

exhibits a minimum, but where conductivity and osmotic coefficient are still falling off.

It is shown, in agreement with most writers at the present time, that more than one kind or composition of colloid must be present in such solutions of colloidal electrolytes.

Occasion is taken to correct a common misconception of the significance of transport of material in a colloid particle or a complex ion as distinguished from the true or electrolytic transport number.

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VOLATILE BORATES OF POLYHYDRIC ALCOHOLS AND THE ACTIVATION OF BORIC ACID

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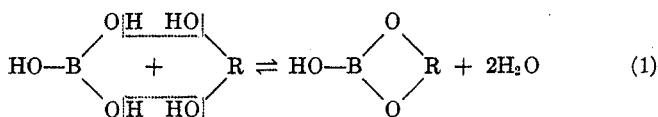
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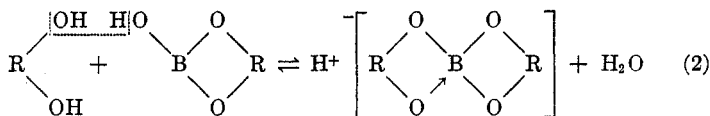
I. INTRODUCTION

Although it is well known that boric acid cannot be titrated satisfactorily by strong base, using phenolphthalein as an indicator, unless a suitable "activator" such as glycerol or mannitol is added (24), there is no generally accepted theory of the remarkable action of these compounds. The increase in effective acidity of the weak boric acid which is found to be produced by polyhydric alcohols in general is variously called "potentiation" (15, 16, 17) or "activation" (1). Some sort of compound formation between the boric acid and the "activator" is generally accepted as the fundamental explanation, but the composition, not to mention the structure, of the compounds is debatable (1, 3).

A number of papers by Böeseken and his collaborators (3, 4, 7) have presented the thesis that the polyhydric alcohols which "activate" boric acid produce esters of the acid and the "activator." These esters are the result of a two-step reaction:



I



II

According to Böeseken, the type I compound does not increase the effective acidity of the boric acid. Only the type II compound, in which the boron atom has been esterified thrice and subsequently has attained a covalence of four, is responsible for the increase in the acidity of the boric acid (4).

At the present time the application of this theory as a quantitative interpretation of the stoichiometric titration of boric acid in the presence of glycerol or mannitol is not satisfactory. Furthermore, no compound of glycerol and boric acid of type I or type II has been isolated nor has the existence of either type been adequately demonstrated. With respect to mannitol and boric acid, no esterified compounds have been isolated and the quantitative interpretations of the "activation" are fragmentary (5). Krantz, Beck, and Carr (16), employing Böeseken's procedures, reported that they were "unable to account for the differences between the results of our investigation and Böeseken's" for the ratio of boric acid to poly alcohol in the levulose-boric acid complex.

We find that when Böeseken's mass-action treatment is applied to Rimbach and Ley's complete data on the acidity of boric acid and mannitol (22), the results are not as consistent as those published by Böeseken in his treatment of selected portions of the data (5).

Kolthoff (14) employs a mass-law treatment of van Liempt's titration curves of boric acid in the presence of glycerol. He claims that a complex containing equimolecular proportions of glycerol and boric acid is formed. This finding is in conflict with the type II compound required according to Böeseken's theory. However, we are unable to confirm Kolthoff's calculated values by his own method of calculation.

Bancroft has raised objections to the assumption that esterified compounds are responsible for the "activation" (1). He has suggested (2) that the interpretation of the "activation" process should be sought in the solution of the boric acid "preferentially in the activating substance," presumably meaning changes in the activity coefficient of boric acid in solvents other than water or a dehydration of the orthoboric acid. Böeseken's reply (6) to Bancroft's objections does not bring us any closer to a quantitative interpretation of the titration curves of boric acid in the presence of mannitol or glycerol.

It is the purpose of this research to isolate the compounds produced by the

reaction of boric acid with the lowest glycols of the homologous aliphatic series and with glycerol and to establish their composition and structure.

For the purpose of orientation a brief summary of the types of experimental investigation to be employed is given:

- A. Preliminary investigation of possible reactions.
- B. Synthesis and identification of the compounds between boric acid and glycols indicated in the preliminary experiments.
- C. Synthesis and identification of the compounds between boric acid and glycerol or substituted glycerols indicated in the preliminary experiments.
- D. Substantiation of compounds.
- E. Exclusion of other types of compounds.
- F. Structure of the-glycol borates.
- G. "Activation" of boric acid by glycols.
- H. Miscellaneous observations.

II. MATERIALS

Boric acid from the Pacific Coast Borax Company analyzed 99.9 per cent boric acid and was free from sodium (flame test), chloride (silver nitrate test), and sulfate (barium chloride test).

Water-white glycerol from Procter & Gamble Company assayed 97.66 per cent glycerol and was free from chloride and sulfate (tests as above). The mannitol, from the Atlas Powder Company, was also chloride- and sulfate-free. Propylene and ethylene glycols and methyl cellosolve were from Carbide and Carbon Chemicals Corporation, and the 1,3-butylene glycol was from Schurcharadt; all were used without further purification (unless noted). Other chemicals, obtained from the Eastman Kodak Company, were: trimethylene glycol, b. p. 113–121°C. at 20 mm.; 2,3-butylene glycol, m. p. 21–23°C.; isobutylene glycol, b. p. 175–177.5°C. at 760 mm.; glycerol α -monochlorohydrin, b. p. 115–120°C. at 15 mm. and 84–86°C. at less than 1 mm.; glycerol α -monoacetate, b. p. 157–159°C. at 15 mm.

The following chemicals were synthesized according to the methods described in the corresponding references: 1,3-butylene glycol (11), b. p. 66–69°C. at less than 1 mm.; glycerol α -chlorohydrin (20), b. p. 105–107°C. at 6 mm.; glycerol α -monomethyl ether (10), b. p. 68–73°C. at less than 1 mm.; glycerol α -monon-butyl ether (10), b. p. 93–98°C. at less than 1 mm. As the glycerol butyl ether was not reported earlier (10), a sample was analyzed:¹ carbon, calculated, 56.7 per cent; found, 54.3 per cent; hydrogen, calculated, 10.8 per cent; found, 10.4 per cent.

III. METHOD OF ANALYSIS

Boric acid was determined by titration to a phenolphthalein end point with 1 *N* sodium hydroxide, using excess glycerol or mannitol. Potassium acid phthalate (U. S. Bureau of Standards) was used to standardize the sodium hydroxide solution.

¹ Mr. S. Gottlieb of the Laboratories of Columbia University performed the analysis.

Esters of boric acid were completely dissolved before the addition of mannitol or glycerol. The phenolphthalein end point was tested by boiling with excess of standard alkali, subsequently cooling to room temperature, and back-titrating with standard acid, except in cases in which this test had previously shown itself to be unnecessary.

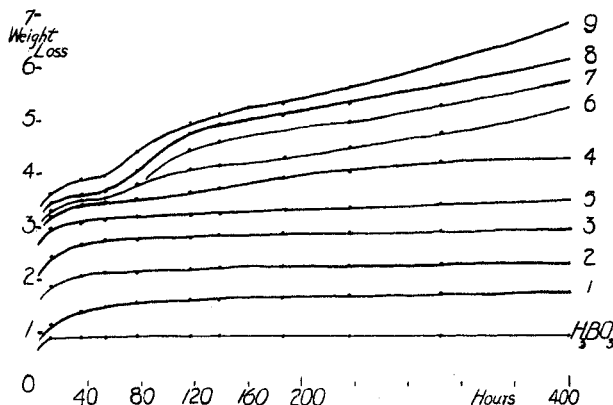


FIG. 1. Boric acid and glycerol. Weight loss calculated as moles of water per mole of boric acid. $T = 100^{\circ}\text{C}$.

EXPERIMENT NUMBER	MOLES GLYCEROL MOLES H_2BO_3
1	0.33
2	0.66
3	1.00
4	1.66
5	1.33
6	2.00
7	2.33
8	2.66
9	3.00

IV. EXPERIMENTAL INVESTIGATIONS

A. Preliminary experiments to determine the amounts of water released by heating boric acid-polyhydric alcohol mixtures of various mole ratios

Charges of boric acid and polyhydric alcohol (total approximately 10 g.) were weighed into similar beakers. Controls of boric acid alone and the alcohol alone were also prepared. The material in each beaker was stirred to hasten solution and then the beaker was placed in a constant-temperature oven ($100^{\circ}\text{C} \pm 1^{\circ}$). At intervals the specimens were removed for weighings to the nearest milligram.

They were kept in a desiccator over calcium chloride when not in the oven. Evaporation occurred at atmospheric pressure.

For calculation and comparison, the losses in weight were assumed to be due to loss of water (the most volatile material in the condensation reaction), and calculations were made of the ratios of moles of water lost to moles of boric acid originally weighed out. These ratios were plotted against hours of heating in the oven (see figures 1, 2, and 3).

Because experiments Nos. 14, 15, 21, and 23 resulted in the complete evaporation of the charges and No. 13 lost 94 per cent of the charge, the following tenta-

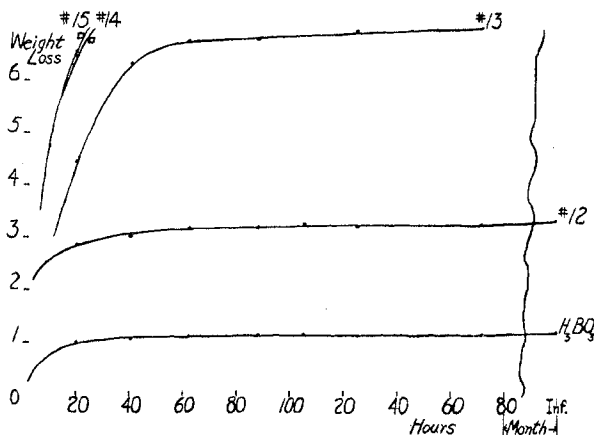


FIG. 2. Boric acid and propylene glycol. Weight loss calculated as moles of water per mole of boric acid. $T = 100^{\circ}\text{C}$. \square = total evaporation.

EXPERIMENT NUMBER	MOLES GLYCOL MOLES H_2BO_3
12	0.50
13	1.00
14	1.51
15	2.01

tive conclusions were drawn: (1) Boric acid and glycols may form compounds which are volatile. (2) These volatile compounds may have various compositions. The mixtures initially 1:1 in mole composition indicate that 1 mole of glycol is the smallest amount that will volatilize 1 mole of boric acid. (3) Boric acid and glycerol, at least, evolve water and perhaps may form volatile compounds. The mixtures of glycerol and boric acid do not give as definite evidence (complete volatilization) of the existence of volatile compounds of boric acid, as do the glycol and boric acid mixtures. The object of the following experiments was to establish these conclusions for the various glycols.

B. Synthesis and identification of the compounds formed by boric acid and glycols

(1) Propylene glycol

(a) 0.20 mole of propylene glycol and 0.20 mole of boric acid were mixed, heated until clear, and distilled at 10 mm. from a 100-cc. Claisen flask. Three

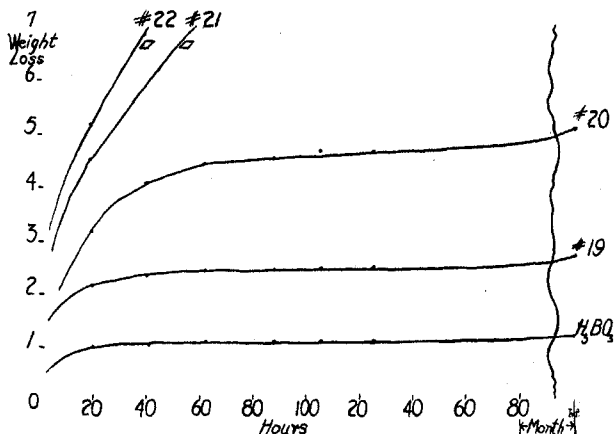


FIG. 3. Boric acid and ethylene glycol. Weight loss calculated as moles of water per mole of boric acid. $T = 100^{\circ}\text{C}$. \square = total evaporation.

EXPERIMENT NUMBER	$\frac{\text{MOLES GLYCOL}}{\text{MOLES H}_3\text{BO}_3}$
19	0.53
20	1.05
21	1.58
22	2.10

fractions were collected. A glassy residue remained. The side arm was clogged occasionally by the viscous distillate.

FRACTION	BOILING RANGE	PRODUCT
No. 1.....	30 to 140°C .	Identified as water and some glycol
No. 2.....	135 to 137°C .	Non-homogeneous
No. 3.....	136.5 to 139.5°C . (at 9 mm.)	Viscous colorless liquid containing 10.77 per cent boron

The viscous layer from No. 2 was added to No. 3, and this was redistilled at 10 mm. without leaving a residue. It was redistilled again at $155\text{--}158^{\circ}\text{C}$. at

15 mm., and a portion (75 per cent) was collected and analyzed. This portion was found to contain 10.65 per cent boron.

(b) 100 g. of propylene glycol and 90 g. of boric acid (mole ratio 1.0:1.1) were mixed and dehydrated under water suction (11 mm.). The product was distilled from a 300-cc. Claisen flask, using an air-cooled condenser having a diameter of 15 mm. Two fractions were collected. A glassy residue remained.

FRACTION	BOILING RANGE	PRODUCT
No. 1.....	125°C. at 3.8 mm. to 115°C. at 1.5 mm.	Intermediate fraction
No. 2.....	110-114°C. at 1 mm.	23 g. yield; product contained 10.65 per cent boron

(c) 100 g. of propylene glycol and 85 g. of boric acid (mole ratio 1.00:1.05) were heated for 40 hr. in an oven at 104°C., and then boiled over a free flame to a total weight loss of 100 g. The product was distilled from the 300-cc. Claisen flask used in experiment (b). An intermediate fraction up to 135°C. was collected. A large amount of non-volatile residue remained in the flask. The fraction boiling at 135-137°C. at 8 mm. was found to contain 10.67 per cent boron.

(d) 2.0 moles each of propylene glycol and boric acid were mixed, placed in a layer $\frac{5}{8}$ in. deep in a crystallizing dish in an oven at 105°C. and removed 24 hr. later. The product contained 11.61 per cent boron. This product was distilled and three fractions were collected. A glassy residue remained.

FRACTION	BOILING RANGE	PRODUCT
No. 1.....	Up to 122°C. above 2 mm.	Intermediate fraction
No. 2.....	122-118°C. at 1.8 mm.	45 g. yield; intermediate fraction
No. 3.....	118-114°C. at less than 1 mm.	15 g.; product contained 10.67 per cent boron*

* Calculated for $C_3H_7O_2B$, a type I compound, 10.62 per cent boron.

(2) Ethylene glycol

(a) A mixture of 2 moles each of boric acid and ethylene glycol was partially dehydrated by being heated uncovered for 23 hr. in an oven at 100°C. The weight lost was 100 g. The remainder of the material was distilled from a 300-cc. Claisen flask, using a condenser 15 mm. in diameter. The distillation was terminated suddenly by the distillate clogging the condenser (Data obtained during the last 5 min. are given below.) A 20-cm. section was immediately cut from the condenser, and the ends were sealed. The sample for analysis was melted from the upper end of this section, which contained a clear glassy material. The sample analyzed was found to contain 12.28 per cent boron.

The bulb of the flask shattered during the cooling of the residue from the distillation.

TIME	PRESSURE	OIL-BATH TEMPERATURE	VAPOR TEMPERATURE (DISTILLATE)
<i>minutes</i>	<i>mm.</i>	<i>°C.</i>	<i>°C.</i>
0	8	270	147.0
2	8	283	156.5
5 (end)	7	295	162.5

(b) A mixture of 2.0 moles each of boric acid and ethylene glycol was partially dehydrated during 20 hr. in the oven. 100 g. of material evaporated. The remainder was distilled from a flask (figure 4). Data are given for the last minutes during which the receiver was filling and clogging at the neck. The

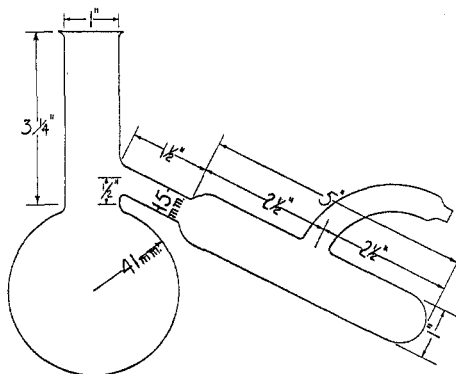


FIG. 4. Flask used in preparation (b) with ethylene glycol

receiver bulb was flamed from the flask. The distillate had the glassy characteristics of that obtained in other experiments and was also melted from the bulb for analysis. It was found to contain 12.25 per cent boron (calculated for $C_2H_6O_3B$, a type I compound, 12.32 per cent boron).

TIME	PRESSURE	OIL-BATH TEMPERATURE	VAPOR TEMPERATURE (DISTILLATE)
<i>minutes</i>	<i>mm.</i>	<i>°C.</i>	<i>°C.</i>
0	1	246	176
2	1	248	177
4 (end)	1	257	187

(3) Other glycols

Mixtures of boric acid and these glycols in 1:1 mole ratio were heated and dehydrated first under filter-pump vacuum and then at less than 1 mm. until

refluxing occurred, and were then distilled under reduced pressure. The borates of trimethylene glycol and 2,3-butylene glycol were distilled from a 50-cc. Claisen flask. The borates of 1,3-butylene glycol and isobutylene glycol were

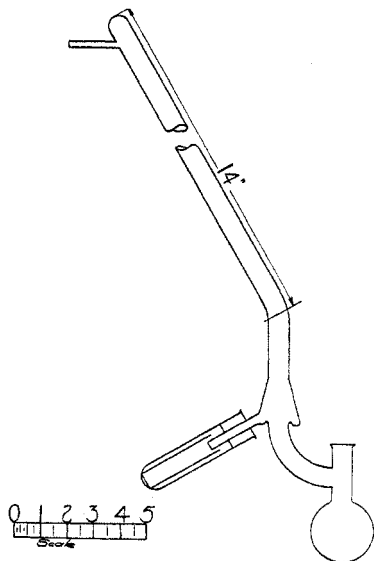


FIG. 5. Flask used in preparation with 1,3-butylene glycol and isobutylene glycol

distilled from another flask (figure 5). Very little residue was left in the distilling flask in each case.

BORATE OF	VAPOR TEMPERATURE	PER CENT BORON	
		Found	Calculated*
	°C.		
Trimethylene glycol.....	147-151 at 3 mm.	10.72	10.62
2,3-Butylene glycol.....	112-117 at less than 1 mm.	9.53	9.34
1,3-Butylene glycol.....	107-109 at less than 1 mm.	9.46	9.34
Isobutylene glycol.....	76-79 at less than 1 mm.	9.66	9.34

* Per cent boron calculated for the type I compound of Böseken.

The reaction of diethylene glycol and boric acid is mentioned under glycerol and boric acid, as the experimental results in both cases were essentially the same.

C. Synthesis and identification of the compounds formed by boric acid and glycerols

The object of the following experiments was to determine whether a borate of these polyhydric alcohols could be distilled.

(1) Glycerol

Six attempts were made to dehydrate and distil *in vacuo* 2:1 and 1:1 mole mixtures of glycerol and boric acid. Water and glycerol were removed from the reaction mixtures, but with vacua of less than 1 mm. and oil-bath temperatures from 150° to 225°C., the reaction mixtures charred.

With a mercury-vapor pump connected through a trap cooled with dry ice, a 1:1 mole mixture of glycerol and boric acid did not show signs of refluxing up to charring temperature. The reaction mixture foamed and became increas-

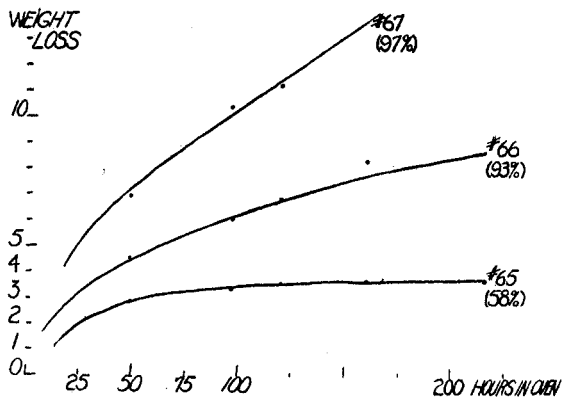


FIG. 6. Boric acid and α -methyl ether of glycerol. Weight loss calculated as moles of water per mole of boric acid. $T = 100^\circ\text{C}$. (%) = per cent evaporated.

EXPERIMENT NUMBER	MOLES ETHER MOLES H_3BO_3
65	0.50
66	1.00
67	2.00

ingly viscous during the release of the third mole of water as the temperature of the oil bath was raised.

(A 1:1 mole mixture of diethylene glycol and boric acid behaved similarly to the experiments with glycerol. It charred at 225°C. and at less than 1 mm. without yielding a volatile borate.²)

(2) Monomethyl ether of glycerol

Weight evaporation experiments similar in all essential details to the previous preliminary experiments were conducted, employing mixtures of the α -monomethyl ether of glycerol and boric acid (see figure 6). The experiments were

² These experiments were performed to ascertain, by using a glycerol with two functional hydroxyl groups, whether the failure to obtain a volatile glycerol borate was due to the three free hydroxyl groups of glycerol.

discontinued when the beaker containing experiment No. 65 cracked by expansion of the contents during cooling.

EXPERIMENT	MOLES OF GLYCOL PER MOLE OF BORIC ACID	LOSSES OF INITIAL WEIGHT
		<i>per cent</i>
No. 65.....	0.50	57.9
No. 66.....	1.00	93.1
No. 67.....	2.00	96.2

A volatile borate of the ether and boric acid in either 2:1 or 1:1 mole ratio was formed.

One-half mole each of boric acid and the α -monomethyl ether of glycerol were mixed, dehydrated by heating for 2 hr. under the reduced pressure furnished by a water aspirator, and distilled at less than 1 mm. pressure, leaving very little residue. No charring occurred during the dehydration or distillation.

VAPOR TEMPERATURE	BORON (BY ANALYSIS)	BORON (CALCULATED)*
$^{\circ}\text{C.}$	<i>per cent</i>	<i>per cent</i>
145-150	7.99	8.20

* Calculated for $\text{C}_4\text{H}_9\text{O}_4\text{B}$, a type I compound.

(3) Monobutyl ether of glycerol

α -*n*-Butyl glycerol ether produced a volatile borate under the same procedure described for the methyl ether of glycerol.

VAPOR TEMPERATURE	BORON (BY ANALYSIS)	BORON (CALCULATED)*
$^{\circ}\text{C.}$	<i>per cent</i>	<i>per cent</i>
162-165 at less than 1 mm.....	6.20	6.23

* Calculated for $\text{C}_7\text{H}_{15}\text{O}_4\text{B}$, a type I compound.

(4) Chlorohydrin of glycerol

A 1:1 mole mixture of boric acid and the α -chlorohydrin, dehydrated and distilled at 160-165 $^{\circ}\text{C.}$ at less than 1 mm., yielded a volatile borate (or borates) with decomposition. Very little residue was left in the distilling flask.

(5) Glycerol α -monoacetate

A 1:1 mole mixture of boric acid and glycerol α -monoacetate, dehydrated and distilled at less than 1 mm., produced triacetin but no volatile borate. A glassy residue remained.

The apparatus used for the distillation of the borates of 1,3-butylene glycol and of isobutylene glycol was used for the distillation of the borates of the two glycerol ethers, the chlorohydrin, and the monoacetate.³

³ These experiments were conducted to show that the distillates were compounds.

D. Substantiation of compounds: summary of distillations conducted at different pressures

(1) Propylene glycol borate

Three portions were collected by distillation from a 50-cc. Claisen flask fitted with an 8-mm. side arm.

FRACTION	BOILING RANGE	BORON
		<i>per cent</i>
No. 1.....	167°C. at 37 mm.	10.67
No. 2.....	165°C. at 35 mm.; 164°C. at 33 mm.	10.58
No. 3.....	163-162°C. at 32 mm.	10.59
Original material.....	113-118°C. at less than 1 mm.	10.59
Theoretical per cent of boron for the type I compound.....		10.62

Three portions were collected from the same flask, which was connected to a manostated vacuum train.

FRACTION	BOILING RANGE	BORON
		<i>per cent</i>
No. 1.....	147-148°C. at 12.4 mm.	10.45
No. 2.....	148-148.2°C. at 12.6 mm.	10.43
No. 3.....	148.5-149°C. at 13.0 mm.	10.44
Original material.....	113-118°C. at less than 1 mm.	10.59
Theoretical per cent of boron for the type I compound.....		10.62

(2) 2,3-Butylene glycol borate

Two portions were collected from the same 50-cc. Claisen flask. After the first portion had been collected, the distilling flask and contents were cooled, the manostated vacuum train reset, and the distillation continued at the lower pressure.

FRACTION	BOILING RANGE	BORON
		<i>per cent</i>
No. 1.....	139-144°C. at 12.5 mm.	9.42
No. 2.....	118-123°C. at 2 mm.	9.42
Original material.....	112-117°C. at less than 1 mm.	9.52
Theoretical per cent of boron for the type I compound.....		9.34

(3) α -Monomethyl glycerol ether borate

A portion of approximately 5 g. was collected from the original 100-cc. distilling flask (connected to the manostated vacuum train) used to isolate this

material. Further fractions were not collected, as the residual material had gradually turned brown during the heating.

FRACTION	BOILING RANGE	BORON
		<i>per cent</i>
No. 1	201°C. at 15.0 mm.	8.41
Original material	144-154°C. at less than 1 mm.	8.80
Theoretical per cent of boron for the type I compound		8.20

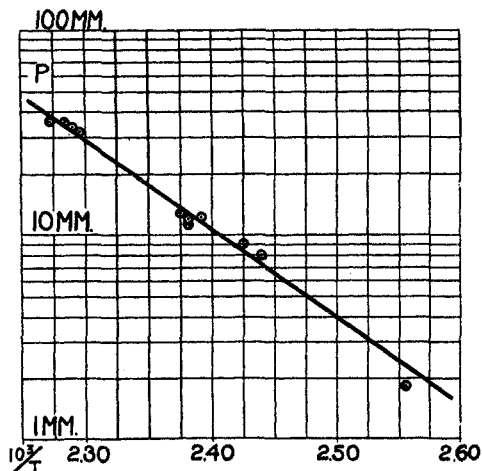


FIG. 7. Logarithmic plot of distillation pressures (P) against the reciprocal of the absolute vapor temperatures (T). Data for propylene glycol borate.

(4) Trimethylene glycol borate

Three portions were collected by distillation at less than 1 mm., utilizing a 500-cc. Claisen flask.

FRACTION	BOILING RANGE	BORON
		<i>per cent</i>
No. 1	135-137°C. at less than 1 mm.	11.12
No. 2	136-140°C. at less than 1 mm.	11.14
No. 3	142-150°C. at less than 1 mm.	11.00
Original material	134-147°C. at less than 1 mm.	11.07
Theoretical per cent of boron for the type I compound		10.67

The third portion was utilized in the following two experiments: Three portions were collected from the 100-cc. flask (see figure 5). Reduced pressure was furnished by a water aspirator pump. The residue had turned brown by the time the last portion was collected.

FRACTION	BOILING RANGE	BORON
		<i>per cent</i>
No. 1.....	201°C. at 35 mm.	11.03
No. 2.....	200°C. at 33 mm.	11.11
No. 3.....	199.5°C. at 32 mm.	
Original material.....	142-150°C. at less than 1 mm.	11.00
Theoretical per cent of boron for type I compound.....		10.62

The next experiment was an attempt to separate the trimethylene glycol borate from an added 0.5 per cent of boron. Three grams of "metaboric acid" was dissolved in 89 g. of the glycol borate. Two portions were collected from the same flask. Reduced pressure was furnished by the water aspirator pump. The residue turned brown and viscous by the end of the second portion.

FRACTION	BOILING RANGE	BORON
		<i>per cent</i>
No. 1.....	201°C. at 35 mm.	11.03
No. 2.....	200-201°C. at 34-35 mm.	11.16
Original material, 142-150°C. at less than 1 mm. (before metaboric acid addition).....		11.00
Calculated percentage after addition of "metaboric acid" but before distillation.....		11.48
Theoretical per cent of boron for type I compound.....		10.62

Distillation of trimethylene glycol borate at 33-35 mm. pressure from an added excess of 0.5 per cent of boron produced the same distillate as was obtained from the borate without the added boron.

To ascertain the structure of propylene glycol borate, the following experiments were performed: (1) Propylene glycol borate, dissolved in acetic anhydride and heated, was found to yield an organic acetate which was identified by boiling point and saponification as the glycol diacetate. This experiment showed that the glycol in the glycol borate was not changed by esterification with boric acid.

(2) Propylene glycol borate dissolved slowly in acetyl chloride, and this solution could be refluxed gently for at least 30 sec. and then cooled without evolving hydrogen chloride gas at any stage. Ethylene glycol monomethyl ether (cellosolve), when added to the above solution or to acetyl chloride alone, immediately evolved heat and hydrogen chloride. These results showed that an alcoholic hydroxyl group was absent from propylene glycol borate.

(3) Dry ammonia gas was passed through a solution of propylene glycol borate in dry toluene and yielded immediately a gelatinous white precipitate. The process could be reversed by boiling the toluene. When dry ammonia gas was passed through a solution of tributyl borate in dry toluene, no precipitate was formed. Hence propylene glycol borate is acidic.

E. The exclusion of compounds of a different composition

(1) Propylene glycol and metaboric acid

In order to determine the type of compound formed from metaboric acid (dehydrated orthoboric acid) and propylene glycol, 400 g. of propylene glycol (5.25 moles) and 225 g. of "metaboric acid" (5.0 moles)⁴ were mixed and heated for 2 hr. between 120° and 150°C. at a pressure of 35 mm. The mixture was then refluxed at less than 1 mm. and distilled from a 1-liter Claisen flask, using a condenser having a diameter of 15 mm. Three portions were collected; the first was rejected. The residue was about 60 cc.

FRACTION	BOILING RANGE	BORON
		<i>per cent</i>
No. 1.....	Up to 122°C. at less than 1 mm.	
No. 2.....	118-112°C. at less than 1 mm.	10.56
No. 3.....	113-115°C. at less than 1 mm.	10.60
Calculated for $C_3H_7O_3B$ (a type I compound).....		10.62

(2) Propylene glycol borate and excess metaboric acid

In order to determine whether propylene glycol borate would combine with additional boric acid, 2.3 g. of "metaboric acid" (44.7 g. per mole of boron) was dissolved in 28 g. of propylene glycol borate and two portions were collected by distillation from a manostated 50-cc. Claisen flask. The residue became progressively thicker as the distillate was collected.

FRACTION	BOILING RANGE	BORON
		<i>per cent</i>
No. 1.....	143.5-145.5°C. at 12.5-12.2 mm.	10.54
No. 2.....	147°C. at 12.2 mm.	10.79
Original material.....	163-162°C. at 32 mm.	10.59
Theoretical value for type I compound.....		10.62
Calculated composition, after addition of "metaboric acid" but before distillation.....		11.60

(3) Propylene glycol borate and excess propylene glycol

This experiment was performed to determine whether water was released according to Böeseken's reaction, forming the type II compound from the type I compound and glycol.

⁴ The metaboric acid used = 44.7 g. per mole of boron.

Eighteen grams each of propylene glycol borate and redistilled propylene glycol (65–69°C. at less than 1 mm.) were mixed and subjected to a pressure of less than 1 mm. No water was obtained in the dry ice–alcohol cooled trap in the vacuum line in 20 min. with the mixture at room temperature (26–27°C.). The temperature of the mixture was then raised and held between 60° and 70°C. for another 20 min. Refluxing occurred to a small extent and $\frac{1}{3}$ cc. of glycol was collected in the trap.

(4) Propylene glycol borate and sodium propylene glycolate

This experiment was performed to determine whether the type II compound could be formed from the type I compound and glycol in the presence of the base sodium propylene glycolate.

Sodium propylene glycolate dissolved in propylene glycol (21) was prepared by adding slowly 0.5 mole of sodium to a mixture of 75 cc. of methyl alcohol and 50 cc. of ether in a flask fitted with a reflux condenser and a calcium chloride guard tube. After complete reaction of the sodium, the flask was connected to a water aspirator pump and heated gently. Propylene glycol was added in small amounts until 200 g. had been added, and the contents of the flask was then boiled at 35 mm. and 186°C. (also at 0.8 mm. and 60°C.). The replacement of solvent required about 3 hr.

Fifty-three grams of propylene glycol borate (0.5 mole) was added to 20 g. of propylene glycol, heated slightly with shaking until homogeneous, and cooled to room temperature.

The sodium propylene glycolate in propylene glycol, at room temperature, was placed in an all-glass flask and reflux column which was attached directly to a trap cooled by a dry ice–alcohol mixture and then to the manometer and vacuum pump. Pressures less than 1.0 mm. were obtained. The solution of propylene glycol borate in propylene glycol was then added and the pressure again reduced to less than 1.0 mm. After 30 min. at the pressure of 0.8 mm., during which period ebullition did not take place, the trap was inspected. No condensed vapor was found. The trap was returned to the same cooling bath and the temperature of the flask was raised at a uniform rate during 60 min. from room temperature (29°C.) to 92°C. No ebullition nor condensation in the trap was observed up to 92°C. After this temperature had been maintained for 40 min., the trap contained approximately 1 cc. of liquid.

Evidently propylene glycol borate and sodium glycolate (mole for mole), dissolved in propylene glycol, do not react instantaneously at room temperature to liberate the third mole of water, as would be required by the reaction for the formation of compounds of Böeseken's type II.

(5) Methyl cellosolve and the boric acids

Methyl cellosolve, the monomethyl ether of ethylene glycol, is functionally a monohydric alcohol, although derived from a glycol. Experiments were performed to determine the number of cellosolve molecules which esterify with orthoboric and metaboric acids.

(a) *Methyl cellosolve and orthoboric acid*: Sixty-four grams of methyl cellosolve

and 20 g. of orthoboric acid (0.84 mole : 0.32 mole) were mixed and heated in a 125-cc. distilling flask for $3\frac{1}{4}$ hr., until the distilling vapors reached a temperature of 130°C. (atmospheric pressure) and the oil bath a temperature of 197°C.

The solution was transferred to a vacuum distilling flask (see figure 5) and 8 cc. of intermediate distillate was collected up to 128°C. at 13.4 mm. (oil-bath temperature, 181°C.). Then the following fractions were collected:

FRACTION	BOILING RANGE	OIL-BATH TEMPERATURE °C.	DISTILLATE VOLUME	BORON per cent
No. 3.....	130-131°C. at 13.0 mm.	191-197	3 cc.	4.48
No. 4.....	161-164°C. at 12.8 mm.	224	1 cc.	5.38
No. 5.....	148°C. at 15 mm.	230	Few drops	5.54
Calculated for $B(OC_2H_4OCH_3)_3$				4.60

(b) *Methyl cellosolve and metaboric acid*: Thirty-four grams of "metaboric acid" (44.7 g. per mole) and 175 g. of methyl cellosolve (mole ratio 1:3) were mixed in a 250-cc. flask and heated. In the first half hour the vapor temperature rose to 110°C. No distillate was collected. In the next 3 hr. the vapor temperature rose to 128°C., and the oil-bath temperature to 208°C. Thirty-five cubic centimeters of distillate was collected. Twenty-seven cubic centimeters of water was calculated to be liberated by the esterification. The flask was connected to the water aspirator pump (pressure 45 mm.), and in three quarters of an hour the vapor temperature rose to 86°C. and then diminished (oil bath at 176°C.). Approximately 30 cc. of additional distillate was rejected.

The residue was then distilled at less than 1 mm. pressure and the following portions were collected:

FRACTION	VAPOR TEMPERATURE °C.	OIL-BATH TEMPERATURE °C.	DISTILLATE VOLUME cc.	BORON per cent
No. 1.....	94-103	137-139	5	4.53
No. 2.....	98.8-99.1		7	
No. 3.....	97.8-102		7	4.65
No. 4.....	100.8-103.0		7	
No. 5.....	96-107	141-149	5	
No. 6.....	96	156	1	4.78
Calculated for $B(OC_2H_4OCH_3)_3$				4.60

Approximately 50 per cent remained as residue.

The six portions were combined and redistilled at less than 1 mm. from a 50-cc. Claisen flask. Three portions were collected:

FRACTION	VAPOR TEMPERATURE °C.	OIL-BATH TEMPERATURE °C.	BORON per cent
No. 1.....	93-99	145-147	4.60
No. 2.....	91-96	134-150	
No. 3.....	93-99	141-157	4.54
Calculated for $B(OC_2H_4OCH_3)_3$			4.60

Evidently both orthoboric and metaboric acid esterify with methyl cellosolve to form a compound of the same type as trimethyl borate.

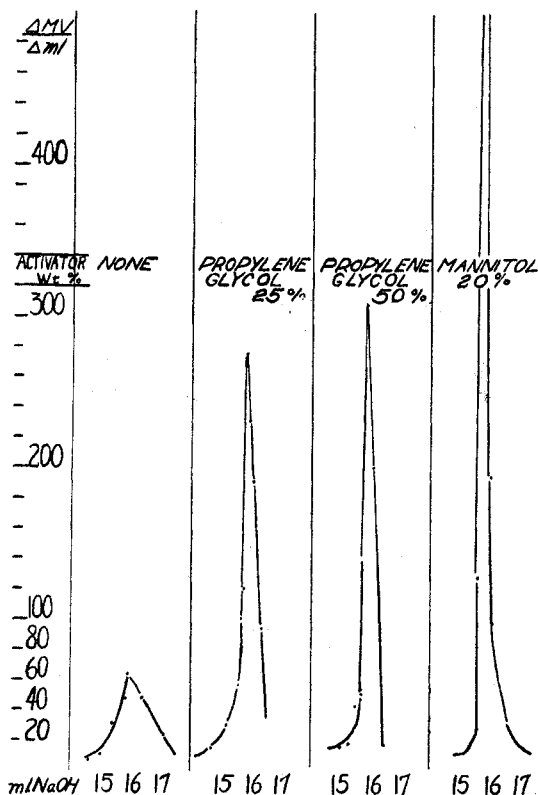


FIG. 8. End points of differential electrometric titrations of boric acid with various activators.

G. Comparison of "activating" properties

- (1) Differential electrometric titrations of boric acid in the presence of (a) no activator, (b) mannitol, (c) propylene glycol

1.000-g. charges of boric acid were titrated with 1.013 *N* sodium hydroxide, using the familiar sheltered-electrode apparatus described by MacInnes and Jones (18). The electrodes were cut from the same piece of wire and after assembly were heated in concentrated nitric acid, while short-circuited, until the difference in potential between the electrodes, when immersed in dilute acid, was less than 0.1 mv. This treatment was repeated between titrations.

During an experiment, the potentiometer was read when additional stirring

of the main portion of the solution or renewing of the sheltered solution did not change the potential difference more than 1 mv.

The 1-g. charges of boric acid were dissolved in 160 cc. of solutions of the weight concentrations shown in the figure (figures 8 and 9). By the end of the titration, the concentration of the "activator" had been reduced 10 per cent, owing to the dilution caused by the sodium hydroxide solution.

The "integrated" curves were constructed by adding the successive potential differences to those preceding.

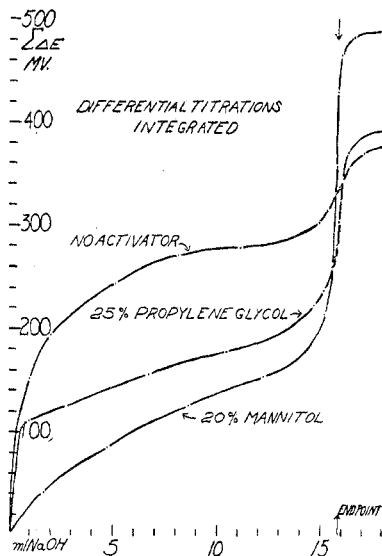


FIG. 9. Effect of propylene glycol "activator"

(2) Indicator titrations in the presence of (a) propylene glycol, (b) ethylene glycol, (c) mannitol

These experiments were performed to demonstrate that by using propylene or ethylene glycol as the "activating" agent, boric acid could be determined within 1 per cent of the value obtained using mannitol.

Charges of boric acid were titrated with 0.959 *N* sodium hydroxide, using phenolphthalein as indicator in the presence of excess redistilled propylene glycol (65–69°C. at less than 1 mm.) or redistilled ethylene glycol (73–77°C. at 4 mm.). In experiments A, B, C, and D the boric acid was dissolved in the sodium hydroxide and the tared glycol was added until the indicator changed color sharply with addition of one drop of the base. The end points were tested by adding excess mannitol and 10 cc. of water to dissolve the mannitol.

0.880 *N* sulfuric acid was used for back-titration. In experiment E the charge was first dissolved in 20 cc. of water. This end point was tested with 20 g. of propylene glycol added slowly. The end point was not changed. The results are given in table 1.

H. Miscellaneous observations

Propylene glycol borate, when added to an equivalent amount of sodium propylene glycolate dissolved in a small excess of glycol, produced heat and a white insoluble material. The borate is a colorless, extremely viscous material at room temperatures. Heating to 80° to 100°C. decreases its viscosity to the extent that it may be poured readily. Propylene glycol borate is soluble, without separation of boric acid, in dry toluene, ether, pyridine, and benzene, and is insoluble in petroleum ether. It hydrolyzes rapidly, liberating heat.

TABLE 1
Titration of boric acid

EXPERIMENT	BORIC ACID	"ACTIVATOR"	WATER ADDED AS		MG. H ₃ BO ₃ ML. 1 <i>N</i> BASE	MANNITOL ADDED AT END POINT	BASE REQUIRED
			Base	Acid			
	GRAMS		ml.	ml.		grams	ml.
A.	1.878	136 g. propylene glycol	31.70	0.50	62.70	5	0.07
B.	1.808	104 g. propylene glycol	30.10	0.10	62.84	5	0.05
C.	1.687	142 g. ethylene glycol	28.06		62.71	8	0.07
D.	1.854	183 g. ethylene glycol	31.20	0.49	62.89	8	0.08
E.	2.033	15 g. mannitol	33.90		62.57		

The solubility of propylene glycol in toluene is increased in the presence of propylene glycol borate (shown by the disappearance of the propylene glycol layer upon the addition of propylene glycol borate).

Ethylene glycol borate is a glassy material. All other glycol borates are viscous liquids. α -Monomethyl glycerol ether borate is more viscous than the corresponding *n*-butyl compound.

No difference from the reactions of propylene glycol borate was observed for the other borates.

V. LIMITATIONS OF THE EXPERIMENTAL METHODS

Each experimental method involves limitations which now require discussion.

A. Weight loss curves

The decomposition of the organic materials, evidenced by the appearance of a yellow and then brown color, is one limitation to the extensive use of this method. Additional factors such as depth of material in the beaker, rate at which solution took place, interval during which the material was coming up to temperature, and the rate of transfer of the liquid from the interior to the sur-

face make exact repetition of each curve difficult; such repetition was therefore not attempted.

B. Vacuum distillation

The general observation that distillations at low pressures (less than 10 mm.) are difficult to conduct without variations of 10°C. in the boiling point (13) is recognized in this work. The distillations at pressures of less than 1 mm. (indicated on the manometer but recognized as not the true pressure at which the distillation took place) were employed because of the lower temperatures which could be utilized and the speed with which the distillation could be completed. It must be recognized that vacuum distillations at less than 1 mm. were employed for the purpose of obtaining the borate compounds.

When necessary, vacuum distillations were conducted at higher (than 1 mm.) pressures, but too high pressures can lead to the thermal decomposition of the organic matter in the borate compound. These higher pressures are good to within 0.2 mm.

The plot of available pertinent data was prepared to determine how closely the distillation temperatures and pressures conformed to the linear relationship found with a compound. As the distillations were conducted at a rate suitable for distillation, the pressures can be regarded as approximating closely to the vapor pressures of the material. The selection of data from many experiments minimizes the chances of error involved in basing the plot on only one experiment. Schierholtz and Staples (23) have utilized this dynamic method of reduced-pressure distillation to obtain the relation of vapor pressure to temperature for various glycols and have obtained the linear relationships.

In attempts to observe the reaction of propylene glycol borate with additional propylene glycol or sodium propylene glycolate, it is recognized that water could have been present in an amount in which its partial pressure would be less than 0.8 mm. This is the extent to which we could not observe water to be liberated instantly from propylene glycol borate and additional propylene glycol or the sodium glycolate.

C. Differential titrations

The irreversibility of electrodes, electrode differences, stirring errors, and other sources of error have been reduced to less than 1 mv. This seemed to be the practical limit in obtaining the differential titration curves and will produce the greatest error in the curve for the differential titration of boric acid without an "activator." The percentage error is inversely proportional to the height of the peak. Thus the error does not affect the demonstration of "activation" of boric acid by propylene glycol and mannitol.

The "integrated curves" of the differential titrations are not well adapted for quantitative comparison of the acidity displacements, because the initial acidities were not measured. Also, the E.M.F. intervals for each curve are not rigidly comparable, as the dielectric constants of the solvents for each experiment were not necessarily the same.

D. Titrations of boric acid

Repeated titrations showed that the analysis of boron by titration (employing mannitol) was reproducible within 0.2 per cent.

VI. DISCUSSION

A. Preliminary investigations

Where the loss exceeds the moles of water calculated from any possible reactions, the excess loss must be due to volatilization of alcohol or alcohol combined with boric acid. The curves representing the lowest weights of glycol generally show a rapid initial loss, followed by a much slower loss. This first portion of the curve is due to the rapid loss of water produced by the esterification and dehydration reactions. The second portion of the curve is due to the slower evaporation of glycol and glycol combined with boric acid. The curves representing the greatest weights of glycol rise smoothly up to the point of complete evaporation of the charge.

The boric acid controls showed only a slow uniform loss in weight beyond the 1 mole of water lost in the formation of metaboric acid. This slow loss could not account for the 100 per cent loss of boric acid in the experiments with added glycol.

Several experiments are worthy of discussion: *Experiment No. 3.* Weight ratio of 1 mole of glycerol to 1 mole of boric acid. In the first 10 hr., 2.5 moles of water were lost, but in 400 hr. only 3 moles were lost. For each mole of boric acid and glycerol there was a total loss of 3 moles of water, indicating esterification of all three hydroxyls of each molecule of reactant, the last mole of water being eliminated very slowly.

Experiment No. 1. Weight ratio of 1 mole of glycerol to 3 moles of boric acid. Over 5 moles, but not more than 5.5 moles, of water per mole of glycerol were lost. These 5 moles can be accounted for on the assumption that, as in experiment No. 3, 3 moles of water were lost as the result of the interaction of 1 mole of glycerol and 1 mole of boric acid, and that each of the two additional moles of boric acid lost 1 mole of water by dehydration to metaboric acid, which dissolved in the glycerol borate. Had 6 moles of water been lost per mole of glycerol, or 2 moles of water per mole of boric acid, the loss could have been due to the formation of the trimetaborate ester of glycerol.

Experiment No. 21. Weight ratio of 3 moles of ethylene glycol to 2 moles of boric acid, corresponding to the reacting ratios reported by Dupire (9). Evaporation was complete.

Experiment No. 20. Weight ratio of 1 mole of ethylene glycol to 1 mole of boric acid. Evaporation was not complete.

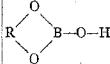

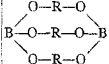
Experiment No. 13. Same ratio as No. 20, but with propylene glycol. Ninety-four per cent of the total charge evaporated.

Experiments No. 15 and No. 22. Weight ratios of 2 moles of propylene glycol to 1 mole of boric acid and 2 moles of ethylene glycol to 1 mole of boric acid, respectively. This is the composition required for the type II compounds postulated by Böeseken. The charges evaporated completely.

Experiment No. 38. Weight ratio of 1 mole of 2,3-butylene glycol to 2 moles of boric acid. After evaporation, there was a residue of dehydrated boric acid. Assuming that 1 mole of boric acid and 1 mole of glycol formed a volatile borate and the second mole of boric acid remained as metaboric acid, the weight of residue was 23 per cent less than it should have been. This extra loss of 23 per cent is duplicated in the boric acid control in the preceding run, in which the loss was 19 per cent more than 1 mole of water for each mole of boric acid.

Experiment No. 6. Weight ratio 2 moles of glycerol to 1 mole of boric acid (the ratio of reactants for Böeseken's type II compounds). The loss was more

TABLE 2
Identification of compounds: percentage of boron in compounds of various types compared to percentage of boron found experimentally in the volatile glycol borates

BORATE OF	BÖESEKEN'S TYPE I 	BÖESEKEN'S TYPE II 	DUPIRE'S (9) TYPE 	VOLATILE GLYCOL BORATE (FOUND)	PER CENT DEVIATION FROM TYPE I
Ethylene glycol (R = C ₂ H ₄).....	12.3	8.2	10.7	12.3	±1
Propylene glycol (R = C ₃ H ₆).....	10.6	6.8	8.9	10.6	±1
Trimethylene glycol (R = C ₃ H ₆).....	10.6	6.8	8.9	10.7	+1
2,3-Butylene glycol (R = C ₄ H ₈).....	9.4	6.3	7.6	9.5	+1
1,3-Butylene glycol (R = C ₄ H ₈).....	9.4	6.3	7.6	9.5	+1
Isobutylene glycol (R = C ₄ H ₈).....	9.4	6.3	7.6	9.7	+3
Methyl ether of glycerol (R = C ₄ H ₉ O).....	8.2	4.9	6.5	8.0	-2
n-Butyl ether of glycerol (R = C ₇ H ₁₅ O).....	6.2	3.6	4.7	6.3	+1

than 5 moles of water per mole of boric acid. As experiment No. 3 showed a loss of 3 moles of water per mole of boric acid, the weight loss equivalent to more than 5 moles of water is assumed to be due to the loss of 3 moles of water and the loss of some glycerol.

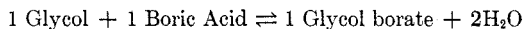
B. Volatile glycol borates

In table 2 are shown values for the percentage of boron in compounds of various types compared to the percentage of boron found experimentally in the volatile glycol borates. Obviously these borates are of the type I composition.

The maximum percentage deviations shown here between the experimental values for boron and those calculated for the type I compound compare favorably with some examples of deviations previously reported in the literature for boron compounds.

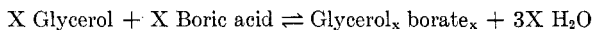
C. Boric acid and trimethylene and the butylene glycols

The first experiments utilizing these glycols confirmed the generalized reaction

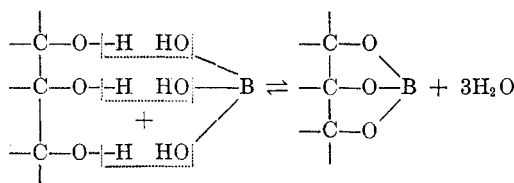


D. Glycerol and boric acid

The behavior of an equimolecular mixture of glycerol and boric acid during an attempt to distil it, is assumed to be due to the formation of the third ester linkage between two diesterified molecules, not within the same diesterified molecule. This reaction,

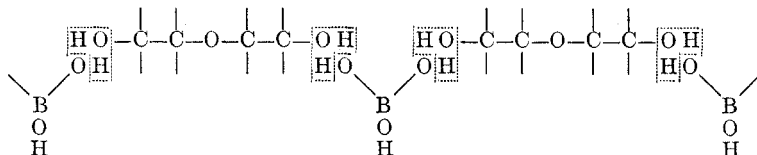


producing a compound of molecular weight too high to volatilize, seems more probable than the reaction



even though neither glyceryl borate was isolated.

No volatile borate was isolated for the reaction of boric acid and diethylene glycol, though water was eliminated. The progressively increasing viscosity of the mixture of these materials while subjected to heating and reduced pressure has been explained tentatively to be due to the formation of ester linkages between two molecules of the glycol and one molecule of boric acid, i.e.



resulting in the formation of a linear ester, similar to the results of Carothers (8) with ethylene glycol and succinic acid.

The presence of the ether linkage in the alcohol molecule is a less possible cause for the non-distillation of the diethylene glycol borate, since the triesterified borate of methyl cellosolve (an ether), as well as the diesterified borates of

the glyceryl monoethers, were distilled and identified without interference produced by the ether linkage in the alcohol molecule.

The experiments with the two monoethers of glycerol confirmed the assumption that, with one hydroxyl group of glycerol occupied or blocked, volatile borates of the resulting functional glycol should be possible. β -Alkyl ethers of glycerol were not tried, as they were not available.

The monochlorohydrin of glycerol and boric acid form a volatile borate with decomposition and are therefore not reported as producing a new boric acid compound. With lower pressures and distillation temperatures it may be possible to isolate the compound in pure condition.

The rearrangement of glycerol monoacetate to yield the triacetate instead of a volatile borate was disappointing, because it eliminated a possible means of locating the unreacted hydroxyl group on glycerol after the first two had reacted with boric acid. The rearrangement strengthened the possibility that the

—C—O—B linkage in the glycol borate esters is labile at elevated temperatures. This instability has been reported (19) in the distillation of $(C_2H_5)_2B-BOCH_2C_6H_4Cl(p)$ (b.p. about $80^\circ C.$), which decomposes to produce $[(C_2H_5)_2B]_2O$. When this instability had been twice noted, attempts were abandoned to prepare esters of the hydroxyl group which we believe to be on the boron atom in the glycol borates. Such preparation had been planned for the purpose of investigating the structure of the glycol borates.

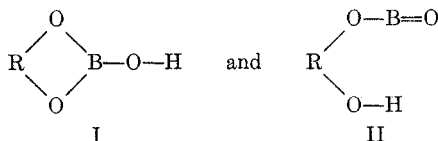
E. Distillations at varied pressures

The distillations of propylene glycol borate from 8 to 35 mm. pressure without more than 2 per cent deviation from the theoretical percentage of boron and the linear character of the plot of $\log p$ against $1/T$ indicate that the distilled product is a compound.

Repeated distillations at increased pressures for 2,3-butylene glycol borate and the methyl ether of glycerol borate with no significant changes in boron content indicate that these also are compounds. The other volatile glycol borates are assumed, also, to be compounds.

F. Structure of propylene glycol borate

The agreement between the percentages of boron found in the volatile borates and calculated for the type I compounds leads to the formulation of these possible structures:



The following reasons indicate that the volatile glycol borates have the cyclic structure (I): Two hydroxyls of the polyhydric alcohol are involved in their

formation, as shown by the behavior of glycerol borate and of borates of the monoalkyl ethers of glycerol when subjected to distillation. The borates are acid in nature, as shown by the precipitation with dry ammonia gas.

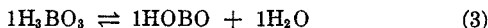
The linear structure (II) is eliminated as a possibility for the following reasons: The alcoholic hydroxyl group is absent, as shown by no evolution of hydrogen chloride gas when the borate is dissolved in acetyl chloride. Excess metaboric acid does not enter into the condensation reaction, as shown by the preliminary experiments Nos. 1 and 38.

Any possible structures containing an ether linkage between glycol molecules are eliminated by the isolation of the glycol diacetate upon heating the glycol borate with acetic anhydride.

G. Exclusion of other types of boric acid compounds

(1) Propylene glycol and metaboric acid

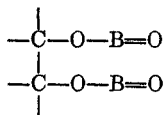
The esterified product is the same, whether 1 mole of the 2 moles of water is eliminated before the condensation, or whether both moles of water are eliminated in the same experimental step. Both reactions yield the same product:



(PG(OH)₂ = propylene glycol)

(2) Propylene glycol borate and metaboric acid

The separation of propylene glycol borate from an added excess of "metaboric acid" without elimination of additional water was interpreted as excluding the formation of diesters of metaboric acid such as



which requires the elimination of one more mole of water if formed from 1 mole of glycol borate and 1 mole of metaboric acid.

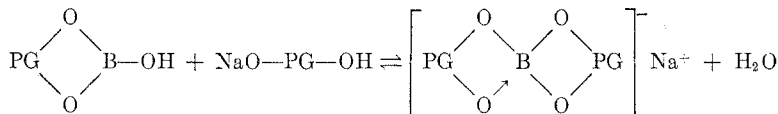
The viscous residues left in the flasks at the end of the distillations are explained as solutions of metaboric acid or dehydrated boric acid in the glycol borate.

(3) Propylene glycol borate and propylene glycol

Propylene glycol borate and additional propylene glycol, heated without loss of water, showed that Dupire's compounds could not be obtained in this manner and partially indicated that Böeseken's type II compound could not be obtained from the isolated glycol borates.

(4) Sodium propylene glycolate and propylene glycol borate

Sodium propylene glycolate was chosen as the donor of alkali ion in the absence of water, or as a base. The reaction expected to take place instantaneously was:



The water was not obtained down to a pressure of 0.8 mm. Heating did not promote the reaction. This further excludes Böeseken's type II compound. The importance of this failure to react is discussed under the "activation" of boric acid by propylene (and ethylene) glycol.

(5) Trimethyl cellosolve borate

A glycol derivative (methyl cellosolve), functioning as a monohydric alcohol in the condensation reaction with boric acid, produces a triesterified borate. No such borate was isolated when unmodified glycols were used; thus monoesterified glycol borate esters are further eliminated. It was again found that the preliminary dehydration of orthoboric acid did not change the proportions of alcohol in the triester of boric acid.

VII. INDICATOR TITRATIONS

The addition of polyhydric alcohols to solutions of boric acid displaces the titration curve towards a more acidic reaction. The greater the mannitol or other polyhydric alcohol concentration, the greater the acidity displacement. If the crossed band (see figure 10) represents the pH range 8 to 9, in which phenolphthalein changes color, then the greater the concentration of polyhydric alcohol, the closer the indicator change is to the stoichiometric point.

In the indicator titrations, the results obtained when propylene and ethylene glycols are used separately as "activators" agree within 4 parts per thousand with the values obtained with mannitol as the "activator." When mannitol was added to a solution "activated" by propylene or ethylene glycol, the additional 0.06 cc. of base was required because the acidity had not been increased sufficiently by the glycol to give the pH color change at the stoichiometric point.

Thus neither propylene nor ethylene glycol, liberated by hydrolysis upon solution of the distilled glycol borate, interfered with the titration for boron content.

VIII. DIFFERENTIAL ELECTROMETRIC TITRATIONS

These experiments confirm by an additional method the "activation" of boric acid by propylene glycol. The "activation" with propylene glycol in 25 per cent initial concentration is conclusively shown by comparison of the end

point with that of the same amount and concentration of boric acid without "activator." It is recognized that the propylene glycol "activation" of boric acid is not as extensive as that obtained with mannitol.

Significance of the "activation" titrations for Böeseken's theory of "activation"

In the "activation" titrations the water present and the type II compound, if it is required for the "activation," would be in equilibrium with the reactants forming the type II compound and water. In the experiments attempting to detect the formation of the type II compound, the concentrations of the reac-

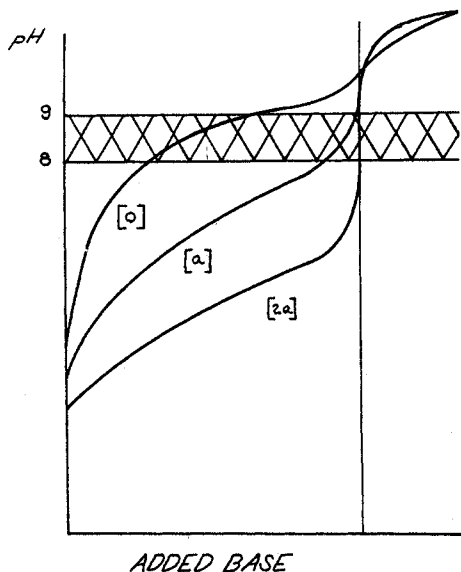


FIG. 10. Titration curves of boric acid: effect of activator concentration

tants were many times greater than in the titrations. It would therefore be expected that the reaction would produce enough water to satisfy the equilibrium constant and that this water could be removed by reduced pressure. But in the experiments in which an attempt was made to detect the reaction between propylene glycol borate and propylene glycol or sodium propylene glycolate, the water, if any was formed, did not have a vapor pressure greater than 1 mm., while the concentrations of water in the titration solutions in which "activation" has been conclusively demonstrated have vapor pressures many times greater than 1 mm.

Obviously this conflict may be resolved by assuming: (1) that the experimental conditions were inadequate in the reactions attempting to produce the

type II glycol borate, or (2) that Böesecken's type II compound is not a prerequisite for "activation."

IX. GENERAL CONCLUSIONS FOR THE EXPERIMENTAL WORK

The work thus far conducted may be summarized in the form of these general conclusions:

1. The lowest members of the aliphatic glycol series and boric acid produce volatile compounds of type I.
2. No other type of compound was isolated.
3. Glycerol and boric acid react with the formation of triesterified linkages, though no product was isolated and characterized.
4. Glycerol monoalkyl ethers and boric acid produce volatile borates of type I.
5. Metaboric acid did not form a monoesterified ester. It is the equivalent of orthoboric acid in the reactions studied.
6. The glycols, propylene and ethylene, used to isolate volatile borates of type I, "activate" boric acid in a titration in the presence of water.

X. COMPARISON OF THE CONCLUSIONS WITH THE RESULTS AND CONCLUSIONS IN THE LITERATURE

1. The prediction of P. Hermanns (12) has been confirmed as regards the type of boric acid esters of propylene and ethylene glycols.

2. Propylene (and ethylene) glycol has an "activating" effect on boric acid in the presence of water, in agreement with the published data of Rimbach and Ley (22), but not in agreement with the findings of Krantz and collaborators (15) for 0.1 molar boric acid in the presence of 4 per cent propylene glycol.

This is not in agreement with P. Hermanns (12), who expected no "activation" from these glycols (propylene and ethylene). He attributes this expected lack of "activation" to extreme hydrolysis preventing the formation of esters.

3. No evidence for the type II compound of propylene glycol and boric acid was found. Böesecken and P. Hermanns believe this type of compound to be prerequisite to "activation."

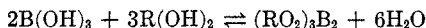
4. Kolthoff's application (14) of the mass law to van Liempt's data for the "acidity" changes during the titration of boric acid in the presence of glycerol has yielded a 1:1 complex of uncertain structure between glycerol and boric acid. Insofar as the ratios of boric acid and the glycerol structure are concerned we are in agreement, though not in agreement as to the type of binding between boric acid and the glycerol structure, which is not described by Kolthoff. We do not believe that the esterified boric acid-glycerol linkage can exist in water solution.

At the same time we question the validity of Kolthoff's mathematics, which involves the solution of mass-law relations for the amount of undissociated complex ion by simultaneous equations. The simultaneous equations which Kolthoff employed cannot be reproduced when his final values are substituted into these equations.

5. Our findings are in agreement with Dupire's work (9) only to the extent

that boric acid can eliminate water in condensing with propylene, ethylene, or butylene glycol or glycerol chlorohydrin, and that the product is volatile at reduced pressures.

We believe that Dupire's claims in reporting compounds resulting from the reaction



are not valid for the following reasons: (1) The weights of reactants required by the theoretical reaction were treated only until the residue had been reduced to the weight demanded by theory and not beyond. (2) The product was not distilled and therefore the distillate was not analyzed, though the temperature of boiling under reduced pressure and the pressure are reported. (3) The calculated and found percentages of at least one element in the new compounds are omitted. (4) The reported calculated and found molecular weights (340 and 335, respectively) are approximately 20 per cent larger than demanded for the theoretical equation. (5) Experimentally it was found that, although 3 moles of glycol will volatilize 2 moles of boric acid, one of the moles of the glycol does not condense with the boric acid.

XI. APPLICATION TO FUTURE STUDIES IN THE FIELD

If the viewpoint of Böeseken and collaborators concerning no "activation" of boric acid by the lowest aliphatic glycols because of hydrolysis and steric factors is accepted, then the "activation" encountered by indicator and differential electrometric titrations must be ascribed to some other cause. Perhaps the cause is the dielectric constant of the medium or a solvation in which glycol instead of water molecules are involved without esterification. This cause must hereafter be included in the treatment of the problem of "activation" of boric acid. An effect such as the change in the height of the end point (or the slope of the titration curve at the end point) in the differential titration curves, which with propylene glycol is 20 per cent (or 300/1500) of the value obtained with mannitol and 500 per cent (or 300/60) of the value obtained with only boric acid can not be neglected in the future treatment of "activation" and should not be overlooked as a source of further investigation.

We do not believe that enough work has been done up to the present in this field to enable a complete mathematical explanation of the neutralization curves of boric acid in the presence of even the least structurally complex "activators." Our work is hereby presented as a starting point for the synthesis of type II esters, if such can be accomplished, and for further physicochemical study of the acidity and hydrolysis of the isolated esters.

XII. SUMMARY

1. Orthoboric acid and the first three members of the homologous series of glycols have been shown to react in equimolecular proportions with the elimination of two molecules of water to form volatile esters of definite composition.

2. Six new glycol borates have been prepared. Their behavior on distillation and their salient chemical properties have been described.

3. These findings are in accord with the predictions of P. Hermanns. The reaction reported by Dupire and the reaction predicted by Böeseken for the "activators" of boric acid could not be confirmed with propylene glycol.

4. Propylene and ethylene glycols have been shown to be strong "activators" of boric acid in acid-base titrations.

5. Glycerol monoalkyl ethers produce volatile borates of the same type.

6. Three moles of ethylene glycol monoethyl ether and 1 mole of boric acid combine to form a volatile borate of the trimethyl borate type.

7. Metaboric acid is the equivalent of orthoboric acid in the preparation of the new esters reported.

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