Decaborane as an Oxidizing Agent

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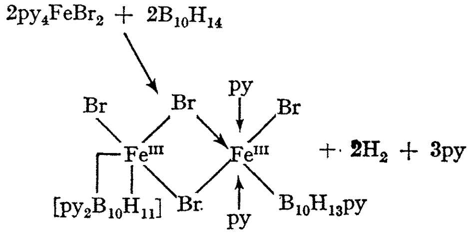
Summary Decaborane, which has not previously been known to act as an oxidizing agent, reacts with py_4FeBr_2 in benzene to give a compound which, on treatment with tetrahydrofuran yields the high-spin tetrahedral iron(III) complex py $FeBr_2B_{10}H_{13}py$ in high yield.

DECABORANE is electron deficient and normally reacts as a reducing agent, as an acidic hydride, or as a substrate for substitution reactions or framework rearrangements.[1] No reactions have previously been reported in which it behaves as an oxidizing agent. We now report that decaborane reacts in benzene solution with certain iron(II) complexes to form new types of Fe^{III}–B_{10} compounds and that analogous though more involved oxidations also occur with complexes of Co^{II} and Sn^{II}.

Decaborane, when reacted for one hour with an equimolar quantity of py_4FeBr_2 in boiling benzene under nitrogen evolves hydrogen and gives a 94% yield of a light brown, ether-insoluble compound A which can be formulated analytically (though not structurally) as $(py_{2\cdot5}FeBr_2B_{10}H_{12})_2$. The structure of this novel intermediate A will be discussed later. Tetrahydrofuran (thf) cleaves A to give an insoluble complex py $FeBr_2B_{10}H_{11}py_2$ and a thf-soluble compound which, on recrystallization, gives a 96% yield of a brown, tetrahedral, high-spin iron(III) complex, py $FeBr_2B_{10}H_{13}$py (by analysis) which is monomeric and non-conducting in acetonitrile [μ_{eff} 5·60 B.M. μ_{calc} (spin only), 5·91 B.M.]. I.r. spectroscopy confirmed the presence of pyridine co-ordinated both to iron and to the boron cluster respectively[2] and the absence of the pyridinium ion. It seems likely that the iron(III) atom and boronco-ordinated pyridine substitute the 6,9-positions of decaborane respectively.

Hydrolytic cleavage of the intermediate A with water gives various iron, pyridinium, and B_{10} species in solution and a quantitative precipitation of the rest of the iron and boron as a bromine-free iron(III) complex in which pyridine is complexed only to the boron. Analytical data are consistent with the formulation $[Fe^{III}(B_{10}H_{11}py_2)_2][B_{10}H_{13}py]$. The iron atom is envisaged as being common to the pentgonal faces of two molecules of the new bidentate chelating ligand $[B_{10}H_{11}py_2]^-$; this ligand can be formally considered to be derived by loss of a proton from $B_{10}H_{12}py_2$ in the $B_{10}H_{14}{}^{2-}$ series in the same way that the bidentate ligand $B_{10}H_{12}{}^{2-}$ is related to $B_{10}H_{14}$ itself by loss of two protons. As might be expected when iron is chelated by two B_{10}-clusters in which there is extensive electron delocalization the bulk magnetic moment is lowered, and the experimental value for μ_{eff} is 3·80 B.M. However, Mössbauer spectroscopy[4] confirms the presence of high-spin Fe^{III} and rules out the presence of Fe^{II} in this complex; chemical isomer shift $\delta = 0{\cdot}87$ mm.sec.$^{-1}$ with respect to sodium nitroprusside; quadrupole splitting $\Delta = 0{\cdot}69$ mm. sec.$^{-1}$. It was not possible to obtain the Mössbauer spectra of intermediate A or of the compounds py $FeBr_2B_{10}H_{13}$ py and py $FeBr_2B_{10}H_{11}$ py because of the large mass-absorption of the bromine atoms. The structure of the intermediate A has not been rigorously established but its i.r. spectrum suggests the presence of both bridging and terminal bromine atoms and the presence of pyridine molecules co-ordinated both to iron and to the boron cluster, respectively. On the basis of the compounds isolated after treatment of A with thf and water, the initial preparative reaction and the structure of A may be tentatively formulated as follows:



The observed room temperature magnetic moment is 7·45 B.M. per dimer unit.

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