

Ab initio studies of the bromination of benzene

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ABSTRACT: The reaction of elemental bromine with benzene was followed using *ab initio* modeling. Two mechanisms were considered as possibilities based in part on tradition and in part on more current experimental evidence. Consideration of transition state energy rules against the conventional picture involving direct formation of the Wheland intermediate via electrophilic attack by bromine. The preferred pathway is calculated to be through the cation–anion radical pair which then goes to the Wheland intermediate. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: benzene; bromination; *ab initio* modeling

INTRODUCTION

The subject of electrophilic aromatic substitution has a history extending back over ca 150 years. The mechanism(s) by which the reaction occurs has been well reviewed.¹ A recent edition of a popular introductory textbook, however, states: ‘Unlike simple alkenes, benzene fails to react with Br₂ or Cl₂.’ In fact, it has been known for some years² that bromine reacts directly with benzene in acetic acid as solvent. A summary of current thinking is given in Scheme 1. First recognized as a potential reaction intermediate, the σ -complex was initially proposed by Pfeiffer and Wizinger.³ Subsequently, Wheland⁴ carried out an early theoretical quantum mechanical study on the nature of this complex, now often referred to as the Wheland intermediate. Experimental data have now firmly established the existence of Wheland intermediates.⁵ When coupled with arguments based on the Pauling–Wheland⁶ theory of resonance, the concept has provided organic chemists with justifications when discussing the relative reactivity and directional preferences in a wide range of substituted benzenes and arenes in general.

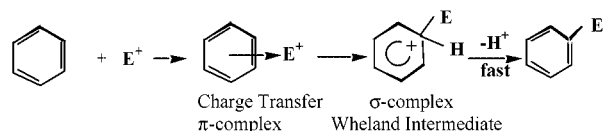
Dewar⁷ was the first to propose the formation of a charge transfer (CT) π -complex as a step on the substitution pathway. Over the years, the role of π -complexes has been extensively examined. Olah and co-workers⁵ made observations of rates and product distributions for the benzylation of various arenes supporting the role of the CT. More recently, Fukuzumi and Kochi⁸ carried out detailed spectral examinations of a wide range of arene donor–acceptor complexes. They noted^{8b} that for a series of arene halogenations and mecurations, the spectral CT bands decreased in direct

proportion to the rate of formation of the substituted products. The solvents employed were acetic and trifluoroacetic acid. Their data on this system were consistent with earlier studies.^{2,9}

In their studies, Olah and co-workers⁵ proposed that the complexes preceding formation of the Wheland intermediate may form a continuum of structures with varying degrees of π -complex to σ -complex character depending on the nature of the components and the solvent. Subsequent workers have embraced this concept.¹⁰ Hubig and Kochi¹¹ gave a very detailed experimental demonstration of the transition from a pure π -complex to a pure σ -complex.

It should be mentioned that the mechanism for alkene halogenation has many of the aspects just reviewed. Ruasse¹² provided experimental evidence that the bromination may proceed by two paths. Formation of a bromine–ethylene CT complex may precede the formation of the ethylene bromonium ion, or the reaction may go directly to the σ -complex (2-bromoethyl cation). The pathway depends both on the alkene structure and on the solvent polarity. Theoretical calculations relating to these mechanisms and including the role of the solvent have been published by Assfeld *et al.*¹³ and by Cossi *et al.*¹⁴ These studies provide an insight into possible routes to be modeled in studying the uncatalyzed reaction of bromine with benzene.

Recent computational work¹⁵ has supported the concept of a family of benzene complexes from the



Scheme 1

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extremes of the π -complex to the covalently bonded σ -complexes originally proposed as intermediates in aromatic electrophilic substitution.

COMPUTATIONAL METHODS

Calculations at the MP2/6-311++G** level were employed in the modeling of the transition from π - to σ -arene complexes.¹⁵ All structures here were optimized with Gaussian 98¹⁶ at the same level. It was established in the earlier study that basis set superposition error was of the order of 0.4–0.6 kcal mol⁻¹ (1 kcal = 4.184 kJ) with this basis set. Since the error in molecular energies is generally considered to be of the order of ± 2 kcal mol⁻¹ for single method calculations, no additional corrections for BSSE were carried out. Synchronous transit-guided quasi-Newton methods (QST2 and QST3)^{17,18} were used to obtain the required transition structure, which was refined and tested by frequency calculations (MP2/6-311++G**). Structures, vibrations and pertinent molecular orbitals were examined visually by Gaussview (Gaussian, Pittsburgh, PA, USA). The transition structure gave a single imaginary frequency with motions consistent with a valid transition structure (Fig. 1) for the reaction under consideration. Subsequently, frequency calculations were carried out for all structures at the HF/6-31G* level providing a thermal enthalpy and zero point energy corrections at 25 °C and following the precedent established by Curtiss *et al.*¹⁹

Corrections to the energies of pertinent structures due to the solvent dielectric constant (acetic acid, $\epsilon = 6.15$ D) were carried out using the isodensity surface polarized continuum model.²⁰ Charge densities were calculated from the electrostatic potential by the method of Merz and co-workers.²¹

Calculations via the polarizable conductor method (COSMO)²² were employed to determine the role of solute cavity formation in the solvent and the variation in dispersion energy for the various species in this study. For five structures containing one benzene moiety and one bromine equivalent, the average cavitation energy with average deviation was 15.01 ± 0.68 kcal mol⁻¹ and the dispersion contribution was -20.05 ± 1.45 kcal mol⁻¹. Since the interests in this study require only differences in energy between two structures, the cavitation and dispersion terms were considered to cancel out for the present purposes.

RESULTS AND DISCUSSION

The enthalpy values for all pertinent structures corrected to 25 °C and to the dielectric constant of acetic acid are given in Table 1. The reaction enthalpy change for the formation of bromobenzene and hydrogen bromide is exothermic by 17.2 kcal mol⁻¹. Before discussing poten-

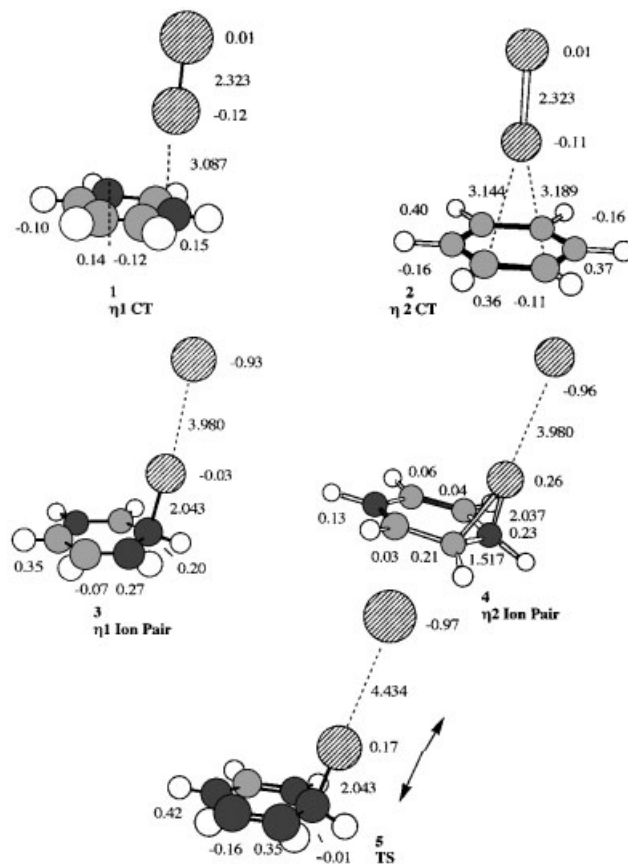


Figure 1. Ball and stick representations of the two CT complexes 1 and 2, the two ion pairs 3 and 4 and the transition structure 5. The double-headed arrow denotes the sense of the molecular vibration corresponding to the reaction coordinate. Bond distances (Å) and charges (e) are shown. The charges are C—H summed together

tial mechanistic pathways, four structures important to that discussion will be described.

In a recent study, the modeling of various electrophiles in forming complexes with benzene employed the MP2 method since it was important for dispersion forces not be neglected.¹⁵ The CT complex of bromine with benzene was initiated from a structure with the bromine axis placed parallel to the plane of the arene ring and 4 Å above the ring plane. The final η^1 structure is shown in Fig. 1 as **1**. This structure is 0.3 kcal mol⁻¹ above the enthalpy of the starting reagents. Since single method calculations are generally considered accurate within the range of ± 2 kcal mol⁻¹, caution should be observed with regard to the slight endothermicity calculated here. However, Fukuzumi and Kochi^{8a} reported that the formation constant for the bromine–benzene complex was too small for direct measurement.

The influence of the solvent is a matter of concern for any reaction in which polar species are involved. The principle solvent correction methods in Gaussian 98 employ variations of the polarized continuum model in which the shape and size of the solvent cavity are defined

Table 1. IPCM solvent-corrected energies plus thermal corrections to 25 °C for the various structures in this study at the MP2/6-311 ++ G** level^a

Species	Energy (hartree)
Bromine	-5144.968689
Benzene	-231.484962
Sum of bromine + benzene	-5376.453651
η^1 CT (1)	-5376.453217
η^2 CT (2)	-5376.458915
Wheland ion (6)	-2803.729083
Bromide ion	-2572.653818
Sum of 6 + bromide	-5376.382901
Wheland ion-bromide Ion pair (3)	-5376.395370
η^2 -Bromobenzonium ion (7)	-2803.713087
η^2 -Ion pair (4)	-5376.386880
TS to Wheland (5) ion pair	-5376.350447
Bromine anion radical	-5145.133013
Benzene cation radical	-231.218572
Sum of cation and anion radicals	-5376.351585
Bromobenzene	-2803.398244
Hydrogen bromide	-2573.082794
Sum of bromobenzene and HBr	-5376.481038

^a The numbers refer to the structures in Figs 1 and 2. Supplementary information can be obtained from author.

by the molecule under consideration. The external medium about the molecular cavity is given a uniform charge determined from the solvent dielectric constant. The interaction between the molecule and the external medium is then iterated until an energy minimum is reached. The isodensity polarized continuum method of Foresman *et al.*²⁰ was chosen for this study as a compromise between accuracy in modeling the cavity and computational time constraints. The Gaussian code at this point in time limits IPCM calculations by the MP2 method to single point calculations. Indeed, the IPCM method will not perform optimizations in the solvent cavity by any method. To surmount this difficulty for cases where optimization in the cavity was desired, the polarized continuum method (PCM) of Miertus and Tomasi²³ was employed using the HF/6-31 + G* method. Single point calculations were then done on these structures at the MP2/6-311 ++ G** level as reported in Table 1.

An earlier study established that the energy change upon dissolving arenes in solvents of low dielectric constant is fairly small.²⁴ The amount of charge transferred in forming **1** is of the order of 0.1 e, and the solvent-corrected energy was found to be only 0.2 kcal mol⁻¹ below the energy determined in a vacuum. The question of a change in the geometry of **1** by interaction with the solvent was addressed by optimizing the structure in the solvent cavity employing HF/6-31 + G* for the calculation. The only perceived change was 0.1 Å in the C—Br bond length. The change in the Br...Br distance was nil. The adjacent bromine, C-1 and C-4 define a plane of symmetry for the ring with the

calculated atom charges (Fig. 1) symmetrically distributed.

During the course of the earlier study, Vasilyev *et al.*²⁵ reported the low-temperature x-ray structure of the CT complex of bromine and benzene. The structure indicated the bromine to be located above one of the C—C bonds with C—Br distances of 3.36 and 3.18 Å, respectively. They described this structure as having a hapticity of $\eta = 1.52$. The x-ray structure served as a starting point for an optimization pictured as **2** in Fig. 1. With trivial variations in the third decimal place, the C—C bonds in the ring are all 1.40 Å, the same as for benzene. The calculated C—Br bond lengths (3.14 and 3.19 Å) have shifted towards a near η^2 structure. In both **1** and **2** the Br—Br distance has elongated from the isolated Br—Br distance of 2.284 Å to 2.323 Å. Vasilyev *et al.*²⁵ reported this distance in their crystal structure as 2.303 Å and pointed out the sensitive response of this bond length to the state of bromine coordination. Small differences between x-ray bond lengths and those from *ab initio* calculations are to be expected as the former measure centers on electron density whereas the latter calculates nuclear separations.

The MP2 structures for the Wheland intermediate ions **6** and **7** are shown in Fig. 2. The bond lengths for **6** are consistent with the resonance structures that one can write for the pentadienyl cation. Foresman and Frisch²⁶ have pointed out that agreement among the various methods for calculating atomic charges is often better achieved by employing group charges (C—H in this case). This method of comparison has been used here throughout. The atomic charges for **6** correspond to the possible resonance structures for the ion with virtually no charge on the attached bromine. In contrast, the η^2 -bromobenzonium ion **7** shows a considerably larger amount of charge on the bromine. The C—C bond in the three-membered ring is close to that expected for an sp³—sp³ single bond. The other ring-carbon bond lengths are alternating sp²—sp² single and double bonds. Ion **7** is

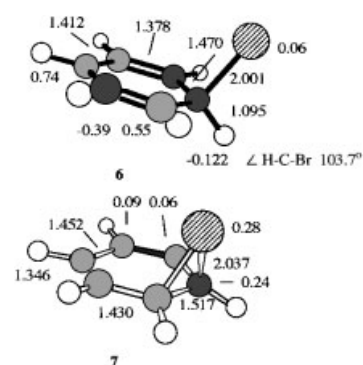


Figure 2. The Wheland ion **6** and the Olah bromobenzonium ion **7** showing bond lengths (Å) and atomic charges (e). The charges shown are the sums for each C—H combination

5.4 kcal mol⁻¹ higher in energy than ion **6**, presumably owing to the strain of the three-membered ring.

Intuitively, one might expect the first-formed Wheland intermediate to exist as a tight ion pair in the low dielectric constant of acetic acid. Initially it was assumed that the bromide ion would be as close as the van der Waals contact distance (3.98 Å) to the ring-bound bromine. The contact distance was determined by importing the MP2 geometries into graphical CPK models in the program SPARTAN (Wavefunction Inc., Irvine, CA, USA). This structure is shown as **3** in Fig. 1. As can be seen, the added bromine has taken on the aspects of a bromide ion with a charge of -0.93e. It was necessary to fix this distance as otherwise the optimization of the ion pair resulted in the formation of bromobenzene and hydrogen bromide.

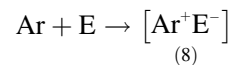
The first test of structure **3** was carried out by a series of single point MP2 calculations in which the Br...Br distance was increased over a range of values keeping a linear arrangement the C—Br...Br atoms. This process requires that Coulomb work be done to separate the ionic charges. As expected, the energy of these structures increased in a regular fashion above that given for **3**.

The arene ring of **3** in Fig. 1 carries the bulk of the the positive charge and only a trivial amount is on the bound bromine. Again, a series of solvent-corrected MP2 calculations were carried out with the bromide ion at various distances along the original benzene sixfold axis. It was necessary to fix each of the trial distances as otherwise the structures spontaneously formed *syn*-1,4-dibromo-2,5-cyclohexadiene. The closest approach of the bromide ion was just above the π -charge cloud. This structure poised at 3.5 Å above the ring plane represented the lowest energy in this series but was still at a higher energy than that for **3**. In a similar fashion, an ion pair was generated from the benzenium ion **7**. The optimized energy for this structure **4** (Fig. 1) is still 5.4 kcal mol⁻¹ above **3**, presumably owing to ring strain.

The transition structure (TS) for the direct conversion of starting materials to the ion pair **3** was obtained by synchronous transit-guided quasi-Newton methods.^{17,18} Shown in Fig. 1 as **5**, the imaginary vibration corresponding to the reaction coordinate showed a stretching mode involving the C...Br...Br structure as shown. Since the MP2 method would not allow optimization of **5** in the solvent cavity, a series of solvent-corrected HF/6-31 + G* single point calculations with accompanying frequency calculations were carried out by incrementing the C—Br bond length by 0.1 Å from 1.94 to 2.54 Å. The structures with C—Br at 1.94, 2.04 and 2.14 Å all displayed one negative frequency. While the energy surface at these adjacent points indicated an almost flat profile, all points other than the found TS (C—Br 2.043 Å) were of a higher energy, confirming **5** as the correct TS. As Fukuzumi and Kochi^{8b} pointed out, it is not possible to declare unequivocally that the CT(s) are directly on the reaction path from starting materials. The

similarities in energies for the starting materials compared with CTs **1** and **2** render the question of which lies on the reaction path moot.

Finally, the complete transfer of an electron from the benzene to bromine would result in the formation of a radical ion pair. Fukuzumi and Kochi^{8b} wrote the expression for this process as follows:



Further, they proposed that 'the ion pair [Ar⁺E⁻] is a reasonable approximation to the transition state for electrophilic aromatic substitution.' They pointed out that the radical ion pair is attained in an adiabatic process, which would require a change in solvation energy, while the formation of the CT is a vertical Franck–Condon transition requiring at best a minimal solvation change. In going from the energy calculated in a vacuum to the solvent-corrected energy, the CT energy is lowered by 0.9 kcal mol⁻¹ while the solvent change in energy for the ion pair **3** is -35.6 kcal mol⁻¹.

The energy determination for the radical ion pair **8** starts with the solvent-corrected values for the individual radicals (see Table 1). Comparison of the isolated Wheland ion **6** and the bromide ion with the ion pair structure **3** shows a difference in energy due to Coulombic interaction of 7.8 kcal mol⁻¹. The magnitude of this correction was confirmed by calculating the energies in acetic acid for the lithium and fluoride ions at infinity versus the LiF ion pair. The found Coulomb energy difference was 12.8 kcal mol⁻¹, the higher value being consistent with a stronger solvent interaction with the smaller, less polarizable inorganic ions.

Two mechanisms employing the entities just described may be considered. The first of these is the conventional early picture in which the arenes and the electrophile collide, forming the Wheland ion pair intermediate that collapses to the reaction products. The TS for this process is shown as **5** in Fig. 1. The activation enthalpy as shown in Fig. 3 is 64.7 kcal mol⁻¹. With benzene there is no way to determine what role, if any, the η^2 structure **4** plays in this process. However, Olah^{5b} had proposed such an intermediate as a possible explanation for his observations of low substrate but high positional selectivities in highly exothermic electrophilic aromatic substitutions.

The second pathway follows from the mechanism put forth by Fukuzumi and Kochi.^{8b} The cation–anion ion radical pair forms either directly from the reactants or the CT complexes yielding **8**, a process requiring 55.2 kcal mol⁻¹. Given that the activation enthalpy from CT **1** may be slightly less in energy than from the neutral starting materials and that partial electron transfer has already occurred, it is tempting to postulate that **1** is on the reaction path. Certainly this possibility is consistent with their observations that the rate of disappearance of the CT spectral bands coincides with the rate of

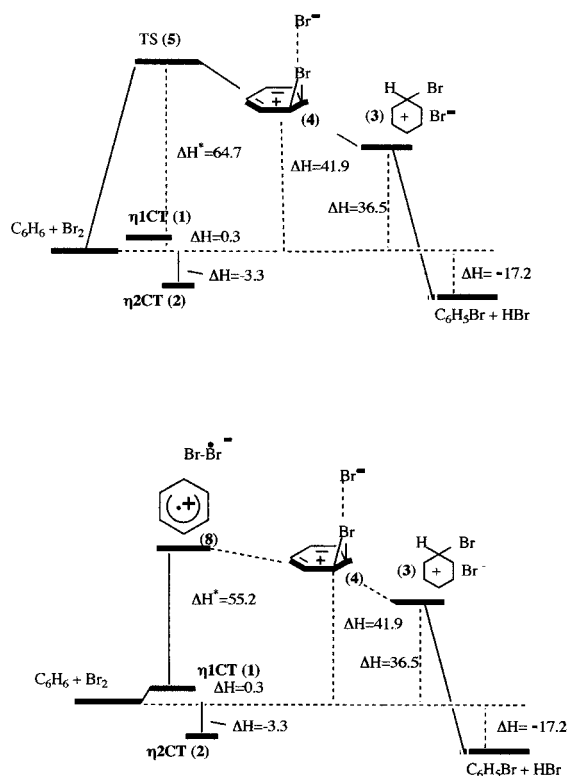


Figure 3. Energy diagram for two possible mechanisms. Energies are in kcal mol⁻¹. Structures are numbered as in Fig. 1

bromination. The intermediate **8** then collapses either directly to ion pair **3** or passes through the η^2 -ion pair **4** to **3**. Recently, it has been mentioned that a transition state may exist between the cation–anion radical pair and the formation of the Wheland intermediate (J. K. Kochi, personal communication). This matter is currently under examination.

The application of the cation–anion radical pair mechanism to the bromination of toluene was modeled by attaching a methyl group to the ring in structure **4** first at **C-3** and then at **C-4**. The resulting two structures were then optimized (MP2/6–311 ++ G**), yielding the two CTs **9** and **10** shown in Fig. 4. These structures were then carried through the cycle of calculations corresponding to those in the lower half of Fig. 3. The relevant energies including the two Wheland intermediates are shown in Fig. 4. These results are consistent with Olah's thinking in that the formation of the radical ion pair from toluene involves less energy than that for benzene and the formation of *o*-bromotoluene is favored over the *meta* isomer. The reaction enthalpies forming CTs **9** and **10** are -5.5 and -5.6 kcal mol⁻¹, respectively.

It is less clear in the toluene case what role the CT may play, as several geometries may be conceived from the starting materials. Two computational experiments were carried out exploring these CTs. In the first the bromine was placed at 4 Å above and parallel to the ring and

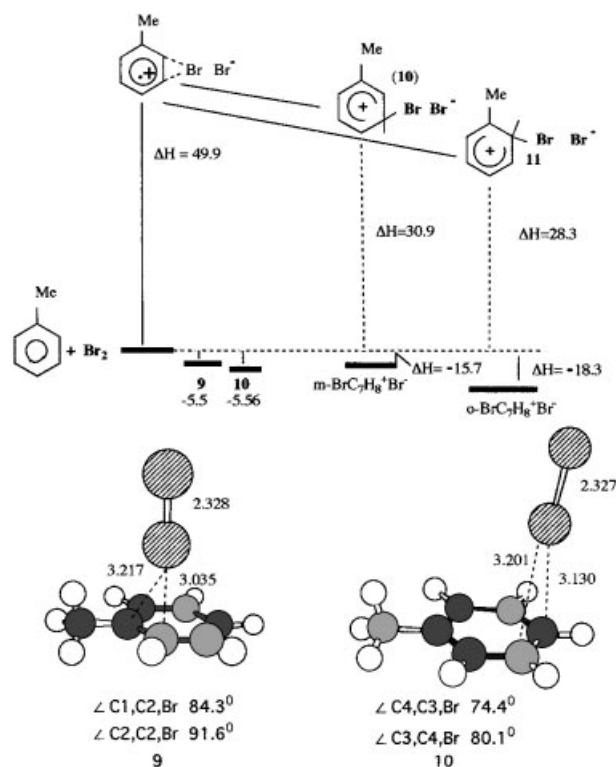


Figure 4. Energy diagram for the bromination of toluene (above) and the structure of toluene CTs (below)

aligned forming a plane with CH₃...C-1...C-4 and poised over the CH₃—C1 bond. The course of the optimization was followed with Gaussview. The bromine molecule turned out as shown as **9** in Fig. 4. This CT was clearly the η^1 -complex. For the second experiment the bromine was translated to a position midway over C-4. The resulting CT was identical with **10** also shown in Fig. 4. CT **10** appears closer to a true η^2 -complex although the bromine is marginally closer to C-4 than to C-3. The amount of charge transferred in each case was 0.1e. The formation of both CTs is exothermic, in contrast to the benzene case. However, this difference is on the borderline of computational accuracy, and mechanistic conclusions are subject to reservations.

In summary, the study of the two most likely pathways for the direct reaction of bromine with benzene supports the conclusion of the lower energy path to be via the formation of a cation–anion radical pair that collapses to the Wheland ion–bromide ion pair and then to products. The lower energy of formation of the toluene–bromine radical ion pair is consistent with expectations regarding the greater reactivity of toluene. The lower energy of formation of the two CTs studied here is also consistent with expectation.

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