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THE HYDROLYSIS OF ALKYL BORATES

BY

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A THESIS
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ABSTRACT

The rate of hydrolysis of methyl, n-propyl, n-butyl and n-amyl borate as well as the equilibrium constant for the reaction involved were determined. An analytical procedure was used whereby the concentration of unhydrolysed ester at any definite time interval could be measured. It was found that the methyl borate was completely hydrolysed in less than one minute. The n-propyl compound was hydrolysed completely in about 80 minutes, whereas about two hours were needed for the n-butyl and n-amyl borates.

The following equilibrium constants were found: methyl borate, 15.81; n-propyl borate, 2.695; n-butyl borate, 2.034 and n-amyl borate, 1.805. ~~A plot of equilibrium constant versus number of carbon atoms in the borate seemed to indicate a linear relationship.~~

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING
NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: _____

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PREFACE

Previous work on organic borates was more or less confined to refined methods of preparation and determination of their structure. Here and there mention was made of their rapid reaction with water based on qualitative observation. The heats of formation for a few borates were calculated using the heat of hydrolysis.

The work done in this research project will be devoted to quantitatively determining the rate of hydrolysis as well as the equilibrium constant for the reaction for methyl, n-propyl, n-butyl and n-amyl borates. It would not have been possible to successfully carry out the project without the assistance and inspiration of my advisor, Professor J. A. Bradley of the Department of Chemical Engineering.

Grateful acknowledgement must also be made here for the cooperation and help of Professors T. J. Tully; J. A. Bishop and G. L. Ram, all of the Department of Chemistry.

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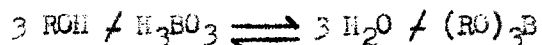
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CHAPTER I

INTRODUCTION

Relatively little work has been done on the organic esters of boric acid. Maurice Arquet¹ observed the loss of boric acid on standing in ethyl and methyl alcohols due to the formation of ester and its evaporation, and that the velocity of esterification was rapid. He noticed that 68% of a quantity of boric acid was lost overnight in a solution of 99.5% methyl alcohol solution and also a loss of 30% of the acid in absolute ethyl alcohol. He isolated the trimethyl ester and found it to boil at 56°C. and that it was readily affected even by the moisture in the air. The esterification took place at room temperature without the addition of mineral acids.

A general method for preparing alkyl esters of boric acid is cited by W. J. Bannister.² The alcohol is treated with boric acid and the resulting water formed is removed by vacuum distillation. The reaction may be represented as follows:



It was found most difficult to prepare the trimethyl and triethyl borates by this general method, due to the rapid rate of hydrolysis of the two borates in the water formed during the course of the reaction.

Special methods of preparing these borates are used.

An idea as to the structure of the esters was found through the calculation of the dipole moments of the n-propyl, isobutyl and sec-butyl borates in benzene at 25°C. from the dielectric constant and

¹Bull. soc. chim. 5, 3, 1422-4 (1936).

²J. R. Johnson and S. W. Tompkins, "Organic Syntheses" 13, 16 (1933).

density³. The small variation of polarisation with concentration showed the intermolecular action to be very small in the three esters studied, which was attributed to the effective screening of the dipoles from one another by the hydrocarbon groups. In cases of large intermolecular action there was present an imperfectly screened semipolar bond. Equations were derived for the calculation of the resultant moments of the trialkyl borates on the assumption of equal probabilities of all the positions of rotation around the B-O bonds. Strong steric repulsion between the alkyl groups in the borates lowered their moments to less than one half of the values calculated on the basis of free rotation as well as on that of the B-O bonds stiffened by double bond character. Later work ⁴ on the measurement of the parachors of several trialkyl borates confirmed their planar structure.

Comprehensive information on the physical constants and analyses of trialkyl borates may be found in a paper by A. Scattergood, W. H. Miller and J. Gammon, Jr.⁵ In that piece of work, twenty-one alcohols were allowed to react with boric acid according to the general method of Bannister. Eighteen borates were secured, sixteen of which had never before been obtained by this method. Ten of the borates were new and three were crystalline. Physical constants of the new borates and missing constants and analyses of previously known borates were determined. A qualitative attempt was made to determine the rate of

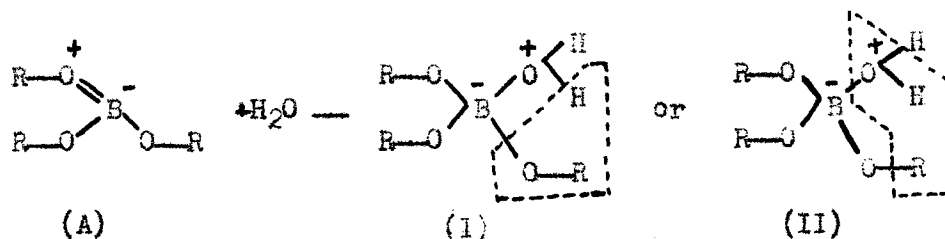
³G. L. Lewis and C. P. Smyth, *J. Am. Chem. Soc.* 62, 1529-33 (1940).

⁴B. A. Arbuzov and V. S. Vinogradova, *Compt. rend. acad. sci. U.R.S.S.* 55, 411-13 (1947)(in French).

⁵*J. Am. Chem. Soc.* 67, 2150-2 (1945).

hydrolysis of the trialkyl borates. This was done by shaking one millilitre of each ester with three to five drops of water at room temperature. The time needed for boric acid to crystallise was noted. Another qualitative observation of the rate of hydrolysis was also made during the analysis for boron. On the basis of the results found, the following generalisations were made: the n-alkyl borates were rapidly hydrolysed and the branched chain primary alkyl borates hydrolysed at rates varying from those of the n-alkyl borates to the unusually slow rate found for the tri-neopentyl borate; the secondary alkyl borates were more slowly hydrolysed than the n-alkyl borates, branching of the chain having the same effect as with the primary alkyl borates. Of the borates studied, the most resistant to hydrolysis was found to be tris-(diisopropylcarbinyl) borate, which defied all attempts at hydrolysis even in an alkaline solution at 100°C.

The paper also offered a possible explanation as to the dependence of the rate of hydrolysis upon the branching of the alkyl group by assuming the rate-determining step to be the addition of a molecule of water. Using the structure (A) of the borate as suggested by the work of Lewis and Smyth (ref. 3), the hydrolysis was pictured as follows:



Since the boron atom is here pictured as lying at the centre of an equilateral triangle with the oxygen atoms at the three apices, large compact alkyl groups would be expected to hinder the approach of the

water molecule to the boron atom, thus resulting in a slow rate of hydrolysis with such borates.

The fact that the n-alkyl borates were hydrolysed rapidly even in N HCl seemed to discount the possibility that the addition of OH^- was the first step in the hydrolysis by water, since the rate of such an addition would presumably be decreased by an increase in hydrogen ion concentration. The loss of a molecule of alcohol from the borate-water adduct was suggested as proceeding by either mechanisms (I) or (II). In mechanism (II), the C-O bond is depicted as breaking, whereas in formulation (I) the bond remains intact. Since Whitmore had shown that when a bond between a neopentyl radical and the rest of the molecule was broken, rearrangement of the neopentyl radical resulted, this criterion was used to determine which of the two mechanisms was true. Neopentyl borate was prepared and subjected to hydrolysis. Neopentyl alcohol was recovered unchanged, showing that the C-O bond was unbroken and thus establishing mechanism (I) as the one by which the hydrolysis proceeded. By contrast, the esters of sulfuric acid are known to hydrolyse by mechanism (II).

Mention is also made of the hydrolysis of trialkyl borates in connection with the determination of the heats of formation of methyl, ethyl, n-propyl and n-butyl borates.⁶ In this work, the heat of hydrolysis for the four borates was measured. With this information and also a knowledge of the heats of formation for water, boric acid and the four corresponding alcohols, it was possible to calculate the heats

⁶Charnley, Skinner and Smith, J. Am. Chem. Soc. 74, 2288-91 (1952)

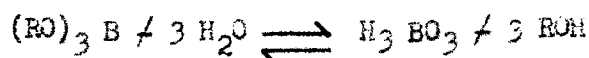
of formation of the esters. The following results were found:

<u>ester</u>	<u>heat of hydrolysis</u> <u>(kcal. / mole)</u>	<u>heat of formation</u> <u>(kcal. / mole)</u>
methyl	-4.615 \pm 0.05	-224.0 \pm 0.8
ethyl	-5.380 \pm 0.06	-251.3 \pm 1.0
n-propyl	-4.600 \pm 0.06	-272.7 \pm 1.4
n-butyl	-4.660 \pm 0.06	-291.9 \pm 1.5

CHAPTER II

DISCUSSION OF THE PROBLEM AND THE METHODS USED FOR ITS SOLUTION

It will be the purpose of this work to determine the rate of hydrolysis of methyl, n-propyl, n-butyl and n-amyl borate. The reaction involved is that between the ester and water to form boric acid and the corresponding alcohol, as follows:



The following methods for the solution of the problem were suggested: (1) determine the change in volume produced, if any, by using a dilatometre; (2) measure the rate of change of boric acid concentration as a function of the decrease of pH; (3) remove all substances with the exception of boric acid by low-temperature vacuum sublimation; (4) determine the amount of unhydrolysed ester after definite time intervals by titrating against standard alkali.

Method (3) was carried out as follows: a weighed sample of the borate was added to a weighed 200 ml. bomb type flask and the vessel with contents allowed to come to constant temperature (30°C.). A known amount of water was then added to the flask, and after a measured time interval the flask was plunged into an acetone-dry-ice mixture (ca. 60-80°C. below zero). Theoretically the hydrolysis would be completely stopped at this low temperature. As soon as the flask was in contact with the freezing mixture, all of the contents solidified and the vessel was immediately connected to a good vacuum pump and evacuated for 12-24 hours. It was believed that by this treatment, everything in the flask would be removed by sublimation with the exception of the boric acid formed during the hydrolysis. Much difficulty was encountered in keeping the freezing mixture replenished with

✓ round-bottom

in a thermostat
thermostat

✓

dry ice over the long periods of time needed to sublime even small amounts of liquid. A manifold was constructed which could be used to evacuate twelve flasks at a time, but unfortunately no good pressure-measuring gauge was available for testing the efficiency of the pump and lack of time prevented further work on this method.

Method (4) was carried out as follows: A 30°C. constant temperature bath was set up and molal solutions of the ester in acetone and water in acetone were prepared. These solutions were allowed to come to constant temperature and then mixed at a recorded time and again allowed to come to constant temperature in the bath. After definite time intervals a sample of the mixture was pipetted into a measured volume of benzene contained in a 600 ml. beaker. Theoretically the benzene would serve to stop the hydrolysis by dissolving ~~off~~ the unhydrolysed ester and the alcohol formed during the hydrolysis. The boric acid formed and any excess water would not be miscible with the benzene and would therefore appear as a dispersed white cloud. It then became necessary to separate the cloud from the rest of the benzene solution. This was done by adding some filter-cell, / stirring, allowing to settle and filtering off the cell, / which presumably had absorbed the boric acid. A clear filtrate resulted. An aliquot of the clear filtrate was pipetted into an Erlenmeyer flask, excess water added, some mannitol and a few drops of phenolphthalein indicator also added and the mixture titrated against standardised sodium hydroxide to a permanent pink end-point. A simple calculation could be made to determine the amount of unhydrolysed ester at this point. Equilibrium could be assumed after 3 or 4 consecutive readings on the burette were the same

sp ?
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or very nearly so. When the data was plotted (ie. time versus concentration of unhydrolysed ester in a definite volume), the portions of the curve where equilibrium was realized were linear. By averaging the linear portions of the curves that fell close together it was possible to calculate the equilibrium constant for the reaction (~~see sample calculations, appendix~~). As the work proceeded the following refinements were found necessary; (1) since the borates hydrolysed at too rapid a rate at 30°C., the reaction was slowed down by making the determinations at 0°C.; (2) it was easier to prepare molar solutions of the ester and water in acetone instead of molar solutions; (3) the differences in volume of standard alkali ^{used in the various borates} ~~from one borate to another~~ were so small that a very accurate microburette had to be used; (4) the cloud that formed when the hydrolysed sample was dropped into benzene could be removed by ordinary gravity filtration without the need for using filter-cell; (5) large changes in concentration of the hydrolysed ester-benzene mixture occurred due to evaporation losses in the open beaker, so subsequently the mixture was kept in a tightly rubber-stoppered Erlenmeyer flask. The final procedure that was used will be described in detail in the next portion of the thesis.

CHAPTER III

FINAL PROCEDURE USED

The alkyl borates that were used were the methyl, n-propyl, n-butyl and n-amyl compounds. Solutions were prepared containing one hundredth ^a of a mole of the ester per one hundred millilitres of acetone solution and three hundredths ^b of a mole of water per one hundred millilitres of acetone solution in a 100 ml. volumetric flask. The two solutions were placed in an ice bath and allowed to come to 0°C. At a definite time the solutions were mixed together in a 250 ml. volumetric flask which was also kept in an ice bath. After recorded time intervals a 25 ml. sample was drawn off with a pipette and dropped into 100 ml. of anhydrous benzene. The benzene was contained in a tightly stoppered 250 ml. Erlenmeyer flask and the reaction flask was itself covered with parafilm to prevent evaporation. A cloud was formed at this point due to the insolubility in benzene of the boric acid formed during the hydrolysis and the unreacted water. After allowing the cloud to stand for a while, it was removed by ordinary gravity filtration, leaving a clear filtrate. A 25 ml. aliquot of the filtrate was then pipetted into another 250 ml. Erlenmeyer flask, water was added plus some phenolphthalein indicator and mannitol. Using a microburette, the mixture was titrated with standard sodium hydroxide solution to a permanent pink end-point. The volume of alkali used was recorded, this being a measure of the amount of unhydrolysed ester at the observed time.

don acetone ?

	<u>Reacting Solutions</u>	<u>Sample</u>
<u>On mixing:</u>	0.1 molar ester	25 ml
0.05 mole ester	0.3 molar water	dropped into
0.15 mole water		100 ml benzene
		25 ml of this = Vec base
		of normality, N

TABLE 1

METHYL BORATE

<u>Run Number</u>	<u>Date</u>	<u>Time (min.)</u>	<u>Moles of Unhydrolysed Ester in 25 ml. of Acetone Solution</u>
1	3/15/54	1	4.040
		2	4.028
		5	4.012
		10	3.841
		15	3.755
		30	3.813
		60	3.925
2	3/15/54	1	4.381
		15	4.467
		30	4.723
		45	4.210
		60	4.154
		75	4.524
		90	4.210
3	3/16/54	15	4.666
		30	4.609
		45	4.494
		60	4.494
		90	4.494
		105	4.494
4	3/22/54	1	4.438
		2	4.438
		5	4.381
		10	4.353
		25	4.268
		45	4.268
		60	4.268
5	3/22/54	1	4.097
		2	4.210
		5	4.210
		15	4.210
		20	4.154
		30	4.210
		60	4.210
6	3/31/54	1	4.135
		2	4.135
		5	4.135
		10	4.135
		15	4.135
		30	4.135

<u>Run Number</u>	<u>Date</u>	<u>Time (min.)</u>	<u>Moles of Unhydrolysed Ester in 25 ml. of Acetone Solution</u>
7	4/22/54	1	4.054
		5	4.082
		10	4.082
		15	4.054
		20	4.028
		25	4.082
		30	4.082

Figure 1- Plots showing the relationship between time of hydrolysis and moles of unhydrolysed Methyl Borate in 25 ml. of acetone solution.

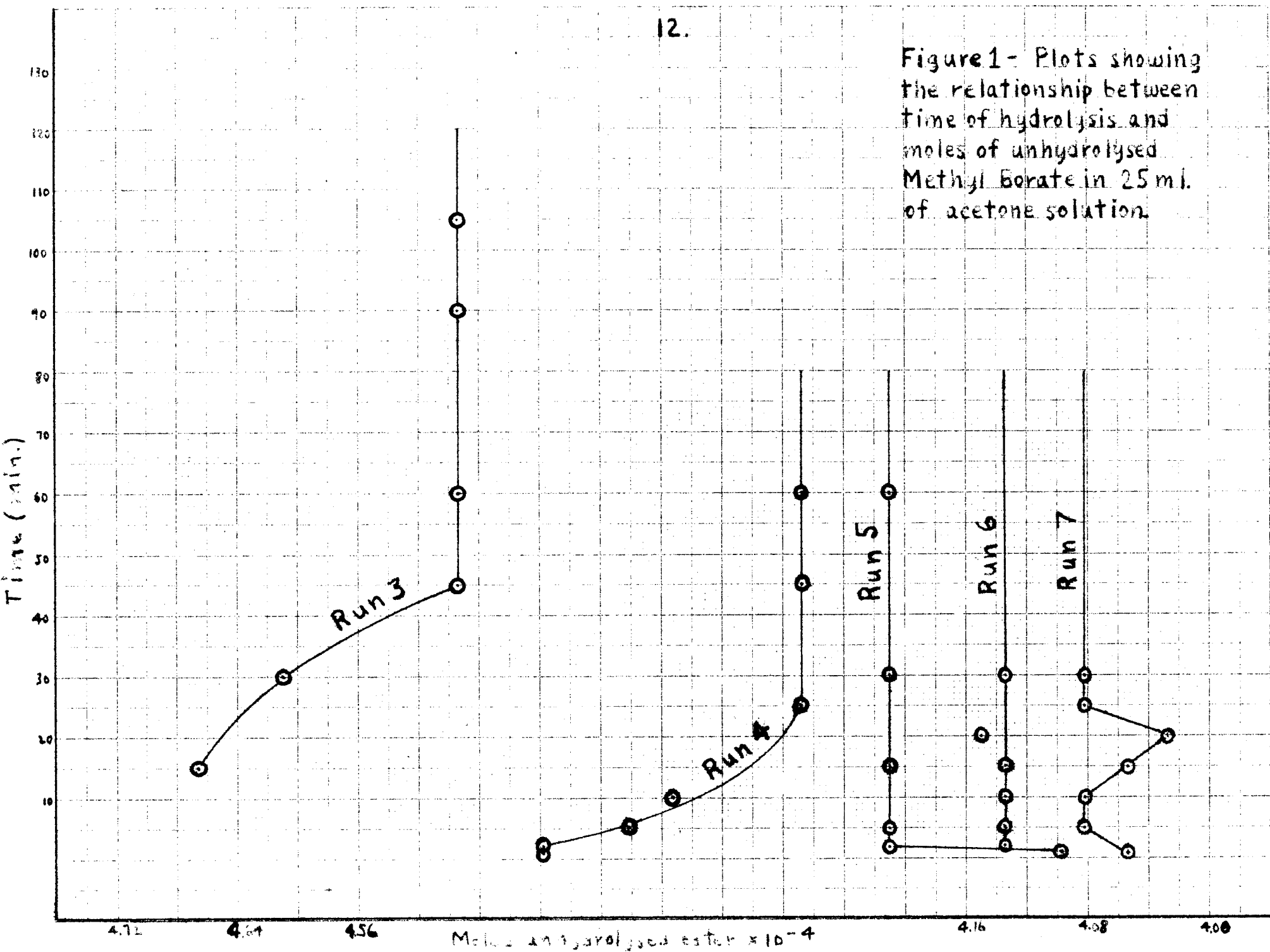


TABLE 2

n-PROPYL BORATE

<u>Run Number</u>	<u>Date</u>	<u>Time (min.)</u>	<u>Moles of Unhydrolysed Ester in 25 ml. of Acetone Solution</u>
1	3/25/54	45	7.396
		60	6.969
2	3/26/54	50	8.478
		60	7.226
		70	7.055
		80	6.630
		90	6.543
3	3/27/54	60	7.652
		90	6.543
		120	5.632
		150	5.576
		180	5.632
		210	5.661
4	3/29/54	60	6.430
		120	5.576
		180	5.405
		240	5.376
		270	5.376
5	4/1/54	60	6.311
		70	5.720
		80	5.343
		160	5.316
		190	5.316
		300	5.343
6	4/2/54	60	6.040
		75	5.693
		90	5.611
		105	5.558
		120	5.585
		135	5.585
		150	5.585

x 10⁻⁴

Figure 2 - Plots showing the relationship between time of hydrolysis and moles of unhydrolysed n-Propyl Borate in 25 ml. of acetone solution.

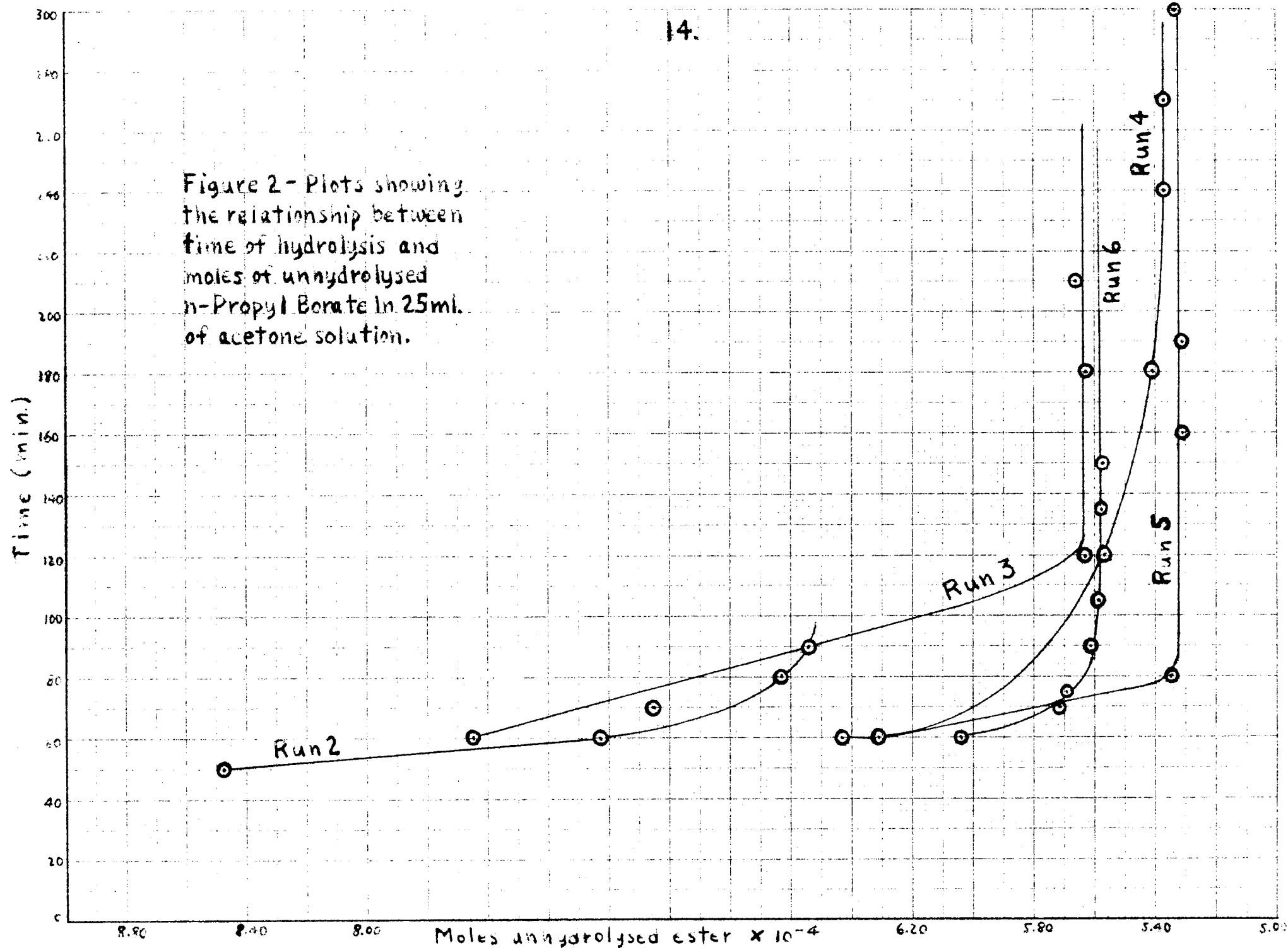


TABLE 3

n-BUTYL BORATE

<u>Run Number</u>	<u>Date</u>	<u>Time (min.)</u>	<u>Moles of Unhydrolysed Ester in 25 ml. of Acetone Solution</u>
1	4/5/54	60	5.853
		75	5.828
		90	5.853
		105	5.853
		120	5.746
		135	5.720
		150	5.720
2	4/6/54	75	9.802
		90	8.486
		105	8.459
3	4/8/54	60	9.397
		75	8.700
		90	8.269
		105	7.330
		210	6.498
		315	5.853
		330	5.828
4	4/9/54	60	9.963
		75	9.315
		90	8.486
		105	7.949
		120	7.679
		135	7.303
		150	7.249
5	4/10/54	60	9.397
		90	8.726
		120	7.036
		150	6.606
		180	6.552
		210	6.311
		240	6.203
6	4/24/54	60	6.122
		90	5.987
		120	5.666
		150	5.531
		180	5.424
		210	5.370
		240	5.370

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<u>Run Number</u>	<u>Date</u>	<u>Time (min.)</u>	<u>Moles of Unhydrolysed Ester in 25 ml. of Acetone Solution</u>
7	4/26/34	90	6.176
		165	5.585
		195	5.343
		220	5.262
		250	5.289
		280	5.262
		300	5.262

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Figure 3- Plots showing the relationship between time of hydrolysis and moles of unhydrolysed n-Butyl borate in 25 ml. of acetone solution.

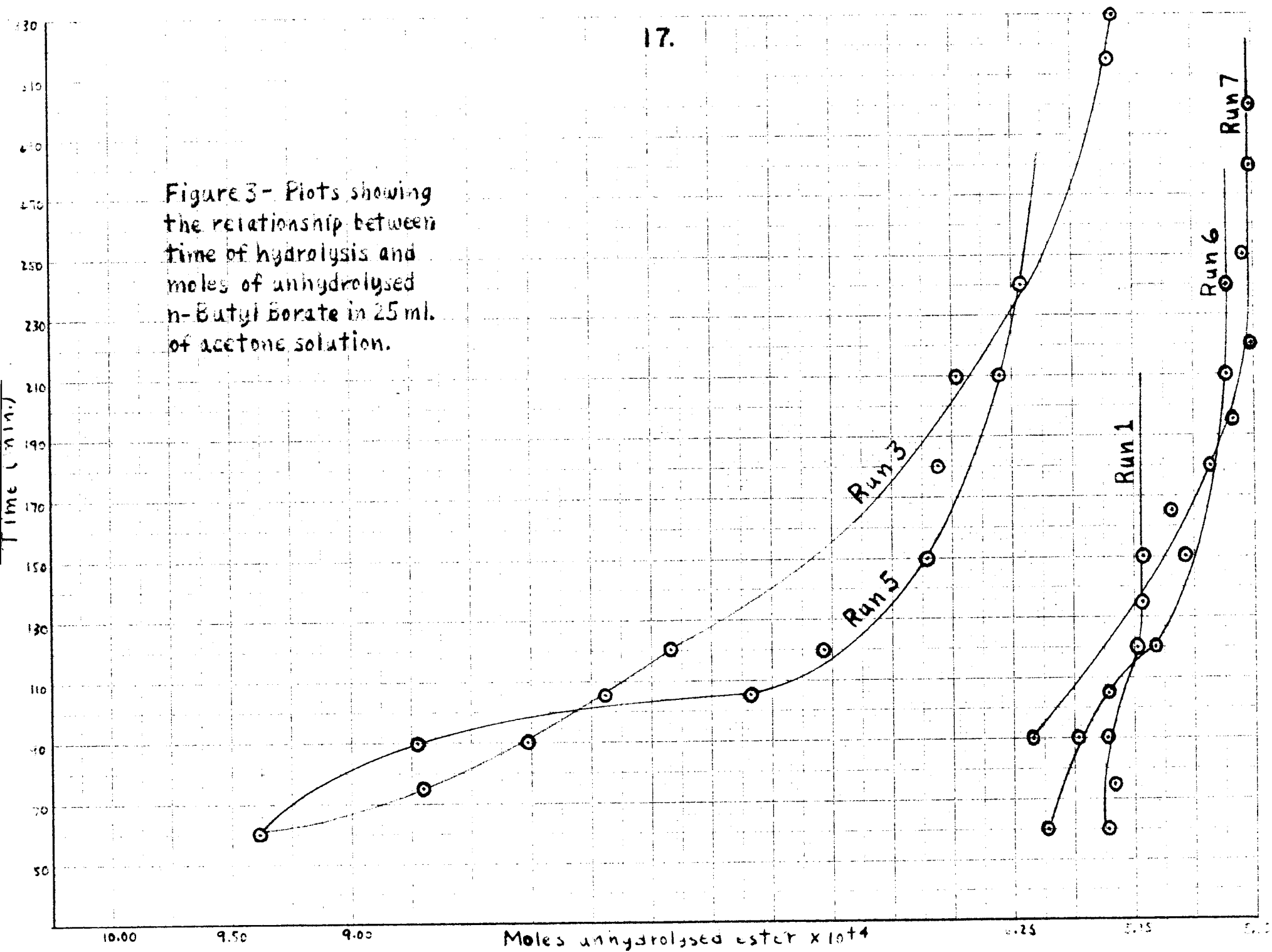
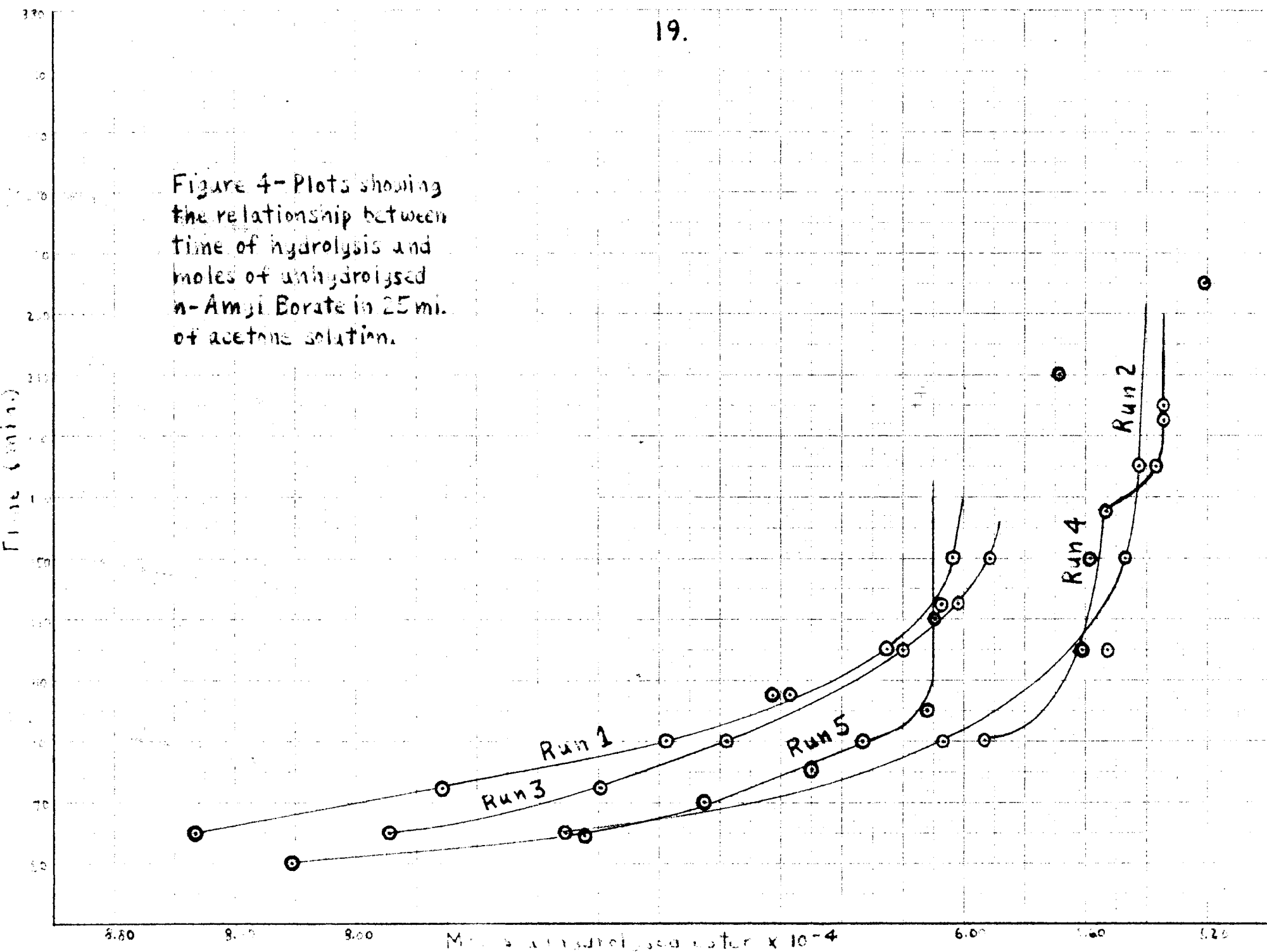


TABLE 4

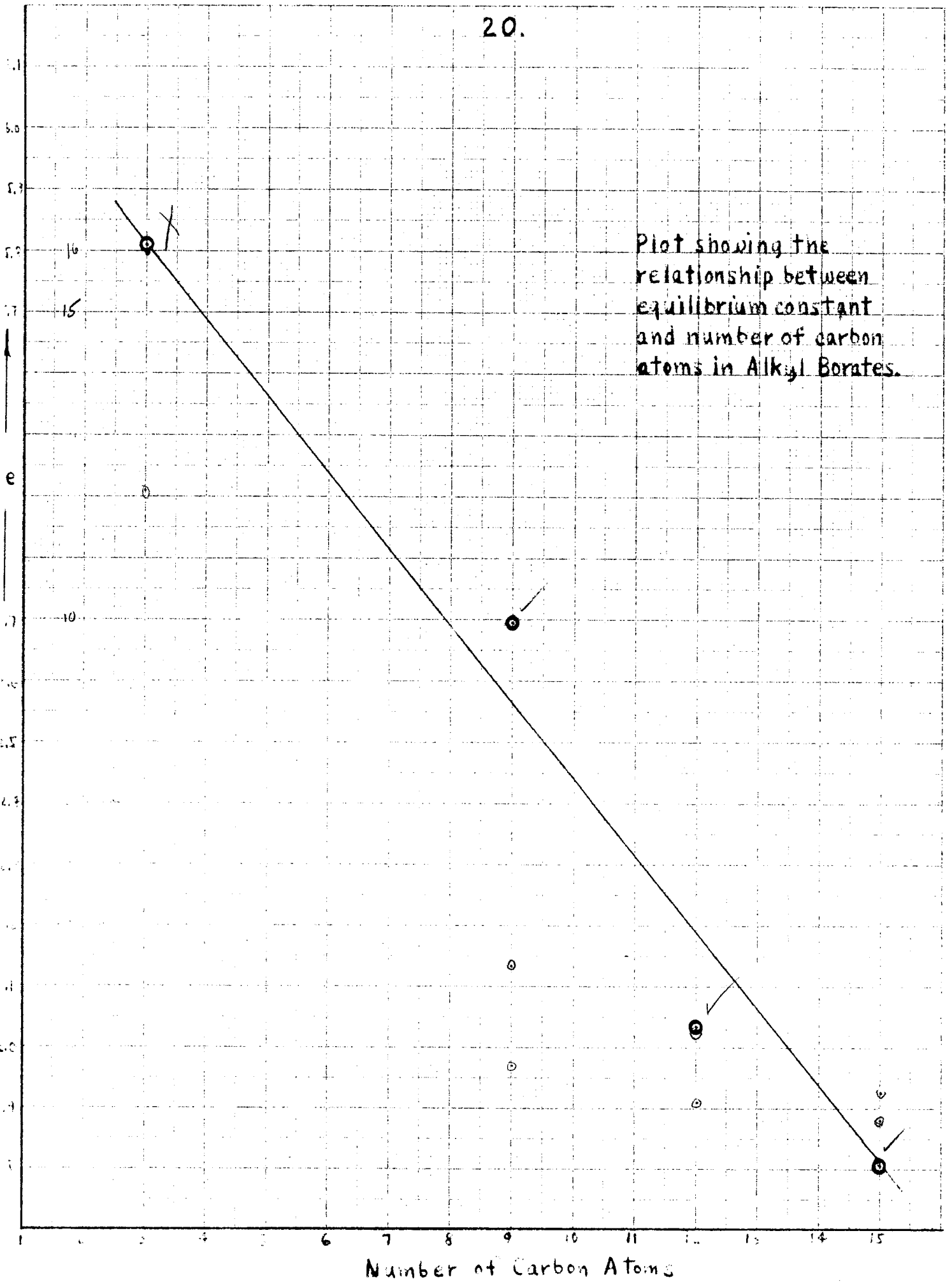
n-AMYL BORATE

<u>Run Number</u>	<u>Date</u>	<u>Time(min.)</u>	<u>Moles of Unhydrolysed Ester in 25 ml. of Acetone Solution</u>
1	4/13/54	60	8.539
		75	7.705
		90	6.981
		105	6.631
		120	6.258
		135	6.068
		150	6.040
2	4/14/54	60	7.303
		90	6.068
		120	5.531
		150	5.478
		180	5.424
		210	5.693
		240	5.210
3	4/19/54	60	7.894
		75	7.196
		90	6.794
		105	6.579
		120	6.203
		135	6.015
		150	5.907
4	4/20/54	90	5.933
		120	5.611
		150	5.585
		165	5.531
		180	5.370
		195	5.343
		200	5.343
5	4/23/54	50	8.217
		60	7.249
		70	6.847
		80	6.498
		90	6.337
		100	6.122
		130	6.095

Figure 4- Plots showing the relationship between time of hydrolysis and moles of unhydrolysed n-Amyl Borate in 25 ml. of acetone solution.



20.



CHAPTER IV

CONCLUSIONS

The rates of hydrolysis of four alkyl borates were determined. It was found that methyl borate was completely hydrolysed in less than one minute. The n-propyl compound came to equilibrium in about eighty minutes, whereas approximately two hours were observed for the n-butyl and n-amyl borates. A fifth borate was available, the n-lauryl compound, but attempts to determine its rate of hydrolysis were unsuccessful due to the fact that it froze out of solution at the working temperature of 0°C.

Using a simple calculation (see appendix) it was possible to calculate the equilibrium constant for each of the borates. The average equilibrium concentration of unhydrolysed ester in 25 ml. of acetone solution was picked off from the linear portion of the curve showing the relationship between concentration and time of hydrolysis, (figs. 1, 2, 3 and 4). The following values for the average equilibrium concentration of unhydrolysed ester (mole per 25 ml. acetone solution) and the corresponding value of ml. of 0.1138N NaOH were found: methyl borate, 4.175×10^{-4} , 0.7336; n-propyl borate, 5.481×10^{-4} , 0.9634; n-butyl borate, 5.697×10^{-4} , 1.001; n-amyl borate, 5.791×10^{-4} , 1.018 ml.

Using these values, the following equilibrium constants were calculated: methyl borate, 15.81; n-propyl borate, 2.695; n-butyl borate 2.034 and n-amyl borate, 1.805.

A plot of equilibrium constant versus number of carbon atoms in the ester (fig. 5) seems to indicate a linear relationship between the two.

CHAPTER V

RECOMMENDATIONS

The successful culmination of this research project was dependent on the method of analysis used. Although every precaution was taken in preventing concentration changes due to evaporation of the solvent and a good microburette used, the correlation between the various runs was not very good. If time permitted the taking of more runs, the curves produced for the n-butyl and n-amyl borates could have been more symmetrical (figs. 3 and 4). It is felt, however, that the relative velocity of reaction as a function of increasing molecular weight is in conformance with results previously predicted.

It would have been interesting to attack the problem using changes in volume as measured by a good dilatometre. This probably would have been the simplest of the four methods suggested (see page 6, Chapt. II). The method of observing the drop in pH as a function of increasing amounts of boric acid formed during the hydrolysis would probably have been quite difficult to perform. A set of standards would have to be made up containing known amounts of boric acid in definite amounts of acetone and their pH measured. The unknowns could then be compared with the standards.

The method of low-temperature vacuum sublimation could no doubt have been used to solve the problem, but lack of time and the difficulties encountered in physically setting it up and maintaining it through the long periods of evacuation prevented its adoption.

There is little doubt in the authors mind that the relationship between K_0 and number of carbon atoms in the ester is linear. If a

few more borates had been available this relationship could have definitely been proven. The relationship referred to here involves only straight chain normal borates.

As further work the following suggestions may be made: (1) Observe the rate of hydrolysis of branched chain alkyl borates as a function of molecular weight and calculate the K_m for the reaction. (2) Carry out the reaction at constant temperatures other than 0°C.

APPENDIX

SAMPLE CALCULATIONS

Calculation of the concentration of unhydrolysed ester after a definite time interval: Run 6, (4/2/54), n-propyl borate, after 150 min. hydrolysis. A volume of 1.040 ml. NaOH (0.1074N) was required.

$$\left(\frac{125}{25} \right) (1.040 \text{ ml. NaOH}) \left(\frac{0.1074 \text{ meq. NaOH}}{\text{ml. NaOH}} \right) \left(\frac{\text{meq. NaOH}}{1000 \text{ meq. NaOH}} \right)$$

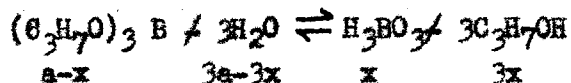
$$\left(\frac{\text{mole n-propyl borate}}{\text{eq. NaOH}} \right) = 0.0005585 \text{ mole n-propyl borate in 25 ml. sample}$$

Calculation of equilibrium constants: For n-propyl borate, the average equilibrium concentration of unhydrolysed ester was found using the curves for runs 3, 4, 5 and 6 (from the portions of the curves that were straight lines). This value for a 25 ml sample was 5.481×10^{-4} mole. (5.481×10^{-4}) = 0.021924 mole/litre. The initial concentrations would be,

$$0.01 \left(\frac{1000}{200} \right) = 0.05 \text{ mole/litre of ester.}$$

$$0.05 (3) = 0.15 \text{ mole/litre of water.}$$

The reaction involved is the following:



$$K_e = \frac{[\text{H}_3\text{BO}_3][\text{C}_3\text{H}_7\text{OH}]^3}{[\text{H}_2\text{O}]^3[(\text{C}_3\text{H}_7\text{O})_3\text{B}]} = \frac{(x)(3x)^3}{(a-x)(3a-3x)^3}$$

$$= \frac{x^4}{(a-x)^4} = \left(\frac{x}{a-x} \right)^4$$

x = amount of ester used = amount of H_3BO_3 formed at equilibrium.

$a-x = 0.021924$ mole ester at equilibrium.

$x = 0.05 - 0.021924 = 0.02808$ mole H_3BO_3 at equilibrium.

$$K_e = \left(\frac{0.02808}{0.02192} \right)^4$$

$$= 2.695$$