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Article

Hydride Affinities of Borane Derivatives: Novel Approach in Determining the Origin of Lewis Acidity Based on Triadic Formula

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The problem of intrinsic Lewis acidities of simple boron compounds ($BH_{3-m}X_m$, $m = 0$–3, X = F, Cl, Br, CH_3, and OH) is assessed by their gas-phase hydride affinities (HAs). A simple and intuitively appealing picture of the interaction process including detachment of an electron from the hydride ion H^-, capture of the pruned electron to the investigated Lewis acid (LA), and subsequent formation of the homolytic chemical bond between two newly created radicals is proposed. It enables transparent and straightforward dissection of the initial and final state effects, which taken together with the intermediate relaxation stabilization determine the trend of changes in the hydride affinities. The former effect is reflected in the electron affinities of the neutral Lewis acids given within Koopmans' approximation, while the final state effect involves properties of the formed Lewis acid–base adducts mirrored in the bond dissociation energy of the formed $[LA–H]^-$ chemical bond. It is demonstrated that unexpectedly low Lewis acidity of fluoroboranes relative to the corresponding chlorine and bromine derivatives can be traced down to the unfavorable Koopmans' electron affinities. Hence, it is a consequence of the initial state effect. In contrast, chloroboranes are more potent Lewis acids than fluoroboranes, because the relaxation and final state effects decisively influence their Lewis acidity. Finally, bromine-substituted borane compounds provide the most powerful studied Lewis acids. Their hydride affinities are result of a synergic interplay of the initial state, intermediate stabilization via relaxation, and final state effects. It is shown that Pearson's global hardness indices defined within his hard and soft acid–base (HSAB) principle fail to adequately predict and interpret the calculated hydride affinities.

Introduction

Acidity and basicity belong to the most important concepts in chemistry. There are several different definitions of acids and bases available, but in Lewis theory[1] they are specified in the most general terms as the electron pair-acceptors and electron pair-donors, respectively. The importance of Lewis' conceptual approach is rooted in the fact that it can be applied to compounds such as BF_3 and CO, which do not contain protons. An important family of compounds is given by borane derivatives, which due to the electron deficiency of the central B atom represent Lewis acids par excellence. Therefore, it is not surprising that boron complexes with

Lewis bases have been extensively studied from both experimental[2–7] and theoretical points of view.[8–19] In par-

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ticular, it is well established by now that the hierarchy of Lewis acidity of the boron halides toward strong bases is $BF_3 < BCl_3 < BBr_3$.[20,21] Such sequence of the acidity strengths is unusual and counterintuitive at first sight, if relative electronegativities and steric requirements of the halide atoms are taken into account. This seemingly puzzling behavior of boron halides triggered considerable controversy in the literature in the past, which calls for a clear-cut resolution. For this purpose, we deemed it worthwhile to examine complexes of $BH_{3-m}X_m$ (X = F, Cl, Br, CH_3, and OH and m = 0, 1, 2, 3) with H^- anion, which in turn provides the simplest nucleophile and the smallest Lewis base. It is noteworthy that boron halides are interesting per se, because they play an important role as catalysts in many organic, organometallic, and inorganic reactions.[22,23] Interactions between this family of boron compounds and hydride ion will be scrutinized by a carefully selected theoretical model, and the results will be interpreted in a new and fresh way, thus shedding more light on the ladders of Lewis acids and on the strengths of their interactions with Lewis bases.

Theoretical Framework

Let us briefly discuss the most important theoretical achievements obtained so far, in order to put the present results in a proper perspective. An early rationalization of the stability of Lewis acid−base complexes was given by Pearson's concept of hard and soft acids and bases (HSAB).[24,25] According to this principle, hard acids prefer hard bases, whereas soft acids favor soft bases. This idea was put into a simple MO language by Klopman.[26] According to Klopman, a dominant interaction between hard acids and bases is embodied in the electrostatic term. In contrast, the soft acids and bases are stabilized via the electron delocalization of the frontier orbitals. Unfortunately, neither HSAB criterion nor Klopman's simple MO models can quantitatively describe the interaction energies between Lewis acids and bases.

A possible explanation of the anomalous order of Lewis acidity of boron trihalides was advocated by the lone pair π-electron back-donation effect of the halogens to the empty

2p orbital of boron. This back-donation mechanism should be stronger for the smaller halogen (e.g., fluorine) due to a better $p\pi-p\pi$ overlapping. This would lead to a larger energy required for distortion of BF_3 upon complexation[27,28] and, as a consequence, a weaker acidity of BF_3 compared to BCl_3 and BBr_3. Branchadell and co-workers[29,30] analyzed the nature of the B−X bonds in boron trihalides and demonstrated that the pyramidalization energies for BX_3 were increased indeed in the sequence $BBr_3 < BCl_3 < BF_3$, which seemed to be in harmony with previous proposition. However, Brinck and co-workers[31] showed, by using the atomic charges and electrostatic potentials, that the π-conjugation is not necessarily stronger in BF_3 compared to other halides. According to their analysis, the charge capacity κ could explain the observed trend in Lewis acidity rather than the pyramidalization energies. In other words, the more polarizable congeners can accommodate an additional electron more easily. The κ value was defined[32,33] as an inverse of the difference between the experimental ionization energy and electron affinity of the molecules in question. This picture is in disagreement with theoretical results of Frenking and co-workers[34] who employed an NBO partitioning scheme and have shown that there was no simple relation between the charge transfer and bond strength. More recently, several new concepts emerged, offering alternative interpretations of the Lewis acid strength using the ligand close-shell packing (LCP) model[35,36] and energies of the LUMO orbitals.[37] The former model is based on the assumption that geometry of a molecule AX_n is mainly determined by the repulsion between the substituents X rather than by the nature of the A−X bonding.

In contrast to the hierarchy of Lewis acidities toward strong bases mentioned above, an opposite trend in acidity of boron trihalides is observed if the interactions with weak bases such as CO, HCN, and CH_3F are considered.[38] Despite many efforts made in elucidation of Lewis acidity of boron compounds in the past, there are still many puzzling features, which are not completely understood, thus requiring rationalization and transparent interpretation.

We believe that a deeper and more comprehensive insight into the nature of Lewis acid−base properties in general is given by a recent triadic formula, which offered quantitative estimates of the initial and final states effects in determining Brønsted basicities[39] and acidities[40] of organic molecules in the gas phase. The underlying physical picture behind this

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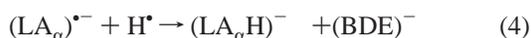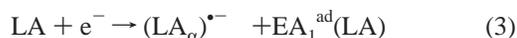(40) Maksić, Z. B.; Vianello, R. *ChemPhysChem* **2002**, *3*, 696.

approach is the separation of the protonation process of neutral organic base (Brønsted basicity) or conjugate base anion (reversed process related to Brønsted acidity) into the three sequential steps: (1) ionization of the base/anion in question by pruning an electron, (2) attachment of the ejected electron to the incoming proton and formation of the neutral hydrogen atom, and finally (3) formation of the homolytic chemical bond between created radical(s) and the hydrogen. It has been shown that our approach had a certain advantage compared to some other models aiming to interpret Brønsted acidities and basicities as discussed in great detail by Deakyne.[41] By generalizing the procedure described above, one can treat the interaction of any Lewis acid (LA)−Lewis base (LB) pair in an analogous way by decomposing the process into three stages: (1) electron ionization of the LB in question, (2) electron addition to LA under scrutiny, and (3) homolytic chemical bond formation, which binds two radicals.

Presently, we shall analyze the gas-phase hydride affinities (HAs), which are defined by the reaction

$$LA + H^- \rightarrow (LA_\alpha H)^- - (HA)_\alpha \qquad (1)$$
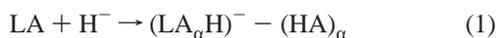
where LA and α denote the Lewis acid in question and the site of the hydride ion attack, respectively. The latter will be the "empty" 2p orbital of the central boron atom. The following three equations are important in describing addition of the H^- anion to the Lewis acid:

$$H^- - e^- \rightarrow H^\bullet \quad -IE(H^-) \qquad (2)$$

$$LA + e^- \rightarrow (LA_\alpha)^{\bullet -} \quad +EA_1^{ad}(LA) \qquad (3)$$

$$(LA_\alpha)^{\bullet -} + H^\bullet \rightarrow (LA_\alpha H)^- \quad +(BDE)^- \qquad (4)$$

Equation 2 illustrates ionization of the hydride ion with concomitant formation of the hydrogen atom. This step is associated with the energy loss mirrored through the ionization energy of H^-, which is an experimentally determined quantity of 17.4 kcal mol^{-1}. The next equation, eq 3, describes electron attachment to the Lewis acid under consideration, which gives a Lewis acid radical anion with an energy gain being equal to the first adiabatic electron affinity of Lewis acid $EA_1^{ad}(LA)_\alpha$. The last equation, eq 4, gives the energy of the homolytic bond energy (BDE)$^-$ between two radicals forming a new B−H covalent bond in producing the $LA_\alpha H^-$ anion. By combining eqs 1−4, one obtains

$$(HA)_\alpha = EA_1^{ad}(LA) + (BDE)^- - 17.4 \text{ kcal mol}^{-1} \quad (5)$$

For interpretative purposes, it is useful to delineate the initial state effects inherent in properties of the Lewis acid under study and the final state effects exhibited by the formed hydride adduct. It would be incorrect, however, to identify $(EA)_1^{ad}$ values entering formula 5 with properties of the initial Lewis acid itself, because the adiabatic electron attachment involves relaxation of both electronic and geometrical

parameters upon electron addition. Consequently, $(EA)_1^{ad}$ does not reflect properties of the initial Lewis acid alone. To separate properties of the initial state from those belonging to the final state and the electron redistribution upon the LA_α reduction, Koopmans' theorem[42] has to be invoked. The latter states that the electron affinity $(EA)_n^{Koop}$ of a given molecule is approximately given by the negative of the corresponding unoccupied orbital energy $-\epsilon_n$ calculated within the clamped nuclei and frozen electron density picture. In a widely accepted Koopmans' approximation, one assumes that the spin-orbitals in the $(N + 1)$ electron states are identical to those of the N-electron state of the neutral molecule. Despite their highly approximate nature, the calculated $(EA)_n^{Koop}$ values are useful when applied in a family of closely related molecules.[43,44] It is worth mentioning that $(EA)_n^{Koop}$ does not necessarily correspond to the first electron affinity ($n = 1$), because the empty boron 2p orbital may be associated with a molecular orbital higher in energy than LUMO. This detail deserves a few words of comment. First, it is not difficult to identify the molecular orbital in question, since it describes the electron density localized around boron atom. Second, if an additional electron is placed in a virtual LUMO $+ m$ orbital, where m is a positive natural number, the corresponding state might be unbound. Nevertheless, even in this case our approach retains its cognitive value in a formal sense. Employing Koopmans' approximation, eq 5 can be rewritten in the following triadic form:

$$(HA)_\alpha = EA_n^{Koop}(LA)_\alpha + E(ea)^{(n)}_{rex} + (BDE)^- - \\ 17.4 \text{ kcal mol}^{-1} \quad (6)$$

where $E(ea)^{(n)}_{rex}$ is reorganization energy spurred by electron attachment being defined as a difference between adiabatic and Koopmans' electron affinities.

$$E(ea)^{(n)}_{rex} = EA_1^{ad}(LA) - EA_n^{Koop}(LA)_\alpha \qquad (7)$$

It should be realized that relaxation of geometric and electron density parameters after electron addition is a part of the hydride anion attachment process. Hence, it represents interplay between the initial and final state effect, where the latter are given by formation of an adduct between the relaxed $(LA)_\alpha^-$ anion and H atom.

As a final comment related to the applied theoretical framework, we would like to emphasize that the underlying picture embodied in eq 6 is a simple extension of a familiar thermodynamic cycle, where $EA_1^{ad}(LA)$ is substituted by a sum of $EA_n^{Koop}(LA)_\alpha$ and $E(ea)^{(n)}_{rex}$ values. It should be kept in mind that inclusion of the Koopmans' electron affinity $EA_n^{Koop}(LA)_\alpha$ is pivotal, because it mirrors genuine properties of the initial state.

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Computational Model

As a good compromise between reliability of results, feasibility of the method, and economy in terms of the computer time, we employed a fairly accurate and practical G2(MP2) computational procedure.[45] G2(MP2) is a composite method designed for accurate predictions of molecular thermodynamic parameters such as atomization energies, proton affinities, ionization energies, and electron affinities, which are usually predicted with chemical accuracy, i.e., with error margin of ± 2 kcal mol^{-1}.[46] G2(MP2) methodology should give reasonably accurate hydride affinities as well. It involves several steps, which effectively correspond to QCISD(T)/6-311+G(3df,2p)//MP2(full)/6-31G(d) total energy with zero-point vibrational energies (ZPVEs) and thermal corrections obtained at the HF/6-31G(d) level. The latter are weighted by a common scaling factor 0.89.[47] Koopmans' electron affinities are computed by the HF/6-311G(d,p)//MP2(full)/6-31G(d) model. Radical anions of the Lewis acids under consideration were treated by unrestricted approach. All computations were performed using a GAUSSIAN 98 suite of programs.[48]

Results and Discussion

Energetic Properties. Before numerical results are discussed, a word on the interpretation of eqs 5 and 6 is in place. In discussing the trend of changes of hydride affinities, the situation is somewhat more complex than with Brønsted acidities and basicities considered earlier.[39,40] It has been shown[39] that all proton affinities of neutral organic bases are higher than the average $[X-H]^+$ homolytic covalent bond formation energies, since the adiabatic electron ionization energies of all neutral bases are substantially lower than the electron affinity of the proton. The latter value is 313.6 kcal mol^{-1}. This is a consequence of the well-known fact that ionization of any neutral base is endothermic. In other words, the corresponding IE values are all positive. On the other hand, attachment of an additional electron to a neutral molecule sometimes proceeds spontaneously (with energy gain), but in other cases an energy investment is required for the electron attachment.[49] Therefore, in the former instance, the electron affinity values are positive, thus contributing to the hydride affinity according to eq 5, whereas in the latter case the EA quantities are negative, hence lowering the HA values. It can be safely stated that the hydride affinities will be larger than the average homolytic boron−hydrogen bond energies provided that a boron

Table 1. Hydride Affinities (HAs) Obtained by a Triadic Formula (Equation 6) Resolved into Various Contributions Calculated by the G2(MP2) Method[a]

molecule	$(EA)_n^{Koop}$	$(EA)_1^{ad}$	$E(ea)^{(n)}_{rex}$	$(BDE)^-$	(HA)
BH_3	$-(43.2)_1$	-3.1	40.1	93.6	73.1
		$[0.9 \pm 0.3]^b$			$[74.2 \pm 2.8]^b$
BH_2F	$-(61.4)_1$	-16.9	44.5	97.1	62.8
BHF_2	$-(82.1)_1$	-23.8	58.3	101.4	60.2
BF_3	$-(108.1)_1$	-17.9	90.2	106.1	70.8
BH_2Cl	$-(43.8)_1$	-1.7	42.1	99.2	80.1
$BHCl_2$	$-(44.9)_1$	2.8	47.7	101.6	87.0
BCl_3	$-(45.4)_1$	9.5	54.9	102.4	94.5
		$[7.6 \pm 4.6]^b$			
BH_2Br	$-(39.1)_1$	3.6	42.7	100.1	86.3
$BHBr_2$	$-(36.3)_1$	11.5	47.8	101.7	95.8
BBr_3	$-(33.2)_1$	19.0	52.2	101.4	103.0
		$[18.9 \pm 4.6]^b$			
BH_2Me	$-(59.2)_1$	-11.9	47.3	95.7	66.4
$BHMe_2$	$-(74.4)_1$	-17.5	57.2	96.5	61.1
BMe_3	$-(86.4)_1$	-19.3	67.1	95.4	58.7
$BH_2(OH)$	$-(78.5)_1$	-28.1	50.4	93.8	48.3
$BH(OH)_2$	$-(112.5)_3$	-44.6	67.9	97.9	35.9
$B(OH)_3$	$-(152.9)_4$	-46.9	106.0	99.0	34.7

^{a} All values are in kcal mol^{-1}. Koopmans' electron affinities are calculated at HF/6-311G(d,p)//MP2(full)/6-31G(d) level. ^{b} Experimental data are taken from ref 55 and are given within square brackets.

compound in question can accommodate an additional electron in exothermal fashion, with energy larger than 17.4 kcal mol^{-1}. This is usually not the case, as the forthcoming discussion will show.

Another point of interest is Koopmans' electron affinities. It is a common knowledge that Koopmans' approximation neglects correlation and relaxation effects. These errors tend to cancel in the case of the electron ionization energies of neutral molecules,[50] but they add up in the calculation of electron affinities producing too negative values.[51] However, if $(EA)_n^{Koop}$ values are discussed in a family of closely related molecules, they very well reproduce experimentally observed trends of changes in electron affinities and provide a valuable tool in interpreting the electron attachment spectra.[52−54]

In order to examine substituent effects on hydride affinities in a systematic way, all mono-, di-, and trisubstituted derivatives $BH_{3-m}X_m$ ($m = 1, 2, 3$) for X = F, Cl, Br, CH_3, and OH are considered. Results of the analysis offered by eq 6 are given in Table 1. Calculated HA quantities span a range of values from 34.7 to 103.0 kcal mol^{-1} found in $B(OH)_3$ and BBr_3, respectively. This would imply that boric acid $B(OH)_3$ is the weakest, while BBr_3 is the strongest Lewis acid measured against the hydride ion. In order to estimate contributions of the initial and final state effects to the hydride affinities, it is useful to select parent BH_3 molecule as a reference system and compare increments of the three terms entering eq 6 for all other molecules. These numbers

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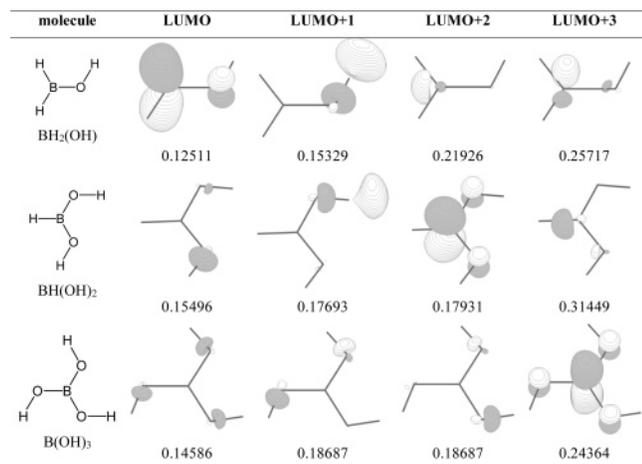(54) Tong, J.; Li, X.-Y. *Chem. Phys.* **2002**, *284*, 543.

Figure 1. Selected molecular orbitals of hydroxyboranes, together with their orbital energies (in atomic units) obtained by HF/6-311G(d,p)//MP2-(full)/6-31G(d) model.

Table 2. Relative Contributions to Hydride Affinities of the Investigated Molecules Obtained by Triadic Formula (Equation 6) Taking BH_3 as a Gauge Molecule[a]

molecule	$\Delta(EA)_n^{Koop}$	$\Delta E(ea)^{(n)}_{rex}$	$\Delta(BDE)^-$	$\Delta(HA)$
BH_2F	−18.2	4.4	3.5	−10.3
BHF_2	−38.9	18.2	7.8	−12.9
BF_3	−64.9	50.1	12.5	−2.3
BH_2Cl	−0.6	2.0	5.6	7.0
$BHCl_2$	−1.7	7.6	8.0	13.9
BCl_3	−2.2	14.8	8.8	21.4
BH_2Br	4.1	2.6	6.5	13.2
$BHBr_2$	6.9	7.6	8.1	22.7
BBr_3	10.0	12.1	7.8	29.9
BH_2Me	−16.0	7.2	2.1	−6.7
$BHMe_2$	−31.5	17.1	2.9	−11.5
BMe_3	−43.2	27.0	1.8	−14.4
$BH_2(OH)$	−35.3	10.3	0.2	−24.8
$BH(OH)_2$	−69.3	17.8	4.3	−37.2
$B(OH)_3$	−109.7	65.9	5.4	−38.4

[a] All values are in kcal mol^{-1}.

are presented in Table 2. It is useful to bear in mind that the negative sign implies that a term in question is smaller than its counterpart in BH_3 (and vice versa for the positive sign).

Inspection of the data in Table 1 reveals some general features. Koopmans' electron attachment energies $(EA)_n^{Koop}$ correspond to the LUMO orbital in all instances but in BH-$(OH)_2$ and $B(OH)_3$, where the vacant boron 2p orbital is a part of the LUMO + 2 and LUMO + 3 molecular orbitals, respectively (Figure 1).

Perusal of adiabatic electron affinities shows that a majority of investigated molecules do not spontaneously bind an electron as revealed by the corresponding negative $(EA)_1^{ad}$ values. There are, however, some exceptions given by mono-, di-, and tribromo derivatives $BH_{3-m}Br_m$ ($m = 1-3$) and molecules $BHCl_2$ and BCl_3, where the corresponding radical anions are more stable than the initial neutral closed-shell molecules. Theoretical adiabatic electron affinities for BCl_3 and BBr_3 are in good agreement with experimental results, which unfortunately have a large error margin. A discrepancy is found in BH_3, but the calculated hydride affinity is on the other hand in good accordance with a measurement.[55]

Perhaps the most striking finding offered by the numerical analysis obtained by eq 6 is that bond dissociation energies $(BDEs)^-$ vary in a rather narrow range between 93.6 kcal mol^{-1} (BH_3) and 106.1 kcal mol^{-1} (BF_3). In other words, they do not affect hydride anion affinities to a significant extent, particularly since the $(BDE)^-$ values cluster around the average value of 98.9 kcal mol^{-1} in most cases. This is in full analogy with a constancy of the C−H bond energy in substituted hydrocarbons for the $C(sp^3)$ carbons. It is surprising that it takes nearly the same amount of energy to homolytically break the B−H chemical bond and form two separate radicals within the same family of halide derivatives irrespective of the number of halide substituents. On the other hand, hydride affinities exhibit much more pronounced variations.

Let us consider the parent borane molecule BH_3 and its halogenated derivatives in some more detail. In a planar BH_3 system, an "empty boron 2p orbital" is located in LUMO, and the price, which has to be paid for attachment of an additional electron within Koopmans' approximation, is 43.2 kcal mol^{-1}. This investment (loss) in energy is approximately recovered by the relaxation energy $E(ea)^{(n)}_{rex}$, which together with bond dissociation energy of 93.6 kcal mol^{-1} leads to a hydride affinity HA of 73.1 kcal mol^{-1}. Sequential substitution by fluorine atoms induces attenuation in Lewis acidity. At first sight, these changes in Lewis acidity are not in harmony with the high electronegativity of fluorine atoms, which would suggest that BF_3 should provide a much stronger Lewis acid than BH_3. However, a closer look reveals that a strong electron withdrawing power of fluorine stabilizes the occupied bonding MOs and destabilizes unoccupied antibonding MOs. This feature explains via the trichotomy formula (eq 6) a counterintuitive behavior of BF_3 acid, because unoccupied orbital energies assume higher values.

The π-electron back-bonding effect provides a rationale for a large change in relative values arising in the relaxation energy $E(ea)^{(n)}_{rex}$ upon fluorine substitution (Table 1). The latter is two times higher in BF_3 than in fluoroborane BH_2F. Moreover, it is important to realize that differences in relaxation energies as well as variations in bond dissociation energies between fluorinated derivatives and BH_3 are positive (Table 2). This would suggest that the effects of the final state and intermediate relaxation energy act in synergic fashion leading to the enhancement of Lewis acidity in $BH_{3-m}F_m$ ($m = 1-3$) with each additional fluorine atom, thus alleviating unfavorable Koopmans' EAs. To be specific, this feature is pronounced the most in BF_3, which would be, if only the relaxation and final state contributions were taken into account, stronger Lewis acid toward H^- than BH_3 by 62.6 kcal mol^{-1}. However, perfluorination leads to lowering of Lewis acidity as a consequence of the highly unpropitious Koopmans' electron affinities, which exert a decisive influence. It can be safely stated that the intrinsic Lewis acidity of fluoro-substituted boranes in the gas phase is determined by properties of the initial acids mirrored in Koopmans' electron affinities, which in turn are a consequence of the

(55) *NIST Chemistry WebBook*; Linstrom, P. J., Mallard, W. G., Eds.; NIST Standard Reference Database Number 69, March 2003; National Institute of Standards and Technology: Gaithersburg, MD (http://webbook.nist.gov).

pronounced electronegativity of F atoms. It should be noticed that only in this series of molecules the trend of changes in Lewis acidity is not linear. The reason behind this is that the $E(ea)^{(n)}_{rex}$ term in BHF_2 is only 58.3 kcal mol^{-1}, which is far too low compared to the average relaxation energy taking place in BH_2F and BF_3 being 67.4 kcal mol^{-1}. As a consequence, Lewis acidity of BHF_2 is slightly smaller than that in BH_2F.

Chlorine derivatives display somewhat different properties. Specifically, consecutive replacement of hydrogen atoms in BH_3 with chlorines boosts its Lewis acidity by increments of 7.0, 13.9, and 21.4 kcal mol^{-1} for mono-, di-, and trisubstitution, respectively. This implies a linear enhancement by 7 kcal mol^{-1} for each Cl atom meaning that the substituent effect is additive. The most striking feature is the fact that the $(EA)_1^{Koop}$ values are nearly identical spanning a narrow range of only 1.6 kcal mol^{-1} (Tables 1 and 2). Consequently, unlike in fluorine compounds, the effects of the initial state do not significantly contribute to the higher Lewis acidity of multisubstituted chloroboranes or its variation between the $BH_{3-m}Cl_m$ series. Rather, chlorine-substituted boranes exhibit pronounced acidities relative to the parent BH_3 molecule owing to a combination of the favorable $(BDE)^-$ energies and relaxation effects. As a final comment, we would like to compare our results with the recent paper of Bessac and Frenking.[37] They discussed the origin of higher acidity of BCl_3 compared to BF_3 and demonstrated that it occurred because of the energetically lower LUMO of BCl_3, which has led to stronger covalent interactions in BCl_3 complexes. In order to check this result, it is useful to express a difference of the corresponding hydride affinities by a triad of terms $HA(BCl_3) - HA(BF_3) = [(EA)_1^{Koop}(BCl_3) - (EA)_1^{Koop}(BF_3), E(ea)^{(n)}_{rex}(BCl_3) - E(ea)^{(n)}_{rex}(BF_3), (BDE)^-(BCl_3) - (BDE)^-(BF_3)]$, where the square brackets imply summation of three terms by convention. Our analysis yields $HA(BCl_3) - HA(BF_3) = 23.7$ kcal mol$^{-1} = [62.7, -35.3, -3.7]$. It appears that BCl_3 is by 23.7 kcal mol^{-1} a stronger Lewis acid than BF_3, since its LUMO orbital is indeed lower in energy by a substantial amount of 62.7 kcal mol^{-1}. This effect prevails over contributions associated with the relaxation energy and the final state effects thus leading to amplified acidity of trichloroborane. Therefore, our interpretation is in harmony with that suggested by Bessac and Frenking.[37]

Let us turn attention to bromine derivatives. Bromine-substituted compounds are stronger Lewis acids than BH_3 and the corresponding fluoro- and chloroboranes. Their acidity increases with the number of Br atoms reaching its maximum for BBr_3, where HA takes a value of 103.0 kcal mol^{-1}. A closer scrutiny of the data given in Tables 1 and 2 leads to a conclusion that $(EA)_1^{Koop}$ values of $BH_{3-m}Br_m$ ($m = 1-3$) molecules do not exhibit significant variation. Moreover, Koopmans' electron affinities are negative, albeit relatively small in absolute values thus contributing to the higher Lewis acidity of bromine derivatives relative to BH_3. Similarly, variations in relaxation energies upon electron attachment $E(ea)^{(n)}_{rex}$ and the bond dissociation energies $(BDEs)^-$ are both higher in bromine-substituted boranes than

in BH_3 (Table 2). Consequently, they contribute to Lewis acidity of bromoboranes in a synergistic way. We note in passing that higher relaxation energies in bromine derivatives are a result of the positive first adiabatic electron affinities in mono-, di-, and tribromo derivatives. It is interesting to point out that the initial state, finite state, and intermediate relaxation contribution to HAs are percentagewise roughly equal to $^1/_3$ each in all bromoboranes.

Methyl (CH_3) and hydroxyl (OH) groups attached to boron act as electron withdrawing substituents, which exhibit a characteristic pseudo π-electron or π-electron donation via hyperconjugation and π-back-bonding mechanisms, respectively. It is, therefore, reasonable to assume that substitution of the BH_3 molecule with these groups would decrease electron-deficiency of the central boron atom and, consequently, lower their Lewis acidity. Perusal of the data presented in Tables 1 and 2 justifies this supposition. Since a hydroxyl group is a better σ-electron-acceptor than CH_3, hydroxyl derivatives $BH_{3-m}(OH)_m$ ($m = 1-3$) are less potent Lewis acids, with $B(OH)_3$ exhibiting the lowest hydride affinity of all systems investigated here. Its HA value is 34.7 kcal mol^{-1}, which is two times smaller than predicted for BH_3. This is a consequence of a fact that the electronegative substituent stabilizes bonding and destabilizes virtual antibonding MOs as discussed in the fluoroborane series. Moreover, it is important to keep in mind that the "empty boron 2p orbital" in $BH(OH)_2$ and $B(OH)_3$ corresponds to LUMO + 2 and LUMO + 3 molecular orbitals (Figure 1), respectively, with a consequence that the respective Koopmans' electron affinities $(EA)_3^{Koop}$ and $(EA)_4^{Koop}$ are extremely low (-112.5 kcal mol^{-1} and -152.9 kcal mol^{-1}). One thing in common to both groups of compounds is given by the fact that consecutive addition of substituents increases $E(ea)^{(n)}_{rex}$ values. This is in accordance with the general notion that the polarizability of a molecule increases with a number of the alkyl groups. However, the overwhelming influence is exerted once again by Koopmans' electron affinities, which in turn reflect properties of the initial state. It is worth pointing out that the decrease in Lewis acidity of $BH_{3-m}X_m$ ($m = 1-3$, $X = CH_3$, OH) systems occurs linearly as m increases in all compounds, boric acid $B(OH)_3$ being a notable exception. Its HA value is close to that in $BH(OH)_2$. This unexpected finding can be rationalized by favorable H-bonding interactions among OH groups in the resulting $B(OH)_3$ and H^- adducts (Figure 2).

More specifically, it turns out that boric acid assumes distorted tetrahedral spatial arrangement upon the H^- addition, which enables three OH groups to form strong OH$\cdots$O hydrogen bonds with H$\cdots$O bond distances as low as 2.198 Å. The same holds for the $B(OH)_3$ radical anion, where an additional shortening of the OH$\cdots$O hydrogen bond distance by 0.2 Å upon electron attachment takes place (Figure 2). This leads to very high relaxation energy of 106 kcal mol^{-1} (Table 1). It should be mentioned that the initial boric acid $B(OH)_3$ is planar, where the hydrogen bonding effect is somewhat less pronounced.

It is of some interest to try to interpret calculated hydride affinities (HAs) in Table 1 by Pearson's hard and soft acid
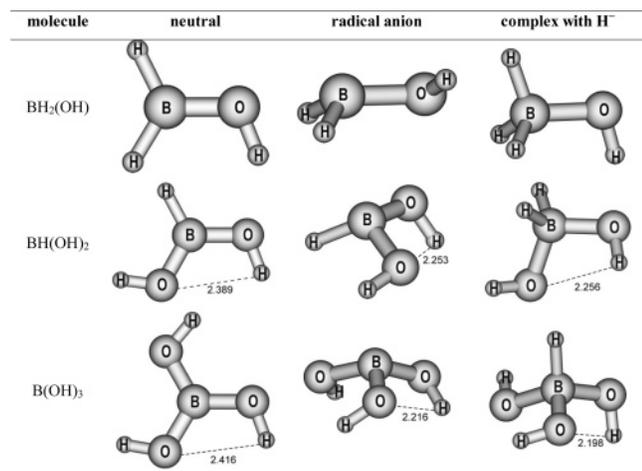
Figure 2. Spatial arrangements of the BH_3 hydroxy-derivatives as obtained by MP2(full)/6-31G(d) level of theory.

Table 3. The First Adiabatic Ionization Energies $(IE)_1{}^{ad}$'s, Electron Affinities $(EA)_1{}^{ad}$'s, and Pearson's Hardness Parameters Calculated by the G2(MP2) Method[a]

molecule	$(IE)_1{}^{ad}$	$(EA)_1{}^{ad}$	η
BH_3	281.0	−3.1	6.2
	(277.3 ± 0.6)		
BH_2F	285.1	−16.9	6.5
BHF_2	304.5	−23.8	7.1
BF_3	364.1	−17.9	8.3
	(362.0 ± 6.9)		
BH_2Cl	265.4	−1.7	5.8
$BHCl_2$	274.2	2.8	5.9
	(274.7 ± 0.5)		
BCl_3	268.2	9.5	5.6
	(268.4 ± 0.5)		
BH_2Br	252.0	3.6	5.4
$BHBr_2$	245.5	11.5	5.1
	(251.8 ± 0.5)		
BBr_3	246.3	19.0	4.9
	(242.4 ± 0.5)		
BH_2Me	265.0	−11.9	6.0
$BHMe_2$	244.8	−17.5	5.7
BMe_3	231.0	−19.3	5.4
	(239.8 ± 4.6)		
$BH_2(OH)$	261.3	−28.1	6.3
$BH(OH)_2$	276.6	−44.6	7.0
$B(OH)_3$	276.4	−46.9	7.0

[a] η values are given in eV, while $(IE)_1{}^{ad}$ and $(EA)_1{}^{ad}$ are in kcal mol^{-1}. The experimental IE results are given within parentheses and are taken from ref 55.

and base (HSAB) principle. Pearson's classification of acids and bases hinges on the global hardness parameter η, which he defined as[25,56]

$$\eta = \left(\frac{IE - EA}{2}\right) \qquad (8)$$

where IE and EA denote the first adiabatic ionization energy and electron affinity of the acid or base under scrutiny, respectively. Employing the G2(MP2) method and eq 8 we have calculated ionization energies and electron affinities of all considered systems. The corresponding hardness parameters η are presented in Table 3. A graphical plot of Pearson's η parameters versus calculated hydride affinities (Figure 3) shows a large scatter of the data. Regression analysis using
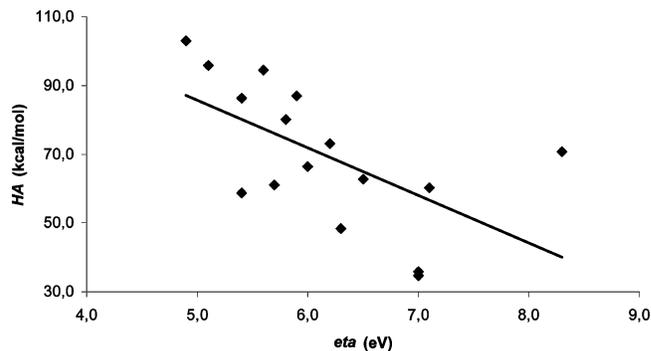
(56) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.

Figure 3. Calculated hardness parameters η vs hydride affinities of borane derivatives.

the least-squares fit method yields a very poor correlation as evidenced by regression coefficient $R^2 = 0.356$. It can be safely stated that Pearson's HSAB concept is unable to quantitatively interpret the calculated trend of changes in HA values of the studied molecules. This is not surprising, because there exist many other examples in the literature, where HSAB principle does not apply.[57]

It is interesting to associate hydride affinities with the adiabatic electron affinities instead. One obtains a fair linear relation

$$(HA) = 1.059 \cdot (EA)_1{}^{ad} + 82.2 \text{ kcal mol}^{-1} \qquad (9)$$

with regression coefficient $R^2 = 0.974$. The largest deviations from the straight line are found for molecules BF_3 (7.6 kcal mol^{-1}) and BH_3 (5.8 kcal mol^{-1}). Since in our picture adiabatic electron affinities include both Koopmans' electron affinities $(EA)_n{}^{Koop}$ and relaxation energies $E(ea)^{(n)}{}_{rex}$, the linear relation (eq 9) supports our earlier conclusion that the homolytic bond association energies $(BDE)^-$ are less important in determining hydride affinities of borane compounds.

Geometric and Bonding Parameters. Selected $[B-H]^-$ bond distances and representative bonding parameters are displayed in Table 4. It is important to note that all neutral Lewis acids are planar. Addition of an extra electron leading to anion radicals induces pyramidalization and elongates boron−heteroatom bonds. The reason behind this is that pyramidalization brings substituents closer to each other thus increasing their repulsion. Another reason for B−R bond elongation is redistribution of the p-character. Pyramidal B−R bonds possess higher p-character and consequently longer bonds. The same holds for $[LA-H]^-$ adducts. It is worth pointing out that all B−X bonds in neutral species possess very close bond distances within the same family of compounds. Apart from geometries, we shall make use of the atomic charges, which offer an insight into the redistribution of the electron density upon hydride anion attachment. They are obtained by Löwdin's[58] symmetrical partition of the electron density between pairs of atoms. The formal atomic density of the B atom in anion radicals is increased relative to neutral Lewis acids as expected (Table 4). The

(57) Chandrakumar, K. R. S.; Pal, S. *J. Phys. Chem. A* **2002**, *106*, 11775 and references therein.
(58) Löwdin, P. O. *J. Chem. Phys.* **1950**, *18*, 63.

Table 4. Bond Distances (in Å) and Löwdin Atomic Charges (in |e|) for Studied Borane Derivatives[a]

| | B−X bond distance[a] | | | [B−H]⁻ bond | boron atomic charge | | |
molecule	neutral	radical anion	adduct	distance adduct	neutral	radical anion	adduct
BH₃	1.194	1.223	1.237	1.236	−0.17	−0.86	−0.76
BH₂F	1.329	1.453	1.463	1.244	0.05	−0.48	−0.35
BHF₂	1.324	1.437	1.441	1.244	0.18	−0.23	−0.10
BF₃	1.322	1.425	1.425	1.236	0.29	−0.07	0.05
BH₂Cl	1.733	1.913	1.954	1.219	−0.16	−0.60	−0.52
BHCl₂	1.732	1.873	1.902	1.207	−0.18	−0.45	−0.38
BCl₃	1.736	1.852	1.872	1.198	−0.22	−0.35	−0.31
BH₂Br	1.892	2.098	2.147	1.214	−0.16	−0.58	−0.51
BHBr₂	1.890	2.044	2.075	1.201	−0.17	−0.42	−0.38
BBr₃	1.894	2.019	2.040	1.193	−0.18	−0.31	−0.28
BH₂Me	1.561	1.629	1.648	1.239	−0.08	−0.67	−0.58
BHMe₂	1.567	1.627	1.645	1.242	0.01	−0.51	−0.42
BMe₃	1.575	1.625	1.644	1.246	0.09	−0.36	−0.29
BH₂(OH)	1.359	1.504	1.517	1.251	−0.07	−0.56	−0.42
BH(OH)₂	1.363	1.477	1.488	1.265	0.01	−0.32	−0.21
B(OH)₃	1.374	1.491	1.481	1.248	0.08	−0.15	−0.06

[a] The former values are calculated by the MP2(full)/6-31(d) model, whereas the latter are obtained at the HF/6-31G(d)//MP2(full)/6-31(d) level of theory. A heteroatom is denoted by X, the parent molecule BH₃ being an exception, where X = H.

highest boron atom electron density charge is found in the case of BH₃, whereas the lowest are found in fluorinated boranes. In addition, the electron density is more strongly drifted to fluorine atoms in anion radicals. Interestingly, the boron atom becomes practically electroneutral in BF_3^-. It comes as no surprise that a pronounced decrease in B electron density occurs after formation of covalent bond between the radical anions and the H atom. This is followed by (deformed) tetrahedral spatial arrangement of substituents around the central boron atom and B−X bond extension. Inspection of the B−H bond distances in formed complexes leads to a conclusion that the trend of changes in hydride affinities (HA) is roughly inversely proportional to the B−H bond distances.

Concluding Remarks

A reasonably accurate G2(MP2) method is utilized to predict hydride affinities (HAs) of selected borane Lewis acids (BH$_{3-m}$X$_m$, m = 0−3, X = F, Cl, Br, CH₃, and OH). The so-obtained HA values serve as a good probe and quantitative measure of their electrophilicity and Lewis acidities. There is a simple and intuitively appealing picture of the process of H⁻ addition to borane derivatives, which offers a new and useful interpretative tool. It is embodied in the triadic formula, which involves separation of the interaction process between Lewis acid and hydride anion into three consecutive steps: (1) the electron ejection from the hydride ion, (2) addition of the pruned electron to the Lewis acid in question, and (3) homolytic chemical bond formation between two formed radicals. This approach enables straightforward delineation of the initial state (neutral Lewis acid),

the final state (hydrided adduct) effects, and the intermediate radical anion reorganization contribution to the HA values. It turns out that the triadic formula serves as a useful vehicle in rationalizing trends of changes in Lewis acidities of the investigated systems, unlike Pearson's crude and qualitative HSAB principle, which is unable to reproduce the ab initio results. The simple picture offered by triadic formula enables classification of simple borane Lewis acids into three categories: (a) those exhibiting hydride affinities determined by initial state effects (fluoro-derivatives as well as methyl- and hydroxy-substituted boranes), (b) compounds whose Lewis acidities are strongly influenced by the relaxation effect and the final state properties (chlorine derivatives of borane), and (c) systems where Lewis acidity is given by an interplay of all three effects, as is the case in bromine-substituted boranes. It appears that all fluoro-, methyl-, and hydroxy-derivatives are weaker Lewis acids than the parent BH₃, whereas the chlorine- and bromine-substituted systems provide more potent Lewis acids compared to BH₃. Finally, BBr₃ is on the top of the hydride affinity scale with HA = 103.0 kcal mol⁻¹.

The unexpectedly large Lewis acidities of bromine and chlorine borane derivatives surpassing those of fluoro-substituted boranes have been the subject matter of much discussion in the past. Our results indicate that fluorine derivatives exhibit low Lewis acidity due to a very strong σ-electron withdrawing power of fluorine(s), which stabilizes bonding and destabilizes antibonding MOs. The latter leads to highly unfavorable Koopmans EA values.

Proposed analysis offers a deeper and more comprehensive insight into the interaction of neutral Lewis acids with the smallest Lewis base, H⁻ ion. This is of paramount importance, since it can guide both the experimental and computational chemists in predicting and designing new molecular systems exhibiting desired properties both in laboratories and in silico, respectively. For example, our calculations reveal that bis-BBr₂-substituted organic molecules provide powerful hydride sponges of unprecedented strength.[59] An important result of the present study is provided by a ladder of gas-phase hydride affinities of small mono-, di-, and trisubstituted borane derivatives. This is the first such ladder to the best of our knowledge.

In summary, it can be safely concluded that the introduced methodology provides a versatile tool in elucidating interactions between Lewis acid and the H⁻ anion, which can be applied to other acid−base pairs. This approach is particularly effective in discussing trends of changes in acidity/basicity of intimately related molecules, which will be discussed in detail in forthcoming papers.

(59) Unpublished results.