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LETTERS

Role of Lewis Acid($AlCl_3$)−Aromatic Ring Interactions in Friedel−Craft's Reaction: An ab Initio Study

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Electrophilic aromatic substitution reactions, which are highly exemplified by the widely used Friedel-Craft's reaction, have been extensively studied using theoretical and experimental techniques. A number of elegant mechanisms have been proposed for the Friedel-Craft's reaction till date. In all the proposed mechanisms, the role of the Lewis acid has been limited to the generation of the electrophile, which subsequently attacks the aromatic system to form either a π or a σ complex. A recent experimental report on the reaction of CO with benzene in zeolite catalysts intrigued us because the presence or absence of $AlCl_3$ was found to govern the reaction product. These clearly indicated that $AlCl_3$ has an additional role in the reaction. We probed this role theoretically by performing high-level ab initio calculations on two model systems $C_6H_6-BCl_3$ and $C_6H_6-AlCl_3$. Our results clearly indicate that one of the benzene carbon tends to become highly nucleophilic, thereby facilitating an attack by an incipient electrophile. There appear unusual molecular orbital interactions including the loss of the benzene nodal plane and back-donation from Cl 3p orbital to the benzene HOMO. In what could be the first high-level theoretical study of Lewis acid−aromatic reactions, we believe our results could help understand the nature of the intermediates in electrophilic aromatic substitution reactions.

The ubiquitous role of novel interactions involving aromatic rings in a number of disparate fields is amply evident from recent literature.[1−3] A recent report on the production of speciality chemicals such as benzaldehyde and benzoic acid from benzene and CO using zeolites as acid catalysts sparked our interest on the role of Lewis acid−aromatic ring interactions, as the presence or absence of $AlCl_3$ (a strong Lewis acid) seems to govern the reaction product.[4−8]

On the other hand, elegant mechanisms have been proposed and investigated for the century-old Friedel−Craft's reaction.[9−11] It is interesting to note that, in all the mechanisms proposed to date, the role of Lewis acid-aromatic substrate interactions has never been considered. Since to our knowledge there has been no theoretical study of Lewis acid−aromatic substrate interactions, we theoretically examined whether the role of the Lewis acid in Friedel−Craft's reaction is limited to the generation of the electrophile or an additional role of activation of the aromatic substrate exists. Our calculations on two model systems $C_6H_6-AlCl_3$ and $C_6H_6-BCl_3$ give unequivocal evidence of such a role. That this role is independent of the kind of Lewis acid employed is evident from similar conclusions obtained from calculations performed on different Lewis acids. Additionally, in a recent theoretical study on the affinity of Lewis acids towards nucleophilic agents, it had been pointed out that the electronic structure of the Lewis acid is not sufficient to determine a priori the affinity towards nucleophilic agents. The nature of the nucleophilic agent was also expected to play a role. Our study suggests that in addition to the above two factors, the relative orientation of the Lewis acids also plays a major role in determining this affinity (Figure 1).[12]

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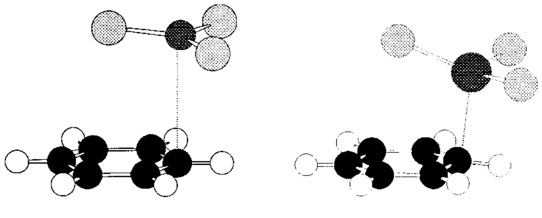
TABLE 1: MP2-Predicted Interaction Energies, Selected Distances, and NPA Charges[a]

	6-31+G*		6-311++G**		6-311++G(3df,2p)[b]
	BCl_3	$AlCl_3$	BCl_3	$AlCl_3$	$AlCl_3$
$-\Delta E_e$	7.13	17.22	8.92	19.00	20.46
$-\Delta E_e^m$	4.46 ± 2.68	12.56 ± 4.66	5.63 ± 3.30	13.74 ± 5.26	16.81 ± 3.65
$-\Delta E_{cor}$	9.47	13.11	11.92	14.96	17.54
$-\Delta E_{es}$	1.27	20.64	1.17	16.23	17.04
$R_{Al/B-C}$	3.256	2.384	3.223	2.384	(2.384)
$R_{Al/B-Cl}$	1.731/1.740	2.095/2.105	1.734/1.743	2.091/2.100	(2.091/2.100)
q(C···Y)	−0.261	−0.447	−0.215	−0.391	−0.394
q(C)	∼−0.241	∼−0.209	∼−0.198	∼−0.165	∼−0.169
q(Cl on Φ)	−0.086	−0.505	−0.092	−0.475	−0.492
q(Cl)	−0.10501	−0.514	−0.110	−0.484	−0.500
q(Y)	0.291	1.403	0.306	1.309	1.361

[a] Energies in kcal/mol. Distances in angstroms. NPA charges in atomic units. $-\Delta E_e$ represents the binding energies without basis set superposition error (BSSE) correction. $-\Delta E_e^m$ represents the median value of the BSSE-uncorrected and BSSE-corrected binding energies as the upper and lower bounds, respectively. The electron correlation energy ($-\Delta E_{cor}$) is the value of the E_e(MP2) subtracted by E_e(HF) at the MP2, optimized geometry. $-\Delta E_{es}$ is the electrostatic (charge−charge) interaction energy evaluated using NPA charges. $R_{Al/B-C}$ and $R_{Al/B-Cl}$ are the distances from B or Al to the C or Cl atoms, respectively. All conformers have C_s symmetry. q(C···Y) represents the charge of C closest to B or Al. q(C) represents the charges of the remaining five C atoms. q(Cl on Φ) represents the charge of the Cl atom lying on the plane of the benzene ring. q(Cl) represents the charges of the remaining two Cl atoms. q(Y) represents the charges of Al or B. [b] MP2/6-311++G(3df,2p)//MP2/6-311++G**.



1 (C_6H_6-BCl_3) **2** (C_6H_6-$AlCl_3$)

Figure 1.

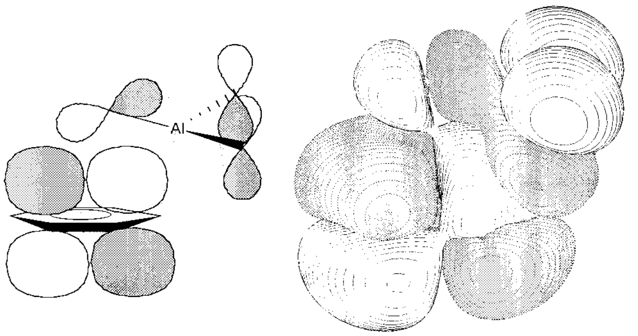


Figure 2. The second HOMO of **2** at the MP2/6-311++G** level. The eigenvalue of the first two HOMOs are nearly degenerate, but the second HOMO exhibits the transfer of charge. Contour level: 0.005 e/au^3.

High level ab initio calculations of C_6H_6−$AlCl_3$ and C_6H_6−BCl_3 have been performed on conformers **1** for BCl_3 and **2** for $AlCl_3$ at the Møller−Plesset second-order perturbation theory (MP2) (Table 1).[13]

It can be seen from Table 1 that, in conformer **2**, Al is very tightly bound to the benzene carbon with an Al−C distance of 2.35 Å. The binding energy of ∼20 kcal/mol, which is predominantly due to electrostatic interactions, suggests a strong charge-transfer stabilization, while the electron correlation energy is compensated by exchange repulsion.[14] Consequent to one of the referee's suggestions, we have carried out a geometry optimization of the C_6H_6−$AlCl_3$ complex at the MP2/6-311++G** level incorporating BSSE corrections. We have found that a 50% BSSE correction[15] improves the interaction energy by only 0.15 kcal/mol, while the intermolecular distance increases by 0.06 Å. Calculations on the C_6H_6−H_2O complex by us had revealed that a 50% BSSE correction led to reliable results which are in agreement with experiment.[2e] Given the magnitude of the total interaction energy and the extremely short distances involved in the C_6H_6−$AlCl_3$ complex, we believe that BSSE corrections are not significant for this particular complex. On the other hand, in conformer **1**, B is less tightly bound to the benzene carbon and the binding (∼9 kcal/mol) is predominantly due to correlation, as the exchange repulsion would be negligible owing to the large B−C distance (3.22 Å) (Figure 2).

In the monomeric state, $AlCl_3$ and BCl_3 possess the D_{3h} geometry. However in the complexed state, the acceptance of charge from benzene leads to a distortion in the geometry. The high charge of Al leads to the close approach of $AlCl_3$ to C_6H_6 with a massive transfer of charge from C_6H_6 to $AlCl_3$, resulting in the pyramidalization of $AlCl_3$ (∠Cl−Al···C = ∼98°). Such a transfer would entail a partial loss of aromaticity in benzene. This is evident from the HOMO displayed in Figure 2. It can be clearly seen that there is a loss of the benzene nodal plane. A similar loss of the benzene nodal plane is observed in the HOMO of protonated benzene.[16] However, a σ bond is eventually formed in that case. This unique loss of the benzene nodal plane in **2** is very novel in a stable complex (Al does not form a σ bond with benzene eventually). The reason for the remarkable stability of this complex inspite of the loss of the benzene nodal plane is due to a unique back-donation of charge from the chlorine 3p orbital to the benzene HOMO (see Figure 2).[17] As a result of this back-donation, the loss of aromaticity in benzene is prevented and an additional stability of the complex is ensured. A similar phenomena is observed in the C_6H_6−BCl_3 complex. The contribution of this back-donation to the overall stability of the complex is partial because of the low electrostatic contribution and the longer distance between the boron atom and benzene. The longer distance also ensures that pyramidalization in BCl_3 is minimal (∠Cl−B···C = ∼91°).

One of the major outcomes of this strong interaction of $AlCl_3$ with C_6H_6 is that the carbon atom of benzene which is closest to the Al atom becomes highly nucleophilic. This is clearly demonstrated in Table 1 wherein the partial charges of all the carbons of benzene in C_6H_6−$AlCl_3$ complex are given (−0.39 au for the carbon closest to Al and −0.16 au for all the other carbons). It should be noted that the charges of the hydrogens are nearly equivalent in both conformers. The strong binding energies of these complexes would lead to an increase in the nucleophilicty of the aromatic carbon, and as a result, one would expect that the activation energy of the aromatic substrate−electrophile interaction would be significantly lowered.

Further evidence for our contention are the benzene−Lewis Acid and Lewis Acid−proelectrophile distances and energies. In the cases of CO (which is a proelectrophile) and BF_3, the experimental B−C distances are 2.886 Å.[18] Our calculations at the MP2/6-311++G** level on the BF_3−CO and C_6H_6−BF_3 gives B−C distances of 2.882 and 2.988 Å, respectively. On a similar note the Al−C distances obtained from calculations on $AlCl_3$−C_6H_6, $AlCl_3$−CO, $AlCl_3$−CH_3Cl at the same level of theory are 2.352, 2.212, 3.300 Å, respectively. The binding energies (BSSE uncorrected)[14] for C_6H_6−$AlCl_3$, $AlCl_3$−CO, and $AlCl_3$−CH_3Cl are 19.00, 14.10, and 3.33 kcal/mol, respectively. Thus, in the absence of any external source of energy, the Lewis acid−aromatic ring interaction energies are stronger than the Lewis acid−electrophile energies.

It should be noted that this Lewis acid−aromatic ring interaction would be significant even in the actual reaction conditions. A typical Friedel−Craft's reaction mixture involves the following components: the substance to be substituted, the reagent which supplies the substituent, a catalyst; a solvent (in most an excess of the substrate or reagent or a nonionizing solvent); subsituted product; and the by product (conjugate acid).[9] Therefore, in a case where benzene is being substituted, benzene itself is used as an solvent. In a recent paper we had evaluated the interaction energies per benzene pair in solution to be about 3 kcal/mol.[3e] Given the interaction energy of two benzene molecules to be about 2 kcal/mol in gas phase, we would only have an interaction energy of 5 kcal/mol. Given the magnitude of the evaluated Lewis acid−aromatic ring interactions in the gas phase, we believe that these interactions would be significant in the actual reaction conditions.

In conclusion, we present for the first time, theoretical evidence that Lewis acids in addition to generation of the electrophile also have an important role in the activation of the aromatic substrate prior to attack by the electrophile. Our results therefore might help explain the presence of different reaction products in the presence/absence of Lewis acids ($AlCl_3$).[4]

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(13) From an evaluation of various possible orientations of BCl_3 and $AlCl_3$ toward C_6H_6 followed by geometry optimizations at the MP2/6-31+G* and MP2/6-311++G** levels, conformer **1** for BCl_3 and **2** for $AlCl_3$ are found to be the lowest energy structures. Thus, only **1** and **2** are discussed in this study, since these are chemically most relevant. All calculations were performed with a Gaussian 94 suite (Frisch; et al. *Gaussian 94*; Gaussian, Inc.: Pittsburg, 1995).

(14) It can clearly be seen that ΔE_e remains somewhat constant regardless of the basis set employed. The exchange energy (ΔE_{exch}) is estimated to be −14 kcal/mol ($\Delta E_{exch} \approx \Delta E_e - \Delta E_{cor} - \Delta E_{es}$; see Table 1 for notation).

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