

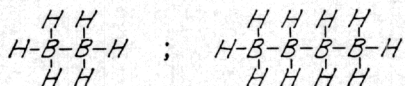
REACTIONS OF BORON TRICHLORIDE

BY

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The chemistry of boron is very interesting when considered from the viewpoint of the modern theories of atomic structure. Boron seems to have a marked tendency to form compounds in which it apparently exhibits a valency greater than would be expected from its position in the periodic table. This is evident when one considers the hydrides, B_2H_6 , B_4H_{10} , etc. Using the regular valence scheme these would have structural formulas as follows:



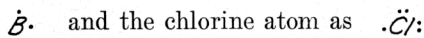
In these compounds boron exhibits a valency of four. If compounds such as triphenylboron are reduced with alkali metals, compounds of the type $NaB(C_6H_5)_3$ are formed, and when suitable solvents are used such compounds add a molecule of the solvent, as for example, $NaB(C_6H_5)_3 \cdot NH_3$.

The extreme reactivity of the halides of boron is also of interest. It is necessary to carry out experiments on these materials in the absence of any moisture, since the halides hydrolyze very readily. With other substances of a similar nature, chemical reactions take place readily.

Interest in the halides of boron is the result of attempts to plate out the element. The prevention of corrosion by plating certain materials with other fairly unreactive materials has been the subject of much discussion and much research work in recent years. It has been thought that if iron, copper, and other industrial metals could be plated with boron, the plated material might have very beneficial properties, and would not corrode as readily as the unplated material. Further, since boron and other elements of that type have not yet been successfully plated, it would be a decided scientific advancement if boron could be plated. Investigations along this line have been conducted at the University of Illinois with the object of plating boron, tungsten, molybdenum, etc. So far it has not been possible to plate out the boron. Since the pure halides are non-conducting, it would not be possible to use them for this work. They can not be used in water solu-

tion, or in solvents which contain water, on account of the hydrolytic action. It may be possible to find some ionizing solvent which will permit the plating of the element.

The reactions of the boron halides may best be explained by studying the electronic mechanism by means of which the atoms are held together. An atom is made up of a nucleus which has a net positive charge, and is surrounded by orbits or shells containing electrons or negative charges of electricity. The outermost electrons in each atom are those which enter into the mechanism of the formation of chemical compounds, and these are generally known as the valence electrons. Disregarding the inner electrons we may represent the boron atom as



Chemical combination consists in the redistribution of the electrons among the atoms forming the molecule so as to produce more stable groupings. This is effected with the formation either of electrovalencies or of normal covalencies or of co-ordinate covalencies. The electrovalencies are more commonly known as the polar, or ionizable, linkages. These are due to the transference of electrons from one atom to another. A molecule in which we find the typical polar linkage is NaCl. The sodium atom gives up one of its electrons to the chlorine atom, with the formation of the sodium ion and the chloride ion respectively. The non-polar non-ionizable, or covalent, linkages are due to the sharing of electrons between the atoms. Two electrons are involved in this sharing. These linkages may arise in two ways: (1) One electron is contributed by each atom, which gives the normal covalent bond, and which is limited like the electrovalencies to the periodic group of each atom. (2) Both electrons are contributed by the same atom, which gives the co-ordinate covalent bond. When these linkages are formed, the numerical value of the covalency is no longer dependent on the periodic group to which the atom belongs. The reason for the formation of these linkages is that they produce more stable groups of electrons than the isolated atoms possess, giving groups somewhat similar to those found in the inert gases.

Boron trichloride is an example of the normal covalent compound. Its structure may be represented thus:

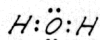


It is observed that the covalent bond is made up of one electron furnished by the boron and one by the chlorine, giving a pair of electrons

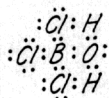
shared by the two atoms. This type of bond is non-ionizable. Hence we see why the halides of boron are non-conductors.

Observing the formula of BCl_3 , as written, more closely, we notice that it is possible for it to share two more electrons with some other atom, providing that the other atom has two electrons which it can share with the boron. A valency bond of this type, wherein two electrons for the linkage are contributed by one atom and shared by two, is called the co-ordinate covalent bond. This type of linkage is the secondary valence bond which is observed in the study of the complex compounds which were first studied in detail by Werner.

With these few facts in mind, it is possible to study some of the reactions of boron trichloride. One of the most characteristic properties of this compound is the ease with which it hydrolyzes. Because of this it is necessary to work with it and the other halides of boron in the absence of even minute traces of water. The difficulty of carrying on reactions with this compound is further complicated by the fact that it is a low boiling liquid, boiling at about 13°C . If we write the structural formula for water in a similar manner to the way we have that of boron trichloride, thus:



we find that the oxygen atom has two pair of electrons which it may share with some other atom provided the other atom is capable of sharing electrons. The boron in the boron trichloride is in a position to act as an acceptor of a pair of electrons, and we obtain as a result:

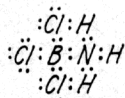


A chlorine atom is then eliminated with a hydrogen from the water and as a result, a hydroxyl group is substituted for one of the chlorines. The repetition of this process causes a complete hydrolysis of the boron trichloride, leaving the boron in the form of boric acid.

A somewhat similar reaction takes place when borontrichloride and liquid ammonia are allowed to react. Ammonia may be used as the medium for a system of acids, bases, and salts, just as water is used. In the ammonia system, the $-\text{NH}_2$ group corresponds to the $-\text{OH}$ group of the water system. The structural formula for ammonia may be written as follows:



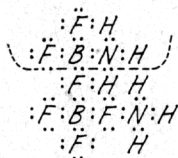
The nitrogen in the ammonia has two electrons which it may share with some other atom. As in the case of water, these electrons are shared with the boron atom, giving us the following arrangement:



Here again, in the presence of the ammonia, a molecule of HCl is split off, giving a molecule of NH_4Cl ; and an amide group is substituted for a chlorine, just as a hydroxide group was substituted in the case of water. The above mechanism may be repeated until all of the chlorine atoms have been replaced by the $-\text{NH}_2$ groups, giving boron amide and NH_4Cl as final products. Joannis¹ reports that the boron trichloride is completely ammonolyzed as mentioned above. Kraus² explains that the weight of the final product is not sufficient proof that the reaction takes place completely as described. He gives the following for the reaction of boron trifluoride and ammonia, which he has been studying:

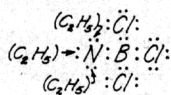


The weight of a mixture of the above two products would correspond to a compound formed by the addition of ammonia to the boron trichloride, BF_3NH_3 . This reaction may be represented in the following way, using two molecules of each of the reacting substances:



After the combination there is a splitting off of the two molecules.

With amines; reactions very similar to those with ammonia, except that there is no splitting of the addition compound formed into other molecules. With triethylamine, the nitrogen of the amine shares two of its electrons with the boron of the trihalide and we have a triethylaminoboron trichloride formed thus:



¹ Joannis, Compt. Rend. 135: 1106 (1902).

² Kraus and Brown, J. A. C. S. 51: 2696 (1929).

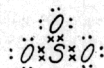
In a similar way, the mono- and diamino dichlorides may be formed, depending on which of the ethylamines was used in the process.

With zinc diethyl, borontrichloride will react according to the following equation:

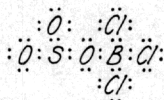


In this case there is, first, a sharing of electrons by the chlorine atoms and the zinc; and then, as the zinc chloride splits off, the ethyl groups are joined to the boron, giving the boron alkide.

With sulfur trioxide, we first have an addition compound formed with the boron halide. Sulfur trioxide may be said to have the formula:



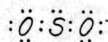
The addition compound can then have the formula:



This addition compound is fairly stable, but if heated to 150° in a sealed tube, three molecules of the sulfur trioxide and two of the boron trichloride will react to give sulfuryl chloride and boric oxide, as follows:



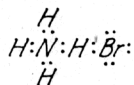
With sulfur dioxide, one would expect an addition compound to form, inasmuch as the formula for sulfur dioxide is:



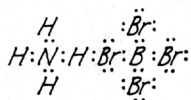
Both the oxygen atoms and the sulfur atom have available electrons which could be shared with the boron. This reaction is now being studied. So far the work has not progressed far enough to give any definite information regarding it. Since sulfur dioxide is an ionizing solvent, there is a possibility that the solution of boron trichloride in the sulfur dioxide might conduct the electric current. This will be tried later.

In the work which has been done at the University of Illinois on the plating of boron, tetraethylammonium bromide was used as the

solvent for boron bromide. Using the simpler substance, ammonium bromide, we observe that the compound



has electrons available to be shared with the boron, and the compound



commonly called ammoniumfluoborate is formed. It was not possible to plate boron from the tetraethylammonium bromide borontribromide addition compound. The tetraethylammonium bromide differs from ammonium bromide in that an ethyl group is substituted for each hydrogen.

There are a number of other reactions in which boron trichloride enters, but they are all of a similar nature to those discussed above. These reactions are nearly always due to the sharing of electrons by the boron and some donor atom, that is, one which has two electrons which it may share with the boron.

* Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry." Longman's Green and Co., London, 1924, Vol. V, p. 122.