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A Theoretical Study of the Fluorohydroxy Boranes $BF_n(OH)_{3-n}$

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The stepwise hydrolysis of boron trifluoride, BF_3, to boric acid, $B(OH)_3$, is studied with ab initio *molecular orbital theory. Restricted Hartree–Fock geometries computed with the 3-21G basis set for BF_3, BF_2OH, $BF(OH)_2$, and $B(OH)_3$ are in satisfactory accord with experimental structures although BF and BO bondlengths are systematically overestimated. The overall hydrolysis reaction is computed* ab initio *to be endothermic by 16.9 kcal mol^{-1} at STP, with the energy change occurring primarily at the Hartree–Fock level with smaller contributions from the correlation and vibrational energies. Each of the three hydrolysis steps contributes approximately equally to the overall endothermicity.*

Introduction

Boron trifluoride resists hydrolysis to boric acid,

$$BF_3 + 3H_2O \rightarrow B(OH)_3 + 3HF \qquad (1)$$

The thermodynamics of this process can be studied through the intermediate steps,

$$BF_n(OH)_{3-n} + H_2O \rightarrow BF_{n-1}(OH)_{4-n} + HF \ (n = 3, 2, 1) \qquad (2)$$

In recent years, there have been several developments in the study of such processes in the gas phase. Good structural and thermodynamic data exists for BF_3 [1]. The intermediate species BF_2OH and $BF(OH)_2$ have been detected by mass spectroscopy [2] and both now have structures determined by microwave techniques [3, 4]. Kawashima, Takeo and Matsumura [4] found that BF_2OH could be obtained from BF_3 and a trace of water but $BF(OH)_2$ only appeared when water was present in excess. No gas-phase structural data appears to exist for $B(OH)_3$ although the heat of formation (298 K) has been estimated from vapor pressure measurements [1].

In a theoretical study of the hydrolysis, all compounds appearing in (2) should be examined at a uniform level of theory so that free energy changes can be assessed. Such a treatment for BF_3 hydrolysis was first described by Armstrong and Perkins (AP) [5] using *ab initio* molecular orbital theory. They concluded that the free energy change in the overall reaction (1) was indeed positive but that most of the change occurred in the first step

$$BF_3 + H_2O \rightarrow BF_2OH + HF \qquad (3)$$

However, in computing free energies, these authors used estimates of unknown vibrational frequencies and also a relatively untested technique for estimating changes in correlation energy. Since then, technical advances in *ab initio* molecular orbital theory have taken place which permit a more reliable computation of all of the energies, structures and vibrational frequencies required. In this paper, we present such a study of H_2O, HF and the fluorohydroxyboranes $BF_n(OH)_{3-n}$ and a new assessment of the free energy changes for the hydrolysis reactions (2).

Theoretical Methods

Standard molecular orbital techniques were used. Initial structures, corresponding to local minima on potential surfaces, were obtained using the RHF/STO-3G model (restricted Hartree–Fock theory with the minimal STO-3G basis) [6]. The geometries of the most stable rotamers were then refined at the RHF/3-21G level with the 3-21G split-valence basis [7]. The RHF/3-21G model was then used for computation of the harmonic vibrational frequencies by analytic second-derivative techniques [8]. The correlation energies were estimated by second-order Møller–Plesset theory [9] with the polarization 6-31G* basis [10] at the Hartree–Fock geometries which we computed using the 3-21G basis. This level of theory is denoted by MP2/6-31G*//HF/3-21G.

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TABLE I. Total Energies (hartrees).

Molecule		RHF/STO-3G	RHF/3-21G	RHF/6-31G*[a]	MP2/6-31G*[a]	RHF/6-31G**[a]
BF_3		−318.66194	−321.46584	−323.19302	−323.77857	−323.19302
BF_2OH		−295.03767	−297.58273	−299.18855	−299.78144	−299.19568
$BF(OH)_2$	*1*	−271.40810				
	2	−271.41192				
	3	−271.41420	−273.69685	−275.18342	−275.78411	−275.19742
$B(OH)_3$	*4*	−247.78357				
	5	−247.79170	−249.80936	−251.17783	−251.78669	−251.19853
HF		−98.57285	−99.46022	−100.00210	−100.18216	−100.01006
H_2O		−74.96590	−75.58596	−76.00977	−76.19649	−76.02228

[a] Single calculations at RHF/3-21G geometries.

TABLE II. Structural Parameters.[a]

Molecule	Parameter	HF/3-21G	Expt.[b,c]
BF_3	R(BF)	1.328	1.307
BF_2OH	$R(BF_1)$	1.345	1.323[d]
	$R(BF_2)$	1.335	1.323[d]
	R(BO)	1.354	1.344
	R(OH)	0.962	0.941
	<(FBF)	117.6	118.0
	$<(F_1BO)$	121.8	122.8
	<(BOH)	121.8	114.1
$BF(OH)_2$	R(BF)	1.349	(1.323)
	$R(BO_1)$	1.362	1.360
	$R(BO_2)$	1.371	1.365
	$R(O_1H_1)$	0.962	(0.941)
	$R(O_2H_2)$	0.962	(0.941)
	$<(FBO_1)$	118.8	118.2
	$<(FBO_2)$	119.9	121.0
	$<(BO_1H_1)$	118.7	(114.1)
	$<(BO_2H_2)$	120.3	(114.1)
$B(OH)_3$	R(BO)	1.377	1.36[e]
	R(OH)	0.962	0.96[e]
	<(BOH)	117.7	114.0[e]
HF	R(FH)	0.937	0.917
H_2O	R(OH)	0.967	0.958
	<(HOH)	107.6	104.5

[a] Distances in angstroms; angles in degrees. [b] Based on references 1, 3, and 4. [c] Bracketed values assumed. [d] BF distances assumed equal. [e] Based on crystal data.

Finally, effects of larger basis sets, including polarization functions on all atoms, are taken into account by single point Hartree-Fock calculations using the 6-31G** basis [10] (RHF/6-31G**//RHF/3-21G).

TABLE III. Vibrational Frequencies (cm^{-1}).

Molecule	HF/3-21G	Expt.[a]
BF_3 (D_{3h})	495 (e')	481 (e')
	691 (a_2'')	697 (a_2'')
	951 (a_1')	888 (a_1')
	1656 (e')	1463 (e')
BF_2OH(C_s)	460 (a')	
	499 (a')	
	515 (a'')	
	705 (a'')	
	947 (a')	
	995 (a')	
	1585 (a')	
	1668 (a')	
	3961 (a')	
$BF(OH)_2$ (C_s)	441 (a')	
	480 (a')	
	493 (a'')	
	539 (a'')	
	716 (a'')	
	937 (a')	
	1036 (a')	
	1038 (a')	
	1564 (a')	
	1647 (a')	
	3954 (a')	
	3958 (a')	
$B(OH)_3$ (C_{3h})	440 (e')	544 (e')
	477 (a'')	652 (a'')
	542 (e'')	209 (e'')
	725 (a'')	824 (a'')
	926 (a')	881 (a')
	1062 (a')	1060 (a')

(continued on facing page)

TABLE III. *(continued)*

Molecule	HF/3-21G	Expt.[a]
	1066 (e′)	1185 (e′)
	1595 (e′)	1440 (e′)
	3949 (e′)	3150 (e′)
	3952 (a′)	3250 (a′)
HF	4061	4138
H_2O (C_{2v})	1799 (a_1)	1595 (a_1)
	3814 (a_1)	3657 (a_1)
	3947 (b_2)	3756 (b_2)

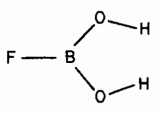
[a] Data from reference 1 and other sources cited therein.

All computations were carried out on a VAX 11/780 computer using the GAUSSIAN-80 [11] program system.

Results and Discussion

Total energies are listed in Table I. Detailed RHF/STO-3G structures are given elsewhere [12] but final RHF/3-21G structures are listed in Table II together with experimental data from the microwave studies [3, 4]. Table III contains theoretical (HF/3-21G) harmonic frequencies and a comparison with experimental frequencies where available.

All RHF/STO-3G structures were found to be planar. For $BF(OH)_2$, the three rotamers *1–3*



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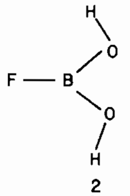

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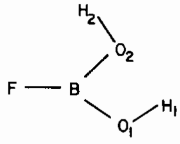

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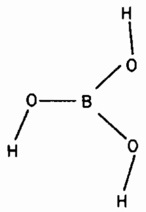
were examined and *3* was found to be most stable, consistent with experiment [4]. *2* is 1.4 kcal/mol less stable than *3* (RHF/STO-3G). This can probably be attributed to the fact that the distorted OH•••F intramolecular hydrogen bond is weaker than the OH•••O bond in *3*. The other C_{2v} structure *1* is 3.8 kcal/mol less stable than *3*, having no internal hydrogen bonds.

For boric acid, the two structures *4* and *5*



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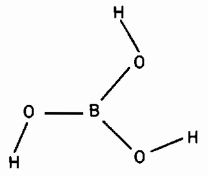

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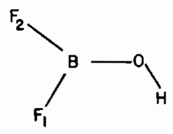

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were examined and *5* found to be more stable by 5.1 kcal/mol, again consistent with the extra internal hydrogen bonds. BF_2OH is found to have only the single planar structure *6*.

We now discuss the theoretical (HF/3-21G) geometrical parameters listed in Table II. It is evident that there are certain systematic deficiencies in the theoretical results. For example, all calculated BF lengths are about 0.02 Å too long. This is a limitation of the 3-21G basis. When the larger 6-31G* basis is used, the calculated BF length in BF_3 is reduced to 1.301 Å in better agreement with the electron diffraction value of 1.307 Å. The 3-21G theory does indicate some lengthening of the BF bonds as the fluorines are successively replaced by OH groups and this is also apparent in the experimental data. For F_2BOH (*6*) there are two distinct BF lengths which were assumed equal in the analysis of the microwave data. The theoretical results indicate that BF_1, the bond *cis* to the OH and forming the distorted hydrogen bond, is longer than BF_2 by 0.01 Å. For $FB(OH)_2$, Kawashima *et al.* assumed a BF length identical with those in F_2BOH; theory suggests some further lengthening.

TABLE IV. *Ab Initio* Theoretical Thermodynamic Quantities (kcal mol^{-1}).

Reaction	ΔE^a_{HF}	ΔE^b_{corr}	ΔE^c_{vib}	ΔH°_0 ^{c}	ΔH°_{298} ^{c}	$-T\Delta S^\circ_{298}$ ^{c}	ΔG°_{298} ^{c}
$BF_3 + H_2O \rightarrow BF_2OH + HF$	+6.0	−0.4	−0.2	+5.4	+5.3	−0.2	+5.1
$BF_2OH + H_2O \rightarrow BF(OH)_2 + HF$	+6.6	−0.7	0.0	+5.9	+5.7	+0.8	+6.5
$BF(OH)_2 + H_2O \rightarrow B(OH)_3 + HF$	+7.0	−1.0	0.0	+6.0	+5.9	+1.5	+7.4
$BF_3 + 3H_2O \rightarrow B(OH)_3 + 3HF$	+19.6	−2.1	−0.2	+17.3	+16.9	+2.1	+19.0

[a] From HF/6-31G**//HF/3-21G results. [b] From MP2/6-31G*//HF/3-21G results. [c] From theoretical harmonic frequencies listed in Table III and the HF/3-21G optimized structures. Pressure = 1 atmosphere.

The BO lengths are also systematically too long at the HF/3-21G level. Again there are increases in these lengths as we proceed from F_2BOH to $B(OH)_3$. For $BF(OH)_2$, there are two BO lengths and BO_2, the bond to the oxygen which acts as a proton acceptor in a distorted hydrogen bond is predicted to be the longer in agreement with experiment.

The other significant difference between theoretical and experimental parameters concerns the BOH angles. Here theoretical values are too large, a deficiency of the 3-21G basis that is apparent in all oxygen valence angles as in water. Nonetheless, it is significant that the BOH angles are substantially greater than the HOH angle. This is a general trend for XOH angles when X is electropositive; for example, LiOH and HBeOH are predicted to be linear (at the RHF/STO-3G level) [13].

The theoretical harmonic frequencies listed in Table III are in reasonable agreement with the limited experimental data. The comparison reflects a general tendency for RHF/3-21G harmonic frequencies to be somewhat larger than experimental fundamental frequencies. The data on boric acid is taken partly from solution and partly from crystal data, so comparison with the theoretical results for the isolated molecule should be treated with caution.

Theoretical results for the reaction energies of the hydrolysis steps (2) are summarized in Table IV. The total heats of reaction (at 0 K) are separated into a Hartree–Fock part, an electron correlation correction and a contribution from changes in zero point vibrational energy (using the theoretical harmonic frequencies from Table III). The internal energy change and entropy change for the reaction at STP are computed utilizing standard statistical mechanical formulas [14] and the HF/3-21G structural and vibrational data. These are combined to provide a totally *ab initio* estimate of the free energy change. Several conclusions may be drawn from this table. In the first place, the dominant part of the reaction energies is clearly the Hartree–Fock energy change. The value of ΔE_{HF} for the overall reaction (1) is +19.6 kcal/mol corresponding to an endothermic process. AP obtained a value of +14.3 kcal/mol using a smaller basis set [5]. For the correlation correction, we obtain a small negative value by the MP2 calculation, decreasing the reaction energy of (1) whereas AP estimated a larger negative change using Hollister–Sinonoglu theory [15]. We find almost no change in zero-point vibrational energy by calculation, whereas AP found a negative value using estimated frequencies. Our overall estimate of the endothermicity of reaction (1) is +16.9 kcal mol. This may be compared with an $\Delta H^{\circ}(298)$ experimental result of +12.2 ± 1.6 kcal/mol using the estimated heat of formation for boric acid [1].

According to our results, the endothermicity of the hydrolysis proceeds in three almost equal steps (2). This is not in agreement with AP who suggest that most of the heat change occurs in the first step (hydrolysis of BF_3 to BF_2OH). Their conclusion arises primarily from changes in zero-point vibrational energy, for which we find no evidence by direct computation.

Conclusions

The principal conclusions reached in this work are:

1. Hartree–Fock theory with the 3-21G basis gives a satisfactory description of the equilibrium geometries of BF_3, BF_2OH and $BF(OH)_2$ although there is some systematic overestimation of BF and BO bond lengths.
2. The overall hydrolysis reaction (1) is endothermic and the total reaction energy is split into three almost equal components for the three hydrolysis steps (2). These energy changes occur primarily at the Hartree–Fock level, correlation and vibrational corrections being smaller.

Acknowledgments

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