The Formation of $K[B_5O_6(OH)_4]\cdot 2H_2O$ from H_3BO_3 and KF in Aqueous Solution

John Emsley * and Jeremy S. Lucas
Department of Chemistry, King's College, Strand, London WC2R 2LS

Potassium pentaborate dihydrate, $K[B_5O_6(OH)_4]\cdot 2H_2O$, has been identified as the product of the reaction of an excess of boric acid with potassium fluoride in water.

From an equimolar aqueous solution of KF and H_3BO_3 grow crystals of composition $KF\cdot H_3BO_3$ which have been interpreted as the salt $K[BF(OH)_3]$ [1] or as a hydrogen-bonded adduct.[2] It was observed in the course of the latter work that with an excess of boric acid over KF other crystals were precipitated. These crystals have now been identified as potassium pentaborate dihydrate, $K[B_5O_6(OH)_4]\cdot 2H_2O$.[3] This salt was first reported in 1855 [4] and can be prepared by boiling a solution of KOH dissolved in a saturated solution of H_3BO_3 in which the K : B ratio is *ca.* 1 : 5. The pentaborate has a low solubility of 2.06 g per 100 cm^3 water (0.07 mol dm^{-3}).[5] A naturally occurring mineral sborgite, $Na[B_5O_6(OH)_4]\cdot 3H_2O$, has the same structure.[6] The rapid formation of $K[B_5O_6(OH)_4]\cdot 2H_2O$ from a solution of KF and H_3BO_3 at room temperature is unexpected.

Experimental

Reaction of KF *and* H_3BO_3 *in Water*.—Potassium fluoride (AnalaR grade, 0.500 g, 8.6 mmol) was added to a stirred solution of boric acid (AnalaR grade, 2.00 g, 32.2 mmol) partly dissolved in water (10 cm^3) at room temperature. The solution became warm, unless cooled, and viscous as the boric acid dissolved. After 6 min a precipitate appeared, the amount of which reached a maximum after 15 min. The product, potassium pentaborate dihydrate (1.20 g, 4.1 mmol, 63%) was filtered, washed with acetone and dried, m.p. >360 °C (Found: H, 2.70; B, 18.9; K, 13.5. Calc. for $H_8B_5KO_{12}$: H, 2.70; B, 18.6; K, 13.3%). The solid was recrystallized from dimethyl sulphoxide–H_2O (2 : 1 v/v) prior to *X*-ray analysis which showed it to be orthorhombic with $a = 11.065$, $b = 11.166$, and $c = 9.041$ Å. The space group is *Aba*, identifying it conclusively as the known $K[B_5O_6(OH)_4]\cdot 2H_2O$,[3] formed according to equation (1). Using more KF than required by equation

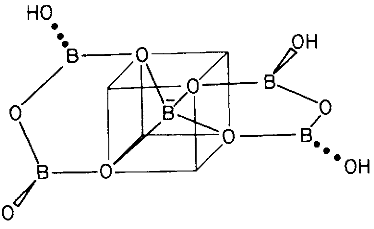
$$5H_3BO_3 + KF \longrightarrow K[B_5O_6(OH)_4]\cdot 2H_2O + 3H_2O + HF \quad (1)$$

(1) reduced the yield of the product although some was still precipitated when the K : B ratio was 0.75 : 1. At higher ratios the insoluble product of the reaction was $KF\cdot H_3BO_3$.

Using CsF in place of KF yielded a salt whose i.r. spectrum was identical with that of potassium pentaborate, even when the reacting ratio of Cs : B was 1 : 1. With this metal there was no evidence of $CsF\cdot H_3BO_3$, only caesium pentaborate. With NaF in place of KF neither the adduct nor a complex borate was formed: only NaF crystallized from such solutions.

Discussion

The solubility of H_3BO_3 in water (6.35 g per 100 cm^3 at 20 °C) [7] is considerably increased by the addition of KF, although the effect is only temporary and either $KF\cdot H_3BO_3$ or $K[B_5O_6(OH)_4]\cdot 2H_2O$ precipitates within a few minutes, depending upon the ratio of K : B in the solution. The system $KF–H_3BO_3–H_2O$ is probably much more complicated than previous investigators, including ourselves, have realised.[1,2,8,9]



(I)

$[B_5O_6(OH)_4]^-$ ion

The ease of formation of $K[B_5O_6(OH)_4]\cdot 2H_2O$, with anion (I), at room temperature, in a reaction which is not of the acid–base type, suggests that the fluoride ion has some role as a catalyst. The behaviour is reminiscent of the catalytic effect of fluoride on the polymerization of silicic acid to polysilicates.[10] In this instance the mechanism is thought to involve HF and SiF_6^{2-}.

However, F^- may operate *via* hydrogen-bond formation, by enhancing the nucleophilicity of an oxygen atom of H_3BO_3 which then is capable of attacking another boron centre. The increasing of oxygen nucleophilicity by fluoride of the hydroxides of carboxylic acids, to the point where they are capable of forming esters with alkyl halides, has been reported.[11]

Support for this theory of a hydrogen-bonding intermediate comes from Mulliken charge densities [2] which for the oxygen atoms of various boric acid species are calculated to be: H_3BO_3, −0.47 e; $H_2BO_3^-$, −0.73 e for O^- and −0.56 e for OH; $(HO)_2BOH\cdots F^-$, −0.81 e for the OH which is hydrogen-bonded to F^-, and −0.49 e for the other OH oxygen. These values suggest that a strongly hydrogen-bonded hydroxide group is more nucleophilic even than a deprotonated oxygen. The species $[BF(OH)_3]^-$ has a charge density on its oxygens of −0.42 e, lower even than H_3BO_3, which opposes the idea of this species being involved as the intermediate in polymerization, unless another mechanism is operative. In any event the role of fluoride as a catalyst seems necessary.

If this explanation of the formation of pentaborate is true then by reverse arguments the role of fluoride in the polymerization of $Si(OH)_4$ might be *via* a hydrogen-bonded species $(HO)_3SiOH\cdots F^-$ rather than SiF_6^{2-}.

Acknowledgements

The authors wish to thank Dr. Reiko Kuroda of the Biophysics Department of King's College London for help with the *X*-ray analysis.

References

1 A. K. Sengupta and S. K. Mukherjee, *J. Indian Chem. Soc.*, 1967, **44**, 658; 1970, **47**, 189, 679.

2 J. Emsley, V. Gold, J. S. Lucas, and R. E. Overill, *J. Chem. Soc., Dalton Trans.*, 1981, 783.

3 W. H. Zachariasen and H. A. Plettinger, *Acta Crystallogr.*, 1963, **16**, 376.

4 C. F. Rammelsberg, *Pogg. Ann.*, 1855, **95**, 199.

5 A. Rosenheim and F. Leyser, *Z. Anorg. Chem.*, 1921, **119**, 1.

6 S. Merlino and F. Sartori, *Acta Crystallogr., Sect. B*, 1972, **28**, 3559.

7 ' Handbook of Chemistry and Physics,' 60th edn., ed. R. C. Weast, CRC Press, Boca Raton, Florida, 1980, p. B-62.

8 M. K. Das, ' Oxyhaloborate Ions,' Gmelin Handbuch der Anorganischen Chemie, Borverbindung 8, ch. 5, pp. 73—80.

9 B. N. Chernyshov, G. P. Shchetinivia, V. A. Kolzunov, and E. G. Ippolitov, *Russ. J. Inorg. Chem.*, 1980, **25**, 815 (translation, *Zh. Neorg. Khim.*, 1980, **25**, 1468).

10 R. K. Iler, ' The Chemistry of Silica,' Wiley–Interscience, New York, 1979, pp. 211—219.

11 J. H. Clark and J. Emsley, *J. Chem. Soc., Dalton Trans.*, 1975, 2129; J. H. Clark, J. Emsley, and O. P. A. Hoyte, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1091.

Received 24*th January* 1983; *Paper* 3/099
