THE CHEMISTRY OF BORON AND SOME NEW ORGANIC—BORON COMPOUNDS.

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While engaged in carrying on a detailed review of the chemistry of several individual elements, among which was boron, I was greatly impressed by the meagre literature on the chemistry of this element. There are but very few compounds, artificially prepared, described; and those which dame nature furnishes us are exceedingly rare, with two or three exceptions, and appear to play very slight rôle in the economy of the world, either mineral or biological. Very likely it is this apparent insignificance in nature and lack of any immediate important, industrial applications of boron and its compounds that has given rise to its neglect by chemists. It was to satisfy my curiosity as to whether this element offers a wide and virgin field of new, synthetic products of curious properties, or presents unsurmountable difficulties which have really baffled chemists, that moved me to attempt some preliminary work during the summer of 1900 at the University of Wisconsin.

If we study boron in the light of the periodic system we find that it occupies a position between metals and non-metals, and also near carbon and silicon, which elements are also near the border-line. We indeed find a strong similarity between boron and these two elements, especially in physical properties, e. g. Amorphous boron is much like amorphous carbon, and has a chestnut-brown color. The corresponding graphitic and diamond boron are also known. However, in most of its com-
pounds boron is trivalent instead of tetravalent as is the case with carbon and silicon compounds. In the latter property boron is more like the members of the nitrogen group, in fact there is some evidence that it may act as a pentavalent element in certain compounds. Theoretically, boron should act very much like aluminum also. Notwithstanding, excepting the oxide B₂O₃, there are not so very many close analogies. In fact there is a very decided similarity to the tri- and pentavalent elements, nitrogen and phosphorous, in chemical behavior, although they are decidedly non-metallic elements. And strange enough, though boron must be regarded as more of a non-metal than a metal yet it reacts far more readily with non-metals than metals; borides of metals are very difficult to prepare.

Among the very few inorganic compounds of importance are the halogen borides. These were merely prepared by several workers but not studied to any extent. Their chemical comportment toward other reagents has remained a virgin field. BCl₃, * is a liquid boiling at 20°; BBr₃ boils at 91°; and BI₃, boils at 210°. The latter compound is decomposed quite readily by light. BBr₃ on account of its stability and high boiling point has been taken as starting material for the synthesis of boron compounds in my work. The action of all the halogen compounds, which are being prepared from time to time by the combustion method as needed in my work, toward typical organic and inorganic compounds, and their physico-chemical properties, as indexes of refraction, latent heat of vaporization, etc., are being studied and will soon be reported on in a separate paper.

In studying the chemical comportment of the halogen borides, the tetrahalogen compounds of carbon and silicon on one hand, of phosphorus and nitrogen on the other, and also of aluminum have been kept steadily in mind. That is for practical purposes, I regard boron as occupying the center of a triangular field bounded by the above mentioned groups of elements and aluminum.

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* Nickles—C. R. 60-800-1865; Moissan—C. R. 112-717-1891; Besson—C. R. 113-78-1891.
A most interesting matter, both from the theoretical standpoint and the properties of the products, is the fact that boron compounds like BBr₃, for example, form a remarkable number of so-called addition products with compounds of the kindred elements on the three sides of the triangular field occupied by boron. Some of these compounds are: 2BBr₃, PCl₅; 2BBr₃, PCl₅; BBr₃, P₃H₅; BBr₃, PBr₅; BBr₅, 4NH₃; but AsBr₅ and SbCl₅ merely dissolve in BBr₃, no definite compounds separate. At the present time I am interested in the preparation of compounds of aluminum halides and boron halides. AlCl₃ and BBr₃ appear to give a definite compound, but as yet I have not completed an analysis of it. However, it appears to break up under high temperature and in hydrogen atmosphere to a boride of aluminum.

Of the compounds mentioned that with ammonia is of most interest to me theoretically. Indeed, it was the study of this compound which lead me to attempt to prepare some new organo-boron compounds by starting with BBr₃ and members of those classes of organic compounds characterized by the presence of an NH₂ group, or the NH group (imido), or N only as in the case of pydرين, quinoline and others. Thus far my work has been principally upon amines and pyridine.

If solutions of BBr₃ and aniline in carbon tetrachloride, carbon bisulphide or benzene are brought together drop by drop an insoluble, amorphous precipitate appears. The action is accompanied by great evolution of heat. When the precipitate is carefully dried in a nitrogen or hydrogen atmosphere and analyzed it is found to be 2BBr₃, C₆H₅NH₂. With an excess of aniline and higher temperature of reacting system there results a yellow substance analyzing up to 2BBr₃, 3C₆H₅NH₂. The first decomposes water quite violently, while the latter acts slowly on water giving B(OH)₃ and aniline hydrobromide. If the 2BBr₃, 3C₆H₅NH₂ is allowed to stand in a strong light in an air tight desiccator in which there is some strong alkali in a separate dish, HBr is evolved from the substance and there remains what analyses up to a sort of boro-nitride of aniline. When the product is placed in water but very slight decompo-
sition occurs, even in several days. But if the water is heated action soon sets in and continues quite rapidly giving aniline and boric acid.

Pyridine and BBr₃ form a white, amorphous precipitate in CCl₄ as medium. It is surprisingly stable in water, not decomposing readily unless boiled for some time. It analyses up to BBr₃, C₅H₅N.

The methods of analysis relied upon in the foregoing work consisted in determining the bromine gravimetrically as silver bromide, and the nitrogen by the Kjeldahl procedure. The combustion method will be worked later but thus far the Kjeldahl method has given sufficiently satisfactory results.

Another phase of boron chemistry which presents interesting aspects is the action of boron halides on the unsaturated hydrocarbons. The olefine and acetylene series. As an example: Dilute solutions of amylene and BBr₃ in CCl₄ as a medium were brought together slowly, the system being cooled with ice-water, and to my surprise, pure, amorphous boron was precipitated in an extremely attenuated, colloidal condition. The boron will, in fact, remain suspended in the reaction mixture an indefinite time. That the material was pure boron, was proved beyond a doubt by evaporating off all the volatile products and washing the residue with carbon tetrachloride and then with ether. As a film it was of a maroon color, very stable in air, even when heated to about 500°. When heated in a glass tube with pure oxygen it was burned to white boric oxide. The gas drawn from the tube and then through lime-water gave no test for carbon dioxide.

The reaction of BBr₃ and the unsaturated compounds is doubtless very complicated, however, and very exact conditions must be maintained to obtain certain definite end-products. If BBr₃ and amylene are brought together directly they react with explosive violence and there is charring of the organic substance, and most irritating fumes evolved. As the other extreme, the passage of BBr₃ fumes carried by a current of hydrogen into amylene dissolved to the extent of 10 to 20 per cent in carbon tetrachloride and the whole reacting mass cooled
in ice water, gives rise to no precipitate but to a most disagreeable smelling solution from which I have not yet succeeded in isolating a definite compound.

As soon as the above work is carried out in detail in several of its many ramifications I expect to study the action of boron halides on aldehydes, ketones and other typical classes of organic compounds and compare the results with those usually obtained with free halogens or the halides of phosphorous and aluminum.