Clustering of H_2SO_4 with BX_3 (X=H, F, Cl, Br, CN,OH) compounds creates strong acids and superacids

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Abstract

The interaction of H_2SO_4 with boron compounds including BH_3, BF_3, BCl_3, BBr_3, $B(CN)_3$ and $B(OH)_3$ was studied computationally using the ωB97xD density functional. All the BX_3 compounds except $B(OH)_3$ bind to H_2SO_4 via both SOH...X hydrogen bonds, and interactions between the B atoms and the S=O oxygen atoms. $B(OH)_3$ interacts with H_2SO_4 solely through hydrogen bonds. $B(CN)_3$ and BCl_3 exhibit the strongest and weakest interactions with H_2SO_4, respectively. Natural bond orbital (NBO) analysis shows that the relative weakness of the H_2SO_4–BCl_3 interaction may be due to π-bonding between the B and Cl atoms, and the occupation of the p_z orbital of the B atom. The strong electron withdrawing groups CN in $B(CN)_3$ intensify electron deficiency of B atom and promote its tendency to capture electrons of oxygen atom of O=S group. Atoms in molecules (AIM) calculations show bond critical points (BCP) between the X groups of BX_3 and the hydrogen atoms of H_2SO_4 for all cases except X = OH. Enthalpies and Gibbs free energies of deprotonation in the gas phase (ΔH_{acid}, ΔG_{acid}) were calculated for $(BX_3)H_2SO_4$ and $(BX_3)_2H_2SO_4$ complexes. These data revealed that clustering of BX_3 with H_2SO_4 enhances the acidity of H_2SO_4 by about 9–58 kcal.mol^{-1}. The $(B(CN)_3)_2H_2SO_4$ cluster had ΔH_{acid} and ΔG_{acid} values of 255.0 and 246.7 kcal.mol^{-1}, respectively, and is the strongest Brønsted acids among the $(BX_3)_2H_2SO_4$ clusters.

Keywords: Boron compounds; H_2SO_4; Superacid; Lewis acid; Molecular clusters.

1. Introduction

Boron compounds are of interest because of their unique properties as Lewis acids [1-4], hydrogen storage compounds [5-8], and as catalysts in chemical reactions [9,10]. Also, because of the electron deficiency of the B atom, boron compounds are used as strong anion receptors [11,12]. Because of the wide application of boron compounds, considerable efforts have been devoted to synthesize these compounds and study their physical and chemical properties [13-15].

The interaction of a Lewis acid with a molecule enhances its acidity and promotes its hydride affinity [16]. This catalytic behavior is used for reduction of substrates by their coordination to the Lewis acids. Interaction of Lewis acids with water increases the acidity of the bound water between 20 to 50 pK_a units, depending on the strength of the Lewis acid [17]. Interaction of BeH_2 and BH_3 (borane) with $CH_2=CHXH_2$, $HC\equiv CXH_2$ (X = N, P, As, Sb) derivatives enhances the acidity of these compounds, however, the acidity enhancement due to interaction with BeH_2 is more than that of BH_3 [18]. Coordination of a molecule to a Lewis acid changes the intrinsic properties of the molecule; for example, conventional bases such as ammonia and aniline become strong Brønsted acids due to coordination to Lewis acids MH_2 (M=Be, Mg, Ca) [19]. Also, the interaction of Lewis acid $BeCl_2$ with weak acid acetic acid increases the acidity of acetic acid so that it can protonate amines in the gas phase [20]. Interaction of Lewis acids with the Brønsted acids increases the acidity so that these complexes could exhibit superacidity [21-23]. Brezeski et al. [21] studied acidity of Lewis-Brønsted acid systems including $HClO_4$ as the Brønsted acid and AlF_3 and SbF_5 as the Lewis acids. They showed that effect of SbF_5 on the acidity enhancement is more than that of AlF_3. Srivastava and Misra [23] theoretically assessed the acidity of some Lewis-Brønsted acids such as $BeCl_2$-HCl, BeF_2-HF, LiF-HF, LiCl-HCl, and BF_3-HF, and showed that $BeCl_2$-HCl with ΔG_{acid} of 272 $kcal.mol^{-1}$ is the strongest acids among this series. Superacids are compounds that are more stronger acids than pure sulfuric acid or have a Hammet acidity function less than -12 [24]. Compounds with ΔH_{acid} value less than 245 $kcal.mol^{-1}$ are classified as hyperacid [25]. Superacids have a wide application in synthesis of organic and inorganic chemistry and as catalyst in chemical industry [26,27]. Therefore, considerable attempts have been devoted to design and synthesis compounds with high acidity.

There are several strategies for designing a superacid, including delocalization of the negative charge of the conjugated base in aromatic rings [28-31], substitution of electron withdrawing groups (EWGs) in the structure of the superacid [32], and formation of a network of hydrogen bonds in the conjugated base [33]. Coordination of a strong Brønsted acid, such as H_2SO_4, to Lewis acids is another strategy, which we employ in this work to produce compounds with superacid or even hyperacid character. H_2SO_4 is a strong Brønsted acid with numerous applications in chemistry and industry. The interaction and clustering of H_2SO_4 with many organic molecule such amines, diamines or carboxylic acids, as well as inorganic compounds such as nitric acid and water, has been extensively studied due to the importance of such clusters for new-particle formation in the atmosphere [34-37]. While boron compounds (with the possible exception of $B(OH)_3$) are unlikely to be found in the atmospheric gas phase, a comparison of H_2SO_4–BX_3 clusters with previously studied H_2SO_4 clusters may provide further insight into how the interactions of H_2SO_4 with other molecules affects its acidity and other chemical characteristics. In this work, the formation of complexes between BX_3 (X=H, F, Cl, Br, CN, OH) and H_2SO_4 are studied using density functional theory, and the acidities of these complexes are assessed in gas phase, and compared to H_2SO_4-$H_2SO_4$and H_2SO_4-HNO_3 clusters.

2-Computational details

The structures of $(BX_3)_{1,2}H_2SO_4$ clusters and their corresponding conjugated bases were fully optimized using the ωB97xD functional and the aug-cc-pVDZ basis set, which includes both diffuse and polarization functions. The electronic energies without thermal and zero point vibrational energy (ZPE) corrections were used to compare the stability of different isomers of each complex. Natural bond orbital (NBO) calculations were carried out at the same level of theory to obtain distribution of the electron in the atoms and bond before and after the interactions. All

DFT calculations were carried out using Gaussian 09 software [38]. Quantum theory of atoms in molecules (QTAIM) was used to calculate density, ρ, its Laplacian, $\nabla^2\rho$, potential, $V(r)$, and kinetic electron energy densities, $G(r)$, at bond critical points (BCP). The QTAIM calculation were performed by AIM2000 software [39]. Benchmarking calculations on $(BH_3)_{1,2}H_2SO_4$ clusters were performed at the CCSD(T)-F12/VTZ-F12 level [40,41] using the Molpro 2015.1 program [42,43]. The results indicate that ωB97xD/aug-cc-pVDZ describes the BX_3 – H_2SO_4 interactions accurately. (Table S1 in Supplementary Materials). To validate our choice of basis set, ΔH and ΔG values for formation of the $(BX_3)H_2SO_4$ clusters were also computed using the aug-cc-pVTZ basis set. Comparison of the values (Table S2) shows that there is a good agreement between the data computed by these two basis sets.

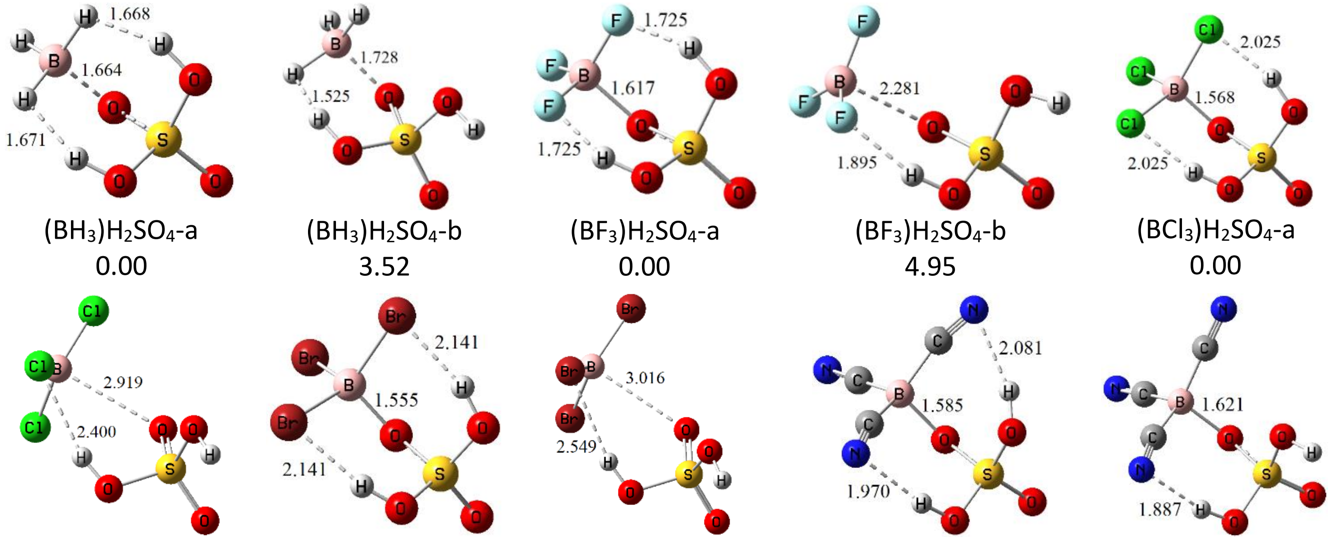
The enthalpy of deprotonation of an acid (HA) in the gas phase, ΔH_{acid}, is usually used as an index of its intrinsic acidity:

$$AH \rightarrow A^- + H^+, \quad \Delta H_{acid} \quad (1)$$

The ΔH_{acid} values (and the corresponding free energies of deprotonation, ΔG_{acid}) were computed at the ωB97XD/aug-cc-pVDZ level of theory at 298 K.

3- Results and discussion

Figures 1 and 2 show the optimized structures of the $(BX_3)H_2SO_4$ and $(BX_3)_2H_2SO_4$ clusters, respectively, with X=H, F, Cl, Br, CN. Because of the electron deficiency of the boron atom, it interacts with the lone pair electrons of the doubly bounded oxygen atoms of H_2SO_4. Furthermore, in the $(BX_3)_1H_2SO_4$ clusters, H_2SO_4 can form one or two hydrogen bonds with the X atoms of BX_3, OH…X. Two different isomers (conformers) for each $(BX_3)H_2SO_4$ cluster were considered, denoted **a** and **b**. The relative energies of the isomers **a** and **b** are shown in Fig. 1 in kcal.mol^{-1}. The isomers $(BX_3)_1H_2SO_4$-**a** with two OH…X interactions are about 3.5–5.0 kcal.mol^{-1} more stable than the corresponding isomers $(BX_3)_1H_2SO_4$-**b** with only one OH…X interaction. In addition, the B-O bond lengths in the $(BX_3)_1H_2SO_4$-**a** isomers are shorter than the corresponding bonds in the $(BX_3)_1H_2SO_4$-**b** isomers, indicating stronger B-O interaction in the former. In the case of $(BX_3)_2H_2SO_4$ clusters (Fig. 2), four isomers were considered (**a**, **b**, **c**, **d**). In the $(BX_3)_2H_2SO_4$-**a** and $(BX_3)_2H_2SO_4$-**b** isomers, the oxygen atoms of the S=O groups interact with boron atoms of two BX_3 molecules. Also, the H atoms of the OH groups can interact with X atoms of one BX_3 molecule, $(BX_3)_2H_2SO_4$-**a**, or two BX_3 molecules, $(BX_3)_2H_2SO_4$-**b**. In the $(BX_3)_2H_2SO_4$-**c** and $(BX_3)_2H_2SO_4$-**d** clusters, the BX_3 molecules interact with each other via a BX-BX interaction. The $(BX_3)_2H_2SO_4$-**c** structures are the most stable isomers except for X=CN, for which the isomer **d** is more stable. We also searched for zwitterionic structures, where one of the protons of H_2SO_4 has migrated to an acceptor site in a BX_3 molecule. However, in no cases were these structures found to be lower in energy than the isomers presented here. The zwitterionic complexes, $(BX_3H^+)HSO_4^-$, converged to the stable $(BX_3)H_2SO_4$ structures after structure optimization. The $(BX3)_{1,2}H_2SO_4$ clusters may participate in different reactions such as formation of HX + X_2B-OSO_3H and/or HX + $(BX_3)X_2B$-OSO_3H and/or 2HX + $(X_2B$-$O)_2SO_2$ which are not the purpose of this work.



$(BH_3)H_2SO_4$-a 0.00

$(BH_3)H_2SO_4$-b 3.52

$(BF_3)H_2SO_4$-a 0.00

$(BF_3)H_2SO_4$-b 4.95

$(BCl_3)H_2SO_4$-a 0.00

$(BCl_3)H_2SO_4$-b 4.41

$(BBr_3)H_2SO_4$-a 0.00

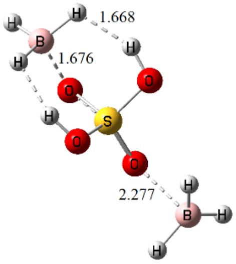
$(BBr_3)H_2SO_4$-a 4.54

$(B(CN)_3)H_2SO_4$-a 0.00

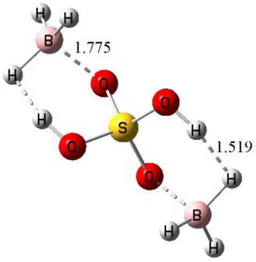
$(B(CN)_3)H_2SO_4$-b 4.11

Figure 1. Comparison of stabilities of different isomers of the $(BX_3)H_2SO_4$ clusters. The relative energies and bond lengths are in kcal.mol^{-1} and Å, respectively. See Table 1 for absolute formation enthalpies and free energies.

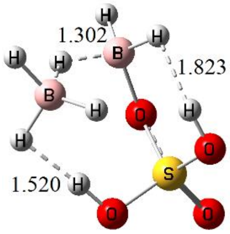
The results of the NBO analysis (Fig. S1-S6) show that in the $(BX_3)_1H_2SO_4$-**a** isomers, a two-center bond (BD) between B and O is formed, while in the $(BX_3)_1H_2SO_4$-**b** isomers, a B-O bond is not formed (except for X=H and X=CN). The reason for this is likely that the two OH…X interactions in the $(BX_3)_1H_2SO_4$-**a** isomers decrease the distance between BX_3 and H_2SO_4, thus facilitating the formation of a B-O bond. Although NBO does not predict a B-O bond in most of the $(BX_3)_1H_2SO_4$-**b** isomers, AIM analysis show a bond critical bond (BCP) between B and O atoms in all of these structures (Table S3). However, the electron density, ρ, at the B-O BCPs of the $(BX_3)_1H_2SO_4$-**a** isomers is higher than that for the $(BX_3)_1H_2SO_4$-**b** isomers, indicating stronger B-O interaction in the former. In addition, AIM calculations shows bonding interactions between the X atoms of BX_3 and the hydrogen atoms of H_2SO_4, X…HO. Interestingly, AIM analysis also finds BCPs corresponding to H…H bonding interactions between the H atom of BH_3 and the H atoms of H_2SO_4 (Tables S3 and S4). NBO results for $(BX_3)_2H_2SO_4$ clusters are analogous to those for $(BX_3)_1H_2SO_4$. According to the NBO analysis, there is one B-O bond in all of the $(BX_3)_2H_2SO_4$-**a** isomers, while B-O bonds are not formed in the $(BX_3)_2H_2SO_4$-**b** isomers (except for X=H and CN). The reason for the existence of B-O bonds in the $(BH_3)_{1,2}H_2SO_4$-**b** and $(B(CN)_3)_{1,2}H_2SO_4$-**b** isomers is likely that the energy required for BH_3 and $B(CN)_3$ to convert from planar to pyramidal form is smaller than for the other BX_3 molecules (See Figure 4). This allows these molecules to interact with the O atoms of H_2SO_4 more easily, and also likely explains why the $(BX_3)_2H_2SO_4$-**b** structure is lower in energy than $(BX_3)_2H_2SO_4$-**a** for these cases.



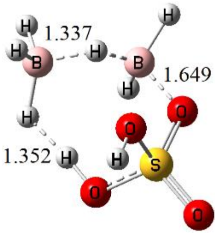
$(BH_3)_2H_2SO_4$-a
16.54



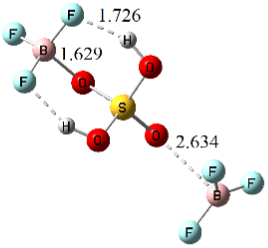
$(BH_3)_2H_2SO_4$-b
14.09



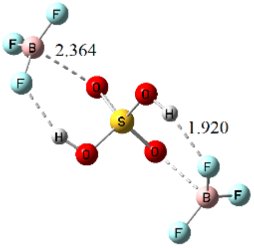
$(BH_3)_2H_2SO_4$-c
0.00



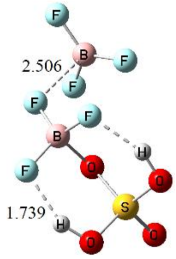
$(BH_3)_2H_2SO_4$-d
4.76



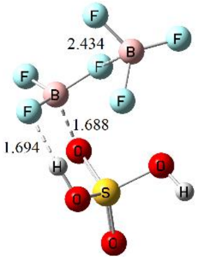
$(BF_3)_2H_2SO_4$-a
1.27



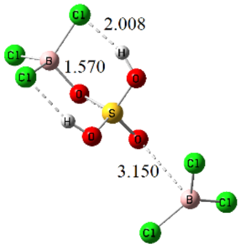
$(BF_3)_2H_2SO_4$-b
2.35



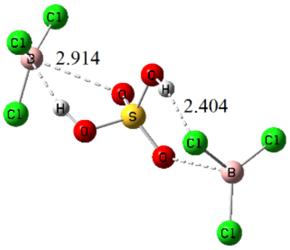
$(BF_3)_2H_2SO_4$-c
0.00



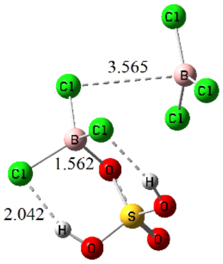
$(BF_3)_2H_2SO_4$-d
3.92



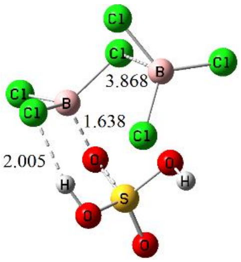
$(BCl_3)_2H_2SO_4$-a
1.71



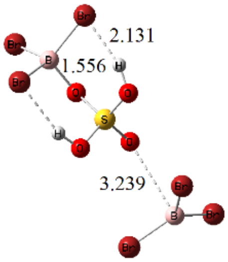
$(BCl_3)_2H_2SO_4$-b
3.75



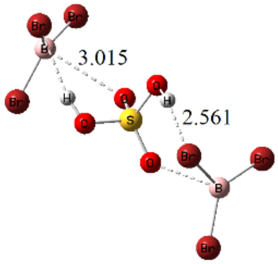
$(BCl_3)_2H_2SO_4$-c
0.0



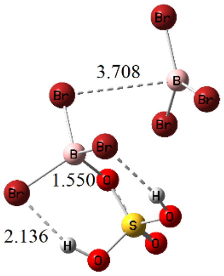
$(BCl_3)_2H_2SO_4$-d
6.59



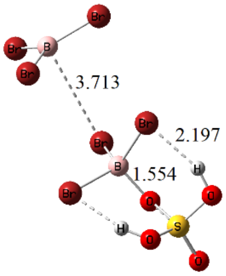
$(BBr_3)_2H_2SO_4$-a
2.57



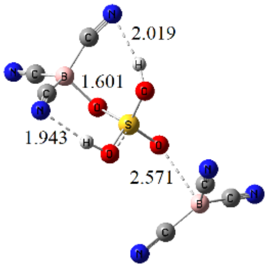
$(BBr_3)_2H_2SO_4$-b
5.02



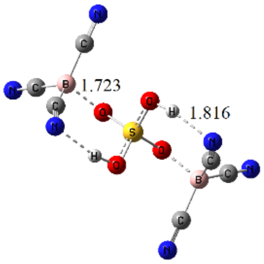
$(BBr_3)_2H_2SO_4$-c
0.0



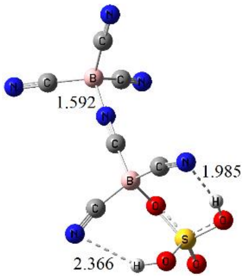
$(BBr_3)_2H_2SO_4$-d
0.91



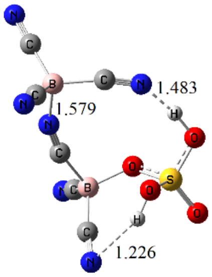
$(B(CN)_3)_2H_2SO_4$-a
36.43



$(B(CN)_3)_2H_2SO_4$-b
34.59



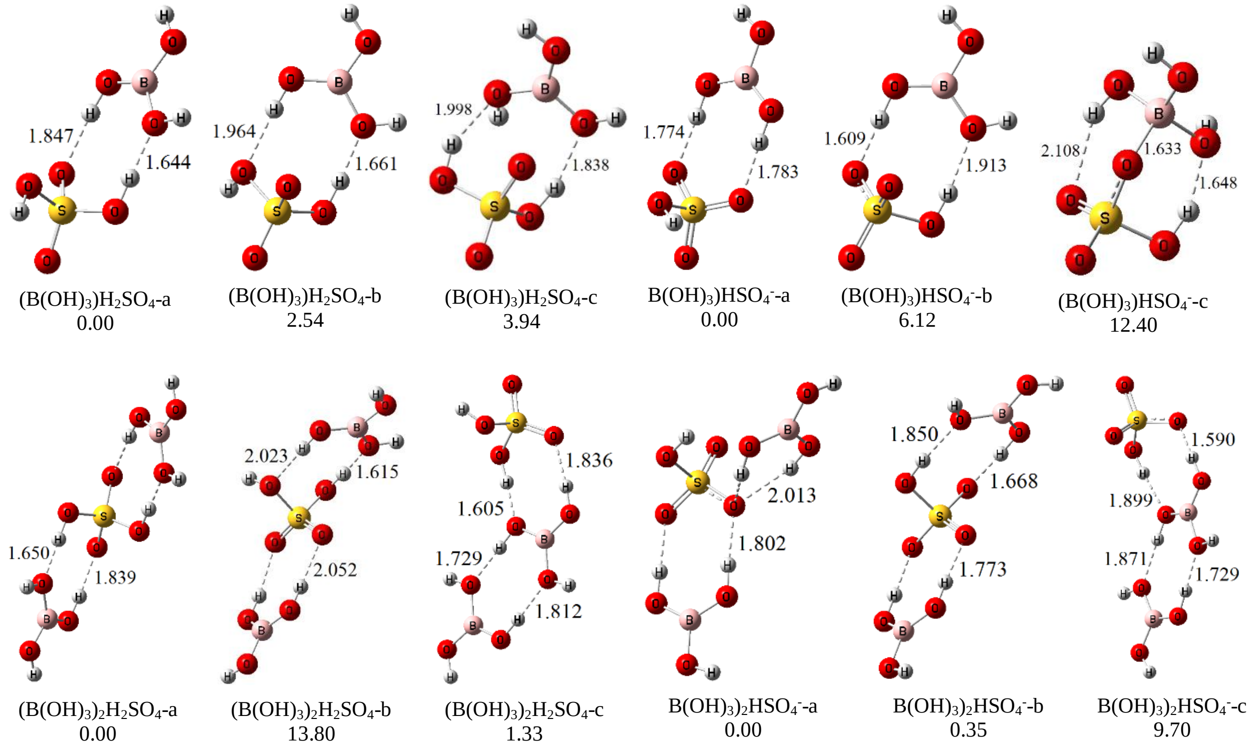
$(B(CN)_3)_2H_2SO_4$-c
12.48



$(B(CN)_3)_2H_2SO_4$-c
0.00

Figure 2. Comparison of stabilities of different isomers of the $(BX_3)_2H_2SO_4$ clusters. The relative energies and bond lengths are in kcal.mol^{-1} and Å, respectively. See Table 1 for absolute formation enthalpies and free energies.

We also studied the interaction of $B(OH)_3$ with H_2SO_4, as $B(OH)_3$ is the most likely boron compound to be found in oxidizing environments such as the atmosphere. The optimized structures of the $(B(OH)_3)_{1,2}H_2SO_4$ and $(B(OH)_3)_{1,2}HSO_4^-$ complexes are shown in Fig. 3. These neutral and anionic structures do not show any B-O interaction between B atom of $B(OH)_3$ and O atoms of H_2SO_4, and the complexes are mainly held together by hydrogen bonds. We obtained an optimized structure with a B-O interaction, $B(OH)_3)HSO_4^-$-c, however, this isomer was by about 12.4 kcal.mol^{-1} less stable than the corresponding isomers with hydrogen bonds. Formation of a B-O bond requires a planar/pyramidal conversion of $B(OH)_3$ and a hybridization change of B from sp^2 to sp^n (n>2). Figure 4 shows that this deformation of $B(OH)_3$ is not energetically favorable.



$(B(OH)_3)H_2SO_4$-a 0.00

$(B(OH)_3)H_2SO_4$-b 2.54

$(B(OH)_3)H_2SO_4$-c 3.94

$B(OH)_3)HSO_4^-$-a 0.00

$(B(OH)_3)HSO_4^-$-b 6.12

$(B(OH)_3)HSO_4^-$-c 12.40

$(B(OH)_3)_2H_2SO_4$-a 0.00

$(B(OH)_3)_2H_2SO_4$-b 13.80

$(B(OH)_3)_2H_2SO_4$-c 1.33

$B(OH)_3)_2HSO_4^-$-a 0.00

$B(OH)_3)_2HSO_4^-$-b 0.35

$B(OH)_3)_2HSO_4^-$-c 9.70

Figure 3. Optimized structures of $(B(OH)_3)_{1,2}H_2SO_4$ complexes and their conjugated bases. The energies and bond lengths are in kcal.mol^{-1} and Å, respectively.

The calculated values of ΔH and ΔG for formation of the $(BX_3)H_2SO_4$ and $(BX_3)_2H_2SO_4$ clusters are summarized in Table 1. Comparison of the ΔH values reveals that formation of approximately all the $(BX_3)_{1,2}H_2SO_4$ clusters is exothermic. The electron withdrawing groups (EWG) F, Cl, and Br intensify the electron deficiency of the boron atom, and hence we expect stronger interactions for BF_3/H_2SO_4, BCl_3/H_2SO_4, and BBr_3/H_2SO_4 relative to BH_3/H_2SO_4. The shorter B-O bond length in the $(BX_3)H_2SO_4$-**a** clusters (X=F, Cl, Br) compared to $(BH_3)H_2SO_4$-**a** indicates stronger interactions in the former. However, the ΔH values do not follow this ordering. This discrepancy may be attributed to the planar/pyramidal conversion energy of BX_3 [44]. In the complexes, the originally planar BX_3 molecule with sp^2 hybridization converts to a less stable bent BX_3 structure (Fig. 4). For example, planar BH_3 is 22.0 $kcal.mol^{-1}$ more stable than its corresponding hypothetical pyramidal isomer (sp^3), while planar BF_3 is by 38.9 $kcal.mol^{-1}$ more stable than its corresponding pyramidal isomer (Fig. 4). Also, π-bonding between the lone pair electrons of the halogens and the empty p_z orbital of the boron atom may decrease the Lewis acidity of BX_3 (X=F, Cl, Br) [45-48]. The results of NBO analysis of the free BX_3 molecules (X= H, F, Cl, Br, CN, OH) in Fig. S1 show a π-bonding interaction in BCl_3 and BBr_3, leading to occupation of the p_z orbital of the boron atom. BCl_3 and BBr_3 accordingly exhibit the weakest interactions with H_2SO_4 among the studied BX_3 compounds. In the other BX_3 molecules (X= H, F, CN), the B-X interaction is a single σ-bond, and the p_z orbital of B is empty, enabling stronger interaction of B with the O atoms of H_2SO_4. Although H_2SO_4-BF_3 interaction is stronger than H_2SO_4-BCl_3, Bessac and Frenking [45] reported a reverse ordering for interaction energies of NH_3-BF_3 and NH_3-BCl_3 systems. They attributed the stronger interaction of NH_3-BCl_3 to energetically lower lying LUMO of BCl_3. Furthermore, exact theoretical analysis showed that effect of electron affinity (lower lying LUMO) of BX_3 on its Lewis acidity is more than the effect of planar/pyramidal conversion [47]. Hence, BCl_3 and BBr_3 should be more acidic than BF_3, and higher interaction energy of the H_2SO_4-BF_3-**a** compared to H_2SO_4-BCl_3-**a** may not be due to higher acidity of BF_3, instead, it may be because of stronger BF…HO hydrogen bonding interaction relative to weaker BCl…HO interaction in the

$(BX_3)H_2SO_4$ clusters. This illustrates that the structure and nature of the Lewis base, such as its ability to form hydrogen bonds, its polarizability and number of the electron lone pairs, may influence the BX_3-Lewis base interactions [49].

Table 1. The calculated values of ΔH, ΔG and equilibrium constants, K_{eq}, for formation of the $(BX_3)_{1,2}H_2SO_4$ clusters in the gas phase and at 298 K. ΔG values are computed using a reference pressure of 1 atm.

reaction	ΔH (kcal.mol^{-1})	ΔG (kcal.mol^{-1})	K_{eq} (1/atm)
$BH_3 + H_2SO_4 \rightarrow (BH_3)H_2SO_4$-a	-13.47	-2.48	6.59×10^{1}
$BH_3 + H_2SO_4 \rightarrow (BH_3)H_2SO_4$-b	-10.13	0.15	7.76×10^{-1}
$BF_3 + H_2SO_4 \rightarrow (BF_3)H_2SO_4$-a	-11.72	0.68	3.17×10^{-1}
$BF_3 + H_2SO_4 \rightarrow (BF_3)H_2SO_4$-b	-6.36	2.86	7.98×10^{-3}
$BCl_3 + H_2SO_4 \rightarrow (BCl_3)H_2SO_4$-a	-9.39	4.93	2.42×10^{-4}
$BCl_3 + H_2SO_4 \rightarrow (BCl_3)H_2SO_4$-b	-3.54	4.01	1.14×10^{-3}
$BBr_3 + H_2SO_4 \rightarrow (BBr_3)H_2SO_4$-a	-9.97	4.38	6.13×10^{-4}
$BBr_3 + H_2SO_4 \rightarrow (BBr_3)H_2SO_4$-b	-3.81	3.63	2.17×10^{-3}
$B(CN)_3 + H_2SO_4 \rightarrow (B(CN)_3)H_2SO_4$-a	-26.08	-11.85	4.91×10^{8}
$B(CN)_3 + H_2SO_4 \rightarrow (B(CN)_3)H_2SO_4$-b	-21.84	-8.37	1.38×10^{6}
$B(OH)_3 + H_2SO_4 \rightarrow (B(OH)_3)H_2SO_4$-a	-13.37	-3.37	2.96×10^{2}
$B(OH)_3 + H_2SO_4 \rightarrow (B(OH)_3)H_2SO_4$-b	-10.78	-0.19	1.36×10^{0}
$BH_3 + (BH_3)H_2SO_4\text{-a} \rightarrow (BH_3)_2H_2SO_4$-a	-2.04	5.69	6.62×10^{-5}
$BH_3 + (BH_3)H_2SO_4\text{-a} \rightarrow (BH_3)_2H_2SO_4$-b	-4.44	5.31	1.27×10^{-4}
$BH_3 + (BH_3)H_2SO_4\text{-a} \rightarrow (BH_3)_2H_2SO_4$-c	-17.75	-6.88	1.11×10^{5}
$BH_3 + (BH_3)H_2SO_4\text{-a} \rightarrow (BH_3)_2H_2SO_4$-d	-12.99	-3.80	6.12×10^{2}
$BH_3 + (BH_3)H_2SO_4\text{-b} \rightarrow (BH_3)_2H_2SO_4$-a	-5.38	3.06	5.69×10^{-3}
$BH_3 + (BH_3)H_2SO_4\text{-b} \rightarrow (BH_3)_2H_2SO_4$-b	-7.78	2.68	1.08×10^{-2}
$BH_3 + (BH_3)H_2SO_4\text{-b} \rightarrow (BH_3)_2H_2SO_4$-c	-21.09	-9.51	9.53×10^{6}
$BH_3 + (BH_3)H_2SO_4\text{-b} \rightarrow (BH_3)_2H_2SO_4$-d	-16.32	-6.43	5.25×10^{4}
$BF_3 + (BF_3)H_2SO_4\text{-a} \rightarrow (BF_3)_2H_2SO_4$-a	-2.01	4.92	2.46×10^{-4}
$BF_3 + (BF_3)H_2SO_4\text{-a} \rightarrow (BF_3)_2H_2SO_4$-b	-0.53	4.93	2.42×10^{-4}
$BF_3 + (BF_3)H_2SO_4\text{-a} \rightarrow (BF_3)_2H_2SO_4$-c	-3.24	4.53	4.73×10^{-4}
$BF_3 + (BF_3)H_2SO_4\text{-a} \rightarrow (BF_3)_2H_2SO_4$-d	0.51	8.71	4.10×10^{-7}
$BF_3 + (BF_3)H_2SO_4\text{-b} \rightarrow (BF_3)_2H_2SO_4$-a	-7.37	2.74	9.78×10^{-3}
$BF_3 + (BF_3)H_2SO_4\text{-b} \rightarrow (BF_3)_2H_2SO_4$-b	-5.89	2.75	9.61×10^{-3}
$BF_3 + (BF_3)H_2SO_4\text{-b} \rightarrow (BF_3)_2H_2SO_4$-c	-8.60	2.34	1.91×10^{-2}
$BF_3 + (BF_3)H_2SO_4\text{-b} \rightarrow (BF_3)_2H_2SO_4$-d	-4.85	6.52	1.65×10^{-5}
$BCl_3 + (BCl_3)H_2SO_4\text{-a} \rightarrow (BCl_3)_2H_2SO_4$-a	-0.54	5.09	1.82×10^{-4}
$BCl_3 + (BCl_3)H_2SO_4\text{-a} \rightarrow (BCl_3)_2H_2SO_4$-b	2.29	4.59	4.30×10^{-4}
$BCl_3 + (BCl_3)H_2SO_4\text{-a} \rightarrow (BCl_3)_2H_2SO_4$-c	-2.23	4.12	9.56×10^{-4}
$BCl_3 + (BCl_3)H_2SO_4\text{-a} \rightarrow (BCl_3)_2H_2SO_4$-d	4.54	10.97	9.00×10^{-9}
$BCl_3 + (BCl_3)H_2SO_4\text{-b} \rightarrow (BCl_3)_2H_2SO_4$-a	-6.39	6.01	3.91×10^{-5}
$BCl_3 + (BCl_3)H_2SO_4\text{-b} \rightarrow (BCl_3)_2H_2SO_4$-b	-3.56	5.51	9.10×10^{-5}
$BCl_3 + (BCl_3)H_2SO_4\text{-b} \rightarrow (BCl_3)_2H_2SO_4$-c	-8.08	5.03	2.03×10^{-4}
$BCl_3 + (BCl_3)H_2SO_4\text{-b} \rightarrow (BCl_3)_2H_2SO_4$-d	-1.30	11.88	1.91×10^{-9}
$BBr_3 + (BBr_3)H_2SO_4\text{-a} \rightarrow (BBr_3)_2H_2SO_4$-a	-1.09	4.92	2.46×10^{-4}
$BBr_3 + (BBr_3)H_2SO_4\text{-a} \rightarrow (BBr_3)_2H_2SO_4$-b	1.65	5.56	8.29×10^{-5}
$BBr_3 + (BBr_3)H_2SO_4\text{-a} \rightarrow (BBr_3)_2H_2SO_4$-c	-3.73	2.38	1.79×10^{-2}
$BBr_3 + (BBr_3)H_2SO_4\text{-a} \rightarrow (BBr_3)_2H_2SO_4$-d	-2.81	3.22	4.28×10^{-3}
$BBr_3 + (BBr_3)H_2SO_4\text{-b} \rightarrow (BBr_3)_2H_2SO_4$-a	-7.25	5.67	6.94×10^{-5}
$BBr_3 + (BBr_3)H_2SO_4\text{-b} \rightarrow (BBr_3)_2H_2SO_4$-b	-4.51	6.31	2.35×10^{-5}
$BBr_3 + (BBr_3)H_2SO_4\text{-b} \rightarrow (BBr_3)_2H_2SO_4$-c	-9.88	3.13	5.03×10^{-3}
$BBr_3 + (BBr_3)H_2SO_4\text{-b} \rightarrow (BBr_3)_2H_2SO_4$-d	8.96	3.98	1.21×10^{-3}

$B(CN)_3 + (B(CN)_3)H_2SO_4\text{-a} \rightarrow (B(CN)_3)_2H_2SO_4\text{-a}$	-3.24	5.61	7.69×10^{-5}
$B(CN)_3 + (B(CN)_3)H_2SO_4\text{-a} \rightarrow (B(CN)_3)_2H_2SO_4\text{-b}$	-5.36	6.87	9.15×10^{-6}
$B(CN)_3 + (B(CN)_3)H_2SO_4\text{-a} \rightarrow (B(CN)_3)_2H_2SO_4\text{-c}$	-26.73	-14.01	1.90×10^{10}
$B(CN)_3 + (B(CN)_3)H_2SO_4\text{-a} \rightarrow (B(CN)_3)_2H_2SO_4\text{-d}$	-39.46	-25.76	7.88×10^{18}
$B(CN)_3 + (B(CN)_3)H_2SO_4\text{-b} \rightarrow (B(CN)_3)_2H_2SO_4\text{-a}$	-7.48	2.13	2.74×10^{-2}
$B(CN)_3 + (B(CN)_3)H_2SO_4\text{-b} \rightarrow (B(CN)_3)_2H_2SO_4\text{-b}$	-9.60	3.39	3.26×10^{-3}
$B(CN)_3 + (B(CN)_3)H_2SO_4\text{-b} \rightarrow (B(CN)_3)_2H_2SO_4\text{-c}$	-30.98	-17.50	6.86×10^{12}
$B(CN)_3 + (B(CN)_3)H_2SO_4\text{-b} \rightarrow (B(CN)_3)_2H_2SO_4\text{-d}$	-43.71	-29.25	2.84×10^{21}
$B(OH)_3 + (B(OH)_3)H_2SO_4\text{-a} \rightarrow (B(OH)_3)_2H_2SO_4\text{-a}$	-13.35	-2.72	9.88×10^{1}
$B(OH)_3 + (B(OH)_3)H_2SO_4\text{-a} \rightarrow (B(OH)_3)_2H_2SO_4\text{-b}$	0.30	9.09	2.15×10^{-7}
$B(OH)_3 + (B(OH)_3)H_2SO_4\text{-a} \rightarrow (B(OH)_3)_2H_2SO_4\text{-c}$	-11.95	-1.35	9.88×10^{0}
$B(OH)_3 + (B(OH)_3)H_2SO_4\text{-b} \rightarrow (B(OH)_3)_2H_2SO_4\text{-a}$	-15.95	-5.90	2.12×10^{4}
$B(OH)_3 + (B(OH)_3)H_2SO_4\text{-b} \rightarrow (B(OH)_3)_2H_2SO_4\text{-b}$	-2.29	5.91	4.67×10^{-5}
$B(OH)_3 + (B(OH)_3)H_2SO_4\text{-b} \rightarrow (B(OH)_3)_2H_2SO_4\text{-c}$	-14.55	-4.54	2.14×10^{3}

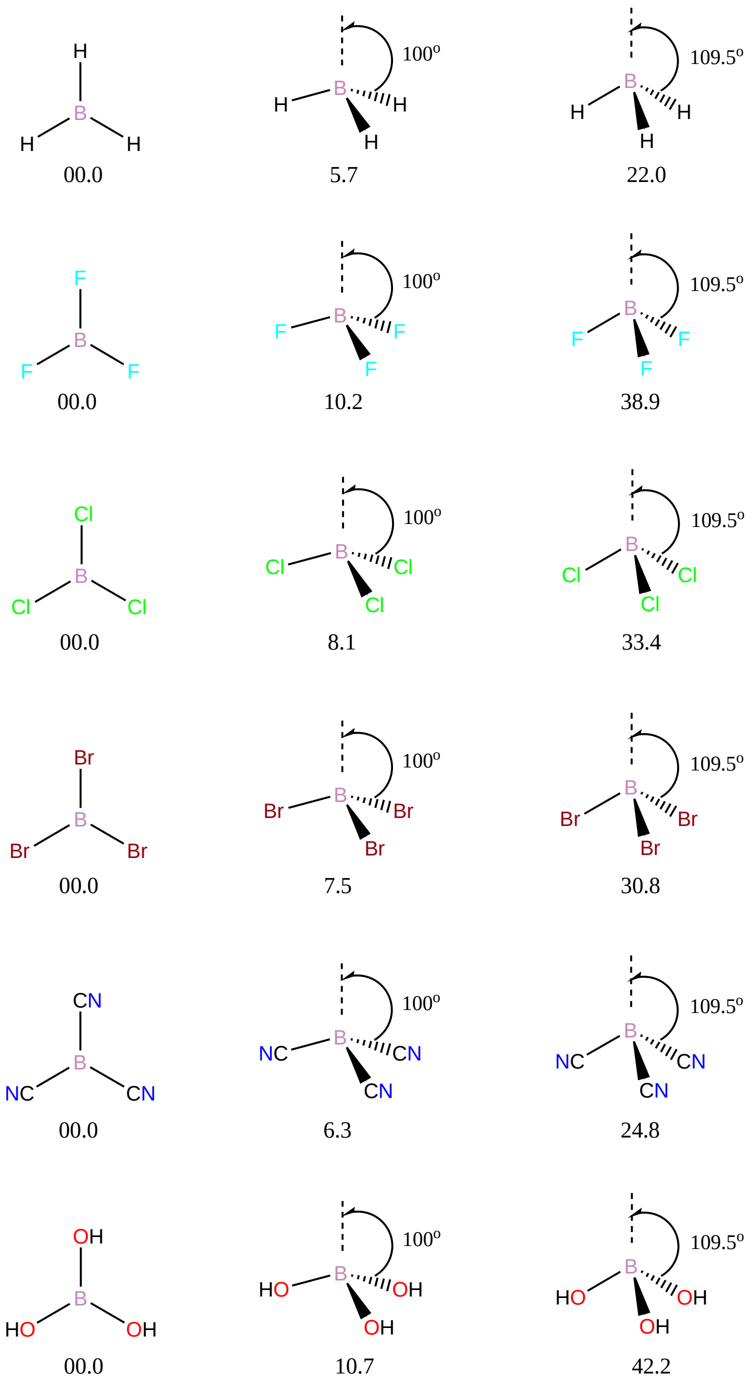
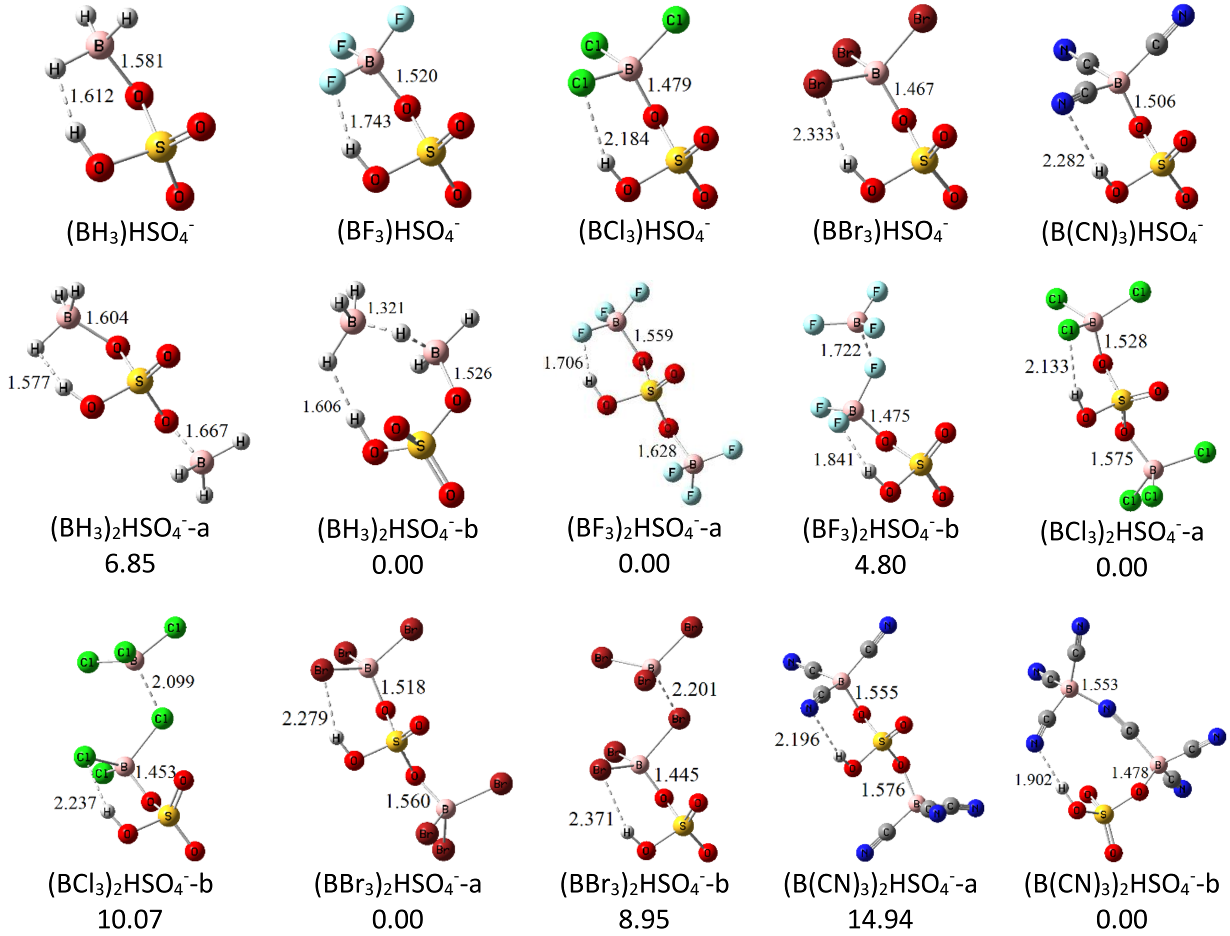


Figure 4. Relative stability of planar and pyramidal forms of BX_3 molecules, computed at the ωB97XD/aug-cc-pVDZ level. The pyramidal structures are not actual minima and their energies were obtained by scanning the angles while the B-X bond lengths were fixed. The energies are in kcal.mol^{-1}.

The ΔG values for the formation of most $(BX_3)H_2SO_4$ clusters are positive, except for $(BH_3)H_2SO_4$-**a**, $(B(CN)_3)H_2SO_4$-**a**, $(B(CN)_3)H_2SO_4$-**b** and $(B(OH)_3)H_2SO_4$-**a**. The relative abundance of each cluster can be obtained from the equilibrium constants, K_{eq}, (Supplementary Materials and Table S5) as a function of the BX_3 concentration (vapor pressure). The boiling points of BF_3, BCl_3, BBr_3, and $B(OH)_3$ at 1 atm are -100, 12.5, 91.3, and 300 °C, respectively [50]. Hence, the saturation vapor pressures of BF_3, BCl_3 and $B(OH)_3$ are about 50, 1.7, and 2×10^{-9} atm at ambient temperature [50,51], while BBr_3 has saturation vapor pressure of 0.13 atm at 33.5 °C [52]. The relative abundances of H_2SO_4, $(BX_3)H_2SO_4$ and $(BX_3)_2H_2SO_4$ as a function of the BX_3 vapor pressure, are summarized in Tables S6-S11. Based on the estimated saturation vapor pressures, the considered vapor pressure range was 0-50 atm for BF_3 and 0-2 atm for other boron compounds. Because of the high saturation vapor pressure of BF_3, formation of significant amounts of $(BF_3)H_2SO_4$ and $(BF_3)_2H_2SO_4$ (in terms of the percentage of total gas-phase H_2SO_4 bound to such complexes) would be feasible in laboratory experiments at ambient temperature (Table S7). For example, at 1 atm of BF_3, clusters account for about 25% of total gas-phase H_2SO_4. For BCl_3, and BBr_3 around 0.2% of total H_2SO_4 might be bound to BX_3-H_2SO_4 complexes when the corresponding BX_3 species are present at their saturation vapor pressure. If H_2SO_4 is also present at the highest gas-phase concentrations achievable at room temperature (i.e. in the ppb-ppm range [53]), these complexes could be detectable at least by mass spectrometric methods. Boric acid, $B(OH)_3$, can be reach up to 2 ppb at ambient condition – roughly the same order of magnitude as the highest H_2SO_4 concentrations in extremely polluted air [54]. While the ΔG values for formation of $(B(OH)_3)H_2SO_4$ and $(B(OH)_3)_2H_2SO_4$ complexes are slightly negative, the low ambient concentrations of reactants imply that the concentration of such complexes will be too small to measure (on the order of 100 cm^{-3} or less).

If the $(BX_3)_{1,2}H_2SO_4$ clusters lose a proton, H^+, the Lewis acids BX_3 can accommodate the resulting negative charge via stronger interactions between the B atom of BX_3 and the O atom of H_2SO_4, and consequently form stable conjugated bases $(BX_3)_{1,2}HSO_4^-$. In other words, BX_3 molecules enhance the acidity of H_2SO_4 via interactions with the O atoms of S=O groups and delocalization of the negative charge. The optimized structures of the conjugated bases,

$(BX_3)_{1,2}HSO_4^-$, of the $(BX_3)_{1,2}H_2SO_4$ clusters are shown in Fig. 5. Comparison of the B-O bond lengths in $(BX_3)_{1,2}H_2SO_4$ (Fig. 1 & 2) and $(BX_3)_{1,2}HSO_4^-$ (Fig. 5) shows that the interaction of BX_3 with negatively charged HSO_4^- is stronger than the corresponding interaction with neutral H_2SO_4. In addition, the calculated electron densities, ρ, at BCP of B-O bond are higher for the conjugated bases compared to the neutral complexes (Tables S3-S4). The NBO results confirm the presence of two B-O bonds in all negatively charged complexes $(BX_3)_2HSO_4^-$-**a**, except for $(BH_3)_2HSO_4^-$-**a**, which only has one B-O bond (Figs. S2-S6).



$(BH_3)HSO_4^-$ $(BF_3)HSO_4^-$ $(BCl_3)HSO_4^-$ $(BBr_3)HSO_4^-$ $(B(CN)_3)HSO_4^-$

$(BH_3)_2HSO_4^-$-a 6.85
$(BH_3)_2HSO_4^-$-b 0.00
$(BF_3)_2HSO_4^-$-a 0.00
$(BF_3)_2HSO_4^-$-b 4.80
$(BCl_3)_2HSO_4^-$-a 0.00

$(BCl_3)_2HSO_4^-$-b 10.07
$(BBr_3)_2HSO_4^-$-a 0.00
$(BBr_3)_2HSO_4^-$-b 8.95
$(B(CN)_3)_2HSO_4^-$-a 14.94
$(B(CN)_3)_2HSO_4^-$-b 0.00

Figure 5. The optimized structures of $(BX_3)_{1,2}HSO_4^-$ clusters, the conjugated bases of the $(BX_3)_{1,2}H_2SO_4$ clusters. The relative energies and bond lengths are in kcal.mol^{-1} and Å, respectively.

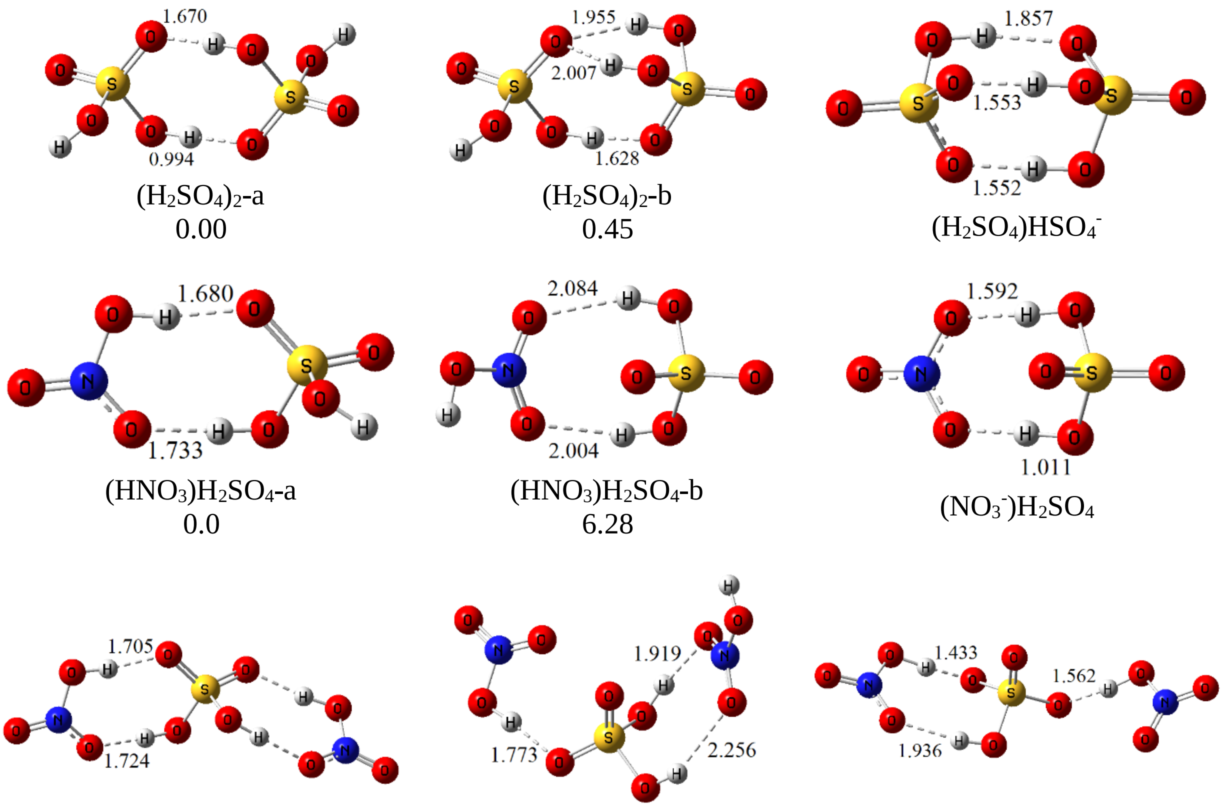
The calculated ΔH_{acid} and ΔG_{acid} values for the most stable isomers of $(BX_3)_{1,2}H_2SO_4$ clusters at 298 K are summarized in Table 2. The ωB97xD computed ΔH_{acid} and ΔG_{acid} values for

H_2SO_4 are 313.44 and 305.33 kcal.mol^{-1}, respectively. These are in reasonable agreement with the experimental values of 309.6 and 302.3 kcal.mol^{-1} [55], and with values obtained by the composite methods G3B3 and G4, which give ΔH_{acid} values of 310.9 and 312.1, and ΔG_{acid} values of 304.4 and 304.5 kcal.mol^{-1}, respectively[56,57]. Inclusion of one BH_3 molecule increases the acidity of sulfuric acid to 294.8 kcal.mol^{-1}. However, since H_2SO_4 can form dimer structures, $(H_2SO_4)_2$, as well as complexes with other acids such as HNO_3 [58], the relevant comparison to answer the question of whether or not BX_3-H_2SO_4 clustering increases the effective acidity of H_2SO_4 is not an isolated H_2SO_4 molecule, but a $(H_2SO_4)_2$ or $(HNO_3)_{1,2}H_2SO_4$ complex (see Fig 6). The calculated ΔH_{acid} values for these complexes are also summarized in Table 2. The ωB97xD computed ΔH_{acid} for $(H_2SO_4)_2$ is 283.7 kcal.mol^{-1}, which is in good agreement with values computed previously using the PW91 and G3MP2 methods; 281.8, and 282.1 kcal.mol^{-1}, respectively [58]. The acidities of $(H_2SO_4)_2$ and $(HNO_3)H_2SO_4$-**a** are comparable with that of $(BCl_3)H_2SO_4$-**a** and $(BH_3)H_2SO_4$-**a**, respectively. The most stable isomer of $(HNO_3)_2H_2SO_4$ (isomer **a**) is as acidic as $(BF_3)H_2SO_4$-**a**. Comparison of the acidity of the complexes $(HNO_3)_{1,2}H_2SO_4$ and $(BH_3)_{1,2}H_2SO_4$ reveals that the effect of HNO_3 and BH_3 on the acidity enhancement of H_2SO_4 is similar. When H atoms are substituted by EWGs F, Cl, Br, and CN, the acidity enhancement is greater, and all the corresponding $(BX_3)_{1,2}H_2SO_4$ clusters are more acidic than bis-trifluoromethylsulfonylimide (TF_2NH), one of the strongest known acids with ΔG_{acid} of 286.5 kcal.mol^{-1} [59]. Also, the simple cluster $(B(CN)_3)H_2SO_4$-**a** with ΔH_{acid} and ΔG_{acid} values of 266.1 and 258.2 kcal.mol^{-1}, respectively, is as acidic as $C_5(CN)_5H$ with ΔH_{acid} of 263.5 kcal.mol^{-1} [60], and $HB(BF_4)_4$ with ΔG_{acid} of 257.7 [61], and stronger than $HAlF_4$ and HAl_2F_7 with ΔG_{acid} of 269.2 and 261.1 [62], respectively. Comparison of the data in Table 2 shows that the effect of the EWGs on the acidity follows the order CN > Br > Cl > F.

Table 2. The calculated ΔH_{acid} and ΔG_{acid} values for the most stable isomers of $(BX_3)_{1,2}H_2SO_4$, $(H_2SO_4)_2$, and $((HNO_3)_{1,2}H_2SO_4$ clusters at 298 K.

deprotonation	ΔH_{acid} (kcal.mol^{-1})	ΔG_{acid} (kcal.mol^{-1})
$H_2SO_4 \rightarrow HSO_4^- + H^+$	313.44	305.33
$(H_2SO_4)_2$-a $\rightarrow (H_2SO_4)HSO_4^- + H^+$	284.24	279.45
$(HNO_3)H_2SO_4$-a $\rightarrow (NO_3^-)H_2SO_4 + H^+$	292.69	286.39
$(HNO_3)_2H_2SO_4$-a $\rightarrow (HNO_3)_2HSO_4^- + H^+$	288.95	280.83
$(BH_3)H_2SO_4$-a $\rightarrow (BH_3)HSO_4^- + H^+$	294.79	287.36
$(BF_3)H_2SO_4$-a $\rightarrow (BF_3)HSO_4^- + H^+$	287.36	279.73
$(BCl_3)H_2SO_4$-a $\rightarrow (BCl_3)HSO_4^- + H^+$	281.17	271.66
$(BBr_3)H_2SO_4$-a $\rightarrow (BBr_3)HSO_4^- + H^+$	278.91	269.30
$(B(CN)_3)H_2SO_4$-a $\rightarrow (B(CN)_3)HSO_4^- + H^+$	266.05	258.26
$(B(OH)_3)H_2SO_4$-a $\rightarrow (B(CN)_3)HSO_4^-$-a+ H^+	304.27	295.76
$(BH_3)_2H_2SO_4$-c $\rightarrow (BH_3)_2HSO_4^-$-b + H^+	287.69	273.24
$(BF_3)_2H_2SO_4$-c $\rightarrow (BF_3)_2HSO_4^-$-a + H^+	273.83	268.63
$(BCl_3)_2H_2SO_4$-c $\rightarrow (BCl_3)_2HSO_4^-$-a + H^+	270.48	265.62
$(BBr_3)_2H_2SO_4$-c $\rightarrow (BBr_3)_2HSO_4^-$-a + H^+	269.43	264.78
$(B(CN)_3)_2H_2SO_4$-d $\rightarrow (B(CN)_3)_2HSO_4^-$b + H^+	255.03	246.69
$(B(OH)_3)_2H_2SO_4$-a $\rightarrow (B(CN)_3)_2HSO_4^-$-a+ H^+	302.92	295.64

The $(BX_3)_2H_2SO_4$ clusters with two BX_3 molecules are even stronger acids. For example, $(BH_3)_2H_2SO_4$-**c** is about 7 kcal.mol^{-1} more acidic than the corresponding cluster with one BH_3 molecule, $(BH_3)H_2SO_4$-**a**. The cluster $(B(CN)_3)_2H_2SO_4$-**d** with ΔH_{acid} and ΔG_{acid} values of 255.0 and 246.7 kcal.mol^{-1} is the strongest acid among the studied complexes. $(B(CN)_3)_2H_2SO_4$-**d** is stronger than $CB_{11}H_{12}H$ (ΔG_{acid}=266.5 kcal.mol^{-1}), $CB_{11}F_1H_{11}H$ (ΔG_{acid}=257.2 kcal.mol^{-1}), $CB_{11}Cl_1H_{11}H$ (ΔG_{acid}=255.3 kcal.mol^{-1}) [63], and $B_{12}F_1H_{11}H_2$ (ΔG_{acid}=265.2 kcal.mol^{-1}) [60]. Its acidity is comparable with $CB_{11}Br_6H_6H$ (ΔG_{acid}=245.9 kcal.mol^{-1}), $CB_{11}(CN)_6H_6H$ (ΔG_{acid}=250.0 kcal.mol^{-1}) [63], and $B_{12}Cl_6H_6H_2$ (ΔG_{acid}=246.6 kcal.mol^{-1}) [64]. Interestingly, boric acid, $B(OH)_3$, did not increase the acidity of H_2SO_4 significantly, indicating that acidity enhancement is due to interaction of B atom of BX_3 and O atom of H_2SO_4, not $(BX_3)_{1,2}H_2SO_4$ cluster formation by any type of interaction.



$(H_2SO_4)_2$-a
0.00

$(H_2SO_4)_2$-b
0.45

$(H_2SO_4)HSO_4^-$

$(HNO_3)H_2SO_4$-a
0.0

$(HNO_3)H_2SO_4$-b
6.28

$(NO_3^-)H_2SO_4$

$(HNO_3)_2H_2SO_4$-a
0.00

$(HNO_3)_2H_2SO_4$-b
10.34

$(HNO_3)_2HSO_4^-$

Figure 6. Optimized structures of $(H_2SO_4)_2$, $(HNO_3)H_2SO_4$, and $(HNO_3)_2H_2SO_4$ complexes and their conjugated bases. The energies are in kcal.mol^{-1}.

4. Conclusion

The interactions of Lewis acids BX_3 (X=H, F, Cl, Br, CN, OH) with H_2SO_4 were studied computationally using the ωB97xD/aug-cc-pVDZ method. All the Lewis acids, except $B(OH)_3$, interacted with H_2SO_4 via both B and X atoms. The $B(OH)_3/H_2SO_4$ complexes were formed mainly by hydrogen bonding interactions. The X atoms interact with the hydrogen atom of the OH groups of H_2SO_4 through an electrostatic interaction, while the boron atom forms a dative bond with the lone pair electrons of doubly-bounded oxygen (O=S). This dative B-O interaction is accompanied by a planar/pyramidal conversion of BX_3. NBO analysis shows that there is an extra π-bond in BCl_3 and BBr_3. Therefore, planar/pyramidal conversion for these compounds is more difficult, and consequently their interactions with H_2SO_4 are the weakest. A comparison of structures and electron densities at bond critical points revealed that the B-O interactions in the negatively charged conjugated bases are stronger than that in the corresponding neutral complexes. Hence, the Lewis acids BX_3 enhanced the acidity of H_2SO_4 by stabilizing the negative charge of the conjugated bases. The studied $(BX_3)_{1,2}H_2SO_4$ complexes encompass a wide range of acidities, with all of the complexes found to be stronger acids than H_2SO_4. The $(B(CN)_3)_2H_2SO_4$-**d** complex, with ΔH_{acid} and ΔG_{acid} values of 255.0 and 246.7 kcal.mol^{-1}, respectively, was the strongest Brønsted acids among the $(BX_3)_{1,2}H_2SO_4$ complexes.

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