

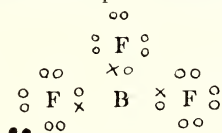
THE REACTION OF BORON FLUORIDE WITH ALCOHOLS AND GLYCOLS

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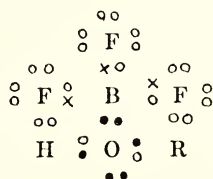
When boron fluoride is passed into methyl alcohol the gas is absorbed in almost uni-molecular proportions and a heavy, fuming, strongly acid liquid results. Vogt, Foohey and Nieuwland¹ have determined the specific conductance of this solution and find that the values obtained are of the same order of magnitude as those observed for the system $\text{H}_2\text{SO}_4\text{-SO}_3$. This acid solution of boron fluoride in methyl alcohol has been used by Vogt, Foohey, and Nieuwland¹ and by Hinton and Nieuwland² in the preparation of acetals of monohydric and polyhydric alcohols from acetylene, using mercuric oxide as a catalyst.

The purpose of the present paper is to assign a possible formula to the acid $\text{BF}_3\cdot\text{ROH}$ and to explain the production of acetals from acetylene by this method.

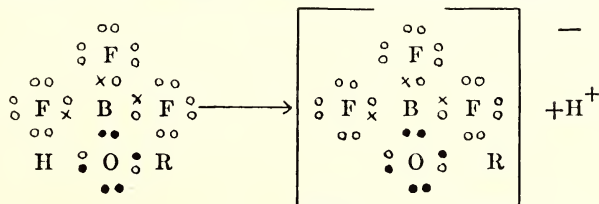
According to the electronic concept of valence boron fluoride is written as:



and methyl alcohol as $\text{H} \circ \text{O} \circ \text{R}$. Since these two compounds react mole for mole we may, using the idea of coordinate co-valence, write the resulting compound as—



In this sharing of electrons the oxygen atom in the alcohol contributes both electrons to its linkage with the boron atom. The oxygen atom by this donation of electrons becomes more positive in nature and thus the bond between it and the hydrogen atom is weakened, causing the compound to ionize.



Proc. Ind. Acad. Sci. 40: 203-206. (1930) 1931.

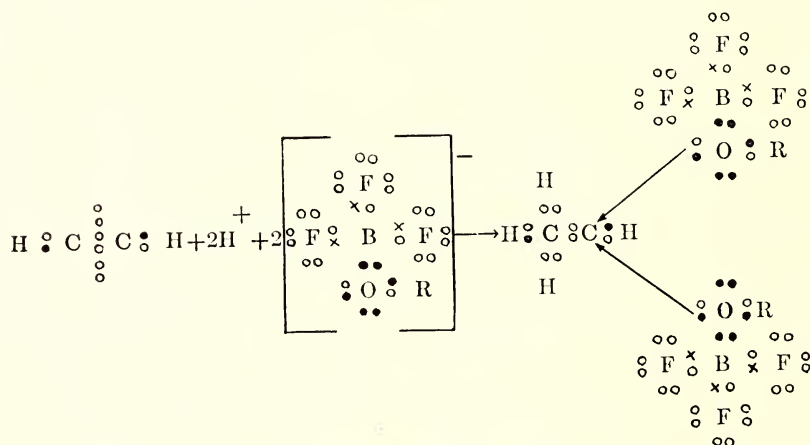
¹J. Amer. Chem. Soc. 52: 1018. (1930)

²J. Amer. Chem. Soc. 52: 2892. (1930)

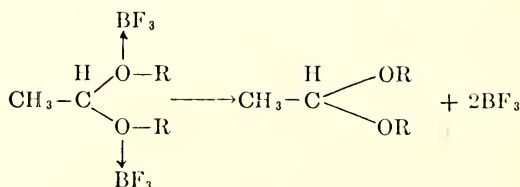
This ionization accounts for the observed high conductivity for solutions of this compound and gives rise to an explanation of the role played by the acid in catalysis.

In practice the following method is used to prepare acetals from acetylene by the use of this acid. Five grams of the methyl alcohol compound is weighed into a tared flask and one gram of mercuric oxide is partly dissolved in it by gentle heating. The flask is then cooled and two to five hundred grams of alcohol added. Dry acetylene from a gasometer is then passed into the closed flask with occasional shaking until the calculated weight has been absorbed.

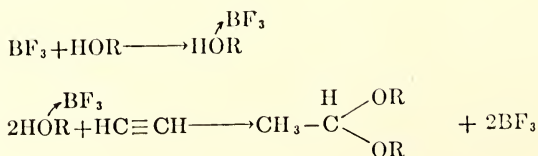
When the acetylene is passed into the mixture two hydrogen ions add on to one of the carbon atoms and the two negative ions add on to the other.



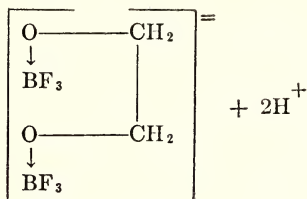
this compound, due to the acquired positive group then splits off boron fluoride and gives acetal.



The boron fluoride then reacts with more alcohol and the cycle is complete. These reactions may be summed up as follows—



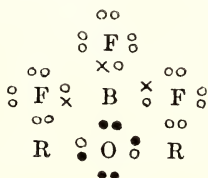
In the case of glycols the boron fluoride merely adds on to both hydroxyl groups giving in the case of ethylene glycol



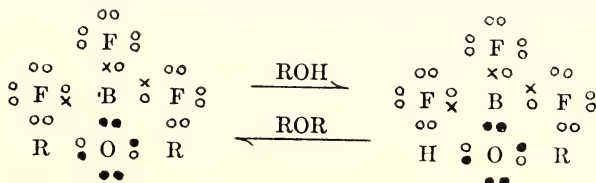
which reacts in a manner similar to that of the monohydric alcohols.

The methyl alcohol contained in the initial five grams of catalyst is soon used up and the boron fluoride then adds on to the other alcohol present. It has been found that boron fluoride will react with those alcohols which give acetals by this method and that in the few cases where no acetal formation takes place boron fluoride will not form a compound with the alcohol in question. Thus Hinton and Nieuwland were unable to prepare the acetal of tertiary butyl alcohol and Bowlus (unpublished work) has found that this alcohol will not react with boron fluoride.

The proposed formula for the alcohol compound also accounts for the following behavior of the compound of boron fluoride with ether. Ether reacts mole for mole with boron fluoride. The resulting compound has a low specific conductance and is not acidic. If the ether compound be placed in alcohol the odor of ether becomes at once apparent. If a rapid stream of air or other inert gas is now bubbled through the solution the odor of ether disappears and catalysis takes place readily. These facts can be explained by assigning to the ether compound a formula analogous to that of the alcohol compound thus—



In this configuration, since there is no hydrogen atom, the compound obviously can not ionize and exhibit a high conductivity. When the compound is placed in alcohol some of the ether is liberated and alcohol takes its place, an equilibrium is finally reached which may be represented in the following manner—



It is very probable that the equilibrium point is reached when only a very small amount of the alcohol compound has been formed. The passage of a rapid stream of air through the solution serves to sweep the ether out of the system and thus pushes the equilibrium toward the right giving the acid compound.

To check up on this equilibrium a small amount of ether was added to an alcohol solution of the boron fluoride which was showing catalysis. Acetal formation immediately stopped and could be restored only by flushing the ether out of the flask. Further evidence of the existence of this equilibrium is found in the fact that specially purified ether will not react with boron fluoride, a trace of alcohol being necessary to start the reaction. We have interpreted this as meaning that the alcohol compound is formed first and then reacts with the ether, producing the ether compound and regenerating the alcohol. The extremely small amount of alcohol sufficient to cause ether to react lends credence to the assumption that the equilibrium point is reached when only a small amount of the alcohol compound is present.

Up to the present, all attempts to prepare salts of the alcohol compound have failed. Zinc, iron, magnesium, and aluminum react with the acid in the order named but the nascent hydrogen liberated reduces the compound and boroethane is produced.

SUMMARY

1. A formula has been assigned to the acid produced by the action of boron fluoride on alcohol.
2. The high conductivity of solutions of this compound in alcohol has been explained.
3. A possible mechanism for the catalytic action of this acid in the formation of acetals from acetylene in the presence of mercuric oxide has been outlined.
4. An explanation of the behavior of ether as a negative catalyst in acetal formation by this method has been offered.