[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Reactions and Properties of Boron Fluoride in Methyl Alcohol

BY L. A. O'LEARY AND H. H. WENZKE

Bowlus and Nieuwland[1] in a recent paper have postulated the existence of methoxyfluoboric acid and have proposed an electronic formula for it. The presence of this acid provides a basis for the explanation of a number of reactions of boron fluoride.

It is the purpose of this paper to prove the existence and structure of methoxyfluoboric acid, to describe a few of its characteristic reactions, to present another explanation of the mechanism of the catalytic formation of acetals from acetylene and to show the extent of its acid properties from conductivity data.

Experimental

Reagents.—Boron fluoride was prepared according to the procedure of Bowlus and Nieuwland.[1] The boron fluoride which was used for conductivity work was further purified by fractional distillation with liquid air in an all-Pyrex distilling apparatus described by Booth[2] with a few minor modifications. The boron fluoride was fractionated five or six times and absorbed directly in an absorption flask containing a weighed quantity of alcohol. The solutions used contained about 15% of boron fluoride by weight.

The methyl alcohol used for the conductivity determinations had a specific conductivity of 1.6×10^{-6}.

Apparatus.—The conductivity apparatus consisted of the usual Kohlrausch assembly with a drum type slide wire bridge and a vacuum tube oscillator as the current source. The entire apparatus was grounded by the method suggested by Taylor and Acree.[3]

A static method was used for the determination of vapor pressures.

Preparation of Compounds.—Mercuric methoxyfluoborate was prepared by adding mercuric oxide a little at a time to methoxyfluoboric acid. If the reaction was allowed to proceed too rapidly, reduction of some of the mercury to the metallic state occurred. No mercuric methoxyfluoborate was obtained if stoichiometric proportions of the reagents were used. This is probably explained by the fact that the water formed in the reaction immediately reacted with the salt and with the acid. The grayish residue which always appeared as the result of decomposition and side reactions was probably a mixture of mercuric fluoride, mercuric fluoborate and mercuric hydroxy fluoride. Attempts definitely to isolate and identify these compounds failed due to their instability. Methoxyfluoboric acid was the only solvent found in which mercuric methoxyfluoborate was both stable and soluble. It crystallized in long, white, needle-shaped crystals from this solution on a steam-bath. In consequence of this the compound was always contaminated to some extent with the solvent.

Monoammono boron fluoride was formed when dry ammonia gas was passed directly into methoxyfluoboric acid or its alcohol solution. The product was filtered, washed repeatedly with ether and dried. Attempts to prepare the sodium salt which resulted in the formation of sodium fluoborate were made by adding sodium methylate

---

[1] Bowlus and Nieuwland, THIS JOURNAL, **53**, 3835 (1931).

[2] Booth, *J. Chem. Ed.*, **7**, 1249 (1930).

[3] Taylor and Acree, THIS JOURNAL, **38**, 2403 (1916).

slowly to an alcohol solution of the acid. An excess of acid was always used. The precipitate was treated in the same manner as the product obtained with ammonia.

Analytical.—The compounds were decomposed in a Parr bomb according to the procedure of Hahn and Reid.[4] The ferric hydroxide was removed by filtration and the carbonate and hydroxyl ions destroyed by adding the calculated quantity of ammonium chloride and digesting to expel the ammonia. The fluoride ion was precipitated as calcium fluoride in a hot slightly ammoniacal solution. The precipitate was filtered, dried, and ignited to constant weight in a platinum crucible. The boron was determined in the filtrate by first removing the ammonium ions with sodium hydroxide, neutralizing with hydrochloric acid, and titrating for boron in the usual manner with one-tenth normal sodium hydroxide in the presence of mannitol. Mercury was determined on a separate sample by White's[5] procedure.

TABLE I

MOLAR CONDUCTIVITY FOR THE SYSTEM CH_3OH-BF_3 AT 25°

V	*L*	*V*	*L*	*V*	*L*
0.8943	23.44	28.618	52.42	1831.5	11.74
1.789	29.26	57.235	55.38	3663.0	6.19
3.577	35.11	114.47	55.02	7326.1	5.86
7.154	41.25	228.94	49.19	14,652	5.27
14.310	47.28	457.88	38.05	29,304	2.05
		915.8	23.78		

V, liters of solution per mole of BF_3. L, molar conductivity.

The molar conductivity of ethyl acetate boron fluoride in methyl alcohol was found to be 53.94 at a dilution of 50 liters and 17.38 at a dilution of 1250 liters.

TABLE II

VAPOR PRESSURE FOR THE SYSTEM CH_3OH-BF_3 AT 25°

Wt. % of BF_3	*P*	Wt. % of BF_3	*P*	Wt. % of BF_3	*P*
4.14	124	33.77	88	57.92	12
9.75	131	40.88	60	64.74	21
18.65	120	43.26	53	65.16	23
20.11	118	48.35	29	67.45	42
21.21	113	49.01	34	68.58	158
		54.89	9		

P, vapor pressure in mm.

TABLE III

ANALYTICAL DATA

Compound		F, %		B, %		Hg, %	
$Hg(CH_3OBF_3)_2$	Found	28.48	28.42	5.55	5.38	49.50	49.15
	Calcd.	28.62		5.44		50.37	
$NH_3 \cdot BF_3$	Found	67.52	67.30	13.02	12.78		
	Calcd.	67.18		12.75			
$NaBF_4$	Found	68.45	68.00	10.53	9.79		
	Calcd.	69.20		9.86			

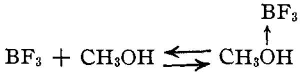
---

[4] Hahn and Reid, THIS JOURNAL, **46**, 1652 (1924).

[5] White, *ibid.*, **42**, 2355 (1920).

Discussion

The vapor pressure curve indicates that an equilibrium exists in the system boron fluoride–methyl alcohol as follows



$$BF_3 + CH_3OH \rightleftarrows \overset{\overset{BF_3}{\uparrow}}{CH_3OH}$$

Since it was impossible to prepare concentrated solutions without some decomposition, the extent of this equilibrium cannot be determined. The maximum in the curve in the dilute region indicated the existence of a constant boiling solution. The fifty mole per cent. solution was found to freeze at $-19.4°$. It is to be noted also that the conductivity curve for the concentrated region published by Nieuwland, Vogt, and Foohey[6] had a sharp break in the vicinity of fifty mole per cent. of boron fluoride, indicating compound formation as shown in the above equation.

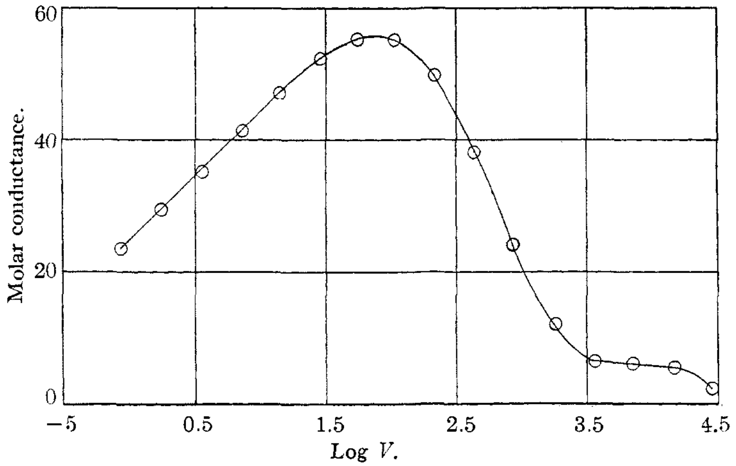
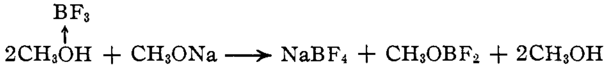


Fig. 1.

A repetition of the work of Gasselin[7] on the quantity of boron fluoride absorbed per mole of alcohol confirms his work in that one mole of methyl alcohol always absorbs very nearly one mole of boron fluoride at atmospheric pressure.

Of the various attempts to prepare salts of this acid, only those with mercury were successful. In the case of the more electropositive metals, the salt if formed immediately broke down into the corresponding fluoborate. When sodium methylate was added in less than the stoichiometric proportions to methoxyfluoboric acid, sodium fluoborate was precipitated.



$$2\overset{\overset{BF_3}{\uparrow}}{CH_3OH} + CH_3ONa \longrightarrow NaBF_4 + CH_3OBF_2 + 2CH_3OH \qquad (I)$$

---

(6) Nieuwland, Vogt, and Foohey, THIS JOURNAL, **52**, 1018 (1930).

(7) Gasselin, *Ann. chim. phys.*, [7] **3**, 5 (1894).

Analysis of the precipitate which was formed when dry ammonia gas was passed into methoxyfluoboric acid showed it to be monoammono boron fluoride. It is probable that ammonium methoxyfluoborate was formed as an intermediate compound according to the following reactions

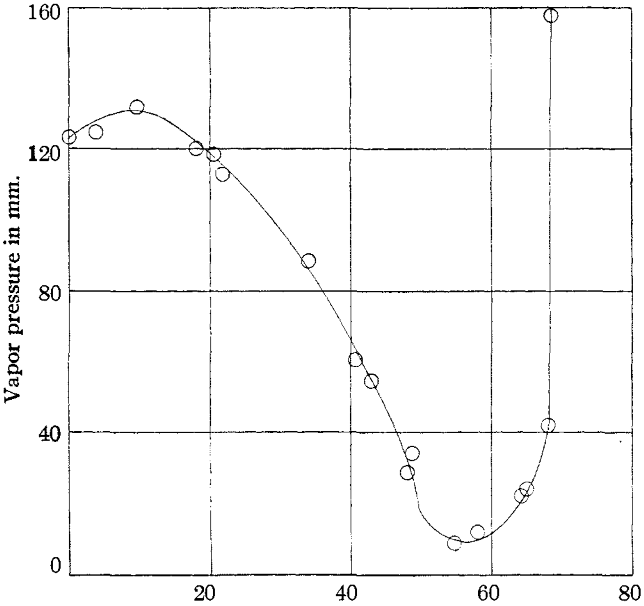
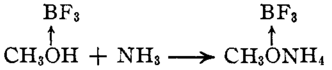
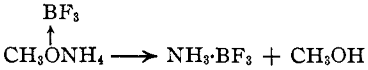


Fig. 2.—Vapor pressure of the system CH_3OH–BF_3.

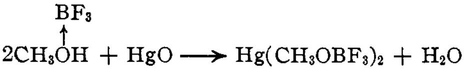


$$CH_3\overset{\overset{BF_3}{\uparrow}}{O}H + NH_3 \longrightarrow CH_3\overset{\overset{BF_3}{\uparrow}}{O}NH_4 \qquad (I)$$



$$CH_3\overset{\overset{BF_3}{\uparrow}}{O}NH_4 \longrightarrow NH_3\cdot BF_3 + CH_3OH \qquad (II)$$

Mercuric methoxyfluoborate was formed according to the following equation



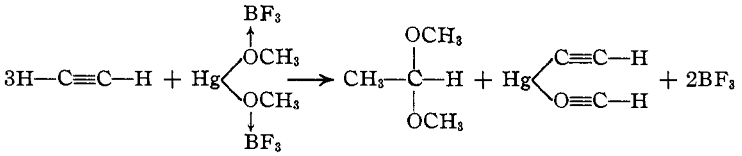
$$2CH_3\overset{\overset{BF_3}{\uparrow}}{O}H + HgO \longrightarrow Hg(CH_3OBF_3)_2 + H_2O \qquad (I)$$

This salt is unstable and readily breaks down into mercuric fluoride as follows

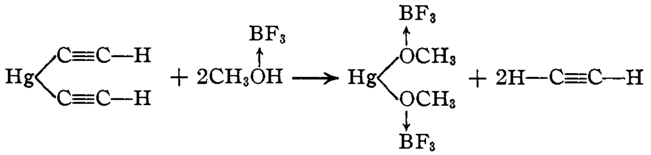
$$Hg(CH_3OBF_3)_2 \longrightarrow HgF_2 + 2CH_3OBF_2 \qquad (II)$$

It is also very deliquescent in air.

It is evident that the existence of mercuric methoxyfluoborate probably explains the role of mercuric oxide in acetal catalysis by means of methoxyfluoboric acid. On this basis the following mechanism for acetal catalysis is offered.

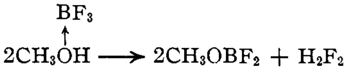


$$3H{-}C{\equiv}C{-}H + Hg\begin{matrix}\overset{\overset{BF_3}{\uparrow}}{OCH_3}\\ \underset{\underset{BF_3}{\downarrow}}{OCH_3}\end{matrix} \longrightarrow CH_3{-}\overset{\overset{OCH_3}{|}}{\underset{\underset{OCH_3}{|}}{C}}{-}H + Hg\begin{matrix}C{\equiv}C{-}H\\ O{\equiv}C{-}H\end{matrix} + 2BF_3 \tag{I}$$



$$Hg\begin{matrix}C{\equiv}C{-}H\\ C{\equiv}C{-}H\end{matrix} + 2CH_3\overset{\overset{BF_3}{\uparrow}}{O}H \longrightarrow Hg\begin{matrix}\overset{\overset{BF_3}{\uparrow}}{OCH_3}\\ \underset{\underset{BF_3}{\downarrow}}{OCH_3}\end{matrix} + 2H{-}C{\equiv}C{-}H \tag{II}$$

The conductivity curve for methoxyfluoboric acid is unusual in that it reaches a maximum in the neighborhood of 60 liters dilution and then gradually decreases and approaches the conductance of the solvent as a limit. The maximum conductivity is approximately one-half of that for hydrochloric acid in the same solvent and at the same dilution. The acid probably breaks up on dilution according to the equation



$$2CH_3\overset{\overset{BF_3}{\uparrow}}{O}H \longrightarrow 2CH_3OBF_2 + H_2F_2$$

The conductivity values of the methyl alcohol solutions of ethyl acetate boron fluoride show that this compound undergoes almost complete alcoholysis. This is perhaps true also of all the organic addition compounds of boron fluoride reported by Bowlus and Nieuwland.[1]

Summary

1. The existence and some of the characteristic reactions of methoxyfluoboric acid have been shown.
2. The ions of methoxyfluoboric acid have been identified by the preparation of mercuric methoxyfluoborate.
3. The vapor pressure–concentration curve for the system methyl alcohol–boron fluoride has been determined.
4. The conductivity curve of the system methyl alcohol–boron fluoride has been determined and a reaction mechanism has been proposed to explain it.
5. It has been shown that the acid characteristics of organic compounds containing a donor atom and an ionizable hydrogen are greatly increased by the addition of boron fluoride.
6. A possible mechanism has been suggested for the catalytic formation of acetals from acetylene and alcohol.

NOTRE DAME, INDIANA

RECEIVED DECEMBER 3, 1932
PUBLISHED MAY 6, 1933