Boron Tris(pentafluoro-orthotellurate), $B(OTeF_5)_3$. Preparation and Lewis Acidity

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Summary The reaction of boron trichloride with pentafluoro-orthotelluric acid leads to the formation of $B(OTeF_5)_3$; its Lewis acid strength, determined calorimetrically, is comparable to that of boron trichloride.

BORON TRICHLORIDE reacts with pentafluoro-orthotelluric acid, $HOTeF_5$[1] at −80° according to equation (1). Boron tris(pentafluoro-orthotellurate), $B(OTeF_5)_3$ forms colourless,

$$BCl_3 + 3\,HOTeF_5 = 3\,HCl + B(OTeF_5)_3 \qquad (1)$$

hexagonal crystals, m.p. 37°. The compound can be sublimed at room temperature *in vacuo* and easily hydrolyses to $B(OH)_3$ and $HOTeF_5$. It is soluble without reaction in $CFCl_3$, nitrobenzene and related solvents. The mass spectrum shows M^+ and fragments arising from the successive dissociation of F_5TeO groups. The 56·4 MHz ^{19}F n.m.r. spectrum is consistent with an AB_4 system, characteristic for F_5TeO compounds,[2] with J_{AB} 179 Hz, δ +47·5 (A), +43·9 (B) (relative to internal $CFCl_3$) and $R = 0{\cdot}89$, calculated by the method of Harris and Packer;[3] ν_{BO} 1330s, ν_{TeF} and ν_{TeO} 740vs, 725vs, and 705s, and δ_{BO} 615m, 430s (KBr, −195°).

Boron compounds like $B(OCF_3)_3$,[4] $B(SCF_3)_3$,[5], and $B(OSO_2F)_3$ with fluorine atoms in the β-position to the boron are, in general, unstable above −20° towards fluoride shifts to vacant boron p-orbitals and formation of BF_3. The thermal stability of $B(OTeF_5)_3$ up to 140° is therefore unexpected. Above 140° the compound decomposes to BF_3, TeF_6, TeO_3, and a colourless, highly viscous liquid with an ill-defined boiling point above 250° according to equations (2) and (3).

$$nB(OTeF_5)_3 = nBF_3 + 3n\langle OTeF_4\rangle \qquad (2)$$

$$3n\langle OTeF_4\rangle = TeF_6 + 2TeO_3 + 3F_5Te(OTeF_4)_{n-3}OTeF_5 \qquad (3)$$

Preliminary molecular weight determinations suggest an average value of about 25 for n. $F_5Te(OTeF_4)_nOTeF_5$ can therefore be looked upon as a modification of the so far unknown tellurium oxide tetrafluoride. Above 200° the chain length is gradually diminished down to $n = 0$ and $F_5TeOTeF_5$[6] is formed. Simultaneously this compound decomposes to TeF_6 and α-TeO_3. Above 350° the thermal decomposition of $B(OTeF_5)_3$ can be formulated according to equation (4).

$$B(OTeF_5)_3 = BF_3 + 2\,TeF_6 + TeO_3 \qquad (4)$$

$B(OR)_3$ compounds are, in general, prevented by oxygen–boron back-donation from being as strong Lewis acids as the boron halides.[7] Despite the bulky F_5TeO-groups, $B(OTeF_5)_3$ forms stable 1:1 adducts with pyridine, tetrahydropyran, and acetonitrile. We have calorimetrically determined the enthalpy of reaction (5) as being −30·0 kcal/mol. Since reference values of the boron halides for

$$C_5H_5N\text{–}C_6H_5NO_2(\text{soln.}) + B(OTeF_5)_3\text{–}C_6H_5NO_2(\text{soln.}) = C_5H_5N,B(OTeF_5)_3\text{–}C_6H_5NO_2(\text{soln.}) \qquad (5)$$

the formation of pyridine adducts are known,[8] the following order of Lewis acidity can be given: BF_3 25·0, $B(OTeF_5)_3$ 30·0, BCl_3 30·8, BBr_3 32·0 kcal/mol.

The surprisingly high acid strength of $B(OTeF_5)_3$ does not seem to be caused solely by the inductive effect of the F_5Te-groups but also by an electronic interaction between oxygen p-orbitals and vacant tellurium orbitals thus significantly reducing the oxygen–boron back-donation.

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