BORON FLUORIDE IN ACETAL CATALYSIS

THOMAS H. VAUGHN, University of Notre Dame

A new method of making acetals from acetylene and hydroxy compounds, using boron fluoride and mercuric oxide as catalysts was reported by Nieuwland, Vogt, and Foohey[1] in 1930. Their work, and that of other investigators[2] has shown that in most instances this new procedure is superior to the older methods of synthesis. This method has also been used in these laboratories for the preparation of ketals from hydroxy compounds and substituted acetylenes.[3]

In 1931, Vaughn, Bowlus, and Nieuwland[4] advanced a formula for the acid formed by the union of boron trifluoride and alcohol and proposed a mechanism to explain the function of this acid in acetal catalysis. The coordination structure assigned to the acid has recently been confirmed by the work of Sugden and Waloff[5] on the parachors of additive compounds of boron fluoride.

In applying this new method of synthesis it has been customary to use 2-5 grams of boron fluoride for each 100 grams of hydroxy compound which was to be ethylidinated. The purification of the resulting acetal has in some instances been complicated by the presence of these large amounts of boron. That the concentrations of boron fluoride used were unnecessarily high is shown by the instance reported by Nieuwland, Vogt, and Foohey[1] where .142 g. of boron fluoride was sufficient to catalyze 200 g. of glycerol to the acetal. Since it was felt that even this concentration was unduly high the present work was undertaken to determine the minimal amount of boron trifluoride necessary for the formation of glycol acetal from glycol and acetylene.

EXPERIMENTAL PART

Materials. The acetylene was obtained from a 40 cu. ft. Prest-O-Lite cylinder and was used without purification. Ethylene glycol was obtained from The Eastman Kodak Company and boiled at 198-200° C. The mercuric oxide was Baker's C.P. red powder. Boron fluoride was prepared from boric anhydride, calcium fluoride and sulfuric acid and was purified by passing through columns of sodium fluoride and fused boric oxide.[6] Glycol acetal was prepared by the action of acetylene on glycol[1] and was carefully purified by repeated fractionation.

[1] Nieuwland, Vogt and Foohey, J. A. C. S. **52**:1018-24   (1930).

[2] Hinton and Nieuwland, J. A. C. S. **52**:2892-6   (1930).   J. A. Nieuwland U. S. Pat., 1,824,963 Sept. 29, 1931.

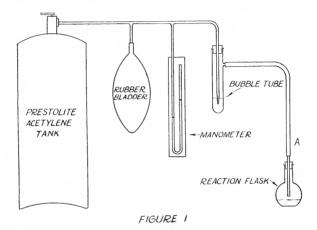[3] The results of this work will be discussed in a later communication.

[4] Vaughn, Bowlus and Nieuwland, Proc. Ind. Acad. Sci., **40**:203-6   (1931).

[5] Sugden and Waloff, J. Chem. Soc., 1932, 1492-96.

[6] Bowlus, "The Action of BF_3 on Organic Compounds," Thesis University of Notre Dame (1931).

Preparation of Boron Trifluoride Solutions. Two hundred grams of powdered boric anhydride was well mixed with 400 gm. of powdered calcium fluoride contained in a 3-1. Erlenmeyer flask. Thirteen hundred grams of concentrated sulfuric acid was then added and the mixture gently heated with a Bunsen burner. After the evolution of gas had continued for about 30 minutes, the stream of gas was purified as above described and passed into an accurately weighed amount (25-30 ml.) of ethylene glycol contained in a 50 ml. volumetric flask, the flask being cooled in cold water during the absorption. When about 5 grams of boron fluoride had been absorbed the flask was again weighed and the solution made up to 50 ml. The concentration of the solution was calculated as grams per milliliter. By careful dilution a series of solutions containing lesser amounts of boron fluoride was prepared.

FIGURE I

Apparatus. The apparatus used in making the determinations is shown in Figure 1. The bladder was a small size swimming tube which was capable of standing pressures up to 150 mm. of mercury. The entering tube of the bubble counter was drawn out to a very fine capillary so that even a very small absorption of gas in the reaction flask could be detected. Ethylene glycol was the liquid used in the bubble counter. Small Florence flasks (150 ml.) were used as reaction vessels. All joints between rubber tubing and glass were securely wired to prevent leaks.

Procedure. Nineteen milliliters of ethylene glycol was measured into the reaction flask from a burette which was allowed to drain for five minutes. 0.30 gram of red mercuric oxide was added to the glycol and the flask connected to the absorption apparatus which had been previously washed with acetylene until free from air. The needle valve on the acetylene cylinder was opened and the pressure in the system raised to 100 mm. of mercury. The stopper was loosened and the flask flushed out with acetylene until the pressure had dropped to 80 mm. The stopper was replaced and the pressure was raised to 100 mm. The flask was then shaken until the glycol was saturated with acetylene. Satura-

tion usually required about 10 minutes and was indicated by the cessation of the flow of bubbles in the bubble counter.

The acetylene supply was shut off at A by means of a pinch clamp and the stopper removed. One milliliter of a solution of boron fluoride in glycol of known concentration was added to the flask from a pipette and the flask flushed out as before until the pressure fell to 80 mm. The pressure was again raised to 100 mm. and the reaction flask shaken. Catalysis was indicated by a gradual increase in the rate of absorption as indicated by the flow of bubbles through the bubble counter and by the formation of a grey deposit on the bottom of the flask. Solutions containing decreasing amounts of boron fluoride were then used in the determination until the signs of catalysis could no longer be observed.

One milliliter of catalyst was used in each run. This, with the 19 ml. of glycol used, gave a total volume of 20 ml. in each run. The results of a number of such runs are listed in Table 1.

TABLE 1.

Glycol in ml.	HgO in gms. $\mp$ .019	g. BF_3/ml. Catalyst	g. BF_3/ml. Reaction Mix.	Catalysis
20	.300	.1455	.00727	+
20	.300	.01455	.000727	+
20	.300	.01164	.000582	+
20	.300	.00873	.000436	+
20	.300	.00582	.000291	+
20	.300	.00291	.0001455	+
20	.300	.001766	.0000883	+
20	.300	.001513	.0000756	+
20	.300	.001455	.0000727	+
20	.300	.001397	.0000698	+
20	.300	.001222	.0000611	+
20	.300	.001134	.0000567	+
20	.300	.001047	.0000523	+
20	.300	.000960	.0000480	—
20	.300	.000873	.0000436	—

To determine whether or not boron fluoride must be present in a certain molal ratio to glycol several determinations were made with mixtures of glycol and glycol acetal. The results of these experiments are shown in Table 2.

TABLE 2.

Glycol in ml.	Glycol Acetal in ml.	HgO in g. $\mp$ .019 g.	g. BF_3/ml. Catalyst	g. BF_3/ml. Reaction Mix.	Catalysis
10	10	.300	.001047	.0000523	+
10	10	.300	.000960	.0000480	—
10	10	.300	.000873	.0000436	—

DISCUSSION

These experiments show that (50 ∓ 2) 10^{-6} g. of boron fluoride per ml. of glycol is sufficient to catalyze the formation of glycol acetal from acetylene. They also show that the same amount is required to initiate catalyses in a mixture consisting of 50 per cent glycol and 50 per cent glycol acetal. These results show that catalysis does not depend on the mole ratio of boron fluoride to glycol, which was 1 to 234,000 in the glycol and 1 to 117,000 in the glycol glycol-acetal solution, but rather on the concentration of boron fluoride.

In the published procedures for the preparation of acetals from acetylene concentrations of about .25 g. of boron fluoride per gram of hydroxy compound have been recommended. The results of the present work show that in the case of ethylene glycol this amount is about 500 times greater than that actually necessary. By using concentrations of catalyst which are near to those actually necessary the isolation and purification of acetals should be materially simplified.

When glycol acetal is prepared by the catalytic method the speed of acetylene absorption increases as the reaction progresses. This increase in speed has been regarded as due to either or both of two causes. First, that as the reaction proceeds, the ratio of boron fluoride to unreacted glycol increases, speeding up the reaction by increasing the relative amount of catalyst present. Second, that as more glycol acetal is formed the effective concentration of acetylene is increased due to its greater solubility in the acetal than in the glycol; the speed of reaction being accelerated by this increased solubility because glycol alone will not absorb acetylene as fast as it can be converted. It was found that in saturating the glycol-glycol acetal mixture with acetylene that much more acetylene was absorbed than by pure glycol and that the absorption was considerably more rapid. This evidence coupled with the fact that very little change in speed of absorption was noticed by greatly increasing the amount of boron fluoride present in the reaction mixture would seem to indicate that the second cause alone is responsible for the increased rate of absorption which has been observed.

The actual role of mercuric oxide as a catalyst in this method of making acetals is not known and has not been taken into account thus far. That it does enter into the reaction is certain since the reaction will not proceed in its absence. Work is under way in this laboratory at present to determine the part played by mercury in the catalysis and to determine the minimal amounts of boron fluoride necessary for the ethylindination of other hydroxy compounds.

ACKNOWLEDGMENT

The author gratefully acknowledges the assistance of Mr. John R. Voss in the conduction of this work.