Lewis Acidity Trend of Boron Trihalides: If Not π Back-Bonding, What Else?

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Abstract

Lewis acidity trend of boron trihalides is a subject that has received a variety of explanations, and still the simple π back-bonding based one is believed by most, perhaps because of its simplicity, irrespective of opposing findings. Herein we try to give an alternative explanation based on qualitative Molecular Orbital (MO) theory, and support that quantitatively by Generalized Kohn-Sham Energy Decomposition Analysis. While the role of orbital overlap on the orbital interaction energy is widely known, the role of electronegativity of the atoms involved is often overlooked. Here we find that the Lewis acidity trend of boron and aluminum halides can be explained by the Wolfsberg-Helmholz (W-H) formula for resonance integral . The MO theory based predictions are valid only when the orbital interactions are strong enough. In the weakly interacting systems the effect of orbital interactions can be overshadowed by other effects such as Pauli repulsion, dispersion etc. Thus the Lewis acidity trend of boron and aluminum halides can vary depending on the strength of interacting Lewis base. We believe that this work would enable one to gain a better understanding not only on the Lewis acidity of boron trihalides and its heavy analogs, but also on a variety of related problems such as the stronger π acidity of CS compared to CO and weaker π bonding between heavy atoms.

Introduction

Trivalent boron compounds are archetypal Lewis acids and are widely used in synthetic chemistry as catalysts and reagents.[1–6] "Lewis acidity" is the property that makes them very attractive for experimental chemists, while the same property poses a challenge to theoreticians. From the experimental data, the relative Lewis acidity of BX_3 (X = F, Cl, Br, I) is $BF_3 < BCl_3 < BBr_3 < BI_3$. This trend is opposite to what one would expect based on electronegativity. Electronegative halogen atoms make B more positive, and hence one anticipates that BF_3 will be the strongest Lewis acid in the series.[7] There are a number of explanations for this anomalous trend, each of which differ, at the same time, all makes sense.[8–12] In other words there is no consensus among scientists regarding this. Nevertheless, the basic inorganic textbook explanation based on π back-bonding remains as the widely believed one.[13]

The unhybridized p orbital on B atom in boron trihalides interact with the lone pairs on the X atoms via lateral overlap; this is the so called π back-bonding. Since B and F have 2p as the valence p orbitals, their overlap in principle should be much more effective. While overlap between 2p of B and p orbitals of Cl, Br, I with higher principal quantum number will be less. The consequent large electron density shift from F to B makes BF_3 less Lewis acidic. This is the most commonly accepted explanation for the lower Lewis acidity of BF_3.

Strength of π back-bonding in planar BX_3 has impact on the energy needed to bring the boron trihalide from its original planar geometry to the final pyramidal structure in the complex. Stronger B-X π bonding will not favor pyramidalization. This will make BF_3 the weakest acid in the series.[14] Though the π back-bonding based explanation is very much conceptually appealing, there are opposing findings. Extended Hückel theory based calculations showed that the perpendicular p orbital on B in BF_3 is more electron-deficient than that in BCl_3.[15] A study by Brinck and coworkers showed that the π back-bonding is actually better in BCl_3 than in BF_3 and that the B in BF_3 is much more positively charged than that in other boron halides, which is against the π back-bonding concept. They found that the ability to accept charge increases in the order $BF_3 < BCl_3 < BBr_3$ and explained the anomalous Lewis acidity trend in terms of charge capacity K, defined by:

$$K = \left(\frac{1}{I - A}\right)$$

where I and A denote the ionization potential and the electron affinity.[16]The value of K was found by using experimentally determined I and A; higher the charge capacity, better will be the Lewis acidity. Also it was shown that the π-donor strength of the halogens in AX_3 and EX_3^+ (A=B-Tl; E=C-Pb) is in the order F < Cl < Br < I.[17]

Gillespie *et al* and Branchadell *et al* have explained the Lewis acidity trend based on the energy cost for pyramidalization–the distortion that would accompany the complex formation with the donor.[4,18] They have reported that the pyramidalization energy is higher for BF_3, which makes it lesser acidic. The work of Gillespie *et al* also contradict the explanation based on charge capacity by showing that BF_3 accepts more electron density from the donor moieties. While the work of Brinck *et al* contradicts the pyramidalization energy based arguments by showing that the pyramidalization energies of BF_3 and BCl_3 are nearly the same if we use the BX_3 fragment in BX_3-base complex.[16]

Frenking *et al* have reported that the higher Lewis acidity of BCl_3 compared to BF_3 is due to its low-lying LUMO, which results in enhanced orbital interactions with the donor.[19] We wondered what is the factor that is responsible for raising the energy of BF_3 π^* and lowering the energy of BCl_3 π^*. Whatever the factor is, its involvement is not limited to boron halides. For example, why CS is a stronger π-acceptor than CO is a question similar to why BCl_3 is a stronger Lewis acid than BF_3.[20,21] We also wanted to know why the Lewis acidity trend is just opposite for heavy group 13 trihalides such as AlX_3. In this work we try to provide a conceptual understanding of the unexpected Lewis acidity trend of boron trihalides and aluminium trihalides via both qualitative and quantitative arguments.

Methodology

All the results in the discussion are based on calculations at PBE0/Def2-TZVP level of theory using Gaussian 16 program.[22,23] Computations with M06-2X functional gave similar results and are given in the supporting information.[24] Natural orbital for chemical valence (NOCV) calculations were done using Orca 4.2, to get an estimate of the orbital interaction energy.[25,26] Visual inspection of molecules and molecular orbitals are done using Chemcraft and Avogadro.[27,28] Generalized Kohn-Sham Energy Decomposition Analysis (GKS-EDA) as implimented in GAMESS was used for dissecting the interaction energy to the physically meaningful terms such as electrostatic, exchange, repulsion, polarization and electron correlation energies.[29–32] The reaction energetics reported are Gibbs free energy with thermal corrections corresponding to 298.15 K.

Results and discussion

In terms of electronegativity perturbation, one would have anticipated that the π^* of BF_3 will be more stable than that of other boron halides.[33] The effect of electronegativity perturbation can be seen when we compare C_2H_2, HCN and CO. The stability of π^* orbitals follows the order C_2H_2 < HCN < CO (Table 1). However, the electronegativity perturbation based explanation fails when elements of different periods are compared, such as CO and CS, or BF_3 and BCl_3. Why the LUMOs of CS and BCl_3 are lower than those of CO and BF_3 respectively? In general, we can see that the splitting between the bonding and antibonding levels decrease with increase in the size of atoms involved (comparison should be made between different periods). Thus CO, BF_3, C_2H_4, C_2H_2 have their π^* levels higher in energy than that of CS, BCl_3, Si_2H_4 and Si_2H_2 respectively. Similarly, C_2H_4 π^* is higher in energy than $CH_2 = SiH_2$.The $\pi - \pi^*$ splitting and the LUMO energy values of the above mentioned compounds are tabulated in Table 1. It is as though, the splitting decreases with increase in bond length, one immediate analogy we can make with the simple particle in a box model. The larger the length of the box (bond length + half the radius of the bonded atoms), the lesser is the splitting of energy levels. A schematic diagram showing the π-π^* splitting in BX_3 is shown in Fig. 1. The larger splitting of BF_3 makes the LUMO very unstable, and hence a bad acceptor of electrons. The small splitting in BI_3 makes its LUMO a strong acceptor.

Table 1: π−π^* splitting, LUMO energy and bond length of BX_3, AlX_3 and some simple π-systems

Molecule	π-π^* separation (eV)	π^*energy (eV)[LUMO+1 for AlX_3]	Bond length (Å)
$CH\equiv CH$	9.30	0.88	1.20
$HC\equiv N$	10.75	0.32	1.15
$C\equiv O$	12.90	-0.62	1.12
$C\equiv S$	7.80	-2.31	1.53
$CH_2=CH_2$	8.04	0.14	1.32
$CH_2=SiH_2$	5.39	-1.23	1.70
$SiH_2=SiH_2$	4.10	-1.98	2.14
BF_3	15.9	0.46	1.31
BCl_3	9.96	-1.69	1.74
BBr_3	8.58	-2.10	1.90
BI_3	7.01	-2.51	2.11
AlF_3	12.64	-0.08	1.63
$AlCl_3$	9.35	-1.12	2.07
$AlBr_3$	8.24	-1.48	2.23
AlI_3	6.88	-1.90	2.45

As we know, resonance integral ($H_{\mu\nu}$) is the measure of the interaction energy of two overlapping orbitals, μ and ν. The Wolfsberg-Helmholtz (W-H) formula for resonance integral will help us gain more insight on the problem. The stabilization of the bonding orbital or the destabilization of the antibonding orbital is proportional to the resonance integral. The W-H formula is:[34]

$$H_{\mu v} = \frac{1}{2} K(H_{\mu\mu} + H_{vv}) S_{\mu v}$$

where K is the constant of proportionality, and $H_{\mu\mu}$ and H_{vv} are the coulomb integrals for the electron in the atomic orbital μ and v respectively and the negative of which are measures of their ionization potentials and hence electronegativity. Thus, for bonds between electronegative atoms, the resonance integral will be very large, even if the overlap is small, resulting in large splitting of bonding and anti bonding orbitals. However in order to achieve the same amount of splitting, less electronegative atoms should undergo significant overlap. In other words, even if the overlap in BF_3 and BCl_3 are same, the splitting between the BMOs and ABMOs will be more in the former. For π bonds, since the overlap is not very good, the separation of bonding and anti bonding MOs is likely to be decided by the sum of coulomb integrals (electronegativity).

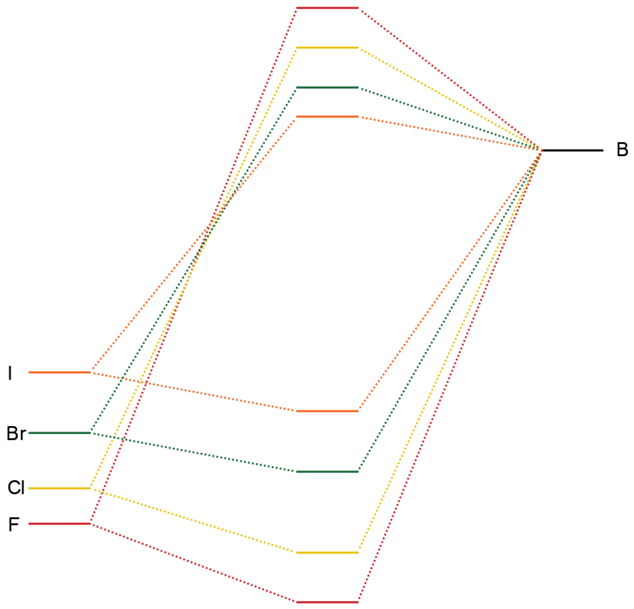

Figure 1: Schematic representation of the π-π^* splitting in BX_3

To get more insight, we performed Generalized Kohn-Sham Energy Decomposition Analysis (GKS-EDA) of EX_3 (E = B, Al) by taking EX_2 as one fragment and X as second fragment (Fig. 2). The total interaction energy decreases as we go from EF_3 to EI_3–so is the polarization energy (orbital relaxation energy or orbital interaction energy). Stabilization due to polarization seems proportional to the electronegativity of the atoms involved.

The electrostatic energy is the Coulomb interaction energy between the fragments with frozen orbitals (not polarized). It includes both the attractive and repulsive interactions between the two fragments. It makes sense to assume that the electrostatic attraction

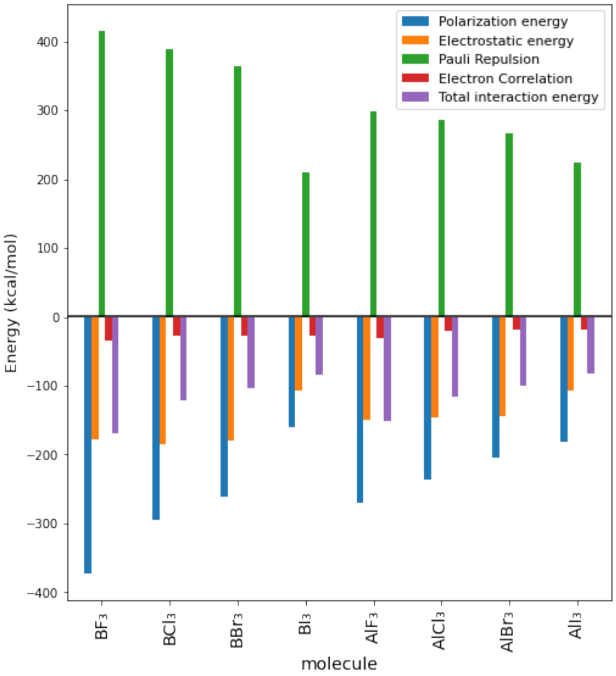

Figure 2: GKS-EDA for the interaction between EX_2 and X fragments in EX_3 (E = B, Al, X = F to I)

between BX_2 and X in BX_3 will be in the order $BF_3 > BCl_3 > BBr_3 > BI_3$, as the positive charge on the B decreases in the same order. The nuclear repulsion should follow the same order due to the same reason. Also, as the screening of nuclear charge is more in heavier atoms, the nuclear repulsion tend to decrease when larger atoms are involved. So, it is not really possible to have a beforehand prediction on the trends in the electrostatic energy. The Pauli repulsion term (sum of exchange energy and repulsion energy) is a destabilization term arising from the antisymmetric nature of the wave function (monomer wave functions are frozen). See Table S1 in Supporting Information(SI) for the exchange and repulsion components of Pauli repulsion. Exchange energy implicitly depends on the overlap. Size match will be a crucial factor here. Notice that exchange energy decreases from BF_3 to BI_3, whereas for AlX_3, the order is $AlF_3 < AlCl_3 > AlBr_3 > AlI_3$, suggesting that the size match is better with BF_3 and $AlCl_3$ (Table S1). Though size match is better with $AlCl_3$, polarization energy is more for AlF_3, confirming that it is not only the overlap that matters, but also the electronegativity of the atoms involved; this provides quantitative support for our explanation based on W-H formula. The repulsion energy is the energy cost of the antisymmetrization requirement and hence it is supposed to have an inverse relation with overlap. However, unlike exchange energy, it includes not only electron-electron interactions, but also electron-nuclear and electron kinetic energy effects.[35] So, it does not always increase in the order of increasing overlap. Overall, we have to admit the fact that it is not possible to single out one factor as decisive in determining the trend in interaction energy. However, it is encouraging to note that the total interaction energy and polarization energy follow the same trend, because predicting trends is the power qualitative molecular orbital theory offer to us.

As we saw from Table 1, the π-π^* splitting in AlX_3 also follows the same trend as in the case of BX_3–i.e. decreases as we go from F to I. Thus one would anticipate that the LUMO of AlI_3 should be more stable than that of other AlX_3. This indeed is the case as can be seen from the LUMO energy values shown in Table 1. Then why is AlI_3 a weaker Lewis acid compared to AlF_3? (See Table 2 which lists the energetics of the complex formation of AlX_3 and BX_3 with NH_3.)

Table 2: Free energy change (ΔG) associated with the complexation of BX_3 and AlX_3 with NH_3.

Complex	ΔG(kcal/mol)
BF_3-NH_3	10.05
BCl_3-NH_3	12.32
BBr_3-NH_3	14.51
BI_3-NH_3	15.99
AlF_3-NH_3	29.35
$AlCl_3$-NH_3	25.71
$AlBr_3$-NH_3	24.87
AlI_3-NH_3	22.73

To understand, the opposite Lewis acidity trends in BX_3 and AlX_3, irrespective of the fact that in both the stability of LUMO increases as we go from F to I, we performed GKS-EDA calculation for dissecting the interaction energy between EX_3 (E = B, Al) and NH_3 (Fig. 3). The polarization energy increases as we go from EF_3-NH_3 to EI_3-NH_3 (An ETS-

NOCV calculation gave the same result; see Table S3). Since the LUMO gets stabilized as we go from EF_3 to EI_3, the electron-accepting ability or electronegativity of the EX_3 fragment increases in the same order. Thus, again we see that the polarization energy follows the order of increasing electronegativity. As mentioned earlier, we cannot predict or explain the trend in electrostatic energy, as it involves both attractive and repulsive coulomb interactions. However, notice that the electrostatic contribution to stabilization increases from BF_3 to BI_3. The Pauli repulsion or exchange repulsion between EX_3 and NH_3 increases from EF_3 to EI_3. This might be due to the fact that the occupied bonding orbitals of EX_3 will have more coefficient on E when X is less electronegative, and hence the exchange repulsion of that with the lone pair on NH_3 will be more. The opposite Lewis acidity trend of AlX_3 can be attributed to the Pauli repulsion, as the stabilization due to polarization and electrostatic interaction increases from AlF_3 to AlI_3. Notice how we fail to predict the Lewis acidity trend in AlX_3 using qualitative molecular orbital theory (MOT). MOT allows us to predict the trend in orbital interaction energy, not total interaction energy. Hence there can be situations where other factors overshadow the orbital interaction energy, and we find surprising trends. *However, it is important to note that this happens when the orbital interaction energy is small.*

Based on the above idea that if orbital interaction energy is small, it is less decisive in determining the interaction energy trend, we decided to check the energy of complexation of AlX_3 with stronger Lewis bases–we chose F^- and I^- for this purpose. The energetics of the complexation of AlX_3 with F^-/I^- are shown in Table 3, and it is evident that now AlI_3 behaves like a stronger Lewis acid. To further support our argument, we did GKS-EDA analysis for dissecting the interaction energy of AlX_3 with F^- and I^- (Figure 4). It is evident that the orbital interaction energy for the complexation with F^-/I^- is much higher than the complexation with NH_3. The total interaction energy and orbital interaction energy follows the same order, and AlI_3 is evidently more Lewis acidic than AlF_3. Thus we would like to conclude that MOT based predictions can be largely successful when the interactions are

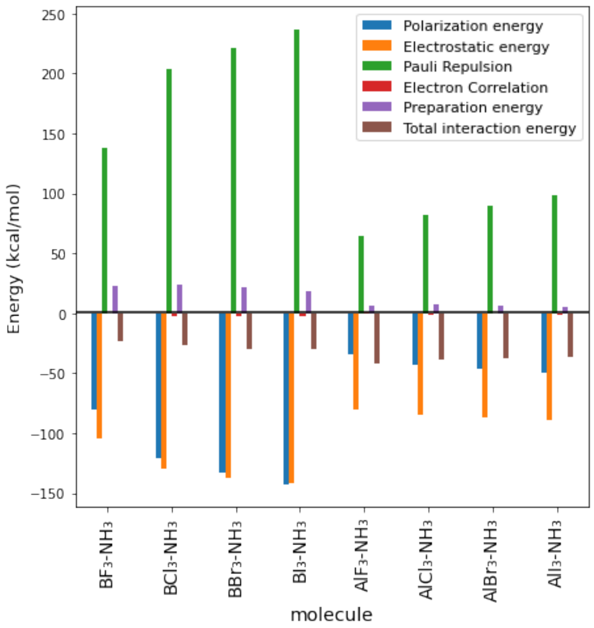

Figure 3: GKS-EDA for the interaction of EX_3 (E = B, Al) with NH_3

strong enough.

Table 3: Energetics of complexation of AlX_3 with F^- and I^-

Molecule	ΔG(kcal/mol)
AlF_4^-	-113.65
$AlCl_3$-F^-	-118.29
$AlBr_3$-F^-	-119.96
AlI_3-F^-	-120.29
AlF_3-I^-	-43.9
$AlCl_3$-I^-	-45.12
$AlBr_3$-I^-	-46.27
AlI_4^-	-46.6

We would like to emphasize that the Lewis acidity trend of boron halides is not anything unexpected, considering the fact that the orbital interaction energy is proportional to both the overlap and electronegativity of the atoms/groups involved. A similar finding, in a different approach was made by Shaik *et al*, while explaining the multiple bonding between heavy atoms.[36] In fact it is the opposite Lewis acidity trend of AlX_3 with NH_3 as the Lewis base that really surprised us. However, we have seen how the Lewis acidity trend of AlX_3 varies depending on the donor strength of the Lewis base. Our explanation for the

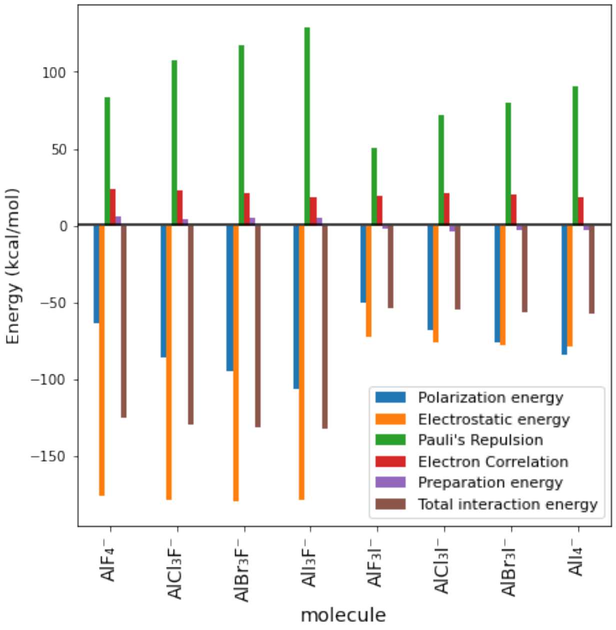

Figure 4: GKS-EDA for the interaction of AlX_3 with F^- and I^-

different Lewis acidity trend of AlX_3 with weak and strong donors also explains the existing report that the Lewis acidity trend of BX_3 with weak Lewis bases is opposite to that with strong Lewis bases–another example where poor orbital interaction is overshadowed by other factors.[37] We also would like to emphasize that the W-H formula can provide a qualitative explanation not only for the Lewis acidity trend, but also for a number of other observations such as the smaller π-π^* splitting of heavy analogs of ethylene and larger π accepting ability of CS compared to CO.

CONCLUSION

To conclude, the trend in orbital interaction energy of BX_3/AlX_3 with Lewis bases can be explained based on Wolfsberg-Helmholz (W-H) formula and quantitatively supported by GKS-EDA analysis. W-H formula suggests that the orbital interaction energy depends not only on the orbital overlap but also on the electronegativity of the atoms involved. The latter can be decisive when the overlap is poor, as in the case of π interactions. This explains the decrease in π-π^* splitting as we go from EF_3 to EI_3 (E = B, Al) and the consequent decrease in the energy of the LUMO in the same order. The lower the energy of the LUMO, the better is orbital interaction with the donor. However if the donor is not strong enough, the effect of orbital interaction can be overshadowed by other effects such as Pauli repulsion, dispersion etc. Thus Lewis acidity trend of EX_3 depends on the strength of interacting Lewis bases. Stronger Lewis bases invoke stronger orbital interaction and hence the total interaction energy will follow the same trend as orbital interaction. In such cases the trends are very much predictable based on qualitative MO theory.

ASSOCIATED CONTENT

Supporting Information Available

Coordinates and energies of all the structures calculated using PBE0 and M06-2X functionals and GKS-EDA data.

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Notes

Authors declare no competing financial interests.

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