Iron–Boron Bromides

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Summary The reaction between iron–boron mixtures and bromine at 1000—1200° at various pressures leads to the iron bromide derivatives $(Br_2Fe)_2BBr$ and $(BrFe)_2BBr$ with iron–boron bonds.

OUR knowledge of metal–boron chemistry has been expanded during the last few years by the synthesis of several new types of compounds. Much of the work in this field has been concerned with covalent metal–boron complexes. It has been assumed that the reason for the stability of σ-bonds between boron and metal atoms is the presence of electron donor ligands bound to boron atoms. These are groups such as Ph, OR, NR_2, or ML_n where ML_n is a group such as $Mn(CO)_5$, $Mn(CO)_4PR_3$,[1] $Co(CO)_3PR_3$,[2] or $Co(diphos)_2$[3] which can compensate for the electron deficiency at the boron atom.

The first indication for the possible existence of simple molecules $(X_nM)_{3-m}BX_m$ or $X_nM(BX_2)_m$ (M = metal or semi-metal, X = halide) was the synthesis of compounds such as $F_2Si(BF_2)_2$, $FSi(BF_2)_3$,[4] or $Si_2F_5BF_2$.[5] Here the substitution of 1, 2, or 3 fluorine atoms leads to molecules with covalent Si–B interactions.

We have demonstrated the ability of boron halide groups to substitute one or more halogen atoms in simple metal halides by synthesising Fe^{II} and Fe^{III} bromide derivatives. When a mixture of iron and boron powder (atomic ratio up to 1 : 10), first sintered at about 1500°, is treated with a slow stream of gaseous bromine at very low pressure and 1100—1200° in a quartz tube, brown crystals of $(BrFe)_2BBr$ sublime on to the colder part of the apparatus. Small amounts of $FeBr_2$ and BBr_3 can also be isolated. The reaction of an Fe–B mixture (1 : 1) at 1000° with gaseous bromine at 10—15 torr leads to bright red-black crystals which sublime out of the hot zone. Analysis indicates that the formula is $(Br_2Fe)_2BBr$ and that the product is very pure with no trace of $FeBr_3$. In polar solvents the two compounds are monomeric: in the solid state they could be polymeric. The formation of these two compounds proceeds initially by way of the formation of iron bromides which then react with boron or boron bromides to form the products which are isolated. At very low bromine concentrations in the hot zone, the main product is $(BrFe)_2BBr$ containing Fe^{II}; at higher bromine pressures, 10—15 torr, the only product is $(Br_2Fe)_2BBr$ with Fe^{III}.

The i.r. spectra of both compounds show only one strong band in the region of 4000—650 cm^{-1} at 720 cm^{-1}, corresponding to the B–Br stretching frequency.

The presence of tervalent boron is indicated by the ^{11}B n.m.r. spectra. $(Br_2Fe)_2BBr$ shows a signal at $-11{\cdot}0$, $(BrFe)_2BBr$ at $-13{\cdot}0$ p.p.m., compared with $BF_3{\cdot}OEt_2$ as an external standard in acetonitrile as solvent. These chemical shifts may be increased by interaction of the boron with acetonitrile, and the real chemical shifts may be at lower field.

The assumption that iron is in the oxidation state +3 in $(Br_2Fe)_2BBr$ and +2 in $(BrFe)_2BBr$ is also supported by Mössbauer spectroscopy. The results of the Mössbauer measurements show an Fe^{III} high-spin state for $(Br_2Fe)_2BBr$ and an Fe^{II} environment for $(BrFe)_2BBr$.

The hydrolysis of the compounds leads to Fe^{III} and Fe^{II} solutions, in agreement with these measurements.

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