

Fig. 2. Effect of hydrogen peroxide with oxygen-bubbled solution, —, No H_2O_2 ; ---, 1×10^{-5} M; - · - ·, 3×10^{-5} ; - - - -, 10×10^{-5} mole $H_2O_2/l.$

Now, the number of moles of oxygen reduced during one cycle can be calculated from the integral of the appropriate portion of the current-voltage or current-time curve of Fig. 1 since the polarization varies linearly with time. This quantity is equivalent to 13 millicoulombs per cm^2 or equal to 2.3×10^{-7} mole for the $3.4 cm^2$ electrode. Therefore, the current of oxidation above 1.0 V would increase in a measurable way if only 1 per cent of this amount of oxygen was converted in H_2O_2 provided that these H_2O_2 molecules remain adsorbed on the electrode during the following anodic sweep. Even if the H_2O_2 molecules were instantaneously released from the electrode, the coverage would never reach 50 per cent of the surface during the cathodic sweep. Otherwise the concentration of hydrogen peroxide liberated in the 10-ml. solution of the working compartment would reach 1×10^{-5} mole and could be detected by the increase in oxidation current above 1.0 V.

The described experiments suggest that hydrogen peroxide is not formed as an intermediate product of the reduction of oxygen in acid solution at the platinum electrode. Hydrogen peroxide observed in other experimental conditions appears most probably as a side-product of reduction of oxygen. Consequently, hydrogen peroxide formation cannot be held responsible for the overpotential of the oxygen electrode in an acidic fuel cell.

Furthermore, the foregoing experiments confirm the hypothesis of Broiter⁶ that the reduction of oxygen proceeds only at the contact of bare platinum atoms since the reduction proceeds during the cathodic sweep only after approximately one-quarter of the monolayer of platinum oxide has already been removed from the surface. The importance of the surface which must be cleared from the monolayer of platinum oxide before the reduction of oxygen occurs suggests, furthermore, that this catalytic reaction proceeds only after a molecule of oxygen has been adsorbed by two adjacent straight platinum atoms.

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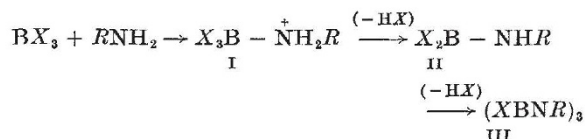
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Reaction of Pentafluoroaniline with Boron Tribromide

THE reactions between boron halides and amines have been examined extensively¹⁻⁵. In theory, it is possible to substitute successively the halogen atoms in a boron halide to form the derivative $B(RNH)_3$ from a primary amine, and the derivative $B(R_2N)_3$ from the secondary amine. Alternative reaction schemes are possible, and in practice, if the amine is not in large excess, the final product from a primary amine is usually a borazine.



Intermediates of type II are unstable though their existence has been inferred, but those of type I have been isolated. With the secondary amines, the reaction stops at the second stage, and compounds such as $(CH_3)_2NBBR_2$ are well known both as simple monomers and as dimers with four-membered boron-nitrogen rings⁶.

We find that approximately equimolar amounts of pentafluoroaniline and boron tribromide react at 25° with the evolution of hydrogen bromide and the formation of a solid mixture. At 50° the mixture melts, more hydrogen bromide is evolved, and a colourless liquid remains. This is pentafluoroanilino-boron dibromide, $C_6F_5NHBBr_2$ (found: B, 2.9; Br, 45.2; $C_6F_5NHBBr_2$ requires B, 3.1; Br, 45.4 per cent). The compound melts at 23° and distils unchanged at 40°–50°. It is moisture sensitive and is decomposed by water to boric acid, hydrogen bromide, and pentafluoroaniline.

At 70° pentafluoroanilino-boron dibromide decomposes quickly, with the evolution of hydrogen bromide, to a white, crystalline solid which melts at 118°–120°, and has a composition close to C_6F_5NBBBr (found: B, 3.2; Br, 26.3; calc. for C_6F_5NBBBr : B, 3.9; Br, 29.4 per cent). The infra-red spectrum of this material shows a weak absorption at $3,425 cm^{-1}$ in the position of the strong N–H frequency of the dibromide, which suggests that this is the contaminant. There is also a strong absorption, nearly absent in the dibromide, at $1,380 cm^{-1}$, which lies in the region ($1,300$ – $1,490 cm^{-1}$) expected for boron-nitrogen ring vibrations in borazines⁷. So far, it has not proved possible to remove the contaminant from the material, which is almost certainly *tris-N*-pentafluoro-phenyltribromoborazine.

In benzene, pentafluoroaniline reacts with boron tribromide at 10° to give a crystalline adduct which appears

to be the addition complex $Br_3B - \overset{+}{N}H_2(C_6F_5)$.

Pentafluoroanilino-boron dibromide is the first example of a type II intermediate to be actually isolated from the reaction between a primary amine and a boron halide. Its reactivity and physical appearance suggest that it is monomeric, as the dimeric dihalides are air-stable solids. On standing, specimens appear to form the borazine slowly even at room temperature, so it is unlikely that the dimer will ever be isolated in a pure state.

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