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An *ab initio* Molecular Orbital Study of Some Coordination Compounds of Boron Trifluoride

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The electronic structures and component energies of the compounds BF_3, BF_2OH, $BF(OH)_2$, and $B(OH)_3$ are reported. Replacement of fluorine atoms in BF_3 by hydroxyl groups is found to be energetically unfavoured and the results are discussed in terms of reactions bringing about the slow hydrolysis of BF_3 in aqueous solution. The hydrolysis of BF_4^- affording BF_3OH^- was also investigated. The rotational energies about the B–N bond for $NH_3 \cdot BH_3$, $NH_3 \cdot BH_2F$, $NH_3 \cdot BHF_2$, and $NH_3 \cdot BF_3$ are calculated. In this series, fluorine substitution causes the rotational energy barrier to decrease.

Introduction

The coordination chemistry of boron trifluoride is of continuing interest and importance and we here focus on two of its aspects; (*a*) the resistance of BF_3 to hydrolysis and (*b*) the energy barriers to rotation about the coordinate bond in complexes.

BF_3 plays an important catalytic role in many industrial processes.[1] This is due mainly to the fact that the main species in an aqueous solution of BF_3 are the adducts $BF_3 \cdot H_2O$, and $BF_3 \cdot 2H_2O$ in which an H^+ ion is labile. Boric acid is present in the solution in only small amounts, since the B–F bond is resistant to conversion to a B–OH bond. This is also true for aqueous solutions of tetrafluoroborates, where the stability of the BF_4^- ion is well established.[2] In order to fully understand the situation, we decided to calculate *ab initio* the energies of the species BF_3, BF_2OH, $BF(OH)_2$, and $B(OH)_3$, in order that the energetics of the series of reaction

$$BF_x(OH)_{3-x} + H_2O \rightarrow BF_{x-1}(OH)_{4-x} + HF$$

for $X = 1, 2, 3$ could be elucidated. Although there have been several non-empirical calculations on BF_3[3–7], there is no electronic structural information on the remaining three species. Such information would be of particular value for $B(OH)_3$, since this would aid in understanding the chemistry of the important borate anions.

A second series of interesting compounds includes $NH_3 \cdot BF_3$, $NH_3 \cdot BF_2$, $NH_3 \cdot BFH_2$, and $NH_3 \cdot BH_3$. In a recent investigation on donor–acceptor complexes of BF_3,[7] it was found that $NH_3 \cdot BF_3$ has a low, almost zero, energy barrier to rotation about the boron-nitrogen bond. This contrasts with $NH_3 \cdot BH_3$, which has a relatively high barrier to rotation.[8] The staggered and eclipsed forms of the two remaining members of the series were, therefore, calculated in order to establish the overall sequence of rotational energies.

Calculational Method

The calculations were performed within the usual LCAO–MO–SCF framework,[9] in which the atomic orbitals were represented by contracted sets of gaussian functions.[10] So as to be able to make a valid comparison with previous calculations[7,8] on complexes of BF_3, we employed the same double-zeta basis. In this basis the 1*s* atomic orbital of hydrogen is represented by four primitive gaussian functions contracted to two basis orbitals, whilst for the other atoms, nine *s* and five *p* gaussian functions were contracted to four *s* and two *p* basis orbitals, respectively.

In the calculation on boric acid, the bond angle and lengths employed were those averaged from various structural determinations,[11] *i.e.,* B–O = 0.1361 nm, O–H = 0.099 nm, and $B\hat{O}H$ = 114.1°. The structural constants are also known for BF_3.[11] However, for BF_2OH and $BF(OH)_2$ no such information is available and hence we assumed appropriate values of BF = 0.131 nm and $F\hat{B}F = F\hat{B}O$ = 120°. For $NH_3 \cdot BF_2H$ and $NH_3 \cdot BFH_2$ the hydrogen atoms were assumed to occupy the same positions as in $NH_3 \cdot BH_3$,[8] whilst the fluorine atoms occupy the same positions as they do in $NH_3 \cdot BF_3$.[11] The B–N bond lengths were then obtained by linear interpolation between the values relevant to $H_3B \cdot NH_3$[8] and $F_3B \cdot NH_3$.[11]

Results and Discussion

The Boric Acid–Boron Trifluoride System

The total energy, selected eigenvalues, and the Mulliken population analysis for the molecules BF_3, $BF_2(OH)$, $BF(OH)_2$, and $B(OH)_3$ are reported in Table I. The four lowest energy levels correspond to the $1s$ orbitals of boron, fluorine, and oxygen where present in the molecule. The results show that all the calculated $1s$ energy levels become less stable as fluorine is replaced by a hydroxide group. The filled π-electronic molecular orbitals also gain energy as the number of hydroxyl groups increases. This trend undoubtedly stems from the larger negative energy of the π-electrons of the fluorine atom. Moreover, the highest filled orbital is of π-symmetry for all the molecules

TABLE I. The Total Energy, Selected Eigenvalues, and Mulliken Population Analysis for BF_3, BF_2OH, $BF(OH)_2$, and $B(OH)_3$.

		BF_3	BF_2OH	$BF(OH)_2$	$B(OH)_3$
Total Energy (au)		−323.171243	−299.143168	−275.117251	−251.090086
Energy Levels					
(a) Four Lowest Filled		−26.36	−26.34	−26.31	−20.56
		−26.36	−26.33	−20.59	−20.56
		−26.36	−20.61	−20.58	−20.56
		−7.85	−7.80	−7.75	−7.71
(b) π-electronic		−0.78	−0.74	−0.70	−0.61
		−0.70	−0.68	−0.58	−0.51
		−0.70	−0.57	−0.53	−0.51
		+0.16	+0.19	+0.22	+0.25
(c) Highest Filled		−0.68	−0.57	−0.53	−0.51
(d) Lowest Vacant		+0.16	+0.17	+0.18	+0.18
Atomic Populations					
Boron	s	2.45	2.47	2.48	2.49
	$p\sigma$	0.83	0.86	0.89	0.94
	$p\pi$	0.29	0.32	0.35	0.37
	Total	3.57	3.65	3.72	3.80
Fluorine	s	3.95	3.95	3.95	
	$p\sigma$	3.63	3.63	3.63	
	$p\pi$	1.90	1.91	1.92	
	Total	9.48	9.49	9.50	
	s		3.95		
	$p\sigma$		3.62		
	$p\pi$		1.91		
	Total		9.48		
Oxygen	s		3.81	3.80	3.79
	$p\sigma$		3.12	3.12	3.13
	$p\pi$		1.86	1.87	1.88
	Total		8.79	8.79	8.80
	s p			3.80	
	$p\sigma$			3.13	
	$p\pi$			1.87	
	Total			8.80	
Hydrogen	s		0.59	0.60	0.60
	s			0.60	
Overlap Populations					
B–F		0.594	0.572	0.580	–
B–F′		–	0.602	–	–
B–O		–	0.662	0.680	0.660
B–O′		–	–	0.646	–
O–H		–	0.594	0.598	0.606
O′–H′		–	–	0.590	–

except BF_3. The orbital in question for BF_3 has a_2' symmetry and is built from a linear combination of the p-orbitals of fluorine which are in the molecular plane and orthogonal to the B–F bond. On replacement of fluorine by a hydroxyl, the corresponding orbitals of oxygen become involved in oxygen–hydrogen bonding. This confers extra stability on the orbital and so in the hydroxyl-substituted molecules it is lower in energy than the highest filled π-orbital.

The lowest vacant orbital of BF_3 has π-symmetry, whilst for the other three molecules this orbital is of σ type and is an antibonding combination of boron s, oxygen s and hydrogen s orbitals. This implies that a nucleophile should interact with these orbitals and so chemical attack should take place at the hydrogens. Reaction at the boron atom, however, will almost certainly happen also if the nucleophile is a strong Lewis base.

The atomic populations listed in Table I reveal that the boron and hydrogen atoms are centres of positive charge. The fluorine atom is shown to be more electronegative than the hydroxyl group, although the oxygen atom carries a greater formal negative charge than fluorine due to extra electron donation from the hydrogen atom.

The free energy, heat of reaction, and component energies for the stepwise hydrolysis of BF_3 to $B(OH)_3$ are presented in Table II. The heat of reaction, ΔH, at T°K is defined as,

$$\Delta H = \Delta E_{\text{total}} + \Delta n\, RT$$

where Δn is the difference between the number of molecules of reactants and products, whilst ΔE_{total} is the difference in total energies between the left- and right-hand sides of the reaction. The total molecular energy is

$$E_{\text{total}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{trans}}$$

where E_{elec} is the electronic energy, E_{vib} is the vibrational energy, E_{trans} is the translational energy, and E_{rot} is the rotational energy. At O° K, the E_{trans} and E_{rot} contributions are zero, while the E_{vib} term is obtained as one-half of the sum of the fundamental vibration energies of the molecule. The fundamental vibrations for $BF(OH)_2$ are unknown and reasonable estimates based on comparable molecules were made. The E_{elec} term comprises the calculated energy value E_{HF} plus the correlation energy contribution, E_{corr}, computed by the pairs population procedure.[13] Kirchoff's equation was then used to obtain $-\Delta H°$ at 298.16° K. In doing this, the specific heats required (C_p) were computed using the vibrational frequencies for known species. The C_p values for BF_3, HF and H_2O are known.[12] Standard entropy changes for all the reactions were then calculated and we assumed, for simplicity, that the vibrational contributions to the standard entropies could be neglected. This will not cause any

TABLE II. The Free Energy, Heat of Reaction and the Component Energies (in kJ mol^{-1}) for Various Gas Phase Reactions involving BF_3 and H_3BO_3.

Reaction	ΔE_{HF}	ΔE_{corr}	ΔE_{vib}	$\Delta C_p \Delta T$	$T\Delta S°$	$-\Delta H°$	$-\Delta G°$	K
$BF_3 + H_2O \rightleftharpoons BF_2OH + HF$	+22.58	−12.79	+7.32	−0.86	+0.28	−16.25	−15.97	1.54×10^{-3}
$BF_2OH + H_2O \rightleftharpoons BF(OH)_2 + HF$	+16.92	−13.91	−3.47	+1.75	+0.28	−1.29	−1.01	6.64×10^{-1}
$BF(OH)_2 + H_2O \rightleftharpoons B(OH)_3 + HF$	+20.19	−11.54	−11.26	+4.35	+0.27	−1.74	−1.47	5.51×10^{-1}
$BF_3 + 3H_2O \rightleftharpoons B(OH)_3 + 3HF$	+59.70	−38.25	−7.42	+5.24	+0.83	−19.27	−18.44	5.67×10^{-4}
$4BF_3 + 6H_2O \rightleftharpoons H_3BO_3 + 3BF_4^- + 3H_3O^+$	+594.41	−246.60	+15.44	−3.14	−126.45	−352.67	−479.12	–
$4HF + H_3BO_3 \rightleftharpoons BF_4^- + 2H_2O + H_3O^+$	+344.90	−31.21	+15.03	−8.04	−43.25	−318.20	−361.45	–
$BF_4^- + H_2O \rightleftharpoons BF_3OH^- + HF$	+95.75	−41.94	−19.90	+0.55	+0.30	−34.46	−34.16	3.27×10^{-6}

gross error in the computed $-\Delta G^\circ$ values. In the last column of Table II are given the equilibrium constants derived from $-\Delta G^\circ$.

It can be seen that reaction to replace the first fluorine of BF_3 by a hydroxyl group is energetically unfavoured. The K value calculated does, however, show that some proportion of BF_3 will have been converted at equilibrium. A further point of interest is that replacement of the first fluorine requires much more energy than subsequent substitutions and this is reflected in the increasing equilibrium constants. We expect the same situation to hold for the hydrolysis of fluoroborate also and, indeed, there is some kinetic evidence for this.[2]

It is of interest to recall that the standard heat of formation of $BF_3 \cdot H_2O$ from gaseous BF_3 and H_2O has been calculated[7] as +103.8 kJ mol^{-1}. Combining this latter result with the present work indicates that H_2O and BF_3 form the adduct almost exclusively, although the material will necessarily be contaminated by small amounts of boric acid if excess of H_2O is present.

By passing smal amounts of BF_3 into water, tetrafluoroboric acid is produced according to,[2]

$$4BF_3 + 6H_2O \rightleftharpoons 3H_3O^+ + 3BF_4^- + B(OH)_3$$

By invoking calculated total energies for H_3O^+, H_2O, and BF_4^- from earlier work,[7] we can compute the overall $-\Delta H^\circ$ and $-\Delta G^\circ$ for this reaction. This is given in Table II. In the gas phase $-\Delta G^\circ$ is −479 kJ mol^{-1}, indicating that the equilibrium will lie heavily to the left-hand side. In practice, the reaction occurs in solution and solvation energies will obviously assist it. This situation is difficult to deal with theoretically, hence we studied the energetics of the reaction

$$4BF_{3(g)} + 6H_2O_{(l)} \rightarrow 3H_3O^+BF_4^-{}_{(s)} + B(OH)_{3(s)}$$

The formation of solids on the right-hand side will delimit the thermodynamics. In the cycle (Figure 1)

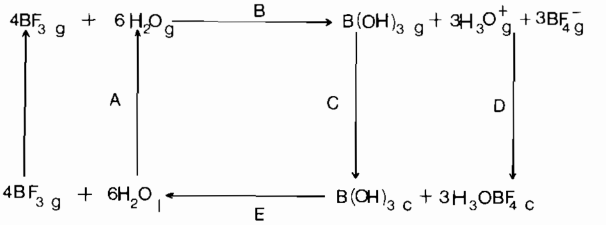

Figure 1. Energy cycle for $4BF_3$, $6H_2O$.

A = −244 kJ mol^{-1} and B takes the calculated value of −360 kJ mol^{-1}. The heat of sublimation of boric acid (c) is −102.0 kJ mol^{-1}.[14] The lattice energy (D) of $H_3O^+BF_4^-$ is not known but may readily be estimated as follows: we take the thermochemical radii of H_3O^+ and BF_4^- as 0.114 nm and 0.228 nm, respectively,[15] and by substitution in Kapustinskii's equation[14] we arrive at a value of 631 kJ mol^{-1} for the lattice energy of $H_3O^+BF_4^-$. Using all these values, the cycle leads to an overall energy of −1390 kJ mol^{-1} for stage E. Clearly, the formation of the solids $B(OH)_3$ and $H_3O^+BF_4^-$ from BF_3 and H_2O is strongly favoured thermodynamically and we can reasonably conclude that the solution reaction is also favoured, though less strongly.

A related reaction is the solution of boric acid in hydrofluoric acid, *i.e.*,

$$B(OH)_3 + 4HF \rightleftharpoons H_3O^+BF_4^- + 2H_2O$$

As before, the gas-phase heat of reaction is highly negative ($-\Delta H^\circ$ = −318.2 kJ mol^{-1}). In the condensed phase, however, using the above value for the lattice energy of $H_3O^+BF_4^-$, the reaction is feasible. We expect, therefore, that solvation and ion pair energies should also render it favourable in HF solution.

The BF_4^- ion is a stable species both in solid compounds and in aqueous solution. Hence, as confirmation, it seemed pertinent to investigate theoretically the reaction

$$BF_4^- + H_2O \rightleftharpoons BF_3OH^- + HF$$

The total energy of BF_3OH^- has been calculated previously.[7] In the gas phase the heat of reaction, $-\Delta H^\circ$, is −34.4 kJ mol^{-1}. This is sufficiently high to keep the equilibrium to the left-hand side. The cycle shown in Figure 2 enables us to compare the energies occurring on both sides of the equation when solid phases are assumed. The lattice energy of K BF_4 (A) is likely to be similar to that of KBF_3OH, since the crystal structures of the two materials are similar,[15] as are the sizes of the F$^-$ and OH$^-$ ions. This means that the thermodynamics depends only on the balance between the heats of vaporisation of H_2O and HF (B, E). Since the latter is the lesser of the two, then stage F will involve a larger energy change than will C. Hence, the equilibrium in the liquid or solid state will be more firmly shifted to the left-hand side.

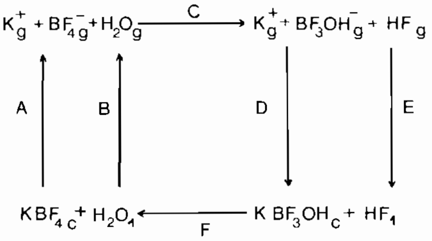

Figure 2. Energy cycle for KBF_4, H_2O.

Energies of Rotation about the B–N Bond in $NH_3 \cdot BH_3$, $NH_3 \cdot BH_2F$, $NH_3 \cdot BF_2H$ and $NH_3 \cdot BF_3$

The differences in energy between the eclipsed and staggered configurations of the B-fluoro-substituted derivatives of $NH_3 \cdot BH_3$ are given in Table III. In all cases, the calculated stable conformation is the stag-

TABLE III. Energy Differences (kJ mol^{-1}) between the Eclipsed and Staggered Configurations for $NH_3 \cdot BH_3$, $NH_3 \cdot BH_2F$, $NH_3 \cdot BHF_2$, and $NH_3 \cdot BF_3$.

	Electronic Energy	Nuclear Energy	Total Energy
$NH_3 \cdot BH_3$	5.88	−15.52	−9.64
$NH_3 \cdot BH_2F$	49.08	−56.49	−7.41
$NH_3 \cdot BHF_2$	65.59	−69.38	−3.79
$NH_3 \cdot BF_3$	+149.61	−149.98	−0.37

gered state, although the rotational energies for the molecules $NH_3 \cdot BF_3$ and $NH_3 \cdot BHF_2$ are low enough for the molecules to be freely-rotating. Inspection of the component total energies reveals that the nuclear energy determines the form of the rotamer. This agrees with a previous observation.[8] The electronic distribution throughout the four molecules (Table IV) reveals that corresponding overlap populations for the eclipsed and staggered configurations are almost identical for every bond except the B–N bond. The order of this particular bond is always greater for the staggered than the eclipsed configuration because there is always a smaller antibonding π-bond order associated with the former. The antibonding π-component probably stems from the long-range interactions between the substituents on the boron and the nitrogen and, in the eclipsed form of $BH_3 \cdot NH_3$, the antibonding overlap population between the eclipsed hydrogens is −0.016, whereas in the staggered configuration the corresponding interactions show a diminished overlap population of −0.006. By contrast, it is found that in all the cases examined, the overlap population between hydrogens which are in diametrically opposite positions has a small positive value. The effect of fluorosubstitution at boron is to reduce the repulsion between the substituents and the corresponding fluorine–hydrogen bond has a small positive overlap population.

Finally, we examine the electron density trends in this series of molecules. The amount of electron density donated overall from the ammonia to the BX_3 moiety (0.28) is virtually constant for each molecule. The sources of this donation are the hydrogen atoms, although as fluorosubstitution increases, there is a bigger electron drift from the hydrogens of ammonia, with a concomitant increase in the electron population of nitrogen. Fluorine atoms dominate the charge distribution in the whole series of molecules: thus, the charge on the boron atom is a function of the number of fluorine atoms present and ranges from +0.12 for $BH_3 \cdot NH_3$ to −1.33 for $BF_3 \cdot NH_3$.

TABLE IV. Atomic and Overlap Populations for $NH_3 \cdot BH_3$, $NH_3 \cdot BH_2F$, $NH_3 \cdot BHF_2$ and $NH_3 \cdot BF_3$.

	$NH_3 \cdot BH_3$		$NH_3 \cdot BH_2F$		$NH_3 \cdot BHF_2$		$NH_3 \cdot BF_3$	
	Staggered	Eclipsed	Staggered	Eclipsed	Staggered	Eclipsed	Staggered	Eclipsed
Electron density								
B	5.12	5.10	4.55	4.52	4.08	4.06	3.67	3.67
N	7.77	7.77	7.79	7.80	7.82	7.83	7.86	7.87
F	–	–	9.54	9.54	9.54	9.54	9.54	9.54
$H(1)_N$	0.65	0.65	0.64	0.64	0.64	0.63	0.62	0.62
$H(2,3)_N$	0.65	0.65	0.65	0.64	0.63	0.64	0.62	0.62
H_B	1.05	1.06	1.09	1.10	1.11	1.12	–	–
Overlap populations								
B–N σ	0.220	0.206	0.142	0.138	0.138	0.134	0.214	0.212
π	−0.038	−0.066	−0.022	−0.048	−0.018	−0.034	−0.016	−0.024
Total	0.182	0.140	0.120	0.090	0.120	0.100	0.198	0.188
B–F	–	–	0.444	0.472	0.520	0.524	0.564	0.564
N–H(1)	0.646	0.648	0.654	0.600	0.596	0.656	0.630	0.628
N–H(2)	0.646	0.648	0.622	0.648	0.642	0.608	0.630	0.628
B–H	0.860	0.862	0.844	0.844	0.846	0.846	–	–

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