

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

THE ACTION OF BORON FLUORIDE ON ORGANIC COMPOUNDS

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Although a number of investigators have mentioned the reaction which takes place between alcohol and boron fluoride, Gasselin¹ was the first to make any effort to isolate the reaction products; the acid solution which he obtained has been used by Nieuwland, Vogt and Foohey² and by Hinton and Nieuwland³ in the catalytic preparation of acetals from acetylene. Cannizzaro⁴ obtained what he thought was stilbene from the products of the reaction of boron fluoride upon benzyl alcohol. Landolph⁵ stated that boron fluoride exercised a dehydrating effect upon acetic acid, and that some acetic anhydride was formed; Meerwein⁶ found that boron fluoride acted upon acetic acid to produce a compound $(\text{CH}_3\text{-COOBF}_3)\text{H}$ boiling at 59° (13 mm.). Patein⁷ prepared a compound of acetonitrile and boron fluoride. Recently Kraus and Brown⁸ have investigated the action of boron fluoride upon the ethylamines.

It is the purpose of this paper to discuss some new compounds which have been prepared with the aid of boron fluoride, to attempt to assign a structure to them and some of those which are mentioned in the literature cited, and to formulate a possible explanation of the mechanism of the catalytic formation of acetals from acetylene.

Experimental

The reagents used in this work were Eastman Practical grade. The boron analyses were made by heating a sample with fuming nitric acid in a sealed tube at 200° for two hours, and titrating the boric acid formed. The combustions were performed with a tube lined with thin asbestos paper and packed with a mixture of two parts of copper oxide and one part of lead chromate. All of the molecular weight determinations, except that of the acetic anhydride compound, were made by the Victor Meyer vapor density method; most of the compounds were found to be completely dissociated in the vapor phase.

Description of a Typical Preparation.—Boron fluoride, prepared by warming a mixture of 200 g. of boric oxide and 400 g. of calcium fluoride with 1300 cc. of concentrated sulfuric acid, was passed through columns of sodium fluoride and fused boric

¹ Gasselin, *Ann. chim. phys.*, [7] 3, 5 (1894).

² Nieuwland, Vogt and Foohey, *THIS JOURNAL*, 52, 1018 (1930).

³ Hinton and Nieuwland, *ibid.*, 52, 2892 (1930).

⁴ Cannizzaro, *Ann.*, 92, 113 (1854).

⁵ Landolph, *Compt. rend.*, 85, 39 (1877).

⁶ Meerwein, *Ann.*, 455, 250 (1927).

⁷ Patein, *Compt. rend.*, 113, 85 (1891).

⁸ Kraus and Brown, *THIS JOURNAL*, 51, 2690 (1929).

oxide, and then into 50 g. (1 mol) of ethyl acetate which was placed in a flask carrying a long glass tube and a drying tube in a two-holed stopper; boron fluoride was passed in, keeping the flask at a temperature of about 25° until 39 g. (1 mol) had been absorbed. The viscous liquid in the flask was then distilled directly in a system protected from water vapor; a second distillation sufficed to give a pure, constant boiling product.

I. **Alcohols.**—It is believed that the compounds obtained by Casselin from the distillation of the solution of boron fluoride in methyl or ethyl alcohol were the products of a decomposition which takes place readily under the influence of heat; and that the solution of boron fluoride in methyl or ethyl alcohol forms but one compound.

An investigation of a portion of the freezing point curve of the system $C_2H_5OH-BF_3$ has been made in these Laboratories and seems to point to the existence of a compound, since a maximum in the curve was obtained at fifty mole per cent. of boron fluoride and at a temperature of -19° .

Nieuwland, Vogt and Foohey² showed that the conductivity of the system $C_2H_5OH-BF_3$ is of the same order as that of the system $H_2SO_4-SO_3$. It is believed by the present authors that this high conductivity is due to the presence of the compound mentioned above, which ionizes in alcohols in such a way, as will be explained later in this paper, as to give hydrogen ions and complex organic anions.

The presence of hydrofluoric acid in the products of the reaction as noted by Casselin is doubtful, and was probably a result of thermal decomposition, for the alcohol compounds were not found to attack glass.

All alcohols were found to absorb slightly more than one mole of boron fluoride. On passing boron fluoride into aliphatic alcohols other than methyl or ethyl alcohol, hydrocarbon oils were obtained.

n-Butyl alcohol absorbed one mole of boron fluoride, forming a dark solution from which a clear, supernatant oil separated on standing for about two days. The production of this oil was hastened by warming the mixture, when boron fluoride and an olefinic gas were evolved. The oil seemed to be a mixture of aliphatic and aromatic hydrocarbons with a small amount of unsaturates, and boiled from 85° (25 mm.) to over 330° (25 mm.). The lower layer was a strongly acid, fuming liquid, similar to the methyl and ethyl alcohol solutions of boron fluoride; it could be substituted for them in the catalytic preparation of acetals from acetylene.

II. **Acids.**—In repeating Meerwein's work the distillation of the saturated solution of boron fluoride in acetic acid was carried out at atmospheric pressure. There was a large evolution of boron fluoride before distillation began. The compound which finally distilled was similar to Meerwein's compound, but seemed to contain a smaller amount of boron fluoride; analyses pointed to the formula $(CH_3COOH)_2BF_3$. By the use of a very small quantity of this acetic acid compound it was found

that esterification rates about equivalent to those produced by the presence of hydrogen chloride could be obtained.⁹

Propionic acid was found to absorb one mole of boron fluoride which it lost completely when a distillation was attempted at normal pressures; a boiling point of 62–63° (17 mm.) was obtained. The analytical values were too low for $(C_2H_5COOH)_2BF_3$, but too high for $(C_2H_5COOH)BF_3$.

No reaction could be obtained with monochloroacetic or trichloroacetic acid.

Benzoic acid, dissolved in chloroform, absorbed boron fluoride to the extent of one mole, and a dark liquid was precipitated, which on standing solidified. No solvent could be found which was suitable for purification purposes; the crude product melted at about 98°.

III. **Nitriles.**—On repeating the work of Patein it was found that the compound of acetonitrile with boron fluoride melted at 87° and boiled at 101° (752 mm.).

IV. **Esters.**—Esters of the aliphatic monobasic acids were found to react with boron fluoride to form monomolecular compounds, of which the lower members were solids.

The esters of the dibasic acids also reacted, but did not admit of easy purification. Diethyl malonate and diethyl oxalate each absorbed one mole of boron fluoride to form crystalline compounds, which lost boron fluoride, with partial decomposition, when vacuum distillation was attempted.

Glycol diacetate reacted similarly; on standing for some time, long acicular crystals separated from the viscous liquid. Some tarry decomposition products were formed when vacuum distillation was attempted.

The aromatic esters reacted in a like manner. Phenyl acetate and ethyl benzoate absorbed one mole of boron fluoride to form almost clear, viscous liquids, which apparently would not crystallize, and which lost all of their boron fluoride on vacuum distillation.

A similar behavior was noted with ethyl chloroacetate and ethyl trichloroacetate.

V. **Ethers.**—Anisole and phenetole absorbed one mole of boron fluoride to form viscous, clear liquids, which could not be distilled under any conditions without evolution of all of the boron fluoride which they had absorbed.

No reaction could be obtained with diphenyl oxide. Negative results were also obtained with dimethyl ethylidene acetal and glycol ethylidene acetal.

The monomethyl ether of glycol acetate absorbed two moles of boron fluoride, forming a viscous liquid which did not crystallize, and which evolved boron fluoride on attempting to distil with the formation of tarry products.

The conductivity of the ethyl ether compound was investigated and was

⁹ Terre, "Thesis," University of Notre Dame, 1931.

found to be very low in comparison with that found for the ethyl alcohol compound.¹⁰

VI. Acid Anhydrides.—Acetic anhydride absorbed one mole of boron fluoride, giving a product which could be crystallized from acetic anhydride. It seemed to be rather stable, did not fume in the air and had practically no odor. The molecular weight determination was made by the freezing point method using acetic acid as the solvent; the value found was too large, and was evidently due to association. No other suitable solvent could be found for the molecular weight determination.

No reaction was obtained with succinic, benzoic or phthalic anhydrides.

VII. Pyridine Bases.—Pyridine absorbed two moles of boron fluoride to form a compound which could be crystallized from alcohol without any apparent decomposition.

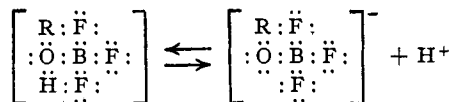
Quinoline and piperidine absorbed one mole of boron fluoride, giving crystalline products.

VIII. Amides.—Acetamide absorbed one mole of boron fluoride and was converted to a viscous, colorless, almost odorless, non-fuming liquid. On long standing a few needle-like crystals separated. On attempting to vacuum distil the compound it decomposed giving boric acid and tarry products.

The Acetal Catalysis; Structure of Some of the Compounds.—According to the electronic concept of valency alcohols may be written as $R : \ddot{O} : H$

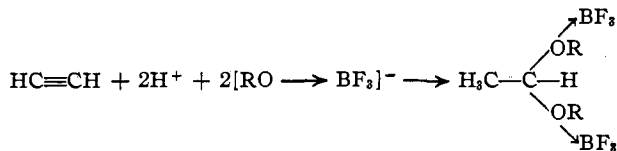
and boron fluoride as $\begin{array}{c} :\ddot{F}: \\ \vdots \\ :\ddot{B}:\ddot{F}: \\ \vdots \\ :\ddot{F}: \end{array}$. Since alcohols absorb one mole of boron

fluoride and appear to form a single compound, the alcohol may be assumed to combine coordinately with the boron fluoride. The compound then ionizes in alcohol, thus



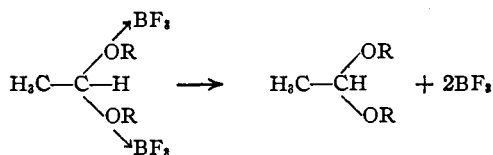
which assumption is substantiated by the large conductivity and acid properties which have been found for it.

In acetal formation the following series of reactions may be assumed to take place. The acetylene reacts with two moles of the ionized compound



¹⁰ Ball and Halter, "Thesis," University of Notre Dame, 1931.

This complex breaks up, giving the acetal



The boron fluoride is then free to combine with more alcohol, and go through the cycle again. In practice the methyl alcohol compound is used to start the catalysis, and is probably used up first, the boron fluoride then combining with the other alcohol which is present.

TABLE I
RESULTS OF EXPERIMENTS

Compound	C, %	H, %	B, %	M. wt.	B. p., °C.(mm.)	m. p., °C.	<i>d</i> ₄
(CH ₃ COOH) ₂ BF ₃							
Found	25.7	4.37	5.75	92.6	140 (748)		1.351 ₂₁
Calcd.	25.33	4.26	5.85	188.0			
(C ₂ H ₅ COOH) ₂ BF ₃							
Found	32.5	5.78	4.90	78.0	62-63 (17)		1.238 ₂₃
Calcd.	33.33	5.56	5.09	216.0			
(CH ₃ CN)BF ₃							
Found	21.8	2.77	8.88	55.7	101 (752)	87	
Calcd.	22.01	2.77	10.09	109.0			
Nitrogen, %		Found,	11.6	Calcd.,	12.84		
(CH ₃ COOCH ₃)BF ₃ ^a							
Found	25.2	4.72	8.19	76.0	110 (759)	60	
Calcd.	25.38	4.23	7.63	141.8			
(CH ₃ COOC ₂ H ₅)BF ₃ ^a							
Found	30.6	5.21	6.95	81.5	119 (759)	26	
Calcd.	30.75	5.17	7.05	156.1			
(HCOOC ₂ H ₅)BF ₃ ^a							
Found	24.1	4.21	7.95	73.9	102 (748)		1.311 ₂₅
Calcd.	25.34	4.23	7.74	142.1			
(CH ₃ COOCH ₂ CH ₂ CH ₃)BF ₃ ^a							
Found	35.4	6.48	6.30	91.1	126 (748)		1.170 ₂₂
Calcd.	35.28	5.93	6.47	170.1			
(C ₂ H ₅ COOC ₂ H ₅)BF ₃ ^a							
Found	35.0	5.80	6.50	83.2	116 (747)	33	
Calcd.	35.3	5.88	6.47	170.0			
((CH ₃ CO) ₂ O)BF ₃ ^a							
Found	28.4	3.30	6.32	409		194	
Calcd.	28.24	3.53	6.47	170.0			
(CH ₃ CONH ₂)BF ₃ ^a							
Found	18.6	3.85	8.47				
Calcd.	18.90	3.94	8.66				
Nitrogen, %		Found,	11.76	Calcd.,	11.02		

^a New compound.

On the basis of the formula proposed for the alcohol compounds of boron fluoride, the ether compounds may be assumed to be the esters of the complex acids; and the ester compounds may similarly be assumed to be the acetoxy derivatives of the same acids. Both of these latter series of compounds should not, according to the above theory, promote catalytic acetal formation since they are incapable of yielding hydrogen ions; such has been found to be the case, and is further substantiated by the low conductivity found for the ethyl ether compound of boron fluoride.

Summary

1. A number of organic compounds of boron fluoride have been prepared, which, in general, contained monomolecular proportions of the constituents, and were dissociated in the vapor phase.

2. These compounds were fuming liquids or solids, difficult to crystallize, decomposed by water and oxygenated solvents, and insoluble in non-oxygenated solvents.

3. The higher aliphatic alcohols were found to form hydrocarbons by the action of boron fluoride.

4. A possible mechanism is formulated for the catalytic formation of acetals from acetylene; and electronic formulas are proposed for some of the organic compounds of boron fluoride.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE STABILITY OF HEXA-TERTIARY-ALKYLETHINYLETHANES. THE EFFECT OF INCREASING THE WEIGHT OF THE ALKYL GROUPS

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Since the discovery¹ that hexa-*tert.*-butylethynylethane (I) had some of the reactions that had previously been thought to be more or less characteristic of the hexa-arylethanes, a considerable amount of work has been done in attempting to determine how this aliphatic molecule could be changed to obtain a substance which would more closely resemble the aryl derivatives. In discussing the causes for the dissociation of ethanes, Lewis² has pointed out that weight and unsaturation are the two important properties of the aryl groups which are responsible for causing the dissociation of hexa-arylethanes into free radicals. This suggested that it would be desirable to study a compound in which the size of the tertiary alkyl group attached to the acetylene residue was greater than *tert.*-butyl,

¹ Salzberg with Marvel, *THIS JOURNAL*, **50**, 1737 (1928).

² Lewis, *Proc. Nat. Acad. Sci.*, **2**, 586 (1916).