The Potassium Fluoride–Boric Acid System. Hydrogen Bonding in $KF{\cdot}H_3BO_3$

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Ab initio LCAO–MO–SCF calculations have been performed on the most likely interactions between F^- and H_3BO_3. These show that the monofluoroborate ion $[BF(OH)_3]^-$ is the most stable, but only by 33 kJ mol^{-1} relative to the hydrogen-bonded system $F^- \cdots HOB(OH)_2$. Infrared analysis of the solid phase of composition $KF.H_3BO_3$, which grows from an aqueous solution of KF and H_3BO_3, shows the hydrogen-bonded structure to be the preferred form. The results of ^{19}F and ^{11}B n.m.r. studies on aqueous solutions of KF and H_3BO_3 are also consistent with hydrogen bonding being the chief interaction although it is possible that an equilibrium exists involving $[BF(OH)_3]^-$ since $[BF_3(OH)]^-$ is detectable in such solutions.

THE tetrafluoroborate ion BF_4^- and its hydroxy-derivatives $[BF_n(OH)_{4-n}]^-$ have a history of investigation going back to the time of Berzelius.[1] In more recent times a clearer understanding of the species and equilibria involved in solutions of BF_4^- has been realised [2] and one review discusses all the possible ions *i.e.* $n = 1, 2,$ or 3.[3] We are of the opinion that evidence for $[BF(OH)_3]^-$ is still lacking.

The ion $[BF(OH)_3]^-$ was first postulated as an intermediate in the hydrolysis of HBF_4 in dilute solutions.[4] The potassium salt, $K[BF(OH)_3]$, was reported to form from an aqueous solution of KF and H_3BO_3 [5a] and the structure was deduced from conductiometric and thermometric calculations supported by an i.r. spectrum which displayed a band at 790 cm^{-1} said to be characteristic of $\nu(B\text{–}F)$.[5b]

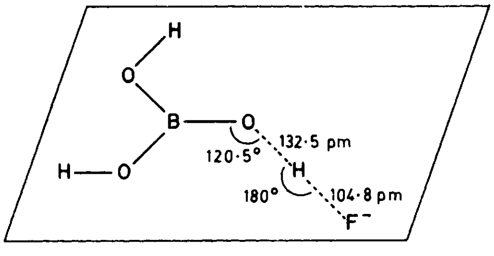
Fluorine-19 n.m.r. investigations of BF_4^- and its hydrolysis products showed clear signals attributable to $[BF_3(OH)]^-$ and $[BF_2(OH)_2]^-$ with J_{BF} *ca.* 14—15 Hz, but the signal for the supposed $[BF(OH)_3]^-$ was absent. Instead a broad band was observed and it was suggested that this represented a time average signal for this ion and for free fluoride in solution, there being rapid exchange of fluorine between these two environments.[6] No explanation for the special mobility of the B–F bond in this ion was advanced, but other evidence, again based on ^{19}F n.m.r. spectroscopy,[7] shows that several equilibria may be involved in these systems and it has been suggested that the ion $[BF_2(OH)_2]^-$ may disproportionate to $[BF_3(OH)]^-$ and F^- without the need for postulating $[BF(OH)_3]^-$.

Recently *ab initio* calculations have been made on several simple boron compounds including H_3BO_3 as a hydrogen-bonded dimer,[8] as well as on the ions $[BF_4]^-$ (ref. 9) and $[BF_3(OH)]^-$.[10] This technique has been used by us to some advantage in probing the very strong hydrogen bonding between RCO_2H and F^-.[11] Considering the well known propensity for hydrogen bonding of H_3BO_3[12] it seemed likely that it too would form a strong hydrogen bond to F^-.

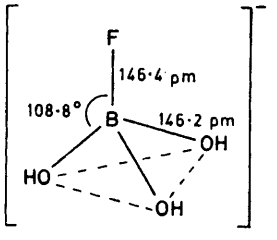
THEORETICAL

Ab initio LCAO-MO-SCF calculations have been performed on boric acid, boric acid–fluoride, the fluorotrihydroxyborate ion, and the borate ion, $H_2BO_3^-$, using a version of the program GAUSSIAN 76.[13] This program has recently been modified to perform level-shifting of the Hartree–Fock Hamiltonian [14] directly in the atomic orbital basis to guarantee the convergence of the iterative SCF calculations.[15]

Geometry optimizations (bond lengths to within ±1 pm, bond angles to within ±0.1°) were performed with the split-valence 4-31G basis set,[16] using standard univariate quadratic interpolation procedures.



(I)



(II)

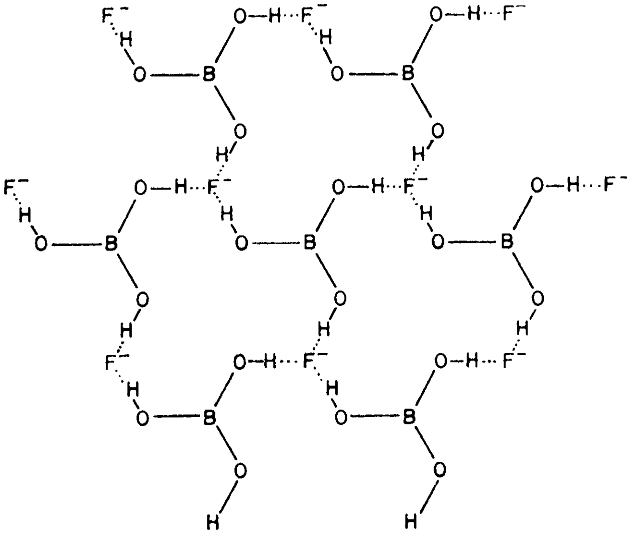
(*a*) *Boric acid,* $B(OH)_3$. Starting from the experimental geometry [17] of $r(BO) = 136.2$ pm, $r(OH) = 94.6$ pm, $BOH = 114.3°$, $OBO = 120°$, the optimization yielded $r(OH) = 95.0$ pm and $BOH = 120.5°$, $OBO = 120°$ and the dihedral angle $OBOH = 0°$, giving C_{3h} symmetry for H_3BO_3.

(*b*) *Boric acid–fluoride,* $[B(OH)_2(O'H'F)]^-$. Starting from the optimized geometry for boric acid above, the optimization yielded $r(BO') = 135.8$ pm, $r(O'H') = 132.5$ pm, $r(H'F) = 104.8$ pm, and $BO'H' = 133.5°$ under the assumption that the hydrogen bond is linear as in (I).

(*c*) *Fluorotrihydroxyborate ion*, $[BF(OH)_3]^-$. Starting from a pyramidal geometry based on the structure for boric acid above, the optimization yielded $r(BF) = 146.4$ pm, $r(BO) = 146.2$ pm, $FBO = 108.8°$, and the dihedral angle $FBOH = 90°$, maintaining C_3 symmetry, structure (II).

(*d*) *Borate ion*, $B(OH)_2O'^-$. Starting from the optimized geometry for boric acid above, the optimization yielded $r(BO) = 143.6$ pm, $r(BO') = 129.5$ pm, and $OBO = 120°$.

The hydrogen-bond energy of (I) and the stability of (II) were then computed using the extended [4*s*2*p*/2*s*1*p*] basis set of Dunning[18] with an *s*-orbital scaling factor of $\sqrt{2}$ and a *p*-orbital exponent of 0.7 for the protons. This basis set has been shown to be sufficiently complete to yield hydrogen-bond energies which are stable against further basis set extensions[11] and against ' ghost orbital ' corrections.[19] Single determinant SCF wavefunctions are generally adequate for calculations of the energies of strong hydrogen bonds between closed-shell molecules since the molecular extra correlation energy and the zero-point vibrational corrections are both small (*ca.* 5%).[20] The results of the calculations are presented in Table 1.



(III)

EXPERIMENTAL

Instruments.—Fluorine-19 n.m.r. spectra were run on a Bruker HFX90 machine operating at 84.66 MHz and the samples were referenced to $CFCl_3$; ^{11}B n.m.r. spectra were run on a Bruker WM250 machine operating at 80.239 MHz and the samples were referenced to $BF_3{\cdot}Et_2O$. Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer the samples being studied as KBr discs.

Solubility.—The solubility of KF in water at 20 °C (94.0 g per 100 cm^3) and H_3BO_3 (4.96 g per 100 cm^3) is significantly increased by the addition of the other. With an equimolar ratio the solubility of H_3BO_3 can reach 128 g per 100 cm^3 but the effect is only temporary. The solution grows viscous and after *ca.* 10 min an amorphous white solid of composition $KF{\cdot}H_3BO_3$ precipitates from solution. This is a homogeneous material, m.p. 84 °C (lit.,[5] 88 °C) (Found: H, 2.50; B, 9.20; K, 32.5. Calc. for $KF{\cdot}H_3BO_3$: H, 2.50; B, 9.00; K, 32.6%). The solubility of this in water at 20 °C is 39.55 g per 100 cm^3 (saturated solution = 3.30 mol dm^{-3}), and the solution is very viscous. The i.r. spectrum of $KF{\cdot}H_3BO_3$ is listed in Table 2. The compound $KF{\cdot}H_3BO_3$ can also be prepared from KF and H_3BO_3 in methanol. Again the solubility of the least soluble component, this time KF, is significantly raised but only temporarily, the adduct precipitating from solution after *ca.* 10 min.

TABLE 1

Total energies (hartrees)[a] of the molecular systems studied

Molecule	4–31G basis	[4*s*2*p*/2*s*1*p*] basis
Boric acid, $B(OH)_3$	−250.836 508	−251.180 042
Boric acid–fluoride, (I)	−350.165 397	−350.659 054
Fluorotrihydroxyborate, (II)	−350.196 349	−350.671 727
Borate anion, $H_2BO_3^-$	−250.216 802	−250.563 689
Fluoride anion, F^-	−99.247 824[b]	−99.414 059[c]
Hydrogen fluoride, HF	−99.887 286[b]	−100.038 590[c]

[a] 1 hartree = 4.35981×10^{-18} J. [b] Ref. 22. [c] Ref. 11.

Sodium fluoride and boric acid do not precipitate material of composition $NaF{\cdot}H_3BO_3$ from solution. From a saturated solution of NaF and H_3BO_3 in water only NaF deposits as crystals.

$K[BF_3(OH)]$.—This was prepared by the published method[4] from KHF_2 and H_3BO_3 in ice-water.

Thermochemistry.—In a simple Dewar flask, equipped with heating coil, the enthalpy of mixing of equimolar, 0.1 mol dm^{-3}, solutions of KF and H_3BO_3 was measured as −6.5 kJ mol^{-1} (±0.5 kJ mol^{-1}) at 20 °C. The enthalpy of solution of $KF{\cdot}H_3BO_3$ at the same concentration measured 42.0 (±1) kJ mol^{-1}.

TABLE 2

Infrared spectra (cm^{-1})

H_3BO_3	$KF{\cdot}H_3BO_3$	$KF{\cdot}(H,D)_3BO_3$	Assignment for $KF{\cdot}H_3BO_3$ and/or $KF{\cdot}D_3BO_3$
	3 300vs	3 300vs	$\nu_{s.}(OH \cdots F)$
3 180vs	3 030vs	3 030vs	$\nu_{s.}'(OH \cdots F)$
	2 450w	2 460w	$2\delta\ (OH \cdots O)$
		2 380s	$\nu_{s.}(OD \cdots F)$
		2 200s	
2 220w	2 220w		$2\delta\ (OH \cdots F)$
1 440s	1 450vs	1 450vs	^{10}B $\nu_{as.}(BO_3)$
1 380 (sh)	1 380vs	1 350vs	^{11}B
	1 240s	1 240s	$\delta(OH \cdots F)$
1 180s	1 130s	1 130s	$\delta'(OH \cdots F)$
882 *	910s	910s	$\nu_{s.}(BO_3)$
	880s	890s	$\gamma(OH \cdots F)$
		830m	$\delta\ (OD \cdots F)$
780s			
	704m	700 (sh)	^{10}B $\pi(BO_3)$
668vw	675s	685	^{11}B
632w		630m	$\gamma(OD \cdots F)$
552m	538m	538m	^{10}B $\delta(BO_3)$
	520m	520m	^{11}B

* Raman active, ref. 30.

DISCUSSION

The addition of KF to boric acid in aqueous solution increases its solubility but only temporarily. Within minutes the solution becomes very viscous, reminiscent of fluoride solutions in acetic acid,[21] and a white solid settles out of composition $KF{\cdot}H_3BO_3$. That a similar substance is not produced from NaF solutions suggests that there is no common ion $[BF(OH)_3]^-$ in these solutions in any appreciable concentration, only F^-. Indeed the object of this paper is to show that $KF{\cdot}H_3BO_3$ is a hydrogen-bonded material of boric acid and fluoride, yet the theoretical results indicate that $[BF(OH)_3]^-$ is slightly more stable.

It has recently been argued that the energies of very strong, asymmetric hydrogen bonds between closed-shell molecules should be defined with respect to the pair of component molecules which is closer, either energetically,[22] or structurally,[23] to the hydrogen-bonded system. Using either criterion it is clear that the boric acid-fluoride hydrogen bond should in fact be defined with respect to the borate anion, $H_2BO_3^-$, and HF, not H_3BO_3 and F^-. Based on this definition we compute the hydrogen-bond energy of the $F^- \cdots H_3BO_3$ system to be 149 kJ mol^{-1},* placing it on a par with other strong hydrogen bonds to fluoride such as $F^- \cdots H_2NCOR$ ($\Delta E = 149$ kJ mol^{-1}),[24] $F^- \cdots HO_2CR$ ($\Delta E = 105$ kJ mol^{-1},) [11] and $F^- \cdots H_2O$ ($\Delta E = 101$ kJ mol^{-1}).[25]

The recently described $F^- \cdots HONO_2$ hydrogen bond may also fall into this category.[26]

There have been only two previous *ab initio* calculations involving boric acid.[8,27] In one of these,[8] a value of 59 kJ mol^{-1} was calculated for the stabilization energy of the boric acid dimer, but unfortunately a minimal STO-3G basis set was used and no geometry optimization was performed so this result must be regarded critically. Our calculations predict that the isolated fluorotrihydroxyborate anion (II) to be more stable than the isolated boric acid–fluoride complex (I) by 33 kJ mol^{-1}.

The fluoride affinity of BF_3 has recently been calculated to be 539 kJ mol^{-1} using the 4-31G basis set,[28] and this may be compared with our 4-31G value for boric acid of 294 kJ mol^{-1}. However, our result with the larger basis set, of 204 kJ mol^{-1}, is almost certainly more reliable.

The compound which has the correct composition for $K[BF(OH)_3]$ does not have the expected i.r. spectrum and we did not observe a strong band at 790 cm^{-1} as did the original discoverers of the solid.[5] The i.r. spectrum of our material (Table 2) shows no absorptions in the region 710—870 cm^{-1}, which is where $K[BF_4]$ has a line at 777 cm^{-1} and $K[BF_3(OH)]$ at 790 cm^{-1} that can be attributed to ν(BF). Nor do we find bands that we can identify as arising from a tetrahedral boron framework such as $[B(OH)_4]^-$ displays at 945 and 754 cm^{-1},[29] and $[BF_3(OH)]^-$ displays at 1 000 and 750 cm^{-1}. These are regions of the spectrum in which $KF{\cdot}H_3BO_3$ shows nothing.

What is most striking about $KF{\cdot}H_3BO_3$ is its i.r. resemblance to H_3BO_3. Thus the modes associated with the vibrations of the planar BO_3 unit are present at 1 380—1 450 [$\nu_{as.}$ (BO_3)], *ca.* 880 [$\nu_{s.}$(BO_3)], 670 [π(BO_3), out-of-plane bend], and *ca.* 550 cm^{-1} [δ(BO_3), in-plane bend] in both compounds.[30] Three of these can be identified by their doublet structure due to ^{10}B and ^{11}B isotopes and the isotope ratio of frequencies 1.029 : 1.

The identification of the hydrogen modes was similarly aided by the recrystallization of the solid from D_2O which gave a partially deuteriated material whose spectrum in Table 2 shows bands at: 2 380, 2 200 [ν(OD)]; 830 [δ(OD)]; and 630 cm^{-1} [γ(OD)] thus identifying the regions of the three hydrogen-bonded OH modes as: 3 300; 3 030; 1 240; 1 130; and 880 cm.$^{-1}$ The 1 240 cm^{-1} band on deuteriation would fall at 918 cm^{-1} which coincides with $\nu_{s.}$(BO_3).

The i.r. spectrum shows $KF{\cdot}H_3BO_3$ not to have structure (II). Nor does it have discrete very strong hydrogen bonds of type (I) since such a system would give rise to the characteristic continuum below 1 600 cm^{-1} caused by very strong hydrogen bonding.[31] Moreover, the stretching and in-plane bending modes of the hydrogen bonds appear as double peaks, which might be explained by their being both $OH \cdots F$ and $OH \cdots O$ hydrogen bonds in the system. It is possible to draw a planar hydrogen-bonded structure for $KF{\cdot}H_3BO_3$ which preserves the planarity of the bonding around the boric acids, as in H_3BO_3 itself, and this is shown in (III). In effect each fluoride ion serves to form three hydrogen bonds thus linking the $F^- \cdots H_3BO_3$ units of (I) into a planar array of hydrogen bonding. Within the three hydrogen bonds at each fluoride it might conceivably be that there is approximate proton transfer as in (I) so that the C_3 symmetry at fluoride is reduced to C_2. The result would be that instead of the expected four hydrogen modes of C_3 symmetry we should observe six modes for C_2. Five of these are observed (Table 2) and labelled $\nu_{s.}$, $\nu_{s.}'$, δ, δ', and γ.

If, as is postulated for $KF{\cdot}H_3BO_3$, the hydrogen-bonding arrangement is like (III) then we would not expect very strong hydrogen-bonding character to display itself and this would explain the absence of an i.r. continuum yet at the same time it would explain why the spectrum resembles that of boric acid itself.

The Figure shows how the chemical shift of the fluoride ion in water varies with concentration, and the effect on this of an equimolar concentration of H_3BO_3. The most striking effect on the signal is its broadening even in dilute solutions: line width, half-height = 42 Hz at 0.2 mol dm^{-3}, 100 Hz at 0.5 mol dm^{-3}, and 166 Hz at 2.8 mol dm^{-3}. At low concentrations the broadening is due to hydrogen bonding and becomes progressively greater through viscosity broadening as the concentration increases.

The upfield shift with concentration is also explained by the increased number of fluorides forming two and even three hydrogen bonds to boric acid in solution. That hydrogen bonding causes an upfield shift of F^- is shown by (^{19}F, HF_2^-) which is at −149.3 p.p.m.[32] However, the observed upfield shift could also be explained by rapid exchange of F^- with $[BF(OH)_3]^-$ since the chemical shift of this can be extrapolated as *ca.* −125 p.p.m. from the chemical shifts of $[BF_4]^-$, −149.5, $[BF_3(OH)]^-$, −140.5, and $[BF_2(OH)_2]^-$ −132.5 p.p.m. However, it is obvious that even if equilibrium (1) is operative it lies to the left-hand side.

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* Calculated with respect to $F^- + H_3BO_3$ the energy is 170.5 kJ mol^{-1}.

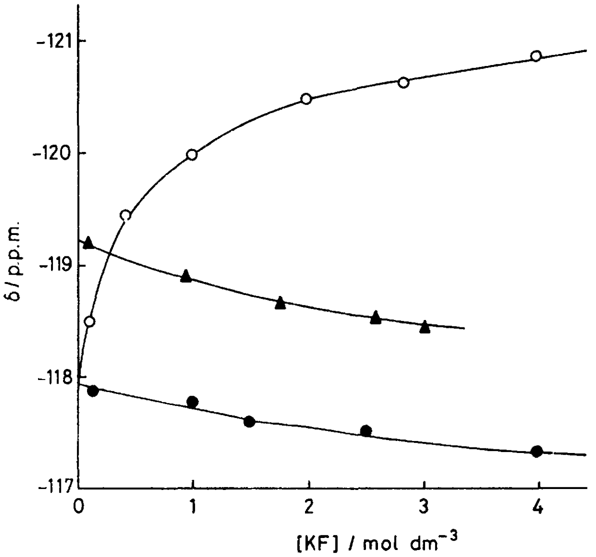
The ^{19}F spectra of equimolar concentrations of KF and H_3BO_3 show a second fluorine signal at -141.6 p.p.m.

$$F^- \cdots H_3BO_3 \rightleftharpoons [BF(OH)_3]^- \quad (1)$$

which we can equate to $[BF_3(OH)]^-$. This signal shows a quartet structure due to J_{BF} of 14.65 Hz. It accounts for *ca.* 5% of the fluorine nuclei at concentrations of 2.8 mol dm^{-3}. The presence of this species, and not $[BF_2(OH)_2]^-$, is consistent with the claim by Maya [7] that the latter exists in equilibrium with $[BF_3(OH)]^-$ as in

$$2[BF_2(OH)_2]^- \rightleftharpoons [BF_3(OH)]^- + F^- + H_3BO_3 \quad (2)$$

(2) and that this equilibrium lies to the right-hand side. It is possible to imagine a system involving $[BF(OH)_3]^-$ and $[BF_2(OH)_2]^-$ but in concentrations too small to be measured by ^{19}F n.m.r. even if they had sufficiently long lifetimes to be observed as separate species.



Fluorine chemical shift (p.p.m., $CFCl_3$) of KF in solution at different molarities: $KF{\cdot}H_3BO_3$ in water (○); $KF{\cdot}H_3BO_3$ in 50 : 50 water–SMe_2O (▲); KF in water (●)

With a mixed solvent, 50 : 50 H_2O : SMe_2O, the ^{19}F n.m.r. spectrum of an equimolar mixture of KF and H_3BO_3 parallelled that of KF in water, but with an upfield solvent shift. This second solvent was chosen as a good hydrogen-bond acceptor, which would compete for H_3BO_3, and at the same time should favour the right-hand side of (1). Clearly this does not happen since the signal moves downfield with increasing concentration as with F^- in water. Thus the upfield shift caused by H_3BO_3 acting on F^- is due to hydrogen bonding and not to the formation of $[BF(OH)_3]^-$.

The ^{11}B n.m.r. spectrum of H_3BO_3 shows a broad signal at 19.3 p.p.m. at 0.1 mol dm^{-3} concentration. At higher concentrations extremely broad resonances appear in the spectrum that arise from polyborate species affected by quadrupole broadening. The presence of equimolar concentrations of KF causes several changes: the boric acid signal broadens considerably and moves upfield to 15.9 p.p.m. at 0.8 mol dm^{-3}; the underlying broad resonances are more intense; and two new signals appear, a broad one at 13.3 p.p.m. and a sharp one at -0.02 p.p.m. The latter displays J_{BF} of *ca.* 15 Hz and is identified as due to $[BF_3(OH)]^-$.[33]

The signal at 13.3 p.p.m. has no counterpart in the ^{19}F spectrum and so does not arise from a B–F species. It is probably a polyborate; H_3BO_3 solutions to which a small amount of KF is added precipitate a polyborate on standing. This material is under investigation.

The ^{11}B spectra show a degree of complexity in these solutions not revealed by ^{19}F n.m.r. spectroscopy. Nevertheless they do show that the primary species is boric acid and that this is shifted upfield by the presence of F^- in solution just as $\delta(^{19}F)$ is shifted upfield by the presence of H_3BO_3. Both signals exhibit considerable broadening * which is anticipated if there is strong hydrogen bonding between them.

The thermodynamic cycle below has been tentatively explored by the measurement of $\Delta H_{mix.}$ and $\Delta H_{sol.}$

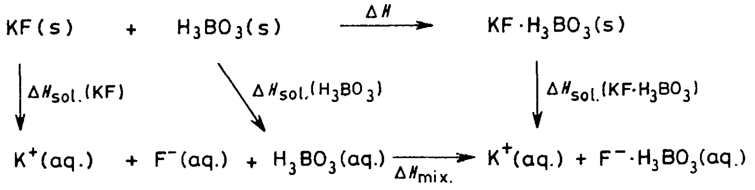
$$\Delta H + \Delta H_{sol.}(KF{\cdot}H_3BO_3) = \Delta H_{sol.}(KF) + \Delta H_{sol.}(H_3BO_3) + \Delta H_{mix} \quad (3)$$

$$\Delta H = -17.7 + 32.5 - 6.5 - 42.0 = -33.7 \text{ kJ mol}^{-1} \quad (4)$$

$(KF{\cdot}H_3BO_3)$. The related equation (3) gives the value of ΔH (4). If the hydrogen-bond energy is defined with respect to F^- and H_3BO_3 by equation (5), and if the lattice energies of KF and $KF{\cdot}H_3BO_3$ are assumed to

$$K^+(g) + F^-(g) + H_3BO_3(g) \xrightarrow{E} K^+(g) + F^-{\cdot}H_3BO_3 \quad (5)$$

be equal, we can calculate the minimum value of E from $-\Delta H + \Delta H_{sub.}(H_3BO_3) = E = 34 + 99 = 133$ kJ



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* The ^{11}B signal of 0.1 mol dm^{-3} $KF{\cdot}H_3BO_3$ is 135 Hz wide at half signal height. The upfield shift of the boron atom of H_3BO_3 is expected if it participates in hydrogen bonding, which will cause partial charge transfer to the oxygen which in turn will raise the electron density at boron.

mol^{-1}. This value we can compare with the calculated value of 170.5 kJ mol^{-1} given as a footnote to p. 785.

In conclusion we have found no evidence for the species $[BF(OH)_3]^-$ either in solution or in the solid $KF{\cdot}H_3BO_3$ despite the fact that *ab initio* calculations show this to be slightly more stable than the hydrogen-bonded complex $F^- \cdots H_3BO_3$. The proposed structure (III) might prove to be more stable than (I) and thus be favoured over structure (II). Since we have found evidence for a hydrogen-bonded complex in both the solid state and in solution, it would seem that the extra stability of 33 kJ mol^{-1} of the fluorotrihydroxyborate ion over a strongly hydrogen-bonded interaction is insufficient to compensate for other forces such as solvation energies and lattice energies, and equilibrium (1) remains firmly to the left-hand side.

[0/1322 *Received, 22nd August*, 1980]

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