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Equilibria in the esterification of boric acid

Richard William Palizay

New Jersey Institute of Technology

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EQUILIBRIA IN THE ESTERIFICATION OF BORIC ACID

BY

RICHARD W. PALIZAY

A THESIS
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ABSTRACT

A solvent extraction method was developed to determine the equilibria in the esterification of boric acid. In this method boric acid was reacted with various alcohols. After equilibrium was reached, the ester was isolated from the reaction mixture by means of a solvent and the amount of ester determined quantitatively. The equilibrium constants were then calculated for the reaction of boric acid with several alcohols.

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING
NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: ______________________

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NEWARK, NEW JERSEY
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INTRODUCTION

Although there are many references to the esterification of boric acid (1), a search of the literature revealed little information concerned with actual equilibrium data in the reaction of boric acid with various alcohols.

Most of the references cite yields of various esters using different alcohols. The yields of ester obtained with a specific alcohol varied widely according to the conditions under which esterification was carried out. Thus the yield does not necessarily reflect the equilibrium condition in the reaction

$$3\ ROH + H_3BO_3 \rightleftharpoons R_3BO_3 + 3\ H_2O$$

Also, it is evident that the determination of the equilibrium constant cannot be based on the yield of free ester if in the course of obtaining the free ester the above reaction is driven further toward completion. An example of this might be the case where an excess of alcohol is added to the boric acid and, after allowing sufficient time for the reaction to reach equilibrium, separation is accomplished by azeotropically removing water with a suitable carrier such as benzene (2, 3, 4). More ester is formed as rapidly as water is removed because of the excess of alcohol and because the esterification of boric acid proceeds at a very rapid rate.

The equilibrium constant calculated from such a run would of course be inaccurate.

In the work described in this paper an effort was made to determine the true equilibria in the esterification of boric acid using a solvent technique. The degree of success which was obtained will be discussed in the section describing the results of experiments.

EXPERIMENTAL

A. Equipment:

The apparatus used in this work was not special in any way. Almost certainly, all of the apparatus would be found in any industrial or college laboratory. In brief, the apparatus required was a constant temperature bath consisting of a battery jar, stirrer, mercury thermometer, mercury thermoregulator, and electrical heating element. An electronic relay between the thermoregulator and the heating element helped to eliminate lag and gave sensitive control over the bath temperature. Erlenmeyer flasks, pipettes, and burettes, as well as glassware for distillation were required.

B. Chemicals:

Benzene was used as solvent in most instances. The benzene was originally of good grade, meeting ACS specifications. All benzene was distilled to azeotropically remove the last traces of moisture.

Petroleum Ether: Baker petroleum ether (meets ACS specifications) was used as solvent in some cases.

N-Pentane: Reilley n-pentane (99 mol per cent n-pentane) was used as solvent in one instance.

Boric Acid: Baker 99.5% boric acid which had been heated to above 100 °C. to remove the last traces of moisture was used in all experiments.

Mannitol: A good grade of mannitol was used in all cases.

Alcohols: Alcohols used were CP grade or equivalent. Methanol was distilled over magnesium to remove traces of moisture and analyzed 0.05% moisture using the Karl Fischer reagent.

Ethyl Alcohol: Absolute ethyl alcohol was used. The moisture content was 0.07% as determined by using the Karl Fischer reagent.

Tertiary Butyl Alcohol: Eastman #820, melting point 24-25.5 °C. was used.

1,3-Dichloro-2-propanol: Eastman #657 was used.

The propyl, butyl, and amyl alcohols were all CP grade and were furnished through the courtesy of Mr. John Roeder of the Newark College of Engineering.

C. Development of the Method:

In undertaking the determination of equilibria in the esterification of boric acid, it was decided the use of a solvent offered the best means of isolating the reaction products.

This method required dissolving the boric acid in the alcohol and, after equilibrium was reached, adding a solvent to remove the ester. The ester could then be hydrolyzed to boric acid by the addition of water. The boric acid could then be titrated with standard sodium hydroxide solution.

Actually, boric acid is such a weak monobasic acid ($K_a = 5.8 \times 10^{-10}$) that it cannot be titrated accurately with 0.1 N standard alkali. However, by the addition of certain organic polyhydroxy compounds, such as glycerol, mannitol, dextrose, or invert sugar, boric acid is transformed into a relatively strong monobasic acid (5).

Through the use of mannitol, then, boric acid could be titrated and the moles of base used would indicate the moles of ester formed. Knowing the weight of acid and alcohol at the start, and knowing the amount of ester formed (from the results of the titration), all the data necessary for calculation of the equilibrium constant would then be at hand.

A solvent was required which would dissolve the ester but not the boric acid or the water. It seemed that these requirements could be met by many organic solvents.

The mole-fraction of water soluble in benzene at 20 °C. is 19.0×10^{-4} (6). To check the solubility of boric acid in benzene, a saturated solution of boric acid in acetone was made. Then small amounts of this solution were added to previously distilled, water-free benzene. The benzene took on a hazy bluish, turbid appearance almost immediately, indicating a very fine precipitate. However, more of the acetone solution was added to assure the formation of a precipitate. A total of 1.4 ml of the acetone solution was added to 100 ml of benzene.

After allowing the precipitate to settle, twenty-five ml aliquots of the benzene were taken and added to water containing mannitol. The mixtures were shaken and then titrated with 0.0995 N sodium hydroxide solution. Each aliquot required 0.11 ml of base. The solubility of boric acid in benzene was 0.0274 grams per liter.

From this preliminary work it appeared that solvents such as benzene, xylene, carbon tetrachloride, and petroleum ether would be suitable, since the ester and alcohol would dissolve in the solvent but the acid and water would not.

The following general method was followed: The first step required the determination of the approximate solubility of boric acid in the alcohol. This was accomplished by placing a small weight of the boric acid in a flask and adding the alcohol in small increments and noting the amount of alcohol required to completely dissolve the acid. This was not the true solubility since some esterification took place. However, the weight of alcohol used represented the minimum amount of alcohol that was necessary to get a homogeneous solution.

When methyl alcohol was used, the boric acid dissolved in relatively small amounts of alcohol at room temperature. However, when alcohols such as isopropyl or butyl were used the boric acid was only sparingly soluble at room temperature. Mixtures of the acid and the alcohols were shaken intermittently for several days at a time without effecting solution. It was necessary to heat the acid-alcohol mixture to obtain complete solution of the acid in small amounts of alcohol. Even with heating the amount of alcohol required was several fold greater than the required amount of methyl alcohol.

If heating was used to dissolve the acid, then the resulting solution was allowed to stand at room temperature for twenty-four hours to be sure that no precipitation of acid occurred on cooling. Then the temperature of the solution was brought to the desired temperature by placing the flask in the bath. The solution was kept at the desired temperature, usually 30 °C., for a period of time long enough to assure the reaction reaching equilibrium. Although the reaction is very rapid, as a matter of caution at least ninety minutes was allowed for equilibrium to be reached.

After sufficient time had elapsed for equilibrium to be reached, the desired amount of solvent was added. The resulting mixture was shaken for two to three minutes and then replaced on the bath for at least two hours.

In the early experiments because the mixture was very turbid and required about a day of settling to give two clear liquid phases, centrifuging was used to speed the experiment. The mixture was centrifuged at 1700 rpm for thirty minutes to give two clear liquids. The centrifuge flask was then carefully replaced in the constant temperature bath and allowed to remain at this temperature for two hours. This last step was taken to avoid any error due to a shift in equilibrium caused by having the temperature of the flask at a lower temperature during centrifuging.

In later experiments the volume of solvent became so large that centrifuging could not be used. Instead of centrifuging after addition of the solvent, the flasks were simply allowed to remain in the bath for about a day until the two liquid phases became clear. The results of each method were equal when equal amounts of solvent were used. The effect of increased solvent will be discussed later.

Once two clear liquid phases were obtained, aliquots were taken of the solvent layer and added to Erlenmeyer flasks which contained water and dissolved mannitol. In some previous experiments the correct amount of mannitol needed for permanent end points was determined. The Erlenmeyer flasks containing the benzene-water mixtures were placed on a shaker for two hours.

It was found that the use of Erlenmeyer flasks with ground glass joints and ground glass stoppers prevented leakage during shaking. The ordinary Erlenmeyer flasks with cork stopper were not satisfactory. Rubber stoppers, although somewhat more satisfactory insofar as leakage is concerned, were unsatisfactory because the solvent extracted chemicals from the rubber.

After hydrolyzing the ester, the mixture was then titrated with standard sodium hydroxide solution using phenolphthalein as indicator. Once an end point was reached, the flask was stoppered and shaken to make sure that the end point was permanent. In some instances, especially where an ester of the longer chain alcohols was used, the end point disappeared on shaking and a small amount of additional base was necessary to attain a permanent end point. A blank was then run on a sample of a mixture of distilled water , mannitol, and benzene. The difference in quantity of base between that used for the sample and that for the control was used to calculate the degree of esterification.

The early runs indicated that about 90 per cent of the boric acid was converted to ester. This seemed unduly high and created doubt as to whether or not the precipitation was complete. To check the effect of more solvent a run was made in which the amount of solvent was varied widely from approximately 190 ml of benzene per gram of acid to 2100 ml of benzene per gram of acid.

The effect of solvent was immediately apparent. For the lower ratio of benzene to acid only a liquid settled out. As the ratio was increased a white precipitate formed. It was evident that the precipitate was boric acid since methyl alcohol and trimethyl borate are both liquids at room temperature. After this experiment all runs were made with the high benzene to acid ratios. The effect of solvent will be treated in greater detail in the Discussion section.

D. Description of a Representative Run:

The method itself will be made clearer by describing an actual experiment and carrying out the necessary calculations: In Run No. 6C, 0.2390 grams of boric acid was weighed out on an analytical balance. The boric acid was then added to a 250 ml Erlenmeyer flask. Using a weighing bottle and an analytical balance, 1.2456 grams of water-free methanol was added to the Erlenmeyer flask and the flask stoppered.

The flask was shaken until all the boric acid was dissolved. Care was taken to make sure that no crystals of boric acid were clinging to the wall of the flask, undissolved. The solution was allowed to stand for 24 hours at room temperature after which time the temperature of the solution was brought to 30 °C. for 90 minutes by placing the flask in the constant temperature bath. Then 200 ml of previously distilled benzene was added to the flask. The flask was removed from the bath and shaken thoroughly for two to three minutes and then replaced in the bath at 30 °C. After two hours at 30 °C., the benzene was not clear and the bath was turned off and the flask left in the bath at room temperature.

After 24 hours the benzene was clear and a precipitate was visible in the flask. The temperature of the flask was raised to 30 °C. for two hours and then two 50 ml aliquots were taken from the benzene phase. Each aliquot was added to a 250 ml Erlenmeyer flask containing 50 ml of distilled water and 4 grams of dissolved mannitol. The flasks were stoppered and placed on a shaker for two hours. After shaking, the mixtures were titrated with standardized 0.0995 Normal sodium hydroxide solution using phenolphthalein as indicator. When the end point was reached, the flasks were stoppered and shaken for two minutes. The end points were permanent.

A total of 5.96 ml of base was required for one aliquot and 5.86 ml for the other. A blank was run on a mixture of 50 ml of benzene added to 50 ml of water containing 4 grams of dissolved mannitol. One drop of the standard base turned the water phase a deep red.

E. Sample Calculations:

The data from the above run will be used to determine the equilibrium constant:

61.84 = molecular weight of boric acid

32.04 = molecular weight of methyl alcohol

$\frac{0.2390}{0.06184}$ = 3.86 millimoles of boric acid charged

$\frac{1.2456}{0.03204}$ = 38.9 millimoles of methyl alcohol charged

0.792 = density of methyl alcohol

$\frac{1.246}{0.792}$ = 1.6 ml of methyl alcohol

Assuming that the volume of the benzene phase formed on adding benzene to the reaction solution is equal to the volume of benzene and alcohol:

200 + 1.6 = 201.6 ml in the benzene phase

$\frac{5.96 + 5.86}{2}$ = 5.91 ml base, average

$(5.91)(0.0995)\frac{(201.6)}{50}$ = 2.37 millimoles of ester at equilibrium

(3)(2.37) = 7.11 millimoles of water at equilibrium

3.86 — 2.37 = 1.49 millimoles of acid at equilibrium

38.9 — 7.1 = 31.8 millimoles of alcohol at equilibrium

From the law of mass action, for any reaction $aA + bB \rightleftharpoons dD + eE$, the equilibrium constant, K_c, at any definite temperature can be calculated from the following relationship:

$$K_c = \frac{C_D^d \times C_E^e}{C_A^a \times C_B^b}$$

where C is the equilibrium concentration of the constituents in moles per liter.

For the reaction $3ROH + H_3BO_3 \rightleftharpoons R_3BO_3 + 3\ H_2O$, the equilibrium concentration would be: $K_c = \frac{(R_3BO_3)(H_2O)^3}{(H_3BO_3)(ROH)^3}$.

The volume of the reaction mixture would cancel out and from the above calculated data: $K_c = \frac{(2.37)(7.11)^3}{(1.49)(31.8)^3}$

$$= 1.77 \times 10^{-2}.$$

The per cent of boric acid reacted is:

$$(100)\frac{(2.37)}{(3.86)} = 61.4\%$$

The benzene to acid ratio is:

$\frac{200}{0.2390}$ = 837 milliliters of benzene per gram of acid.

DISCUSSION

The experimental data for all runs are listed in Table I. Table II lists the values taken for the molecular weights and densities of the alcohols. From the data of these tables the equilibrium constants and percentages of reacted boric acid were calculated by the methods described on pages 12 and 13. The results of the experiments varied somewhat with each alcohol so each alcohol will be discussed in turn.

Methyl Alcohol:

Most of the experiments were run using methyl alcohol. In the first experiments it was noted that the amount of benzene used drastically affected the results.

If only small amounts of benzene were added to the equilibrium mixture, a solution was formed and no separation of solid or liquid occurred. If the amount of solvent was increased, two liquid phases were produced. When the benzene layer was analyzed, the results showed that apparently the reaction had gone almost to completion. However, if greater quantities of solvent were used, a solid precipitate was formed. Now, when the solvent layer was analyzed, the results showed the reaction to have been about 60 per cent complete.

It was decided to check the effect of still greater

TABLE I - DATA FROM ALL RUNS

RUN NO.	A	B	C	D	E	F	G	H	I	J	K	L	M	N	P	Q
	BORIC ACID		ALCOHOL			SOL-VENT	E Plus	ALI-QUOT	G/H	SODIUM HYDROXIDE			AT EQUILIBRIUM			
	Grams	Milli-Moles	Grams	Milli-Moles	Ml.	Ml.	F	Ml.		Ml.	Nor-mality	M.Moles (J x K)	Ester (I x L)	Water (3M)	Acid (B-M)	Alcohol (D—N)
	METHYL ALCOHOL, 30 °C:															
1A	0.5013	8.11	2.683	83.7	3.4	95	50*	20	2.50	29.52	0.1007	2.97	7.43	22.3	0.68	61.4
1B	0.5008	8.10	2.683	83.7	3.4	95	50*	20	2.50	29.45	0.1007	2.97	7.43	22.3	0.67	61.4
2A	0.4949	8.00	2.7912	87.1	3.5	100	103.5	40	2.59	28.36	0.1007	2.86	7.41	22.2	0.59	64.9
2B	0.5108	8.26	2.8285	88.3	3.6	100	103.6	40	2.59	28.73	0.1007	2.89	7.49	22.5	0.77	65.8
3A	0.2593	4.19	1.8141	56.6	2.3	100	102.3	40	2.56	14.65	0.1007	1.48	3.79	11.4	0.40	45.2
3B	0.2609	4.22	2.2205	69.3	2.8	200	202.8	50	4.06	9.54	0.1007	0.96	3.90	11.7	0.32	57.6
4A	0.2584	4.18	1.6958	52.9	2.1	100	102.1	40	2.55	14.93	0.1007	1.50	3.83	11.5	0.35	41.4
4B	0.2551	4.13	1.4066	43.9	1.8	200	201.8	50	4.04	6.05	0.1007	0.61	2.46	7.38	1.67	36.5
4C	0.2505	4.05	1.6355	51.0	2.1	300	302.1	100	3.02	9.34	0.1007	0.941	2.84	8.52	1.21	42.5
5A	0.2513	4.06	1.4697	45.9	1.9	200	201.9	100	2.02	13.07	0.0995	1.30	2.63	7.89	1.43	38.0
5B	0.2521	4.08	1.4171	44.2	1.8	400	401.8	100	4.02	6.77	0.0995	0.674	2.71	8.13	1.37	36.1
6A	0.2415	3.91	1.2686	39.6	1.6	100	101.6	50	2.03	13.09	0.0995	1.30	2.64	7.92	1.27	31.7
6B	0.2436	3.94	1.6642	51.9	2.1	150	152.1	50	3.04	11.16	0.0995	1.11	3.37	10.1	0.57	41.8

TABLE I - (CONTINUED)

RUN NO.	A	B	C	D	E	F	G	H	I	J	K	L	M	N	P	Q
	BORIC ACID		ALCOHOL			SOL-VENT Ml.	E Plus F	ALI-QUOT Ml.	G/H	SODIUM HYDROXIDE			AT EQUILIBRIUM			
	Grams	Milli-Moles	Grams	Milli-Moles	Ml.					Ml.	Nor-mality	M.Moles (J x K)	Ester (IxL)	Water (3M)	Acid (B-M)	Alcohol (D--N)
6C	0.2390	3.86	1.2456	38.9	1.6	200	201.6	50	4.03	5.91	0.0995	0.588	2.37	7.11	1.49	31.8
6D	0.2410	3.90	1.3228	41.3	1.7	400	401.7	100	4.02	6.15	0.0995	0.612	2.46	7.38	1.44	33.9
6E	0.2401	3.88	1.6847	52.6	2.1	500	502.1	100	5.02	6.47	0.0995	0.644	3.23	9.69	0.65	42.9
7A	0.2485	4.02	1.2152	37.9	1.5	200	201.5	100	2.02	11.59	0.0995	1.15	2.32	6.96	1.70	30.9
7B	0.1253	2.03	0.6526	20.4	0.8	200	200.8	100	2.01	5.89	0.0995	0.586	1.18	3.54	0.85	16.9
7C	0.1256	2.03	0.7510	23.4	1.0	250	251.0	100	2.51	5.70	0.0995	0.567	1.42	4.26	0.61	19.1
8A	0.2416	3.91	1.3381	41.8	1.7	200	201.7	100	2.02	12.56	0.0995	1.25	2.53	7.59	1.38	34.3
8B	0.1221	1.97	0.8061	25.2	1.0	200	201.0	100	2.01	7.07	0.0995	0.703	1.41	4.23	0.56	21.0
8C	0.1257	2.03	0.8208	25.6	1.0	250	251.0	100	2.51	6.26	0.0995	0.623	1.56	4.68	0.47	20.9
	Methyl Alcohol, 0 °C.:															
9A	0.2438	3.94	1.4116	44.1	1.8	400	401.8	100	4.02	6.17	0.0995	0.614	2.47	7.41	1.47	36.7
	Ethyl Alcohol, 30 °C.:															
10A	0.5016	8.11	7.06	153.2	8.8	100	108.8	40	2.72	29.31	0.1007	2.95	8.02	24.1	0.09	129.1
10B	0.5114	8.27	6.95	150.9	8.8	200	208.8	100	2.09	38.20	0.1007	3.85	8.05	24.2	0.22	126.7
	N-Propyl Alcohol, 30 °C.:															
11A	0.2297	3.71	3.76	62.6	4.2	200	204.2	50	4.08	9.03	0.0995	0.898	3.66	11.0	0.05	51.6

TABLE I - (CONTINUED)

RUN NO.	A	B	C	D	E	F	G	H	I	J	K	L	M	N	P	Q
	BORIC ACID		ALCOHOL			SOL-VENT	E Plus	ALI-QUOT	G/H	SODIUM HYDROXIDE			AT EQUILIBRIUM			
	Grams	Milli-Moles	Grams	Milli-Moles	Ml.	Ml.	F	Ml.		Ml.	Nor-mality	M.Moles (J x K)	Ester (IxL)	Water (3M)	Acid (B-M)	Alcohol (D-N)
	Isopropyl Alcohol, 30 °C.:															
12A	0.2420	3.91	3.61	60.1	4.6	200	204.6	100	2.05	10.24	0.0995	1.02	2.09	6.27	1.82	53.8
12B	0.2439	3.94	3.67	61.1	4.7	400	404.7	100	4.05	5.53	0.0995	0.55	2.23	6.69	1.71	54.4
	N-Butyl Alcohol, 30 °C.:															
13A	0.2457	3.97	5.10	68.8	6.3	200	206.3	50	4.12	8.98	0.0995	0.893	3.68	11.0	0.29	57.8
	Secondary Butyl Alcohol, 30 °C.:															
14A	0.2418	3.91	4.99	67.3	6.2	200	206.2	50	4.12	5.17	0.0995	0.514	2.12	6.36	1.79	60.9
14B	0.2380	3.85	5.25	70.8	6.4	400	406.4	100	4.06	5.42	0.0995	0.539	2.19	6.57	1.66	64.2
	Tertiary Butyl Alcohol, 30 °C.:															
15A	0.1164	1.88	5.33	71.9	6.8	200	206.8	100	2.07	1.80	0.0995	0.179	0.371	1.11	1.51	70.8
	N-Amyl Alcohol, 30 °C.:															
16A	0.2346	3.79	5.82	66.0	7.1	200	207.1	50	4.14	6.70	0.0995	0.667	2.76	8.28	1.03	57.7
16B	0.2364	3.82	5.20	59.0	6.4	400	406.4	100	4.06	6.34	0.0995	0.631	2.56	7.68	1.26	51.3
	Primary Isoamyl Alcohol, 30 °C.:															
17A	0.2394	3.87	5.14	58.3	6.3	200	206.3	50	4.13	7.96	0.0995	0.792	3.27	9.81	0.60	48.5

TABLE I - (CONTINUED)

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	P	Q
RUN NO.	BORIC ACID		ALCOHOL			SOL-VENT Ml.	E Plus F	ALI-QUOT Ml.	G/H	SODIUM HYDROXIDE			AT EQUILIBRIUM			
	Grams	Milli-Moles	Grams	Milli-Moles	Ml.					Ml.	Nor-mality	M.Moles (J x K)	Ester (IxL)	Water (3M)	Acid (B-M)	Alcohol (D — N)
17B	0.2348	3.80	4.93	55.9	6.1	400	406.1	100	4.06	6.91	0.0995	0.688	2.79	8.37	1.01	47.5

*In these experiments, water was added to the solvent-ester solution to hydrolyze the ester. The water was then separated from the solvent and diluted to 50 ml. Then the 20 ml aliquots were taken and titrated.

TABLE II

MOLECULAR WEIGHTS AND DENSITIES

	Molecular Weight	Density
Methyl Alcohol	32.04	0.792
Ethyl Alcohol	46.07	0.789
N-Propyl Alcohol	60.09	0.804
Isopropyl Alcohol	60.09	0.789
N-Butyl Alcohol	74.12	0.810
Secondary Butyl Alcohol	74.12	0.808
Tertiary Butyl Alcohol	74.12	0.779
N-Amyl Alcohol	88.15	0.810
Primary Isoamyl Alcohol	88.15	0.813
Boric Acid	61.84	1.435

amounts of solvent. Accordingly, in Run No. 6 the amount of solvent was varied FROM about 400 to approximately 2100 milliliters of benzene per gram of boric acid. The results of Run No. 6 showed that the apparent degree of completion of the reaction was high with low ratios of benzene to acid. Then as the ratio was increased the per cent of boric acid reacted dropped to a minimum. But, with still higher benzene to acid ratios the per cent of reacted boric acid increased.

Table III lists the milliliters of benzene per gram of boric acid in various runs as well as the percentage of reacted boric acid and the equilibrium constant, all calculated from the data of Table I in the manner shown on pages 12 and 13. Figure I shows the minimum which occurs when the perdentage of reacted boric acid is plotted versus the ratio of benzene to boric acid.

The minimum which occurs and the trend toward a more complete reaction with increasing amounts of solvent is more apparent when the curve for a single series of runs is shown as in Figure II.

It might be thought that the increase in per cent of reacted boric acid which occurred with higher ratios was due only to a solvent effect of the benzene on the boric acid. From the data of Table III for Runs 6D and

TABLE III - EQUILIBRIUM CONSTANTS OF METHYL ALCOHOL

RUN NO.	GRAMS	BZ (ML.)	BZ/ACID (ML/GRAM)	% REACTED BORIC ACID	EQUILIBRIUM CONSTANT
1A	0.5013	95	190	91.6	5.26×10^{-1}
1B	0.5008	95	190	91.7	5.33×10^{-1}
2A	0.4949	100	202	92.6	5.02×10^{-1}
2B	0.5108	100	196	90.7	3.89×10^{-1}
3A	0.2593	100	386	90.5	1.52×10^{-1}
3B	0.2609	200	767	92.4	1.02×10^{-1}
4A	0.2584	100	387	91.6	2.34×10^{-1}
4B	0.2551	200	784	59.6	1.22×10^{-2}
4C	0.2505	300	1200	70.1	1.89×10^{-2}
5A	0.2513	200	796	64.8	1.64×10^{-2}
5B	0.2521	400	1590	66.4	2.26×10^{-2}
6A	0.2415	100	414	67.5	3.24×10^{-2}
6B	0.2436	150	616	85.5	8.34×10^{-2}
6C	0.2390	200	837	61.4	1.77×10^{-2}
6D	0.2410	400	1660	63.1	1.76×10^{-2}
6E	0.2401	500	2080	83.2	5.73×10^{-2}
7A	0.2485	200	805	57.7	1.56×10^{-2}
7B	0.1253	200	1600	58.1	1.28×10^{-2}
7C	0.1256	250	1990	70.0	2.59×10^{-2}
8A	0.2416	200	828	64.7	1.98×10^{-2}
8B	0.1221	200	1640	71.6	2.06×10^{-2}
8C	0.1257	250	1990	76.8	3.75×10^{-2}
9A	0.2438	400	1640	62.7	1.38×10^{-2}

(9A run at 5 °C. All others at 30 °C.)

1.52×10^{-2}

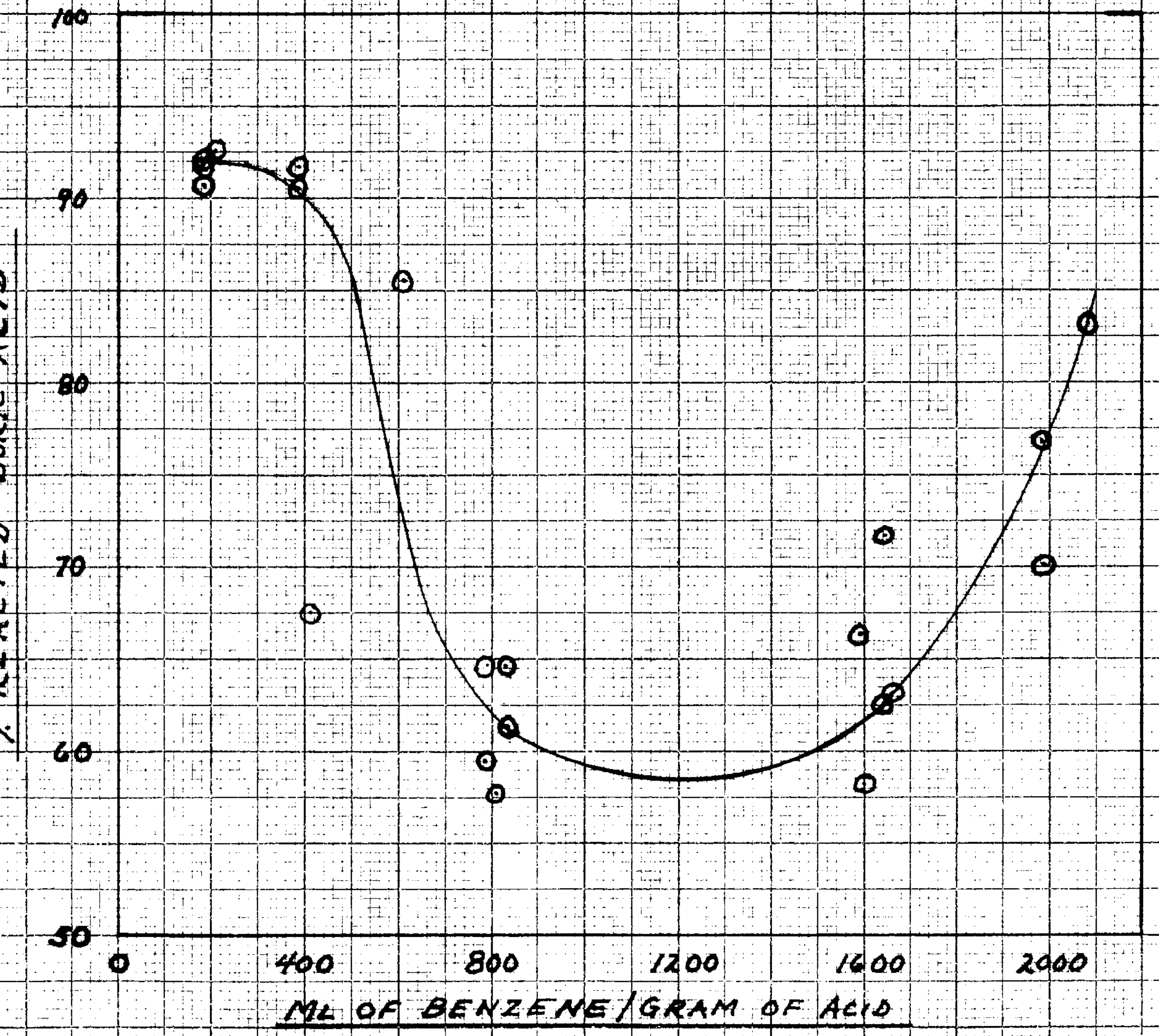

FIGURE I. THE EFFECT OF INCREASED AMOUNTS OF SOLVENT

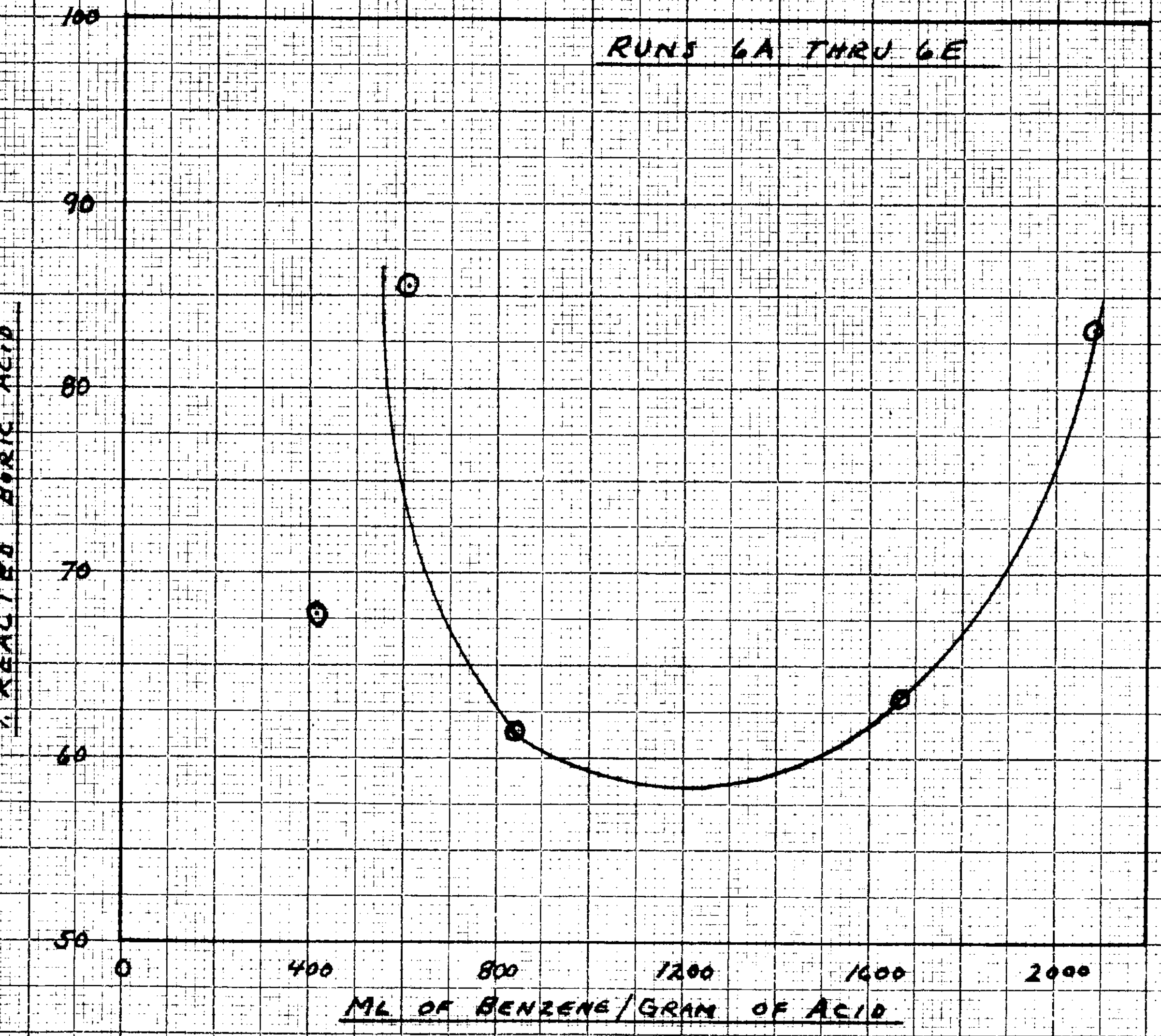

FIGURE II. THE EFFECT OF INCREASED AMOUNTS OF SOLVENT

6E, an increase in benzene of about 420 milliliters of benzene per gram of acid increased the per cent of boric acid reacted 20.1 per cent which is equal to 0.201 grams. However, the solubility of boric acid in benzene as determined by the method described on page 6 was only 0.0274 grams per liter or 0.0115 grams per 420 milliliters. The 0.0115 grams is 5.7 per cent of the the 0.202 grams. Thus, the increase in the amount of boric acid which reacted with increasing amounts of benzene must be largely due to something else besides a simple solvent effect of benzene on boric acid. However, no experiments were made to determine the exact cause for this increase.

Ethyl Alcohol:

The esterification of ethyl alcohol was accomplished in one of the early runs. It was necessary to use large amounts of this alcohol to dissolve the acid because heating was not used. Also, only relatively small amounts of solvent were used. In this case n-pentane was used because benzene did not give separation. This combination of large amounts of alcohol and small amounts of solvent gave a high value for the per cent of boric acid reacted (97.3%). The value for the equilibrium constant was also high (2.57×10^{-1}).

This early run was made before the effect of solvent was known. The use of heat to dissolve the acid so that lower amounts of alcohol could be used plus increased amounts of solvents would probably give better results.

Normal Propyl Alcohol:

The alcohol was heated to get complete solution of the acid with small amounts of alcohol. Refluxing would have been difficult because of the very small amounts of alcohol used so heating was accomplished by tightly stoppering the flask which contained the alcohol and acid. Then the lower part of the flask was immersed in hot water and shaken until the acid completely dissolved. Care was taken to keep the flask tightly stoppered so that alcohol could not escape.

Some preliminary experiments showed that petroleum ether gave better precipitation than benzene. Although about 800 milliliters of petroleum ether per gram of acid was used, it was calculated that 98.7 per cent of the acid reacted. Consequently, the equilibrium constant was high. Probably a series of runs would have to be made to determine the minimum equilibrium constant.

Isopropyl Alcohol:

Heating was used to dissolve the acid. The equilibrium constant was much lower than for the normal propyl alcohol as would be expected. When the amount of solvent was increased the equilibrium constant increased in the same manner as for methyl alcohol.

Normal Butyl Alcohol:

It was nedessary to heat the acid-alcohol mixture in order to get complete solution in relatively small amounts of alcohol. Like normal propyl alcohol, normal butyl alcohol showed a high percentage of reacted acid although 800 milliliters of benzene per gram of acid was used.

Secondary Butyl Alcohol:

Heating was employed to dissolve the acid. The behavior of this alcohol was as expected. The equilibrium constant was lower than the primary alcohol. When the amount of solvent was increased from 800 to 1600 milliliters of benzene per gram of acid, the amount of reacted boric acid increased from 54.2 to 56.9 per cent.

Tertiary Butyl Alcohol:

Heating was used to dissolve the acid. As would be predicted the equilibrium constant was very low, the lowest of all alcohols tested.

Normal Amyl Alcohol:

It was necessary to heat the alcohol-acid mixture in order to obtain complete solution with low amounts of alcohol. The results showed 67.0 per cent reacted boric acid which was lower than the value for n-butyl alcohol and higher than the value for secondary butyl alcohol. It would be expected that the primary alcohol with the longer chain would not go as far toward completion as the shorter chain alcohol, but would be more reactive in esterification than a shorter chain secondary alcohol.

Primary Isoamyl Alcohol:

The equilibrium constant was higher than that for n-amyl alcohol but lower than the value for n-butyl alcohol. This is as expected since the branched hydrocarbon chain would be expected to give properties intermediate between n-butyl and n-amyl alcohols.

1,3-Dichloro-2-propanol:

Heating was used to dissolve 0.1136 grams of acid in 8.87 grams of the alcohol. The standard procedure of extracting with benzene after equilibrium was reached and then hydrolyzing with water was followed. When the hydrolyzed sample was titrated, a permanent end point could not be attained until after adding many times the theoretical amount of base which would be required if the boric acid was completely reacted.

Next a sample of the alcohol was added to distilled water and phenolphthalein added. When base was added the mixture turned pink, but with continued shaking the

the color faded. More base was added and shaking continued until finally a permanent end point was obtained.

Because of the reaction of the alcohol with base, the equilibrium constant could not be determined.

<u>Calculations</u>:

The equilibrium constants and the percentages of reacted boric acid for all runs (calculated from the data in Table I) are listed in Tables III and IV.

TABLE IV

EQUILIBRIUM CONSTANTS FOR VARIOUS ALCOHOLS

RUN NO.	ALCOHOL	BZ/ACID (ML/GRAM)	% REACTED BORIC ACID	EQUILIBRIUM CONSTANT
10A	Ethyl	199	98.9	5.81×10^{-1}
10B	Ethyl	391	97.3	2.57×10^{-1}
11A	N-Propyl	871	98.7	7.11×10^{-1}
12A	Isopropyl	826	53.5	1.81×10^{-3}
12B	Isopropyl	1640	56.6	2.42×10^{-3}
13A	N-Butyl	814	92.7	8.75×10^{-2}
14A	Secondary Butyl	827	54.2	1.35×10^{-3}
14B	Secondary Butyl	1680	56.9	1.41×10^{-3}
15A	Tertiary Butyl	1720	19.7	9.48×10^{-8}
16A	N-Amyl	853	72.8	9.93×10^{-3}
16B	N-Amyl	1690	67.0	6.82×10^{-3}
17A	Primary Isoamyl	835	84.5	4.52×10^{-2}
17B	Primary Isoamyl	1700	73.4	1.51×10^{-2}

CONCLUSIONS

The equilibrium constants for the alcohols studied can be determined by the solvent technique described in this paper. The equilibrium is affected by the amount of solvent used. For a specific alcohol, a series of runs should be made to determine at what ratio of benzene to acid the equilibrium constant is at a minimum. This ratio probably represents the point at which precipitation of unreacted acid is greatest and the point at which the reaction is not driven further toward completion by an excess of solvent.

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