presence of boron fluoride has been described.

The effect of the concentration of catalyst and time upon the yield of esters by acidolysis has been determined.

The acidolysis of ethyl sulfate has been studied with and without catalysts.

A mechanism of the reaction has been proposed.

NOTRE DAME, INDIANA RECEIVED SEPTEMBER 17, 1937

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

Organic Reactions with Dihydroxyfluoboric Acid[1]

BY T. B. DORRIS, F. J. SOWA AND J. A. NIEUWLAND

Dihydroxyfluoboric acid[2] is a liquid with the formula $HB(OH)_2F_2$ (or $HBO_2H_2F_2$). It possesses acid properties and at the same time it is a potential source for boron fluoride under certain conditions. These properties indicate that it should exhibit desirable catalytic activity.

The purpose of this investigation was to study the use of dihydroxyfluoboric acid as a catalyst in organic reactions. A rough comparison with the catalytic activity of boron fluoride was also made.

With very few exceptions it was found that dihydroxyfluoboric acid could be substituted for boron fluoride as a catalyst. This fact can be explained when it is considered that dihydroxyfluoboric acid gives rise to boron fluoride under various conditions. This is particularly true in its reaction with acetyl chloride, with acetic anhydride, with benzenediazonium chloride and with compounds containing oxygen.[3] Two separate experiments, however, have shown quite conclusively that dihydroxyfluoboric acid is not dependent on boron fluoride for its catalytic activity in all cases. In the presence of boron fluoride, phenol and isopropyl alcohol combine to form isopropylphenols and phenyl ethers.[4] This reaction fails to proceed in any concentration of the new catalyst even after very long periods of heating. In esterification reactions, moreover, boron fluoride is decomposed by the water formed while dihydroxyfluoboric acid may be recovered and reused to catalyze further esterifications.[5]

In general it might be stated that boron fluoride is a more powerful catalyst while dihydroxyfluoboric acid is a milder catalyst that promotes less polymerization. Boron fluoride rearranges isopropyl phenyl ether spontaneously,[6] while 30 to 40% of this ether is unchanged after refluxing for two hours with dihydroxyfluoboric acid. The rate of absorption of propylene by phenol is considerably greater when using boron fluoride.[7] This comparison of rates, however, must be interpreted cautiously, due to the very slight miscibility of dihydroxyfluoboric acid with most organic liquids.

Experimental Part

Preparation of Dihydroxyfluoboric Acid.—Dihydroxyfluoboric acid, b. p. 160°, was prepared by action of anhydrous hydrogen fluoride on boric oxide as previously described.[2]

Olefins with Phenol.—One mole of phenol was weighed in a liter Florence flask that was fitted with a two-hole rubber stopper into which were inserted an inlet tube extending to the bottom of the flask and an outlet tube. The outlet tube was connected to a mercury safety trap that also served the purpose of maintaining a safe pressure in the system. After adding 0.1 mole of dihydroxyfluoboric acid, propylene was passed in under a pressure of 7 to 10 cm. of mercury above atmospheric until 28 g. of propylene was absorbed. The solution was transferred to a separatory funnel and washed several times with a solution of potassium hydroxide. The alkaline extracts were acidified in order to recover the phenolic compounds while the alkali insoluble portion contained the alkyl phenyl ethers. The phenols, 2-isopropylphenol (30 mole %) and 4-isopropylphenol (3.4%) along with traces of higher substituted phenols and ethers were isolated. About 63.5% of the original phenol was recovered. The 2-isopropylphenol was shown to be identical with the 2-isopropylphenol formed by the rearrangement of isopropyl phenyl ether. The two phenols gave the same isopropyl phenyl ether derivative.

By using butylene, which was about 80% isobutylene and about 20% *n*-butylene, in place of propylene in an experiment similar to that described above the products were: butylphenol (8.1%), butyl phenyl ether (5.4%), butylphenyl butyl ether (26.8%) residue (55.8%) and recovered phenol (3.8%). The butyl phenyl ethers were proved by the "Zeisel" reaction.

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(1) Original manuscript received June 28, 1937.

(2) Sowa, Kroeger and Nieuwland, THIS JOURNAL, 57, 454 (1935).

(3) Kroeger, Sowa and Nieuwland, *ibid.*, 59, 965 (1937).

(4) Sowa, Hennion, and Nieuwland, *ibid.*, 57, 709 (1935).

(5) Kroeger, Sowa and Nieuwland, *Ind. Acad. Science*, Dec. (1937).

(6) Sowa, Hinton and Nieuwland, THIS JOURNAL, 54, 2019 (1932).

(7) Sowa, Hinton and Nieuwland, *ibid.*, 54, 3694 (1932).

Butylene with Benzene.—One mole of benzene and 8.4 g. of dihydroxyfluoboric acid were weighed in a liter Florence flask which was connected to a butylene tank as previously described. Butylene was passed into the benzene until three moles were absorbed. The catalyst was removed by treatment with a small amount of a 10% caustic soda solution. The butyl substituted benzenes were separated by fractionation. The products were *s*-butylbenzene (32.1%) b. p. 173–176, and polysubstituted butylbenzenes (13.8%). The *s*-butylbenzene gave benzoic acid upon oxidation with dilute (1:3) nitric acid.

Similar attempts to condense propylene with benzene were unsuccessful.

Rearrangement of Isopropyl Phenyl Ether.—One hundred ninety grams of isopropyl phenyl ether and 5 g. of dihydroxyfluoboric acid were weighed in a 500-cc. flask fitted with a reflux condenser and the contents refluxed for two hours. The method of purification was the same as that described under "Propylene with Phenol."

Sixty-seven grams of product was obtained which consisted of phenol (21%), 2-isopropylphenol (58%), 4-isopropylphenol (20%) and a trace of 2,4-diisopropylphenol.

Butylene with Acetic Acid.—Butylene (about 80% isobutylene and about 20% *n*-butylene) was passed into one mole of acetic acid and 2 g. of hydroxyfluoboric acid. The mixture was agitated and maintained at about 30° until 10 g. of butylene was absorbed. The contents were then neutralized with sodium carbonate, dried over calcium chloride and distilled. A yield of 16 g. of *t*-butyl acetate, b. p. 97°, and a small quantity of *s*-butyl acetate, was isolated.

Butylacetylene with Methyl Alcohol.—The procedure was the same as described[8] previously except that 5 g. of hydroxyfluoboric acid with 5 g. of mercuric oxide was substituted for the boron fluoride. A yield of 75% of the theoretical of 2,2-dimethoxyhexane (b. p. 58–60° at 30 mm.) was obtained.

Amylacetylene with Acetic Acid.—The procedure was the same as previously described[4] except that hydroxyfluoboric acid was used in place of the boron fluoride catalyst. A yield of 32% of the theoretical of α-amylvinyl acetate (b. p. 93° at 40 mm.) was isolated.

Acidolysis of Esters.—By treating *n*-propyl propionate with acetic acid in the presence of various catalysts[9] the yields of *n*-propyl acetate were: sulfuric acid 21%, zinc chloride 31%, boron fluoride 40% and dihydroxyfluoboric acid 60%.

Summary

Dihydroxyfluoboric acid has been shown to function as a catalyst in most organic reactions that are catalyzed by boron fluoride.

Dihydroxyfluoboric acid is a milder catalyst than boron fluoride.

An explanation for the similarity between boron fluoride and dihydroxyfluoboric acid as catalysts has been proposed.

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[8] Hennion, Killian, Vaughn and Nieuwland, THIS JOURNAL, **56**, 1130 (1934).

[9] Sowa, *ibid.*, **60**, 654 (1938).

NOTRE DAME, INDIANA RECEIVED NOVEMBER 8, 1937

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Relative Reactivity of Amines in the Aminolysis of Amides[1]

BY MARTHA E. SMITH AND HOMER ADKINS

It was thought that a comparison of the effect of various alkyl groups in modifying the replacement value of amines in the aminolysis of amides would be of value for its own sake. In addition it would be of interest for a comparison of the values so obtained with the strength of the amines as bases in water solution, as well as with the effect of the same alkyl groups in the alcoholysis of esters.[2]

In order to attain these ends, equilibrium has been established in the reaction

$$\mathrm{AcNHR'} + \mathrm{RNH_2} \rightleftarrows \mathrm{AcNHR} + \mathrm{R'NH_2}$$

for a series of amines and amides, and the concentrations at equilibrium of the two amines determined. Equilibrium was established both by starting with $\mathrm{RNH_2}$ and with AcNHR, R′ being either *n*-amyl or phenethyl. These two amines were used for the purpose of the comparison of the amines because their boiling points enable one or the other of them to be separated readily by fractionation from the other amines investigated. They are the most readily available of alkyl primary amines with the exception of cyclohexylamine, whose boiling point is intermediate between them.

It seems unnecessary to describe the many preliminary experiments made before the procedure outlined below for aminolysis and analysis was developed. Equimolecular amounts (0.11 mole) of an amine and an amide were allowed to react in dodecylpiperidine within a steel vessel under hydrogen (100 atm.) for two to five days at 260°. The two lower boiling amines were then separated from each other and from the other reactants by fractional distillation. The reactants were so chosen that one of the amines could be distilled

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[1] This investigation was supported in part by a grant from the Wisconsin Alumni Research Foundation.

[2] Hatch and Adkins, THIS JOURNAL, **59**, 1694 (1937).