Theoretical Study of the Structure of Borate Complex Ions

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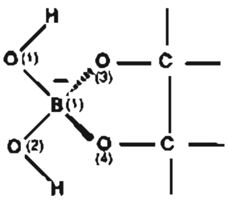
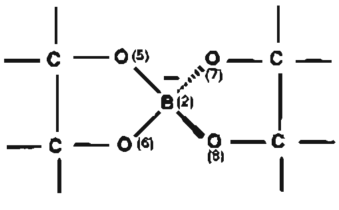
We recently reported[1] the results of two experimental studies on the thermodynamics of formation of 1:1[1a,b] and 1:2[1b] borate complex ions with bidentate chelating ligands. One conclusion of that work[1b] is that there may be "significant differences in boron–oxygen bonds in the various borate complex ions." In a further investigation of this point, we report here the results of a theoretical study of borate complex ions. We have prevously shown[2a] that AM1 is a useful and accurate technique for both structural and thermodynamic studies of anion addition to boron acids in the gas phase and that method is used again here.

General structures of the 1:1 and 1:2 borate complex ions are given below. An atom numbering scheme is included in the figures. Results are reported for the following ligand systems: 1,2-ethanediol (H_2E), 1,2-dihydroxybenzene (H_2Cat), glycolic acid (H_2G), oxalic acid (H_2Ox), and squaric acid (H_2Sq). Calculations on $B(OH)_3$, $(HO)_2BOH_2^+$, $(HO)_2BO^-$ and $B(OH)_4^-$ are also presented.



BX^-



BX_2^-

Computational Method

The modeling scheme and the application of AM1 to borate complex anions are discussed in our earlier work.[2a] Calculations were done here not only using MOPAC[2b] as before but also using HyperChem[2c] and essentially identical results were obtained. Symmetry restrictions were not employed for any of the calculations reported and all molecular degrees of freedom were considered to be independent. In all cases geometries were optimized using the Broyden–Fletcher–Goldfarb–Shanno method.[3] One point should be made, however, about the 1:1 complex ions. The orientation of the hydroxyl hydrogens is a matter of some interest. Bond lengths and angles in the complex ions are functions of the orientation of these protons and, to a lesser extent, so is the standard enthalpy of formation. In order to make direct comparisons of the various 1:1 complex ions, these protons were always initially oriented above and below the plane of the chelate ring and final minimizations retained this orientation in all cases[4] as shown in Figure 1.

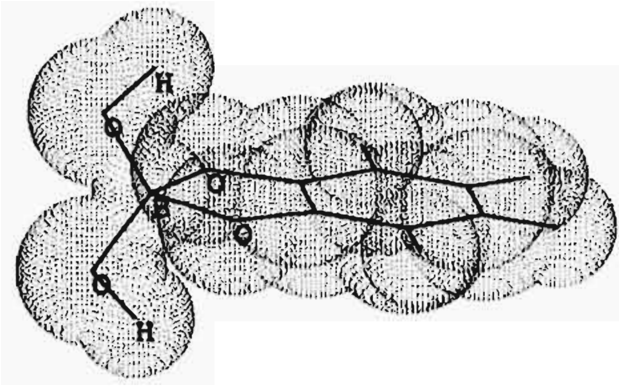


Figure 1. Final minimized structure of $BCat^-$.

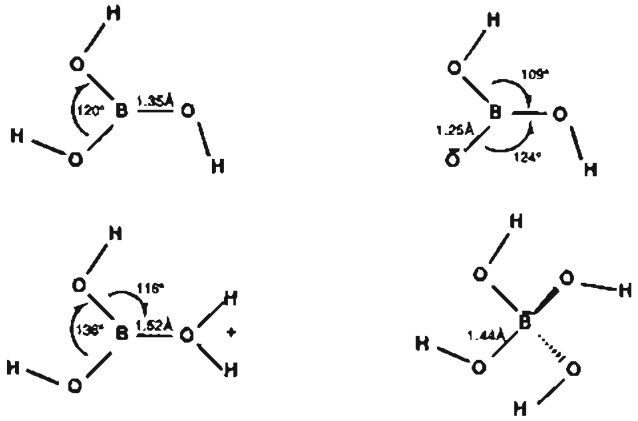


Figure 2. Structural parameters for boric acid and the borate ions.

Results and Discussion

Boric Acid and Borate Ions. Calculations were carried out on boric acid and three ions. Some of the structural results of these calculations are included in Figure 2. Results on $B(OH)_3$ and $(HO)_2BOH_2^+$ can be directly compared with other recent quantum mechanical calculations, and agreement is excellent.[5] Similarly, results on $B(OH)_3$ and $B(OH)_4^-$ are supported by structural studies[6] which show an increase of ~0.1 Å in B–O bond length on addition of hydroxide ion to $B(OH)_3$. Calculations were also done on $(HO)_2BO^-$ which is the conjugate base of $B(OH)_3$ acting as a Bronsted acid as it does in the gas phase.[7] The considerably shortened B–O bond is in agreement with a crystal structure determination[8] of the sodium salt of a doubly deprotonated cyclic borate trimer. Calculated boron–oxygen bond lengths in these species vary from 1.25 to 1.52 Å. The agreement between our AM1 results and other quantum mechanical calculations[5] as well as structural determinations[6,8] supports the validity of AM1 as an appropriate molecular orbital method for describing B–O bonds in borate complex ions.

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(4) For the borate complex of 1,2-dihydroxybenzene ($BCat^-$), initial rotation of one hydroxyl proton by 180° produces a minimized structure in which the initial orientation of the protons is retained. This structure is measurably less symmetric than $BCat^-$ with the two protons oriented above and below the plane of the chelate ring, but it is only 0.5 kcal/mol higher in energy. Initial rotation of both protons away from the chelate ring results in a final minimized structure in which one proton is rotated back toward the chelate ring. In structures of complex borates, these protons are almost always oriented away from the boron atom in order to participate in intermolecular hydrogen bonding.

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Table 1. Structural Parameters for 1:1 and 1:2 Borate Complex Ions

ligand	O(1)−B(1)−O(2), deg	B(1)−O(1), Å	O(3)−B(1)−O(4), deg	B(1)−O(3), Å	O(5)−B(2)−O(6), deg	B(2)−O(5), Å
H_2E	110	1.40	104	1.51	108	1.46
H_2Cat	113	1.39	102	1.57	108	1.49
H_2G	112	1.39	102	1.50[a]	108	1.45[a]
				1.58[b]		1.49[b]
H_2Ox	114	1.38	101	1.56	108	1.47
H_2Sq	117	1.37	103	1.64	109	1.53

[a] B−O (hydroxyl oxygen) bond length [b] B−O (carboxyl oxygen) bond length

BX^- and BX_2^-. Representative boron−oxygen bond lengths and O−B−O bond angles are given in Table 1 for both BX^- and BX_2^-. In all cases the structures are quite symmetrical and bond lengths and angles are effectively identical for all equivalent bonds.

In 1:1 complex ions, the O(3)−B(1)−O(4) bond angle in the chelate ring is always quite a bit less than 109.5° and the O(1)−B(1)−O(2) bond angle is increased relative to $B(OH)_4^-$. The B−OH bond in BX^- is shorter and stronger than the B−OH bond in $B(OH)_4^-$ and this shortening is marginally greater as ligand acidity increases. B−O bond lengths in the chelate ring are always greater than B−OH bond lengths and these bonds generally increase in length as ligand acidity increases. The unsymmetrical ligand, glycolic acid, clearly shows this bond length difference as the boron−hydroxyl oxygen bond is 0.08 Å shorter than the boron−carboxyl oxygen bond. This result is in agreement with a crystal structure determination of potassium boromalate.[9] Similarly, a crystal structure determination[10] of a 1:1 complex of a substituted 1,2-dihydroxybenzene shows shorter B−OH bonds relative to B−O chelate ring bonds by ~0.08 Å. Although we include a calculation on squaric acid, we have shown experimentally[11] that BSq^- does not exist in aqueous solution and the very long calculated B−O chelate ring bond distance supports this result. Squaric acid often acts as a bridging ligand[12] rather than a chelate because of the long O···O distance.

The results of these calculations support the idea that there are significant differences in B−O bonds in the various borate species. Considering just the B−OH bond on going from $B(OH)_4^-$ to BOx^-, a shortening of the bond by 0.06 Å occurs along with an increase in O−B−O angle of almost 5°. Given that the B−O bond length in the chelate rings may be as long as 1.58 Å, there is a surprisingly large difference of 0.2 Å in B−O bond length among the various tetrahedral borates. The strong, short B−OH bond in BOx^- may account for the experimental result[1b,13] that $B(Ox)_2^-$ is not formed in solution. Similarly, compared with the thermodynamics of formation of the 1:1 complex,[1b] addition of H_2E to BE^- is less favorable enthalpically by 15 kJ/mol and addition of H_2G to BG^- is less favorable by 51 kJ/mol. In the series $B(OH)_4^-$, BX^-, and BX_2^-, the shortest, strongest B−O bonds are always the B−OH bonds in BX^-.

On addition of a second ligand to BX^- to give BX_2^-, structures which are quite symmetrical are formed. O−B−O chelate ring bond angles increase and B−O chelate ring bond lengths decrease in BX_2^- relative to BX^-. Shorter and stronger B−OH bonds in BX^- are replaced by longer B−O bonds in the chelate ring of BX_2^-. The calculated $B(Cat)_2^-$ structure (Table 1) is in agreement with two separate crystal structure determinations.[10,14]

Reaction Thermodynamics. From calculated standard enthalpies of formation for the various species, it is possible to calculate in a straightforward way the enthalpies of various borate complexation reactions in the gas phase. We have argued[1b] that the disproportionation reaction ($2BX^- \leftrightarrow BX_2^- + B^-$) is influenced by solvation to only a small extent and comparisons of experimental[1b] and calculated enthalpies of disproportionation can be made for the H_2E, H_2G, and H_2Ox systems. The results are as follows: H_2E {15 kJ/mol (experimental); 16 kJ/mol (AM1)}, H_2G {53 kJ/mol (experimental); 40 kJ/mol (AM1)}, and H_2Ox {89 kJ/mol (AM1)}. The highly endothermic calculated enthalpy of disproportionation for BOx^- provides further evidence to account for the lack of observable $B(Ox)_2^-$ in solution. The fact that all three of these disproportionation reactions are endothermic is explained in part by the relatively strong B−OH bonds in BX^-.

While agreement between calculated and experimental enthalpies of disproportion is obtained, other thermodynamic parameters do not model nearly as well. In particular, the enthalies for ligand exchange ($2BXY^- \leftrightarrow BX_2^- + BY_2^-$) model very poorly as do the entropies of disproportionation. Although the calculated entropies of disproportionation are in the same order as seen experimentally, the values are much lower: H_2E {34 J/(mol K) (experimental); −2.4 J/(mol K) (AM1)} and H_2G {103 J/(mol K) (experimental); 8 J/(mol K) (AM1)}. Clearly, effects of solvation are almost always important, and it is not unexpected that gas phase calculations generally do not agree with thermodynamic parameters measured in solution. Accurate modeling of thermodynamic parameters in solution requires the inclusion of not only the effects of solvation but also the effects of counterions and ionic atmosphere. This is an area of of active, current investigation.[15]

Chelation. If glycolic acid is treated as an ambident, unidentate ligand, the boron oxygen bond in $(HO)_3BG^-$ when glycolic acid bonds via the hydroxyl oxygen is calculated to be 1.52 Å and the average B−OH bond length is 1.42 Å. Coordinated via the carboxyl oxygen, the B−O bond is calculated to be 1.64 Å long[16] and the average B−OH bond is 1.39 Å. On ring closure, both B−O bonds to the chelated ligand decrease in length (Table 1) and so, to a lesser extent, do the B−OH bonds. Chelation in these systems is, then, enhanced by enthalpic as well as entropic factors.

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