TRANSESTERIFICATION OF ALKYL BORATES

BY

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ABSTRACT

An attempt was made to prepare pure methyl borate by an ester interchange using a high-boiling alkyl borate in combination with methyl benzoate or methyl phthalate. The product, assumed to be methyl borate, boiled at about 70°C., which is 5° higher than the expected boiling point, and analyzed at 88 to 95%.

Various catalysts, such as hydrochloric acid, sodium methoxide, p-toluene sulfonic acid, aluminum isopropoxide, and aluminum chloride, were tried before magnesium-aluminum ethoxide was chosen as the best catalyst for this particular transesterification reaction.

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INTRODUCTION

A literature search revealed the fact that in the past a limited amount of work had been done on the transesterification reaction, also known as an ester interchange or the redistribution reaction. It should be mentioned here that the transesterification reaction, which is studied here is an ester interchange and not an alcoholysis.

It has been pointed out by Adkins[1] that "there are few, if any, simple equilibria among organic reactions." For example, the reaction of an aldehyde with an alcohol to form an acetal involves at least three equilibria besides those concerned with the catalyst.

$$RCHO + R'OH \rightleftarrows RCH(OH)(OR')$$
$$RCH(OH)(OR') + R'OH \rightleftarrows RCH(OR')_2 + H_2O$$
$$RCHO + H_2O \rightleftarrows RCH(OH)_2$$
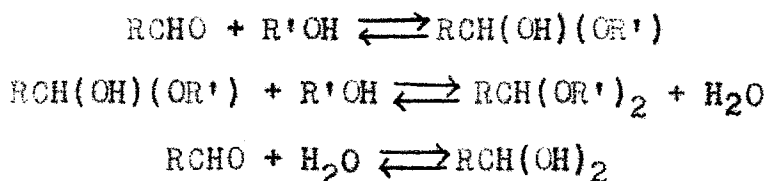
Despite this general rule, it has been found that there does exist a very simple type of organic equilibrium, which occurs in several different classes of reactions. The process leading to equilibrium has been termed the "redistribution reaction," of which the transesterification reaction is an example.

In the organic field, there are a relatively small number of examples of equilibrium reactions of the general

type symbolized by:

$$AY + BZ \rightleftarrows AZ + BY$$
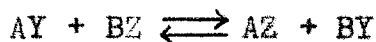
This metathesis is possible only when the components, A, B, Y, and Z, if not atoms, are radicals which retain their structure and identy after recombination. Also, the A, B, Y, and Z components, if not ionized, at least retain sufficient polarity during the interchange to prevent little or no side reaction.[2]

As a result, under favorable reaction conditions (including if necessary the presence of a catalyst) an equilibrium can be reached, as indicated in the above equation.

Catalyzed reactions may be utilized to prepare mixed esters, and it can be shown that the yields of mixed esters approach those corresponding to a statistical redistribution of alkoxy groups. Alternatively, the interchange of alkoxy groups may be driven to completion in cases where one of the products is the most volatile component of the system. This is accomplished by continuous or intemittent removal of the most volatile product[3], which in the case studied here would be methyl borate.

Post and Hofrichter[4] prepared triethyl butyl orthosilicate (22% yield) and diethyl dibutyl orthosilicate (30.4% yield) by refluxing together one-half mole quantities of ethyl and

butyl orthosilicate for 120 hours. The products were separated
by fractionation at reduced pressures.

Interchange of alkoxy groups between two alkyl ortho-
silicates necessarily produces all possible isomeric esters.
There is no reason why one isomer should be more stable than
the other or formed in greater quantity.

Work done by Peppard, Brown, and Johnson[3], covering
various combinations of alkyl silicates, borates, and carboxylic
esters, indicates that the redistribution of alkoxy groups
takes place slowly in the absence of catalysts. However, the
reactions are catalyzed by the more reactive metallic alkoxides,
e.g., by alkoxides of aluminum, magnesium, and antimony, and
also by aluminum chloride. Mixtures of alkoxides, such as
magnesium-aluminum ethoxide, are sometimes more active cata-
lytically than the simple alkoxides.

THE METHOD

Methyl benzoate mixed with an alkyl borate of high
boiling point was placed in a round bottom reaction flask
with a small amount of catalyst (magnesium-aluminum ethoxide)
and heated. As a result of ester interchange, methyl borate
or mixed methyl-butyl borates were formed. These, because of
their lower boiling points distilled out of the mixture,
passed up through a small packed column from the top of
which the vapor passed into a stillhead with thermometer,
condenser, and stopcock, as shown in the diagram on page 10.
Fractions were collected by the fraction-cutter and analyzed.

DISCUSSION

The present work was undertaken for the purpose of studying the possible preparation of methyl borate by the transesterification reaction. This would be valuable in that it would provide a convenient means of preparing pure methyl borate, the direct preparation of which is troublesome because of a difficultly separable azeotropic mixture.[5]

However, trouble was encountered in obtaining pure methyl borate by the proposed method. The most volatile product boiled at about 70°, which is 5° higher than the expected boiling point of pure methyl borate. The analyses from the various runs ranged from 88 to 95%, assuming methyl borate to be the borate present. This matter is described more fully in the section on analysis.

This percentage was realized regardless of what borate was used in combination with methyl benzoate or methyl phthalate.

The results obtained with alkyl borates, as n-propyl, n-butyl, n-amyl, isoamyl, and 2-ethyl hexyl borate in combination with methyl benzoate or methyl phthalate are included in Table I.

Methyl palmitate was also used, but decomposition occurred when the boiler temperature reached about 300°C. This also happened with methyl phthalate when the boiler temperature

reached about 270°C. Xylene was tried as a solvent with
n-amyl borate and methyl phalate, but it held the boiler
temperature too low, (about 156°C.) and made the reaction
extremely slow. Decalin was also tried as a solvent in
another reaction with n-amyl borate and methyl phthalate.
This maintained the boiler temperature at about 210°C. A
reaction took place at this temperature, the results of
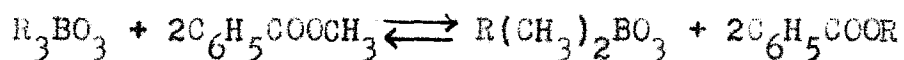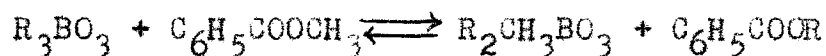which can be seen in Table I.

The general equation for the transesterification reaction
is as follows:

$$R_3BO_3 + 3C_6H_5COOCH_3 \rightleftharpoons (CH_3)_3BO_3 + 3C_6H_5COOR$$
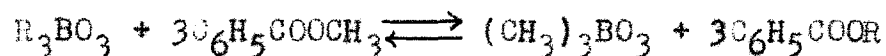
where R_3BO_3 represents a high-boiling alkyl borate. It must
be remembered, however, that mixed esters can be, and probably
are, formed:

$$R_3BO_3 + C_6H_5COOCH_3 \rightleftharpoons R_2CH_3BO_3 + C_6H_5COOR$$

$$R_3BO_3 + 2C_6H_5COOCH_3 \rightleftharpoons R(CH_3)_2BO_3 + 2C_6H_5COOR$$

A catalyst had to be used in every case to achieve
reaction.

Catalysts other than magnesium-aluminum alkoxides were
tried. These were hydrochloric acid, sodium methoxide,
p-toluene sulfonic acid, aluminum isopropoxide, and anhydrous
aluminum chloride. They proved much less effective. Finally,

magnesium-aluminum ethoxide prepared according to Meerwein and Bersun[6], was chosen as the best catalyst for this particular transesterification reaction.

PREPARATION OF MAGNESIUM-ALUMINUM ETHOXIDE[6]

A mixture of 2.4 grams of magnesium, 5.4 grams of aluminum (both cut into very small pieces), and a small quantity of mercuric chloride and iodine was dissolved in 100 cc. of alcohol. It was filtered in a stream of nitrogen. The filtrate was freed of alcohol by distillation. As soon as most of the alcohol was off the residue started to crystallize. The residue was distilled, using an agitator and a short unpacked column (about 3 inches long). It was difficult to establish a definite boiling point (about 225°C. at 4mm.) because the column and condenser had to be heated to prevent the product from crystallizing. No yield was calculated, but Meerwein and Bersin reported a yield of 55%.

APPARATUS

The 0.1 mole runs were made in a 100cc. round bottom flask equipped with a thermometer. The column, packed with one-quarter inch glass helices, was 10 inches long and had an inside diameter of one-half inch. About 8 inches of the column was surrounded by two outer glass tubes, the center one being wrapped with monel wire. This wire was connected to a powerstat to regulate the amount of heat required to push the compound to the top of the column. At the top of the column was attached a standard stillhead equipped with a thermometer, condenser, and a stopcock to regulate the draw-off. The fraction-cutter was of the standard type containing a stopcock to cut the various fractions. This can clearly be seen in the diagram on page 10.

The 0.2 and 0.3 mole runs were carried out in a 250cc. round bottom flask equipped with a thermometer. They were distilled in the same equipment as the 0.1 mole runs, described above.

The 1 mole run was done in a 1 liter round bottom flask equipped with a thermometer. The column, packed with one-quarter inch Berl saddles, was 16 inches long and 1 inch in diameter. This column was also surrounded by a heating jacket. The stillhead was of the automatic type, controlled by an automatic time switch. A standard fraction-cutter was also employed to cut the different fractions.
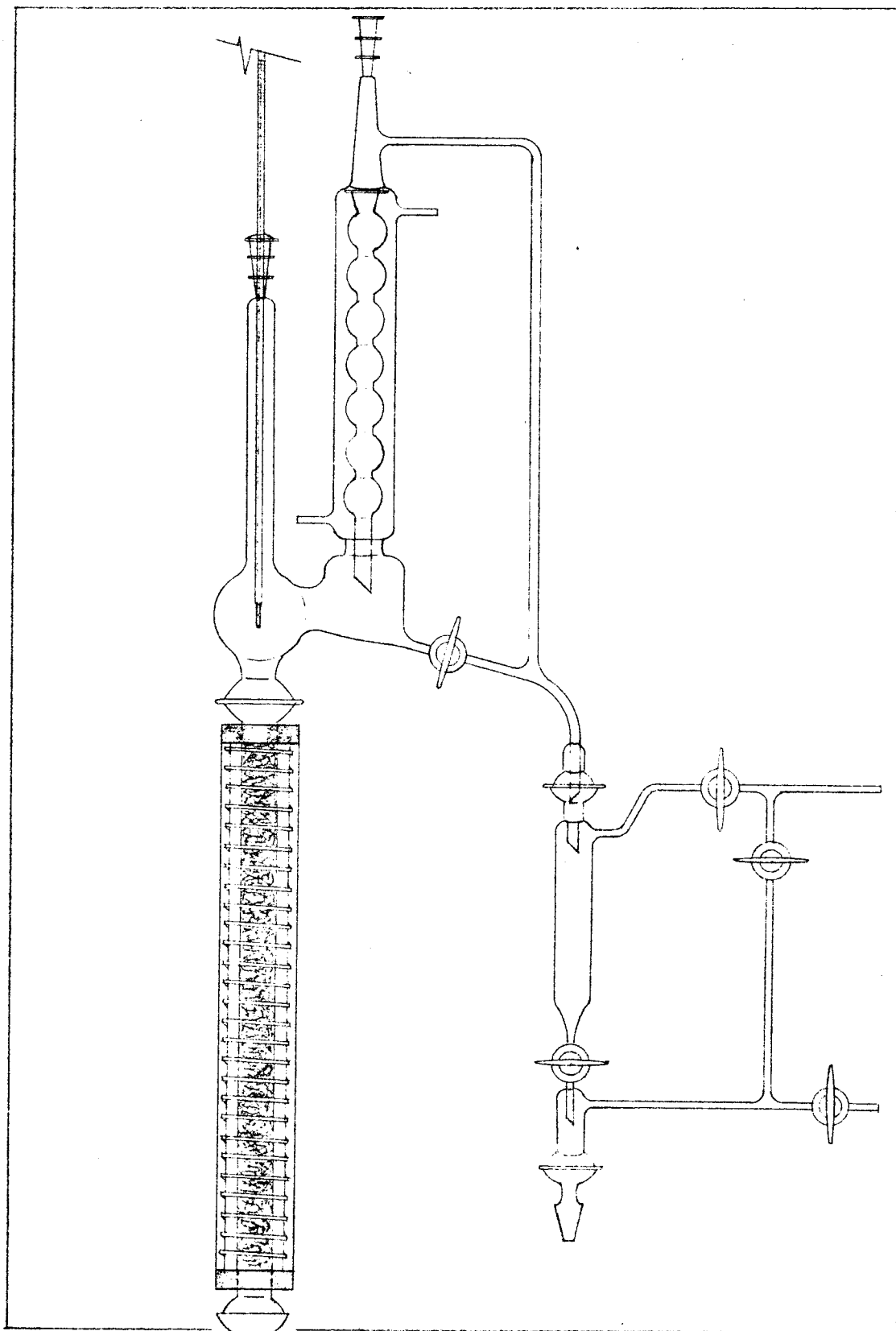
TABLE I

YIELDS OBTAINED IN TRANSESTERIFICATION REACTIONS

The catalyst used in each of the runs was magnesium-aluminum ethoxide (0.03 mol/mol of borate).

ESTER A	B.P. °C.	MOLES OF A	ESTER B	B.P. °C.	MOLES OF B	TIME (hrs.)	YIELD*
n-Propyl borate	175	0.3	Methyl benzoate	199	0.9	6.5	91.5
n-Butyl borate	230	0.3	Methyl benzoate	199	0.9	4.5	90.8
n-Amyl borate	275[a]	1.0	Methyl benzoate	199	3.0	5.5	92.7
Isoamyl borate	255	0.3	Methyl benzoate	199	0.9	3.0	85.2
n-Amyl borate	275[a]	0.2	Methyl phthalate	282	0.3	8.0	70.4 [b]
2-Ethyl hexyl borate	360[a]	0.3	Methyl benzoate	199	0.9	5.0	79.9

* The yield is based on the assumption that the borate distilling over was methyl borate which was drawn from the mixture periodically.

a. Approximated from a pressure-temperature alignment chart from the Matheson Co., Inc., East Rutherford, N.J.

b. Decalin was used as a solvent in this reaction.

TABLE II

COMPARSION OF CATALYSTS TRIED

The runs were all of the 0.1 mole size and the amount of catalyst used was 0.03 mole/mole of borate. Isoamyl borate was used in combination with methyl benzoate.

CATALYST	GRAMS OF PRODUCT	BOILING POINT OF PRODUCT (approx.)
Hydrochloric acid (36.9% assay)	2.6 (wet) 6.0	69 55
Sodium methoxide	no reaction occurred	
p-Toluene sulfonic acid	decomposition occurred	
Aluminum isopropoxide	1.4	60
Aluminum chloride	4.8	70
Magnesium-aluminum ethoxide	2.0 6.2 1.4	55 70 74

The theory for a 0.1 mole run is 10.39 grams.

EXPERIMENTAL

Determining the Best Catalyst:

A number of 0.1 mole runs were made to determine the
best catalyst for this transesterification. A mixture of
27.2 grams (0.1 mol) of isoamyl borate, 40.8 grams (0.3 mol)
of methyl benzoate, and the catalyst (0.03 mol/mol of borate)
were heated to reflux. The methyl borate formed was drawn
off from the top of the column, described on page 9. When
no more of the methyl borate was being formed the reaction
was stopped.

After trying such catalysts as hydrochloric acid, sodium
methoxide, p-toluene sulfonic acid, aluminum isopropoxide,
aluminum chloride, and magnesium-aluminum ethoxide, it was
established that the magnesium-aluminum ethoxide was the
most suitable catalyst for this reaction. See Table II for
a comparison of the catalysts tried.

Preparation Using Propyl Borate and Methyl Benzoate:

$$(C_3H_7)_3BO_3 + 3C_6H_5COOCH_3 \rightleftarrows (CH_3)_3BO_3 + 3C_6H_5COOC_3H_7$$
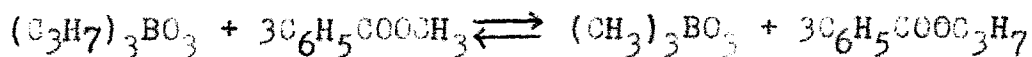
A mixture of 56.4 grams (0.3 mol) of propyl borate,
122.4 grams (0.9 mol) of methyl benzoate, and 3.9 grams (0.03
mol/mol of borate) of magnesium-aluminum ethoxide were
charged to a 250cc. round bottom flask. This flask was
placed on the small still shown on page 10 and the contents

were heated to reflux. As the methyl borate was formed and forced to the top of the column, it was drawn off slowly. The distillation was continued until the formation of methyl borate ceased, as noted by the increase in the column temperature. If the column temperature did not drop to that of the boiling point of methyl borate within one hour, the reaction was stopped. At this point the fractions were analyzed (see analysis) and the yield was calculated (see Table I).

Preparation Using Butyl Borate and Methyl Benzoate:

$$(C_4H_9)_3BO_3 + 3C_6H_5COOCH_3 \rightleftarrows (CH_3)_3BO_3 + 3C_6H_5COOC_4H_9$$
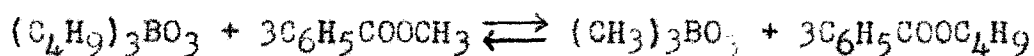
By The procedure described above methyl borate was prepared using 69.0 grams (0.3mol) of butyl borate, 122.4 grams (0.9mol) of methyl benzoate, and 3.9 grams (0.03 mol/ mol of borate) of magnesium-aluminum ethoxide.

Preparation Using n-Amyl Borate or Isoamyl Borate and Methyl Benzoate:

$$(C_5H_{11})_3BO_3 + 3C_6H_5COOCH_3 \rightleftarrows (CH_3)_3BO_3 + 3C_6H_5COOC_5H_{11}$$
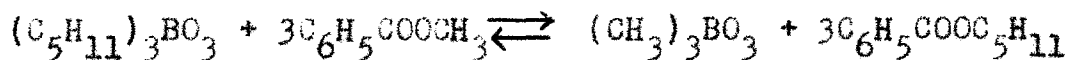
In a like manner methyl borate was obtained using 1.6 grams (0.3 mol) of n-amyl borate or isoamyl borate, 122.4 grams (0.9 mol) of methyl benzoate, and 3.9 grams (0.03 mol/ mol of borate) of magnesium-aluminum ethoxide.

A larger run was also made using 272.2 grams (1 mol) of n-amyl borate, 408.3 grams (3 mol) of methyl benzoate, and 13.2 grams (0.03 mol/mol of borate) of magnesium-aluminum ethoxide. The main fraction (80.8 grams analyzing at 93.7%) was redistilled thru a small packed column. No further purification of the methyl borate resulted from this redistillation. The boiling points and the analyses were in the same range as they were from the original tranesterification.

Preparation Using n-Amyl Borate and Methyl Palmitate:

$$(C_5H_{11})_3BO_3 + 3C_{15}H_{31}COOCH_3 \rightleftarrows (CH_3)_3BO_3 + 3C_{15}H_{31}COOC_5H_{11}$$

An attempt to prepare methyl borate by the above method, using 54.5 grams (0.2 mol) of n-amyl borate, 162.3 grams (0.6 mol) of methyl palmitate, and 2.6 g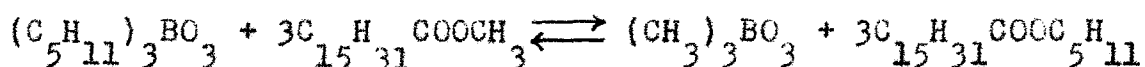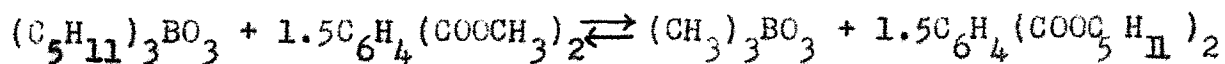rams (0.03 mol/mol of borate) of magnesium-aluminum ethoxide, did not proceed in the same way. As soon as the boiler temperature reached about 300°C. decomposition occurred. The boiler temperature continued to rise and the column temperature receded below the boiling point of methyl borate. The reaction was stopped at this point.

Preparation Using n-Amyl Borate and Methyl Phthalate:

$$(C_5H_{11})_3BO_3 + 1.5C_6H_4(COOCH_3)_2 \rightleftarrows (CH_3)_3BO_3 + 1.5C_6H_4(COOC_5H_{11})_2$$
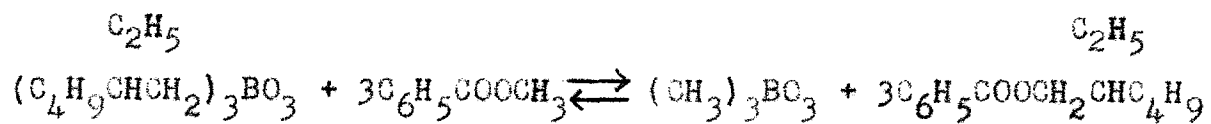
Decomposition was also encountered when endeavoring to prepare methyl borate, using 81.6 grams (0.3 mol) of n-amyl borate, 87.4 grams (0.45 mol) of methyl phthalate, and 3.9 grams (0.03 mol/mol of borate) of magnesium-aluminum ethoxide. The decomposition seemed to commence when the boiler temperature continued to rise until it reached 30 °C. and then began to drop, due to the formation of low boilers. At this point the reaction was stopped.

A run was done using 54.5 grams (0.2 mol) of n-amyl borate, 58.3 grams (0.3 mol) of methyl phthalate, 2.6 grams (0.03 mol/mol of borate) of magnesium-aluminum ethoxide, and 100cc. of xylene. The object of the xylene was to control the boiler temperature, and therefore prevent decomposition. The solvent held the boiler temperature at about 156°C., which proved to be too low. As soon as a couple of drops were drawn off from the top of the column, the column temperature would jump up above 100°C. The reaction was so slow at this temperature that the experiment was discontinued.

Another run, of the same size, was made using 75cc. of decalin in place of the xylene. The decalin maintained a boiler temperature of about 214°C. A reaction occurred at this temperature, the results of which can be seen in Table I.

Preparation Using 2-Ethyl Hexyl Borate and Methyl Benzoate:

$$(C_4H_9\overset{C_2H_5}{C}HCH_2)_3BO_3 + 3C_6H_5COOCH_3 \rightleftharpoons (CH_3)_3BO_3 + 3C_6H_5COOCH_2\overset{C_2H_5}{C}HC_4H_9$$

By the same method as mentioned above, methyl borate was prepared, using 119.5 grams (0.3 mol) of 2-ethyl hexyl borate, 122.4 grams (0.9 mol) of methyl benzoate, and 3.9 grams (0.03 mol/mol of borate) of magnesium-aluminum ethoxide.

ANALYSIS[7]

Although the analysis is that used for boric acid, actually the ester was analyzed. All the esters of boric acid met with in this work hydrolyzed so rapidly (in a few minutes) at room temperature that the analytical method for boric acid could be used without change for the ester.

The analysis is based on a titration of boric acid with standard sodium hydroxide. Boric acid is such a weak acid that it cannot be titrated accurately with 0.1 N standard alkali. However, it can be transformed into a relatively strong acid by adding certain organic hydroxyl compounds containing more than one hydroxyl group per molecule, such as glycerol, mannitol, dextrose, or invert sugar. These polyvalent alcohols form complex acids with boric acid which are much stronger than the boric acid alone.

The sample (0.2 to 0.4 grams) was weighed in a glass stoppered erlenmeyer flask, as rapidly as possible. Distilled water (100cc.) and mannitol (3 grams) were added and the solution was titrated to a faint pink with phenolphthalein as indicator. Then a little more mannitol was added. If the color of the indicator vanished, more alkali was added until the pink color appeared, and then more mannitol was added. This procedure was repeated until the addition of mannitol no longer caused a fading of the pink color. In most cases the first three grams of mannitol were sufficient.

As an example of the analytical procedure the analysis of the main fraction of a large run using n-amyl borate and methyl benzoate may be cited:

To the sample (0.3010 grams) was added distilled water (100cc.), mannitol (3 grams), and phenolphthalein (a few drops). On titration it took 23.1cc. of 0.1175N sodium hydroxide to obtain a faint pink color. Then a little more mannitol was added, and the pink color did not disappear, proving that enough mannitol was used in the beginning. The percent methyl borate in the sample was calculated as follows:

$$\frac{0.1175 \times 23.1 \times 0.1039}{0.3010} \times 100 = 93.65\%$$

All of the analyses for the main fractions were in the same range (92-95%). Because the analyses showed a low purity methyl borate for all the runs it seemed that the analytrical method might be off so an analysis was run on pure freshly distilled isoamyl borate. The results, 100.5% as isoamyl borate, proved that the method was satisfactory.

SUMMARY

Transesterification reactions of high boiling alkyl borates in combination with methyl benzoate or methyl phthalate produced methyl borate or mixed borate of 88 to 95% purity. The rate of reaction varied from 4.5 to 8 hours, depending on the intensity at which the reaction mixture was heated. In no case was a reaction achieved without the aid of a catalyst. The reaction could be effected by the use of catalysts such as hydrochloric acid, aluminum isopropoxide, and aluminum chloride, but it was proved that magnesium-aluminum ethoxide was the best for this transesterification reaction.

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