

Catalytic Esterification with Dihydroxyfluoboric Acid

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The study of the chemistry of dihydroxyfluoboric acid has been the subject of recent investigations in this laboratory. The catalytic reactions, in particular, offer an especially fertile field of research since dihydroxyfluoboric acid is an active catalyst both alone and when combined with certain catalytic metals. As an esterification catalyst this compound combines the best features of hydrogen chloride and sulfuric acid in that it has little or no polymerizing action and is nonvolatile in ordinary esterification mixtures. (The pure acid boils at 159.1°.) This latter property makes possible the use of this catalyst in continuous esterification processes. Such a process was not actually carried out, but it was found that the catalyst could be used repeatedly without loss of activity, which fact indicates the feasibility of the use of dihydroxyfluoboric acid in continuous esterification.

In the majority of the preparations it was found that preliminary removal of the catalyst was unnecessary. Because of this, the pure ester could be obtained simply by fractionation of the crude reaction mixture with consequent improvement in the yield. Removal of the catalyst, when desired, could be effected by the addition of a solution of sodium methylate in methyl alcohol and subsequent filtration to remove the sodium salts formed.

In general, better yields were obtained in the esterification of aliphatic acids than with aromatic acids. Anthranilic acid gave only a 5% yield of the methyl ester. On the other hand, practically quantitative yields of certain aliphatic esters were obtained. Tert-butyl acetate could be prepared with this catalyst but only in very poor yields.

Dihydroxyfluoboric acid is most conveniently prepared in the laboratory by the action of boron trifluoride on solid orthoboric acid.² It can be handled in much the same manner as concentrated sulfuric acid, but it is much less corrosive on contact with the skin. Dihydroxyfluoboric acid when alone is decomposed by water to orthoboric acid, but, peculiarly enough, the water present in an esterification mixture seems to have no effect on the catalyst. Quite frequently it was found that the catalyst could be recovered unchanged after removal by distillation of the alcohol and organic acid and their reaction products.

Experimental

The majority of the esters were prepared in the following manner: The organic acid (0.5 to 1.0 mole) was placed in a 500 ml. flask with an excess of the anhydrous alcohol (3.0 to 6.0 moles) and 1 to 2% by weight of dihydroxyfluoboric acid was added. The flask was then fitted with a reflux condenser and the mixture was refluxed for 2 to 4 hours. The product was then fractionated to recover the pure ester.

¹The major portion of this work was completed before the death of Rev. J. A. Nieuwland, June 11, 1936.

²Sowa, Kroeger, and Nieuwland, 1935. *Jour. Amer. Chem. Soc.*, 57:454.

If removal of the catalyst was considered desirable, a solution of 5 g. of sodium in 25 ml. of methyl alcohol was added to the crude reaction mixture, and the resulting sodium salts were removed by filtration. The filtrate was then fractionated.

The following table (Table I) is a summary of the preparations of the various esters.

TABLE I.

Acid	Alcohol	B. P. Ester °C.	Yield %
Adipic ¹	Methyl	di-111-113°(9 mm.).....	85
		mono-157-160°(9 mm.).....	14
Sebacic ¹	Methyl	174-176°(22 mm.).....	98
Oxalic ²	Methyl	m.p. 52-53°.....	93
Succinic ¹	Methyl	87-89°(7 mm.).....	74
Malic ²	Methyl	m.p. 101-102°(Di methyl fumarate)...	22
Tartaric ¹	Methyl	159-160°(20 mm.).....	55
Anthranilic ³	Methyl	132-136°(15 mm.).....	5
Benzoic ¹	Methyl	195-198°(745).....	19
Acetic ²	Methyl	58-59°(748 mm.).....	57
Acetic ²	Ethyl	76-77°(748 mm.).....	75
Acetic ²	Isopropyl	89-90°(748 mm.).....	85
Acetic ¹	Glycol	186-189°(746 mm.).....	17

¹Catalyst removed with sodium methylate.

²Purified without removal of the catalyst.

³The unreacted anthranilic acid was removed by washing with sodium bicarbonate solution and the ester was extracted with ether.

The dibasic acids mentioned in Table I were completely converted to the dimethyl esters with the exception of adipic acid which gave the results indicated.

A group of preparations of ethyl acetate were run to determine the effectiveness of the catalyst when used repeatedly. The procedure was as follows: The required quantities of acetic acid and absolute ethyl alcohol (see Table II) were weighed into a flask, and 2 g. of dihydroxyfluoboric acid was added. The mixture was refluxed for one hour; then the fraction boiling below 120° was removed by distillation. This fraction was washed with sodium carbonate solution, dried over calcium chloride, and distilled. This distillate consisted of pure ethyl acetate, b.p. 76°-77°.

Fresh acetic acid and alcohol were then added to the residue boiling above 120° (catalyst from first run). The mixture was again refluxed, after which the fraction boiling below the 120° was distilled off and purified as before. A series of eight runs gave the results summarized in Table II.

It may be noted that increase in either the time of reflux or the amount of alcohol caused a slight but definite increase in the yield. On the other hand, increase in the amount of acetic acid caused a decrease

TABLE II.

Number	G. Acetic Acid	G. Alcohol	Time of Reflux (hrs.)	Yield, G. Ethyl Acetate
I.....	60	46	1.00	42
II.....	60	46	2.25	48
III.....	60	46	2.25	47
IV.....	60	46	4.50	50
V.....	60	46	5.00	52
VI.....	60	56	5.00	53
VII.....	70	46	5.00	34
VIII.....	60	60	5.50	60

in the yield. This loss probably took place during the final purification of the ester.

On completion of the eighth run the residue boiling above 120° was transferred to a small flask and distilled. Of the original 2 g. of dihydroxyfluoboric acid used, 1.4 g. were recovered, b.p. 156° - 158° .

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Summary

1. Dihydroxyfluoboric acid has been found to be an efficient catalyst for esterification reactions.
2. As a catalyst, it may be used repeatedly without loss of activity.
3. The preparation of a number of esters is described.