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Lewis Acidity of Boron Trihalides

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The Lewis acidity of BF_3, BF_2Cl, $BFCl_2$, and BCl_3 in acid−base orbital interactions has been studied. We have derived the unoccupied reactive orbitals that show the maximum localization on the boron pπ atomic orbital overlapping with the lone-pair orbital of an electron donor and have evaluated the electrophilicity of the boron center in these compounds. The Lewis acidity of boron is shown to be controlled by two factors: localizability of the unoccupied reactive orbital on the boron pπ atomic orbital and the polarizability of the boron center. The former has been shown to be similar in magnitude in these boron halide compounds. Contrary to common belief, the conjugation between the boron atom and the attached halogen atoms is not necessarily stronger in BF_3 relative to others. The trend observed in experiments and in theoretical calculations for BF_3, BF_2Cl, $BFCl_2$, and BCl_3 is interpreted in terms of these factors.

Introduction

The acid and base are fundamental concepts in chemistry. They are defined, in the Lewis theory, as an electron-pair acceptor and an electron-pair donor, respectively.[1] The acid−base interaction has been utilized very often to interpret the mechanisms of chemical reactions, owing to its simplicity and wide applicability. Pearson has divided Lewis acids and bases into two classes that he has termed *hard* and *soft*.[2,3] He has also proposed the principle of hard and soft acids and bases (HSAB): hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases. This makes it possible to predict the stability of complexes formed between acids and bases. In the complexes between hard acids and hard bases, the electrostatic interactions have been suggested to be the dominant source of stabilization.[4] In contrast, electron delocalization plays an important role in the interaction between soft acids and soft bases.[4] Delocalization of electrons has been demonstrated to result in the the formation of new bonds and the cleavage of old bonds in molecular interactions and therefore to give the principal driving force of organic reactions.[5] Accordingly, it is of profound importance to have clear knowledge of acid−base interactions.

Hardness or softness as well as Lewis acid−base strength of a molecule has often been discussed in terms of the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).[4] Theoretical calculations on BF_3, BCl_3, and BBr_3 have suggested that the relative Lewis acidity can be interpreted in terms of the LUMO energy.[6] We have analyzed the electronic structures of $BH_3−NH_3$ and $BH_3−CO$ complexes, showing the importance of frontier orbital interactions in these small systems.[7] Although this approach has been useful in understanding the chemical reactivity of molecules, we take two significant aspects of chemical interactions into account to have a clearer insight into acid−base interactions: chemical interactions are local by nature, reactivities being determined primarily by the local power of an atom or a functional group in a molecule, and therefore, orbitals other than the HOMO and the LUMO should also take part in an interaction to make it localized on an atom or a functional group.

Boron trihalides are used in synthetic chemistry as typical Lewis acids.[8−11] The central boron has only six electrons in its outer shell, and therefore, it is electron-deficient. To satisfy its octet, boron shows a strong affinity for lone-pair electrons of a Lewis base. In this way, boron halides interact with amines to give stable donor−acceptor complexes having a B−N bond. The complexes of boron halides have been investigated extensively both from experimental[12−17] and from theoretical points of view.[18−31] In general, the Lewis acidity of mixed boron halides, BF_xCl_{3-x} ($x = 0, 1, 2, 3$), is known to increase with decreasing x.[32] It is suggested that BCl_3 is a stronger Lewis acid than BF_3, being opposite to the order expected on the basis of the relative electronegativities and the steric effects of the halogens.[33,34]

It has generally been accepted that the order of Lewis acidity described above arises because the boron pπ orbital is conjugated more strongly with the attached halogens in BF_3 than in BCl_3, bringing a larger distortion energy to BF_3.[33−39] Branchadell et al. analyzed the nature of the B−X bonds in boron trihalides[6] by applying the topology of the charge density $\rho(\mathbf{r})$[40] and its Laplacian $\nabla^2\rho(\mathbf{r})$[41] and the valence bond (VB) method.[42,43] It was concluded that the strength of the B−X π bond should increase in the order $BBr_3 < BCl_3 < BF_3$. They calculated pyramidalization energies for BX_3 by comparing the energy of a pyramidal structure with an X−B−X angle of 113.5° and that of a planar one. The values were found to increase in the order $BBr_3 < BCl_3 < BF_3$. Thus, they conjectured that the relative Lewis acidity of boron trihalides was due, to a certain extent, to the variation in the distortion energy that resulted from the difference in double-bond strength.

On the other hand, there are some studies that suggest that the π conjugation is not necessarily stronger in BF_3.[44−46] Brinck et al. have suggested that the calculated atomic charges and electrostatic potentials are consistent with the electronegativities of the halogen atoms but not with the back-bonding concept.[46] Assuming the same geometries for BF_3 and BCl_3 as those in complexes, the distortion energy has been shown to be greater in BCl_3 than in BF_3 by ~2 kJ/mol at the HF/6-31+G(2d,p) level of theory. The difference in the pyramidalization energies does not seem to determine the Lewis acidity. Thus, they have

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explained the observed trend in the Lewis acidity in terms of the charge capacity κ, which was defined by[47,48]

$$\kappa = \frac{1}{I - A} \tag{1}$$

where I and A denote the ionization potential and the electron affinity, respectively. The value of κ was calculated by using experimentally determined I and A, leading to a conclusion that the charge capacity was the key factor for determining the acidity.

The back-bonding seems to be a familiar concept in organic chemistry. For instance, Brown and co-workers have compared the reactivity of allyl boron reagents bearing different types of chiral auxiliaries and have ascribed the observed reactivity trend to the difference in the strength of back-donation of the lone pair of electrons from the nitrogen and oxygen atoms in the auxiliaries to the pπ AO of the boron center.[49] It is interesting therefore to see if the Lewis acidity is governed by n → 2p (B) back-donation or if some other factors play crucial roles in differentiating the Lewis acidity among boron halides BF_xCl_{3-x}. To evaluate the affinity of the boron center in boron halides toward lone pairs of electrons, we will look at the unoccupied orbital that overlaps most efficiently with the orbital of a Lewis base. The wave function of an acid−base interacting system may be represented in terms of the occupied and unoccupied MOs of the two fragment species when the basis set is fixed. Thus, we utilize the unoccupied MOs obtained in the calculations of the electronic structures of boron halide fragments for a qualitative comparison of several factors that are supposed to affect its Lewis acidity.

Computational Method

The electronic structure of boron trihalides and the complexes with amines have been calculated at the MP2(full)/6-31+G** level of theory by applying the Gaussian 94 program.[50] Evaluations of the affinity of boron for lone pairs of electrons of bases and acidic hardness of the boron center have been carried out by using the MOs obtained with the 6-31G** basis set.

Results and Discussion

Let us describe briefly the method of analysis that we utilize in this study.[51] In the interaction between a BH_3 molecule and an electron donor, such as an NH_3 molecule, electron delocalization takes place predominantly from the HOMO of the latter to the LUMO of the former. The LUMO is localized well on the boron atom. As the hydrogens in BH_3 are replaced by halogens, as in BF_3, the LUMO tends to be delocalized over the halogen atoms. Even in such a case, a σ bond is formed between the boron atom and the electron-donating center of the base. This suggests that the reactive orbital should also be localized well on the boron atom in boron trihalides. Then we should take other unoccupied MOs, as well as the LUMO, into account to describe properly the interaction of boron halides with a base.

The orbital of the boron atom utilized to form a bond with the electron-donating center of the base is an AO function or a linear combination of several AO functions, depending on the structure and the basis set used. We denote this orbital by δ_r. Then the orbital function δ_r is written in the form of a linear combination of the occupied MOs ϕ_i ($i = 1, 2, ..., m$) and the unoccupied MOs ϕ_j ($j = m + 1, m + 2, ..., M$) in a boron halide molecule with the coefficients $d_{i,r}$ and $d_{j,r}$, respectively. The orbital that is localized to the maximum extent on δ_r in the unoccupied MO subspace is given by

$$\phi_{\text{unoc}}(\delta_r) = \left(\sum_{j=m+1}^{M} d_{j,r}\phi_j\right)\Bigg/\left(\sum_{j=m+1}^{M} {d_{j,r}}^2\right)^{1/2} \tag{2}$$

The denominator on the right-hand side is attached for the normalization of this reactive orbital. It ensures a comparison between the reactant molecules that differ in size and structure. The occupied reactive orbital ϕ_{oc} having the maximum localization on δ_r can be determined similarly by projecting δ_r onto the occupied MO subspace of the molecule.

The level of the unoccupied reactive orbital localized on the reaction site r or the affinity of the orbital function δ_r of the boron in the given boron halide molecule to the orbital of lone-pair electrons of an attacking base is estimated then by

$$\lambda_{\text{unoc}}(\delta_r) = \left(\sum_{j=m+1}^{M} {d_{j,r}}^2\epsilon_j\right)\Bigg/\left(\sum_{j=m+1}^{M} {d_{j,r}}^2\right) \tag{3}$$

where ϵ_j signifies the orbital energy of the constituent canonical MO ϕ_j. In this manner, we can take all the unoccupied MOs relevant for the interaction with a base into account. The level of the occupied reactive orbital λ_{oc} in the interaction is estimated similarly by taking the sum over the occupied canonical MOs. By representing the denominator of the right-hand side of eq 2 by $(1 - a^2)^{1/2}$, we obtain

$$\delta_r = a\phi_{\text{oc}}(\delta_r) + (1 - a^2)^{1/2}\phi_{\text{unoc}}(\delta_r) \tag{4}$$

and

$$\lambda(\delta_r) = a^2\lambda_{\text{oc}}(\delta_r) + (1 - a^2)\lambda_{\text{unoc}}(\delta_r) \tag{5}$$

where $\lambda(\delta_r)$ is the energy expectation value for the orbital δ_r in the reactant molecule. Now $-\lambda$ indicates the electronegativity of the reaction site, determined primarily by the kind of atom or group of the reaction site and the orbital δ_r taken as the reference.

We have to define next the orbital function δ_r that is suitable for representing the bond formation between the boron center and a base. For this purpose, we have calculated the interaction frontier orbitals at the 6-31G** level of theory for BF_3-NH_3 and BCl_3-NH_3 complexes.[52] Figure 1 illustrates the orbitals of the BF_3 and BCl_3 parts in these complexes, which play the dominant role in electron delocalization from the NH_3 part. The orbital of BF_3, for example, has been derived by representing first the wave function of BF_3-NH_3 in terms of the electron configurations of the BF_3 and NH_3 fragments[7] and then by applying a pair of unitary transformations of the canonical MOs within the unoccupied MO subspace of the BF_3 part and within the occupied MOs of the NH_3 part.[52] The orbital of the BF_3 fragment is given by a linear combination of the unoccupied canonical MOs, including not only the lowest unoccupied MO but also other unoccupied MOs relevant for the interaction. One sees that the orbitals of BF_3 and BCl_3 look very similar to each other, being localized well on the boron center.

The major components of the boron center in the interaction frontier orbitals have been shown to be the inner functions of the 2s AO and the $2p_z$ AO having an extension toward the nitrogen of NH_3. The contribution of the p-type outer functions to the orbitals is very small, being less than 2% in weight. The difference in electrophilicity of boron trihalides may be discussed in a planar monomeric form, and we assume here that

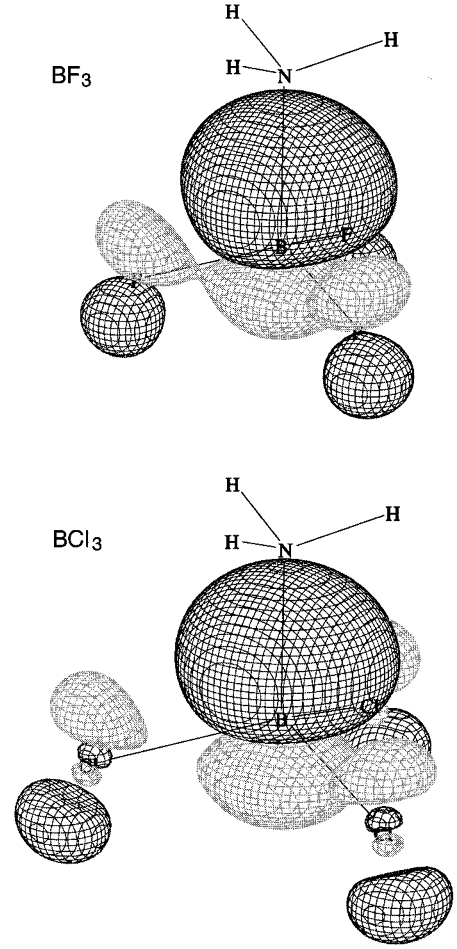


Figure 1. Unoccupied interaction frontier orbitals of BF_3 (upper) and BCl_3 (lower) taking part in electron delocalization from the NH_3 lone-pair orbital in the structures of the BX_3-NH_3 complexes. They were obtained by carrying out simultaneous transformations of the MOs of the BX_3 fragment and of the NH_3 fragment in BX_3-NH_3 complexes to represent the orbital interactions described in the wave function of the complex in terms of pairs of fragment orbitals.

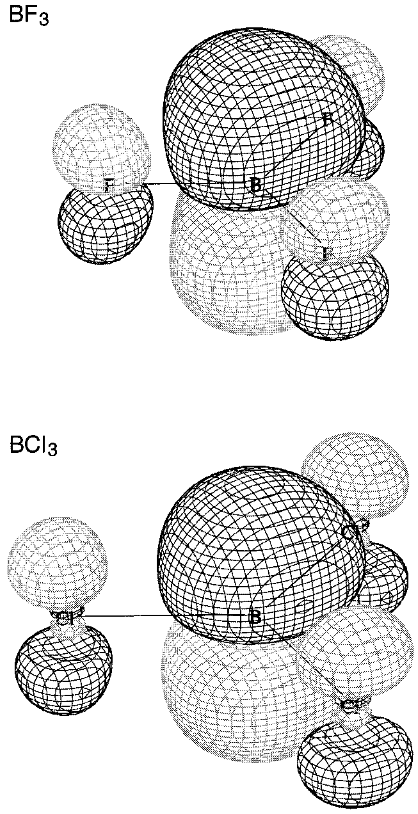


Figure 2. Unoccupied reactive orbitals of BF_3 (upper) and BCl_3 (lower) in the planar forms obtained by projecting the $2p_\pi$ AO of the central boron onto the RHF/6-31G** unoccupied MO subspace of these molecules. The structures were optimized without any symmetry constraints at the MP2(full)/6-31+G** level of theory.

TABLE 1: Comparison of the Elements Determining the Electrophilicity of BF_3, BF_2Cl, $BFCl_2$, and BCl_3 in Planar Forms

	BF_3	BF_2Cl	$BFCl_2$	BCl_3
localizability of reactive orbital $(1 - a^2)^a$	0.740 (0.688)	0.752	0.762	0.769 (0.685)
hardness η (au)^a	0.533 (0.507)	0.493	0.448	0.399 (0.371)
energy of B pπ AO, λ (au) ^{a}	0.040 (−0.052)	0.042	0.046	0.051 (−0.057)
unoccupied reactive orbital level, λ_{unoc} (au)^a	0.318 (0.265)	0.286	0.258	0.235 (0.177)
$(1 - a^2)\gamma/\lambda_{unoc}{}^{a,b}$	2.33 (2.59)	2.63	2.95	3.27 (3.86)
Mulliken charge on B^c	+1.492	+0.959	+0.500	+0.075
distortion energy (kJ/mol)^{c,d}	101.6	102.1	100.8	99.3
B−N bond length (nm)^c	0.1659	0.1645	0.1634	0.1626
B−N bond energy (kJ/mol)^{c,e}	111.9	114.5	117.0	119.1

^{a} Values in parentheses indicate the case in which the reference function δ_r is taken to be a combination of the inner and outer functions of B 2pπ AO with the coefficient ratio of 8:2. ^{b} $\gamma = 1$ au. ^{c} Calculated at the MP2(full)/6-31+G** level of theory. ^{d} Defined by $E[BF_xCl_{3-x}$ (bent)$] - E[BF_xCl_{3-x}$ (planar)$]$, in which the bent structure was taken as the same as in a complex. ^{e} Defined by $E(NH_3) + E(BF_xCl_{3-x}) - E(H_3N-BF_xCl_{3-x})$.

the pπ-type AO function having an extension perpendicular to the molecular plane plays the major role. Thus, we have taken the inner $2p_z$ function of the boron as the reference orbital. The unoccupied reactive orbitals obtained in this manner by using the MOs calculated at the 6-31G** level are presented in Figure 2 for BF_3 and BCl_3.

It has widely been accepted that n (F or Cl) → 2p (B) back-donation of electrons should be stronger in BF_3 than in BCl_3, and hence, the former is weaker as a Lewis acid than the latter.[33] The present analysis shows that this is not likely. It is seen in Table 1 that $(1 - a^2)$ of BF_3 is similar in magnitude to those of BF_2Cl, $BFCl_2$, and BCl_3, being 0.74−0.77. Equation 4 indicates that the pπ-type function of the boron atom is found mainly in the unoccupied MO space but to a similar extent in these boron halides. Accordingly, the reactive orbital is populated by electrons to a similar extent. To examine the importance of the reluctance of BF_xCl_{3-x} toward pyramidalization, we have computed the distortion energy for these compounds by comparing the energies of the planar and the bent structures. The latter has been taken to be the same as the structure in the complexes. The calculated distortion energies are similar in magnitude to each other as given in Table 1. The distortion energy does not seem to interpret the relative acidic strength in the present case. Contrary to common belief, the n → 2p (B) back-donation is not the reason for a weaker acidity of BF_3. The B pπ orbital is partially occupied through conjugation with the F and/or Cl atoms, but it has sufficient room for accepting more than one electron in the planar form.

The projected reactive orbital ϕ_{unoc} is shown to be localized up to ~75% on the boron pπ orbital, since we have $\langle\delta_r|\phi_{unoc}\rangle^2 = (1 - a^2)$. The values in parentheses in Table 1 correspond to the case in which the reference function δ_r has been chosen to be a linear combination of the inner and outer functions of the boron pπ orbital with the coefficient ratio of 8:2. The localization of the projected reactive orbital in the unoccupied MO space and/or on the boron center is seen to be less efficient. This means that the outer function has been utilized for the conjugation with the adjacent halogens, more heavily in BCl_3, at the present level of calculations. However, we find again that the extent of localization of the reactive orbital in the unoccupied MO space is very similar in BF_3 and in BCl_3.

An important factor to be considered here is the gap between the levels of the occupied and unoccupied reactive orbitals, λ_{oc} and λ_{unoc}. Perturbation theory tells us that polarizability of the reaction site r is inversely proportional to this gap.[53] The unoccupied and occupied reactive orbitals are delocalized over the neighboring halogen atoms, and they mix with each other, induced by electron delocalization from an approaching base. This orbital mixing removes the electronic charge from the boron center and places it on the halogen atoms to facilitate electron delocalization from the base. In addition, the mixing of the occupied and unoccupied reactive orbitals weakens the conjugation between the pπ orbital of the boron and the halogen atoms, making the boron orbital engage in bond formation with the base.

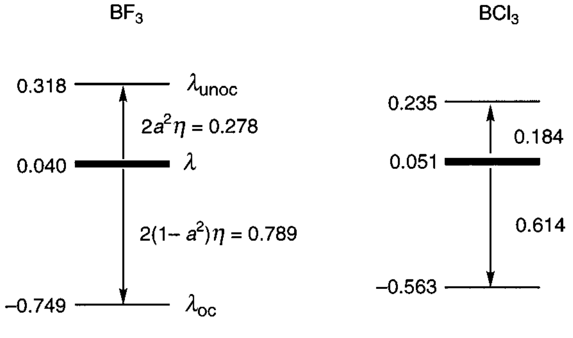
The present treatment includes explicitly the polarization effect. We have determined above the reactive orbital ϕ_{unoc} to show the maximum localization on the boron pπ orbital in the unoccupied MO subspace. Delocalization of the reactive orbital over the adjacent halogen atoms elevates the electron-accepting orbital level λ_{unoc} from λ by $2a^2\eta$,

$$\lambda_{unoc}(\delta_r) = \lambda(\delta_r) + 2a^2\eta(\delta_r) \tag{6}$$

in which η is a measure of the chemical hardness of the boron pπ orbital, defined by[51b]

$$\eta(\delta_r) = (\lambda_{unoc}(\delta_r) - \lambda_{oc}(\delta_r))/2 \tag{7}$$

It is of crucial importance that the hardness η of the reaction site is small to make the electron-accepting level stay low in energy. Efficient localization of the unoccupied reactive orbital on the reaction site leads to a smaller a^2 value and therefore a lower electron-accepting level. One sees in Table 1 that the hardness η and the acidic hardness $2a^2\eta$ of the boron pπ orbital increase in the order $BCl_3 < BFCl_2 < BF_2Cl < BF_3$. That is, the boron center is more polarizable, and accordingly, softer as an acid in BCl_3 than in BF_3.



We have started our discussion from an assumption that boron compounds should provide an unoccupied orbital that has the maximum amplitude on the boron atom to form effectively a new bond with a base. As mentioned above, the construction of the reactive orbital has dual meanings, i.e., the maximum localization in the unoccupied MO space and the maximum localization on the reaction center. To make this more explicit, we may take here $\langle\delta_r|\phi_{unoc}\rangle^2\gamma/\lambda_{unoc}$ as a reactivity scale, where γ is a constant having an energy unit.[54] It is seen in Table 1 that this scale gives the smallest value to BF_3 and increases in the order $BF_3 < BF_2Cl < BFCl_2 < BCl_3$. This agrees with the experimentally observed and/or theoretically calculated strengths of the B−N bond in the boron halide−amine complexes.

TABLE 2: Comparison of the Elements Determining the Electrophilicity of BF_3 and BCl_3 with the Bent Form as in BX_3-NH_3 Complexes[a]

	BF_3	BCl_3
localizability of reactive orbital $(1 - a^2)$	0.843	0.796
hardness η (au)	0.564	0.436
energy of δ_r, λ (au)	0.121	0.036
unoccupied reactive orbital level, λ_{unoc} (au)	0.298	0.215
$(1 - a^2)\gamma/\lambda_{unoc}$[b]	2.82	3.71

[a] The components of the boron in the unoccupied interaction frontier orbital were taken as the reference function δ_r. [b] $\gamma = 1$ au.

In the complexes with amines, the boron center has a pyramidal bond arrangement. To see the effect of the s-type AO function on the electrophilicity, we have calculated the theoretical quantities defined above for the orbitals of BF_3 and BCl_3 presented in Figure 1. One sees in Table 2 that our discussion made above holds also in this case. The electron-accepting level is located higher in BF_3 than in BCl_3. The vacancy of the reactive orbital is slightly larger in BF_3 probably because of less effective conjugation with halogens in this bent structure.

In the interaction of boron halides with a base, electrostatic interaction may be another source of stabilization. As presented in Table 1, the boron center has the largest positive charge in BF_3 among the species examined in this study.[55] On the other hand, the B−N bond has been calculated to be the longest in BF_3. This seems to indicate that the electrostatic attraction does not interpret the relative reactivity of the boron halides toward NH_3. In contrast, in the case of the complexes between boron halides with CH_3F, the B−F bond length has been shown to increase in the order of $BF_3 < BF_2Cl < BFCl_2 < BCl_3$ [56] to reduce primarily overlap repulsion between the lone pairs of electrons.

Parr and co-workers proposed the concept of absolute chemical hardness of a molecule that was given by half the difference between the ionization potential I and the electron affinity A or by half the energy gap between the LUMO and the HOMO, applying a finite difference approximation.[57] By introducing the reactive orbitals, we are allowed to discuss the hardness of a reaction site in a molecule. The electronegativity of a molecule is located in the middle of the HOMO and the LUMO.[58] In contrast, the $-\lambda$ can move between the electron-donating level and the electron-accepting level in our approach, reflecting the efficiency of a reaction site to serve as an acid or a base in a molecule. It represents the power of an atom or a group to attract electrons in a molecule, having a significance in line with the chemist's view of electronegativity.[59] The present argument may be applied to investigate the electronic mechanisms by which an atom or a group is activated specifically as an electron-accepting site or as an electron-donating site in a reactant molecule.

Conclusion

We have studied the Lewis acidity of BF_3, BF_2Cl, $BFCl_2$, and BCl_3 from the orbital interaction viewpoint. By deriving the unoccupied reactive orbital that shows the maximum localization on the boron pπ orbital function, the Lewis acidity of these compounds has been demonstrated to be controlled by two major factors, localizability of the unoccupied MOs on the boron orbital relevant for bond formation with a base and the polarizability of the boron center. The present analysis has revealed that the localizability is very similar to each other, and therefore, the n → 2p (B) back-donation of electrons is not the major factor for differentiating the Lewis acidity of these boron halides. The unoccupied reactive orbital of BCl_3 lies lower in energy compared with that of BF_3, owing to its smaller value of acidic hardness. The trend in reactivity observed in experiments and in theoretical calculations for BF_3, BF_2Cl, $BFCl_2$, and BCl_3 has been found to be understood in terms of these theoretically defined quantities. The present analysis will also be useful in comparing or predicting the electrophilicity of boron reagents having auxiliaries that are different in size and structure for organic syntheses.

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