzene. The case of Cl^+ is somewhat different due to its large size, as discussed below.

The symmetric center-CI is found to lie at a rather high energy, but lower energy curve crossings at other geometries are expected, based on general principles. The rationale for this expectation is the following. After crossing at the center-CI, the two systems (benzene with H^+ or with $\text{C}\equiv\text{CH}^+$), may follow three barrier-less reaction paths to the ground-state product, all ultimately ending at the σ -complex. One path leads initially to a centrosymmetric π/CT complex (center- π), which is a second-order saddle-point with two imaginary frequencies; this complex connects to either the stable σ complex or to a bridged π structure²⁵ with C_s symmetry ($1\text{A}'$) (side- π - $1\text{A}'$), a transition state between two σ complexes. Another reaction path leads to two radical pairs (benzene cation of B_1 or B_2 symmetry and an electrophile radical: $\text{H}\cdot$ or $\cdot\text{C}\equiv\text{CH}$), which can recombine to form the σ complex. The third channel is a direct route from the center-CI to the σ complex. The structures and energies of these species were calculated by allowing the ring system to distort under C_{2v} or C_s symmetry, as appropriate. The two radical pairs are not degenerate anymore, although their energies are still rather similar. The structures of the optimized π/CT complex within C_{2v} symmetry restriction (center- π), the bridged π transition state (side- π - $1\text{A}'$) and the σ complex obtained under C_s symmetry are shown in Figure 2.

Consider now the reaction leading from one σ complex to another. In C_s symmetry, it is readily verified that in addition to the radical pair with A' symmetry (RP- $1\text{A}'$), there is another radical pair of A'' symmetry (RP- $1\text{A}''$) that is a transition state connecting the two σ complexes. (See Figure S2 in the Supporting Information). Both RP- $1\text{A}'$ and RP- $1\text{A}''$ are over-bond structures, shown in Figure 2. Hence, a two-legged phase inverting Longuet–Higgins loop is formed, in which a CI between the side- π - $1\text{A}'$ and RP- $1\text{A}''$ must be present. We term it the side-CI, as the electrophile is located over one of the CC bonds of the benzene ring. The energy of the side-CI for the system H^+ /benzene is $\sim 1.00 \text{ eV}$ lower than that of the center-CI. By symmetry, six side-CIs exist with the same probability. This implies that six σ complexes with the proton added at different carbon atoms of benzene can be equally obtained through these side-CIs. Similar side-CIs are found for the other systems, $\text{C}\equiv\text{CH}^+$ with benzene and Cl^+ with benzene. Due to the larger atomic radius of chlorine, a center- π structure under the restriction of C_{2v} symmetry is reached at $r \sim 2.6 \text{ \AA}$, before the crossing of PESs; therefore, the potential surfaces in Figure 1c look somewhat different than those of Figures 1a and 1b. Thus, for all three EAS systems, H^+ , $\text{C}\equiv\text{CH}^+$, and Cl^+ with benzene, the side-CIs play an important role in the formation of the σ complex. Due to the interaction of the orbital of electrophiles with that of benzene within van der Waals distance, a charge transfer takes place on the excited state surface, prior to the formation of conical intersection.²⁶

2. CH_3^+ with Benzene. In this case, the exothermicity of the reaction is much smaller than in the previous ones. At infinite separation the starting reaction pair is an excited state with an

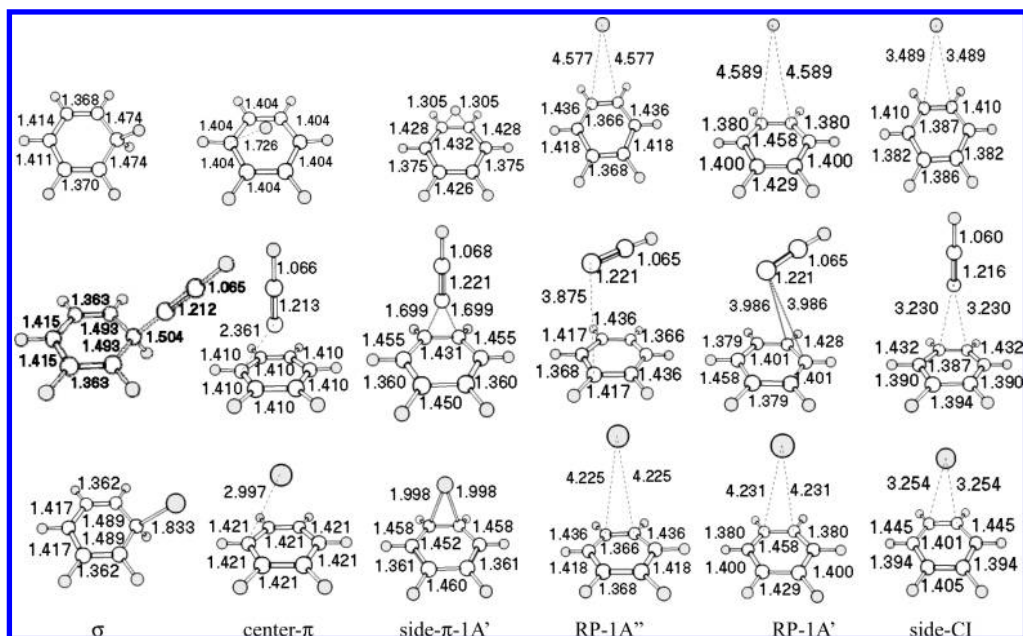


Figure 2. The optimized structures of some critical points (σ , center- π , side- π -1A', RP-1A'', RP-1A', and side-Cl), for the systems of H^+ , $\text{C}\equiv\text{CH}^+$, or Cl^+ with benzene.

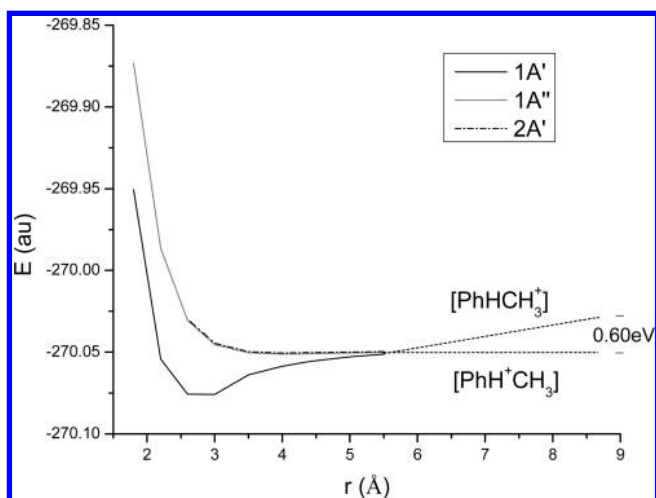


Figure 3. The potential energy surfaces of the three lower-energy electronic states (1A', 2A', and 1A'') as a function of r , for the CH_3^+ /benzene system. The orientation of attack is shown in Scheme 4(4); along the path, the internal geometrical parameters of neutral benzene and of CH_3^+ are preserved. Curve crossing takes place at a large r , an exact calculation is not feasible with the basis set used (the dotted lines stand for this range). The asymptotic separation "0.60 eV" is the energy difference between the electron affinity of CH_3^+ and the ionization potential of benzene.

excess energy of only ~ 0.60 eV. As two reactants approach each other an electron tends to be transferred at relatively large separations by a harpoon-type mechanism, due to the lower excess energy of the original reacting pair. Under C_s symmetry, the potential energy curves of the three lower-energy electronically excited states (1A', 2A', and 1A'') of CH_3^+ with benzene are plotted as a function of r (Figure 3). Two states with A' symmetry correspond respectively to different configurations: a closed-shell configuration $[\text{PhHCH}_3^+]$ and an ET configuration $[\text{PhH}^+\text{CH}_3]$ resulting from promotion of an electron from a higher occupied π orbital with a' symmetry of benzene to the lone pair p orbital with a' symmetry of carbon of CH_3^+ . The 1A'' state is an electron-transfer state $[\text{PhH}^+\text{CH}_3]$ with configuration of two singly occupied orbitals: an a'' π orbital of

benzene and the lone pair p orbital (a') of carbon of CH_3^+ . The planar CH_3^+ and the neutral benzene approach each other head on (cf. Scheme 4(4)), while preserving their original geometries.

Along the r coordinate, a lower-energy π -bonding structure is located at $r \sim 2.8$ Å. Similar to the system of H^+ , Cl^+ , or $\text{C}\equiv\text{CH}^+$ with benzene, the π -bonding structure is not a minimum. Its further optimization under C_s symmetry (cf. the orientation of Scheme 4(4)) leads with no barrier to a stable σ complex, in agreement with previous theoretical studies:²⁷ CH_3^+ inserts without a barrier into benzene to form a σ complex, and no π complex minimum is found. On the other hand, the CH_3 radical and benzene cation radical can combine to form the σ complex, also without a barrier. Therefore, as with the EAS reactions discussed above, both polar and ET mechanisms are possible for the reaction of CH_3^+ with benzene.

3. NO_2^+ with Benzene. As for the previous electrophiles, the EA value of NO_2^+ is larger than the IP of benzene, but only by 0.35 eV. Thus, a crossing between $[\text{PhHNO}_2^+]$ and $[\text{PhH}^+\text{NO}_2]$ may also be involved in the nitration reaction of benzene. Indeed, a crossing is calculated (Figure 4b), but, as shown in Figure 4a, the original system of NO_2^+ interacting with benzene ($[\text{PhHNO}_2^+]$) is on the *ground state*. The difference from the reacting pairs discussed above is due, apart from the fact that EA of NO_2 is only 0.35 eV larger than the IP of benzene, from the large energy change in the bond reorganization process from NO_2^+ to NO_2 radical (cf. Figure 4b), as noted by previous workers,^{2,20} also from a consequence of the Franck–Condon principle: transfer of an electron takes place much faster than nuclear movements.²⁸

Our results of the overall potential surface, which agree with previous workers, are summarized in Figure S3 in the Supporting Information. As pointed out in the Introduction, a SET mechanism including more than one intermediate is favored for the nitration of more-reactive aromatics.

4. NO^+ with Benzene. The calculated energy profiles of 1A₁ (corresponding to $[\text{PhHNO}^+]$), 1A₂, and 2A₁ states (corresponding to benzene cation-radical $[\text{PhH}^+\text{NO}]$), as a function of r , and the potential energy profiles of 1A₁ and 1A₂ states as a

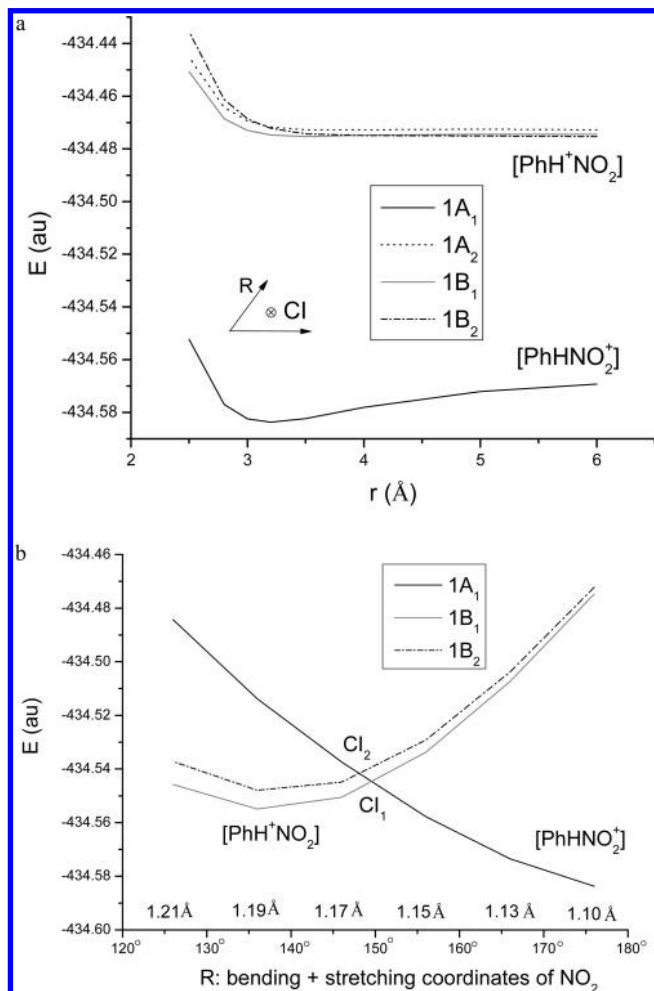


Figure 4. (a) Potential energy profiles of the $1A_1$, $1A_2$, and $1B_1$, $1B_2$ states of the benzene- NO_2^+ complexes for the geometry (neutral benzene and NO_2^+) as a function of the r coordinate; the original system [PhHNO_2^+] is on the ground state. Notwithstanding, a crossing between [PhHNO_2^+] and [PhH^+NO_2] was located when another nuclear coordinate R is considered. (b) Potential-energy profiles of $1A_1$, $1B_1$, and $1B_2$ states as a function of R (the bending and symmetric stretching coordinates of NO_2), at $r = 3.2$ Å. The molecular orientation for both (a) and (b) refers to Scheme 4(5).

function of the stretching coordinate of NO, at $r = 3.2$ Å, are shown in Figure 5, for an orientation within C_{2v} symmetry (Scheme 4(6)). The original reacting species [PhHNO^+] is on the ground-state, as a direct result of relatively low EA of NO^+ . With the benzene cation-radical pair $1A_2$ or $2A_1$ still being on the excited surface even if the stretching of NO is relaxed, it indicates that the radical pair is not involved in the nitrosation of benzene. This result is consistent with the Marcus-Hush type interpretation proposed by Gwaltney et al.²

Compared with NO_2^+ , the lower reactivity of electrophilic aromatic nitrosation by NO^+ has been ascribed to a significant barrier in the conversion of a π complex to the N-protonated nitroso derivative,^{2,29} via the σ complex as a high energy transition structure. An obvious charge-transfer character of the π complex is detected by IR spectroscopy and IR multiple photon dissociation spectroscopy (IRMPD).^{6a,30} Our results³¹ agree with the main conclusion, namely, that the reaction is entirely on the ground state surface.

5. NO^+ with Aniline. Aniline is a much better electron donor than benzene, having a smaller IP value of 7.72 eV. As shown in Figure 6, the original reactants state [PhNH_2NO^+] with positive charge on the NO-electrophile is an excited state, 1.16

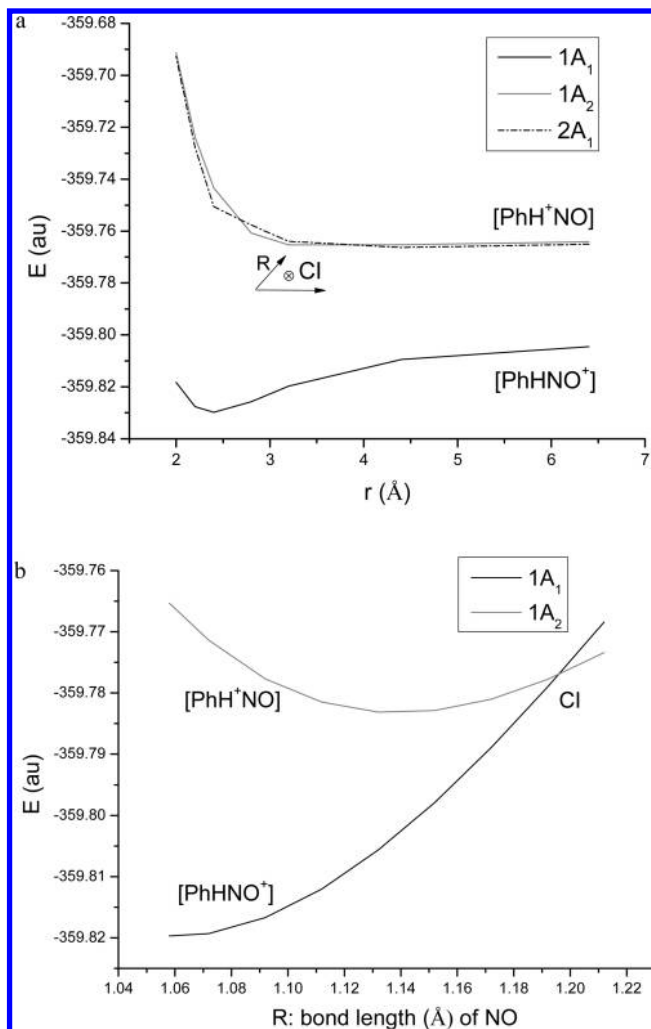


Figure 5. (a) Potential energy profiles of the $1A_1$, $1A_2$, and $2A_1$ states of the benzene- NO^+ complexes for the geometry (neutral benzene and NO^+) as a function of the r coordinate; the original system [PhHNO^+] is on the ground state. A crossing between [PhHNO^+] and [PhH^+NO] was located when the NO stretch coordinate R was allowed to change. (b) Potential-energy profiles of $1A_1$ and $1A_2$ states as a function of R at $r = 3.2$ Å. The molecular orientation for both (a) and (b) refers to Scheme 4(6).

eV higher than the ground-state [PhNH_2^+NO] ($1A''$), in which one electron is transferred from the highest occupied π orbital of aniline to the lowest unoccupied π^* orbital of NO^+ . This is therefore a case of the strong electrophile (Chart 1). A crossing of the two states ([PhNH_2NO^+] (now it is $1A'$ state) and [PhNH_2^+NO] ($1A''$)) is observed at $r \sim 2.6$ Å, only 0.05 eV higher in energy than the adjacent π -bonded structure (not a real minimum).

In fact, at the crossing point, the ET state [PhNH_2^+NO] with A' symmetry, not shown in Figure 6, has the same energy as the two degenerate states. The PESs of NO^+ with aniline is very similar to that of $\text{C}\equiv\text{CH}^+$ with benzene. However, full optimization of the π -bonding structure for the nitrosation of aniline leads to the more stable radical pair with A' symmetry (real minimum), 1.79 eV below the original system, which may be ascribed to the very small barrier (upper limit is only 0.05 eV) between the π complex and radical pair as well as the relative higher stability of the radical pair. In addition, the radical pair with A'' symmetry is also located, and is 2.01 eV below the original system. The two optimized radical pair minimum structures are shown in Figure S5 of the Supporting Information.

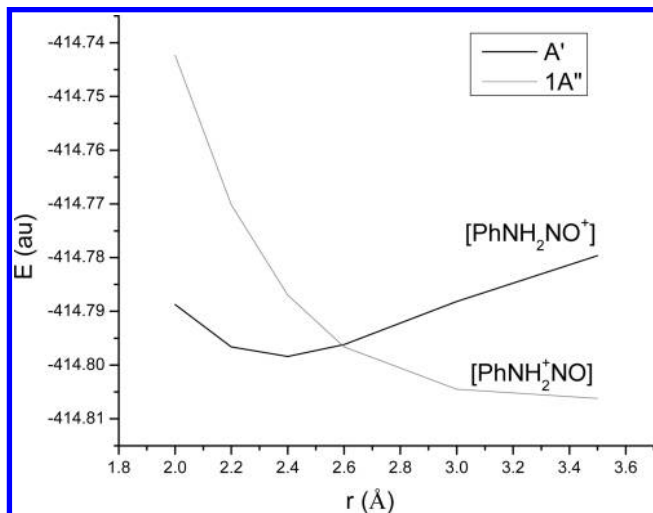


Figure 6. The potential energy curves of the lower-energy electronic state $[\text{PhNH}_2^+\text{NO}]$ ($1A''$) and the closed-shell electronic state $[\text{PhNH}_2\text{NO}^+]$ (A'), as a function of the internuclear separation r . The molecular orientation refers to Scheme 4(7); along the path, the internal geometrical parameters of neutral aniline and of NO^+ are conserved.

Four σ complexes, with NO added to the different position of aniline, ipso-, ortho-, meta- or para-, have been fully optimized and shown in Figure S5. Their relative energies to the original system $[\text{PhNH}_2\text{NO}^+]$ are listed in Table 2. The relative stabilities of the σ intermediates lead finally to the relative ratio of the different substitution products: para-substitution > ortho-substitution \gg meta-substitution > ipso-substitution. The high stability of para- and ortho-substitutions is a result of resonance activating by amino group donating electrons.³²

IV. Discussion

1. Are Excited States Involved in Gas Phase EAS Reactions? The question can be answered based on thermodynamic data collected in Table 3. As shown there, if the electron affinity of the electrophile is higher than the ionization potential of the aromatic molecule ($\text{EA}_E^+ - \text{IP}_{Ar} > 0$ in Table 3), then the original system $[\text{ArE}^+]_0$ is usually found in an electronically excited state at large separations. The situation may be inverted, if the reorganization energy involved in the loss of an electron compensates for the difference between EA and IP. Thus, for H^+ , Cl^+ , and $\text{C}\equiv\text{CH}^+$ with benzene, as well as for NO^+ with aniline, the state in which the system is located initially is an electronically excited one ($\Delta E = E_O - E_{ET} > 0$ in Table 3). In contrast, due to the reorganization energy of NO_2 and NO, the original state $[\text{ArE}^+]_0$ is lower than the ET state $[\text{Ar}^+\text{E}]$ in the cases of the nitration and nitrosation of benzene ($\Delta E = E_O - E_{ET} < 0$ in Table 3). Therefore, in the EAS reaction pathways

TABLE 2: Relative Energies E (eV) of the Optimized Radical Pairs ($1A'$ and $1A''$) and σ -Complexes to the Original System $[\text{PhNH}_2\text{NO}^+]$ (-414.7625 au) for the Nitrosation of Aniline

radical pair	ΔE	σ -complex	ΔE
$1A'$	-1.79	ipso-	-0.56
$1A''$	-2.01	meta-	-1.01
		ortho-	-2.26
		para-	-2.34

of H^+ , Cl^+ , and $\text{C}\equiv\text{CH}^+$ with benzene, and NO^+ with aniline in gas-phase, electronically excited states are involved, and consequently a conical intersection (CI) is likely to play an important role as an effective funnel from the excited state to the ground state of the system. The nitration and nitrosation of benzene are purely ground-state reactions. At the present theoretical level (CAS level), the system of CH_3^+ with benzene is an intermediate case: electron transfer appears to take place at large distances, at which our computational method is not applicable.

The transition through the CI funnel is expected to be very rapid and thus is not expected to be the rate determining step of the overall reaction. However, an important property of CIs is that the decay of excited system through CI in general leads to more than one ground-state product, directly or via transition states. This is due to the fact that a conical intersection is defined by two coordinates and not one. It is becoming increasingly apparent that in thermal reactions the reaction path bifurcations on the ground state may be relatively common,^{33–36} allowing the formation of more than one product through a single transition state. In the present examples involving excited states, the total energy of system significantly exceeds the energy of the controlling dynamical bottlenecks on the ground state PES, often sufficient to reach the region near the conical intersection seam. This region, where electronic states are close in energy, could also lead to efficient transitions from the excited state to the ground state, rather than just the lowest-energy conical intersection.³⁷ Thus, the presence of a conical intersection can naturally account for the formation of the observed various intermediates and transition states, all of the π -complexes, the radical pairs and the σ complexes.

On the basis of the present calculations and the above discussions, EAS mechanisms may be portrayed in one diagram (Scheme 5), based on the energy scheme shown in Chart 1.

Two classes of EAS reactions can be distinguished based on the electronic state of the original reacting pair $[\text{ArE}^+]_0$. In the case of powerful electrophiles (H^+ , Cl^+ , or $\text{C}\equiv\text{CH}^+$) with benzene, or the nitrosation of aniline, the $[\text{ArE}^+]_0$ species lies at a higher electronic state than that of the vertical ET states $[\text{Ar}^+\text{E}]$ in which the positive charge of electrophile has been transferred to the substrate without any structural change. Having sufficient excess energy, the $[\text{ArE}^+]$ state can decay directly to

TABLE 1: Relative Optimized Energies ΔE (eV) of Some Critical Points on PESs of the Reactions of H^+ , $\text{C}\equiv\text{CH}^+$ or Cl^+ with Benzene

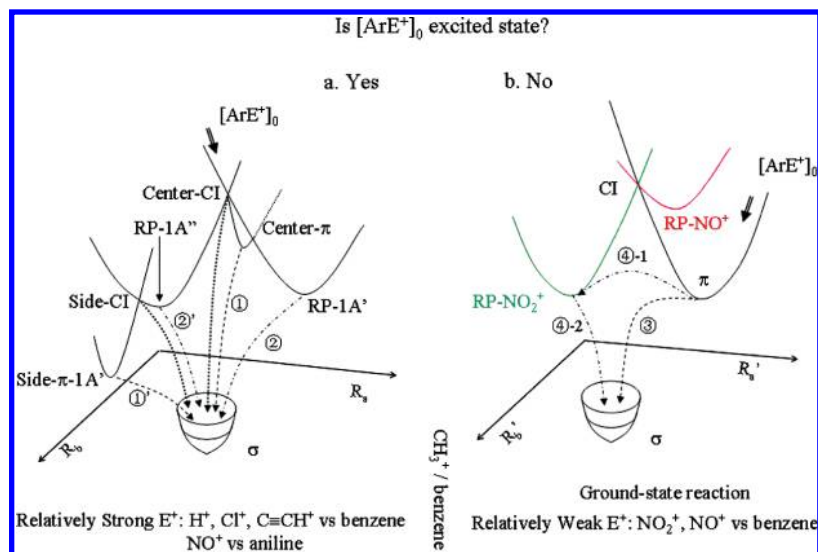
E^+	ΔE							
	σ -complex ^a	$[\text{PhHE}^+]^b$	center- CI^c	side- $\text{CI}^{d,e}$	center- π	side- π - $1A'^d$	RP- $1A''^d$	RP- $1A'^d$
H^+	0 (-231.0904)	6.02	4.31	3.30	2.93	0.54	3.14	3.11
$\text{C}\equiv\text{CH}^+$	0 (-306.8272)	6.35	5.10	3.67	4.92	0.79	3.51	3.51 ^f
Cl^+	0 (-689.9966)	4.43		1.67	4.19	0.56	1.41	1.40

^a The values in brackets are the absolute energies in au. ^b The energy of approaching reactants $[\text{PhHE}^+]$ at $r = 3.0$ Å. ^c Optimized with fixed internal coordinates. ^d Optimized under C_s symmetry. ^e Side-CI is the located CI between side- π - $1A'$ and RP- $1A''$. ^f This RP- $1A'$ of $\text{C}\equiv\text{CH}^+$ /benzene is not a stationary point; further optimization leads to the lower-energy side- π - $1A'$ structure.

TABLE 3: Calculated Energy Difference ($\Delta E = E_O - E_{ET}$ in eV) between the Original State $[ArE^+]_0$ (E_O) and ET State $[Ar^+E]$ (E_{ET}), and the Experimental Thermodynamic Data

	benzene						aniline
	H ⁺	Cl ⁺	C \equiv CH ⁺	CH ₃ ⁺	NO ₂ ⁺	NO ⁺	NO ⁺
$\Delta E = E_O - E_{ET}$	4.85 ^a	5.64 ^{a,b}	2.86	n.a.	-2.49	-1.05	1.16
$EA_{E^+} - IP_{Ar}^c$	4.36	3.73	2.37	0.60	0.35	0.02	1.54

^a The value is crudely estimated at CAS(4,3)/CC-pVDZ level. ^b The singlet state is calculated instead of the more stable triple state for the original system of Cl⁺ with benzene. ^c The experimental data from ref 21.

SCHEME 5: Possible EAS Reaction Paths in the Gas Phase. The arrows with double line mark the starting point of reaction

all ground-state species (the π complexes, the radical cation pairs, and the σ complexes) via an effective funnel of a conical intersection (center-CI and/or side-CI shown in Scheme 5a). The funnel includes also the region around the conical intersections. No barrier needs to be overcome in either of the reaction paths from the CI to these critical points. Besides the direct formation from CI, the σ complexes can be produced along two other reaction paths. One is a polar process via a π complex (center- π and/or side- π -1A') to a certain σ complex, in which one-electron transfer is accompanied by simultaneous formation of a new bond between the electrophile and benzene (path ① in Scheme 5a). The second path is by the collapse of the radical cation pair to a σ complex (path ② in Scheme 5a) (not necessarily the same). Hence, in this class of EAS reaction, the polar mechanism and ET mechanism are initiated after the passage through a CI, and may compete with each other. Which ground-state trajectory is favored might be determined by dynamic calculations. The σ complexes are the only observable intermediates.

In the second class of EAS reactions, the original reacting system $[ArE^+]_0$ is on the ground-state, as shown in Scheme 5b, either by virtue of a low EA (NO^+) or due to a high reorganization energy (NO_2^+ , NO^+). In this case a π complex will be initially formed on the ground-state PES as the two reactants approach each other. From the π complex, the σ complex can be directly formed by a polar path (path ③ in Scheme 5b). In some cases, in which the radical cation pair can be located on the ground-state PES (e.g., for the nitration of benzene, $RP-NO_2^+$ in Scheme 5b), the single-electron-transfer (SET) pathway is also a feasible means leading from the π complex to the radical cation pair, followed by its recombination to form (a possibly different) σ complex (path ④ in Scheme 5b). Since the transition-states pertinent to both SET and polar

pathways are near the real (or avoided) crossing region where a single electron shift happens, any factor (steric, electronic, or geometric) that can affect the coupling process of the two spin-paired electrons following the electron shift will determine which particular pathway is followed.³⁸ In other cases, the PES of ET is lifted so high that the radical pair is located on the excited state (e.g., the nitrosation of benzene, $RP-NO^+$ in Scheme 5b), hence the radical pairs are never involved in this EAS reaction. The polar reaction path is exclusively responsible for the reaction mechanism.

Due to the lower excess energy in the beginning of reaction, the electron transfer in the case of the CH_3^+ /benzene reacting pair takes place at a large separation (a harpoon model). After the crossing, the basic reaction mechanism of CH_3^+ with benzene is expected to be similar to the first class EAS reaction.

2. The π Complex. The present investigation indicates that a π complex is not a necessary intermediate in all EAS reactions. For the very active electrophiles, for example, H⁺, Cl⁺, and C \equiv CH⁺, in their reaction with benzene, or for the nitrosation of more reactive substrates, e.g., aniline, the system $[ArE^+]_0$ is originally in an electronically excited state with a large excess of energy, so that the formation of the σ complex is definitely an exergonic process. The π complex turns out to be one saddle point in one of the channels of the fast reaction process as discussed in the preceding section. According to our calculations, the reaction of CH_3^+ with benzene follows the same pattern as these EAS reactions.

For both nitration and nitrosation of benzene, the π complex has been characterized as a minimum on the PES, with over-atom structure in the case of nitration or over-ring structure for nitrosation. Therefore, our conclusions concerning the π complex and its role in the nitration and the nitrosation of benzene basically agree with those of Gwaltney et al.² As a result of the

weak interaction of electrophile and substrate in π complex, the π complex is responsible for the low substrate selectivity of this class of EAS reaction.

3. Conical Intersections in the First Class of EAS Reaction. In the past few years there is a growing awareness concerning the role of conical intersections in organic reactions. In some cases the CIs are rather low-lying and also strongly affect thermal reactions. Examples are hydrogen or proton-coupled electron transfer³⁹ and organic reactions in which thermal generation of electronic excited states takes place.⁴⁰ The latter have been termed “photochemical reactions without light”.^{41–43} In the present case a similar situation holds: the first class of EAS reaction starts on an excited state surface, even though no light is absorbed in the system. The center-CI connecting to all the critical points is a triple degeneracy in the case of benzene, as a result of symmetry of benzene ring. In Section III.1, it was shown that except for the center-CI which has a high-symmetry over-ring structure, a more stable side-CI with a over-bond structure, almost isoenergetic with the radical pair, is found as an effective funnel connecting the excited state and ground state. For a high-symmetry original system, such as proton with benzene, in principle, six side-CIs with electrophile over different bonds can be formed equally and ultimately lead to the six σ complexes with electrophile added to the different carbon atom, with the same probability. It implies that if a substituted substrate reacts with an electrophile, breaking the high-symmetry of the original system, some side-CI will be favored and finally lead to different rates of formation of σ products, that is, showing high positional selectivity. Therefore, the existence of the side-CI offers a possible explanation for the high positional selectivity (regioselectivity) of the first class of EAS reaction.

The center-CI is a weak-bonding structure and it has the same role as the π -complex does in the second class of EAS reaction: leading to the low substrate selectivity.

4. The Solvent Effect. The present investigations are totally based on the EAS reactions in the gas phase. The original reactants system (ArH plus E^+) is expected to be stabilized in a polar solvent due to preferential solvation of E^+ , which may bring the system down to the ground state. The effect is strongest in the case of H^+ , due to its small size. Therefore, the main reaction mechanism in solution may be basically a ground state event, with the avoided crossing playing the role of the CI in the gas phase. The ArH plus E^+ system is expected to yield ArE plus H^+ , rather than ArE plus H^+ , in agreement with experiment.

5. Comparison with Experiments. The number of detailed mechanistic studies of EAS reactions in the gas is rather limited. A particularly detailed one is presented in ref 13 for the nitration of benzene. In the reaction with “naked” NO_2^+ , the nascent product carries a large amount of excess energy. According to the present model, the nascent σ -complex is formed with a large excess of energy, and under collision-free conditions is expected to dissociate, so that the parent cation will not be observed. This is expectation fully satisfied experimentally. The σ -complex is found to dissociate to form either the PhH^+ ($m/z = 78$) + NO_2 or the NO_2^+ ($m/z = 46$) + PhH one, which are observed in the spectrum as the dominant peaks. Both channels are observed, as the relatively small difference in IPs of benzene and NO_2 makes them almost equally probable. The parent ion ($m/z = 124$) is not observed. When a “solvated” NO_2^+ was used (a cluster with CH_3NO_2), the mass spectrum changed significantly: the parent mass at 124 was clearly observed. In this case the nascent product is not as hot, and therefore the lower IP of

benzene leads to a pronounced increased formation of the PhH^+ ($m/z = 78$) + NO_2 pair over the NO_2^+ ($m/z = 46$) + PhH one.

Experimental production of “naked” protons is much harder. Cacace and Caronna⁴⁴ reported the reaction of HeT^+ with gaseous benzene and toluene. This helium–tritium ion molecule was formed by the radioactive decay of tritium hydride and is expected to react in a fashion similar to the naked tritium. The experiments were conducted at 110 C, at which the vapor pressure of the organic substrates was about 1 atm. Thus, in contrast with mass spectrometric conditions, in this case collisions are frequent. In the case of toluene, tritiated toluene was the major product, as expected for EAS reactions, benzene was a minor product. Positional selectivity was observed, with the ortho and para (major products) produced in almost equal amounts, meta products were found in three times lower yields. The results were rationalized by assuming the formation of a protonated σ -complex, which dissociates to form the substituted toluene. Positional selectivity was attributed to the preferential attack on the aromatic ring, and within the ring, on the ortho and para positions. These results are consistent with our proposal that the side-CI is of central importance in determining the fate of the attack.

V. Concluding Remarks

The present work provides a full portrayal of the potential energy diagram of EAS reactions by a systematic theoretical investigation of seven EAS systems in the gas phase. On the basis of the nature of the original system $[\text{ArE}^+]_0$, composed of an aromatic neutral and a charged electrophile, the reacting pair can be located either on an excited state or on the ground state surface. Subsequently, all EAS reactions are sorted into two classes. In the first class, the reaction begins on an excited state surface. Conical intersections (CIs), acting as effective funnels, connect the excited-state reactant with all the critical points on the ground-state potential surface. From the CI, both a polar path and a SET path are possible for the EAS reaction without a barrier. Which path is favored depends on the character of CI. The weak interaction between electrophile and substrate in the center-CI leads to the low substrate selectivity of reaction; whereas the more stable side-CI with an over-bond structure offers a possible explanation of the high positional selectivity of this class of EAS reactions.

The second class of EAS reactions is a purely ground-state process. The original system $[\text{ArE}^+]_0$ first relaxes to a π complex through weak interaction between neutral aromatic substrate and charged electrophile. Sequentially, a polar reaction path from the π complex is responsible for the producing of σ complex. In some case, for example, the nitration of benzene, a SET process starting from the stable π complex to form radical cation pair, and finally leading to the σ complex, competes with the polar reaction path. The competition between the two reaction paths is controlled by the factors that can accelerate or inhibit the new bonding after one-electron shift. The prevalent mechanism of EAS reaction in solution is expected to be basically a ground state event, as a result of preferential solvation of the electrophile.

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Supporting Information Available: Graphic showing the orbitals used for the active space and calculated structures of

some important species on the potential surface (e.g., π -complexes radical pairs, CIs). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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