

SOLVOLYSIS KINETICS OF THE  
METHYLAMINEBORANES

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## CHAPTER I

### INTRODUCTION

By virtue of an available empty p-orbital on the boron atom, trivalent boron compounds can accept an electron pair from various donor species. Addition compounds between boranes and a variety of Lewis bases have been known for many years, but there is little known about the change in activity with the change in the donor species.

Perhaps the best characterized of these adducts are the amineboranes, and there are several general review articles on the B-N bond.<sup>6,25,28,63</sup> The first methylamineborane to be characterized was trimethylamineborane, which was synthesized in 1937 by Burg and Schlesinger.<sup>13</sup> The compound was originally prepared by a displacement reaction between borine carbonyl and the amine, and subsequently by the direct reaction of the amine and diborane. Trimethylamineborane has also been prepared from hydrogen and trimethylaminetrialkylboranes.<sup>41</sup> The variety of melting points assigned to monomethylamineborane was attributed to small amounts of impurity incurred in the preparation, but Parry *et al.*<sup>50</sup> prepared the pure compound by condensing the amine onto a diborane-tetrahydrofuran solution at  $-75^{\circ}\text{C}$ . Methylamineboranes have also been prepared from the reaction of trimethylamine borontrifluoride and lithium borohydride;<sup>35</sup> from triphenoxyborate, aluminum metal, and hydrogen;<sup>2</sup> and from the electrolysis of sodium borohydride in liquid ammonia and in liquid amines.<sup>64</sup> However, the most convenient route to the methylamineboranes results from the reaction of the methylamine hydrochlorides with

sodium or lithium borohydride in diethyl ether or diglyme<sup>14,22,46,60</sup> according to the overall equation



All of the methylamineboranes are white crystalline solids and show an increasing resistance to water hydrolysis from monomethylamineborane to trimethylamineborane. Mono-, di-, and trimethylamineborane melt at 56°, 37°, and 94°C.,<sup>46</sup> respectively. Trimethylamineborane can be heated for several hours above 100°C. without a detectable change in its physical properties. However, dimethylamineborane forms the amino-borane ( $\text{RCH}_3\text{NBH}_2$ ) when heated,<sup>12</sup> and monomethylamineborane can eventually form N,N,N-trimethylborazine.<sup>68</sup>

Some of the physical-chemical properties of the methylamineboranes which have been determined include the dipole moments;<sup>4,46,50</sup> electron diffraction<sup>3</sup> and x-ray patterns;<sup>26</sup> molecular weight measurements in liquid ammonia,<sup>49</sup> benzene, water, and dioxane;<sup>46</sup> vapor pressure measurements and heats of vaporization;<sup>50</sup> heats of formation from the gaseous amines and diborane;<sup>44</sup> B<sup>11</sup> chemical shifts<sup>53</sup> and other nuclear magnetic resonance studies;<sup>23,50</sup> and infrared spectra, Raman spectra, and B-N bond force constants.<sup>31,32,38,50,55,56</sup>

All of the methylamineboranes react with halogen acids, except HF, to form the monohalogen amineborane according to the overall equation



where X = Cl, Br, or I, and R = CH<sub>3</sub> or H.<sup>48</sup> The methylamineboranes can be used to prepare lithium borohydride by reaction with lithium hydride.<sup>41</sup> The only methylamineborane which has been utilized for hydroboration is

trimethylamineborane,<sup>1,37</sup> and an extensive study of the hydroborating powers of amineboranes has not been undertaken. The borohydride ion and boranes will reduce the iodate ion in aqueous solutions, and this reaction has been made the basis of an analytical procedure to determine the concentrations of amineborane solutions.<sup>42</sup> Monomethylamineborane and other monoalkylamineboranes have been widely used to prepare trialkyl-N-substituted borazines.<sup>5,22,60,66</sup>

Relatively little research has been done, however, on the solution kinetics of the methylamineboranes. Kelly, Marchelli, and Giusto<sup>39</sup> calculated the rate constants for the acid hydrolysis of several amineboranes at room temperature but did not determine the activation energies. Ryschkewitsch<sup>57</sup> made an extensive study of the acid hydrolysis of trimethylamineborane, in which the author determined the activation energy, the ionic strength dependences, and a logical mechanism for the reaction. A report of some of the results of this work has appeared in the literature.<sup>30</sup> In a study of the hydrolysis by DCl, Davis *et al.*<sup>17</sup> found a rapid and quantitative exchange of the boron hydrogens in trimethylamineborane with D<sub>2</sub>O. A large amount of research has also been done on the aqueous hydrolysis of sodium borohydride.<sup>9,16,18,19,20,36,52,62</sup> Kinetics in the gas phase have been studied for the combination of amines and borontrifluoride,<sup>10,24,27,40</sup> but the aqueous hydrolysis has received relatively little attention.<sup>59</sup> The gas phase kinetic studies of other B-N compounds include Brumberger's<sup>11</sup> investigation of the relative reaction rates of diborane with mono- and trimethylamine, and a detailed work<sup>29</sup> on the mechanism of the reaction between diborane and trimethylamine.

Intuitively, one could propose that the solvolysis kinetics of the methylamineboranes involve a dissociation of the adduct into an amine and a borane fragment, attack of an acidic species on a B-H bond, or displacement of an amine from the adduct molecule by the attacking species. As previously noted, solvolysis mechanisms have been proposed, and one of the purposes of this investigation was to test these mechanisms, and possibly elucidate in some detail, a mechanism for the hydrolysis of the methylamineboranes. At the same time, the effect of substituting a methyl group for a hydrogen on the nitrogen atom of the adduct could be observed from a study of the activation energies. It was also proposed to determine the heats of solution of the methylamineboranes in order to calculate the heats of hydration of the compounds. It was thought that a correlation between the trend in activation energies and heats of hydration would be evident. In the hydrolysis of diborane, intermediates of the type  $H_3B \cdot H_2O$  have been proposed,<sup>61,67</sup> and this intermediate was also suspected to be present in an acid hydrolysis of the methylamineboranes. However, the reaction of diborane with water is very rapid and did not lend itself to study by our analytical methods. It was therefore proposed to undertake a study of the acid hydrolysis of trimethylamineborane in 1-propanol-water solutions to see if intermediates of the type  $R_3NBH_2(OC_3H_7)$  and  $R_3NBH(OC_3H_7)_2$  could be detected, and to extend the work of Ryschkewitsch and Birnbaum<sup>58</sup> on the kinetics of substituted pyridineboranes in 1-propanol and water. We also wanted to observe the differences in activation energies in the mixed solvent and in water. It was thought that from the observed trends in activation energies in these two media, we could predict the effects of various

solvent changes on the activation energies. Finally, a brief study of the association of monomethylamineborane in benzene was undertaken in order to investigate a possible error in the literature.

CHAPTER II  
EXPERIMENTAL

A. Materials

Cylinder gases. All of the cylinder gases used were obtained from the Matheson Company.

Benzene. Reagent grade benzene was distilled from  $\text{CaH}_2$  and stored over "dry-Na" or  $\text{CaH}_2$ .

1-Propanol. In order to rid the alcohol of any impurities which might react with the amineboranes, it was treated with trimethylamineborane before distillation. Reagent grade 1-propanol was made approximately 0.02 M in trimethylamineborane and approximately 1 M in HCl, and this solution was stored until gas evolution ceased--about 24 hours. The solution was then neutralized with NaOH, and enough distilled water was added so that the 1-propanol to water ratio did not exceed four. The solution was then distilled, and the fraction boiling at  $87.7^\circ\text{C}$ . was collected. The fraction collected at this temperature was the 1-propanol-water azeotrope, containing 28.9 per cent water and 71.7 per cent 1-propanol by weight.<sup>43</sup>

The alcohol was also distilled from reagent grade 1-propanol which was pre-dried with  $\text{CaSO}_4$ . The fraction collected boiled at  $97-98^\circ\text{C}$ .

Trimethylamineborane. Samples of trimethylamineborane from Callery Chemical Company were sublimed at  $0^\circ\text{C}$ . onto a cold finger at  $-78^\circ\text{C}$ . The pure compound melts at  $94^\circ\text{C}$ .,<sup>46</sup> and the purity exceeded 98 per cent as determined by reducing equivalents.

Dimethylamineborane. Samples of dimethylamineborane from Callery Chemical Company and from Chemical Procurement Laboratories were recrystallized from n-hexane and diethyl ether. The pure compound melts at 37°C.,<sup>46</sup> and the purity exceeded 95 per cent as determined by reducing equivalents.

Monomethylamineborane. Several methods of preparing monomethylamineborane were attempted. No product could be obtained by bubbling diborane through methylamine at -78°C. The method employed by Parry et al.<sup>50</sup> of condensing the amine onto a solution containing diborane and tetrahydrofuran at -78°C. proved inadequate for the preparation of 1 to 10 gm. lots. Larger, pure samples were obtained by a modified method of Nöth and Beyer,<sup>46</sup> using lithium borohydride and monomethylamine hydrochloride.

To prepare the hydrochloride, a 500 ml. three-necked round bottom flask, containing 300 ml. of diethyl ether and equipped with a teflon-coated magnetic stirring bar, was surrounded by an ice bath. The flask was fitted with two gas delivery tubes which extended below the surface of the ether, and with a simple mercury bubbler to observe any pressure differential. A cylinder of anhydrous HCl was connected to one of the delivery tubes through a trap containing concentrated sulfuric acid. A cylinder of anhydrous monomethylamine was connected to the other delivery tube through a mercury bubbler and a trap containing solid potassium hydroxide. Stirring was initiated, and the gases were admitted, adjusting their flow rates so that no pressure differential existed. The product formed immediately, and the reaction was continued until, by visible inspection, the desired amount had been prepared. The product was allowed to settle, and most of the ether was decanted; the remaining ether was

removed on the vacuum line by heating the product at 100°C. for two hours. The purity of the monomethylamine hydrochloride was determined by the adsorption-indicator method for chloride ion<sup>54</sup> and exceeded 99 per cent. After removal from the vacuum line, the product was stored in an inert atmosphere box. Samples could be exposed to the atmosphere for only short periods of time before water absorption affected the weight.

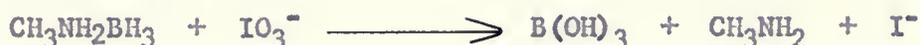
To prepare the monomethylamineborane, an approximately 0.4 M solution of lithium borohydride in diethyl ether was prepared from reagent grade ether and 85 per cent lithium borohydride obtained from Metal Hydrides, Inc. The solution was prepared in the dry box and allowed to stand until gas evolution ceased. Approximately 250 ml. of the solution was decanted into a flask fitted with an airtight rubber syringe stopper. Aliquots were removed by means of a graduated hypodermic syringe, and the normality was determined by the method of Lyttle, Jensen, and Struck,<sup>42</sup> using arsenite instead of thiosulfate to titrate the iodine.

In a typical run, 6.5 gm. (97  $\mu$ moles) of monomethylamine hydrochloride were added to a 250 ml. two-necked round bottom flask fitted with a teflon coated magnetic stirring bar. This operation was carried out in the dry box. The flask was placed on the vacuum line, and approximately 75 ml. of ether were distilled from a lithium borohydride-ether solution onto the monomethylamine hydrochloride at -78°C. The flask was then surrounded by an ice bath and brought to atmospheric pressure with dry nitrogen. A rubber syringe stopper and a mercury bubbler were fitted to the two necks of the flask, and a magnetic stirrer was placed beneath the flask and the ice bath. A graduated hypodermic syringe was used to add 120 ml. of 0.36 M lithium borohydride (43  $\mu$ moles) in ether, and

stirring was initiated. Reaction occurred according to the overall equation



The gas evolution, as indicated by the mercury bubbler, ceased after approximately two hours. The cold solution was then filtered in the atmosphere, the filtrate placed on the vacuum line, and the ether removed at 0°C. The product obtained had a yellowish tint. The impure compound was dissolved in 10 to 15 ml. of benzene and warmed to 40°C. An equal volume of n-heptane was added, and the solution was cooled in an ice bath. This solution was then filtered, and a pure, white crystalline solid was obtained. The product was placed on the vacuum line and was pumped on for several hours at 0°C. It was then sublimed at 25°C. onto a cold finger at -78°C. The pure product melted at 55°-56°C., in agreement with the literature value.<sup>46</sup> The purity was checked by adding a weighed sample to an excess of iodate, acidifying, and titrating the excess oxidizing equivalents present as iodine with arsenite to a starch end point. The following set of equations describe this analytical method:



An alternate analysis was performed by hydrolyzing a weighed sample with a known amount of excess acid and back titrating with sodium hydroxide. The hydrolysis proceeds according to the equation:



The purity as calculated by both methods exceeded 98 per cent. These results and the findings of a commercial analysis are listed below.

	<u>%C</u>	<u>%H</u>	<u>%N</u>	<u>B-H as re- ducing eq./g.</u>	<u>Acid eq./g.</u>
Found:	27.03	18.17	30.99	0.193	0.190
Calculated:	26.75	17.96	31.20	0.193	0.193

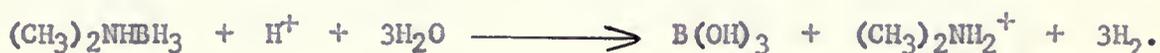
The yield of pure product was 56 per cent.

### B. Procedures

Calibration of the pH apparatus. The pH was followed by a Model SR Sargent Recorder equipped with a resistance-matching adapter, S-72172 Sargent pH adapter, used in conjunction with Beckman glass and calomel electrodes. In the preliminary experiments, the electrodes behaved erratically when placed into the reactant solutions. Several steps had to be taken to produce consistent results. The electrodes were thermostated in the constant temperature bath in order to insure rapid temperature equilibration. Enough solid potassium chloride was added to the calomel electrode, so that a saturated solution was maintained over the temperature range studied. Further stabilization was attained by constructing a barrier junction to fit over the calomel electrode. The junction consisted of a tube with a capillary to allow solution contact while preventing dilution and contamination in the reference cell. Before each run the barrier was filled with a saturated potassium chloride solution, which was also thermostated at all times in the constant temperature bath. The whole apparatus was recalibrated with prepared buffer solutions daily and before runs at a new temperature. The recorder speed

was known, and a pH versus time plot was obtained directly from the recorder chart paper.

The acid hydrolysis of dimethylamineborane in water. The hydrolysis proceeds according to the overall equation



The progress of the reaction can be followed by determining the loss of reducing power of the solution or the change in the hydrogen ion concentration. Trimethylamineborane solutions have been analyzed by the former method by Ryschkewitsch.<sup>57</sup> In this investigation a weighed amount of dimethylamineborane was added to a known volume and concentration of hydrochloric acid. The pH and time were read directly from the recorder plots. The instantaneous dimethylamineborane concentration could then be determined from the stoichiometry of the reaction.

The reaction was studied over the temperature range of 36-50°C. The initial dimethylamineborane concentration varied from 0.008 to 0.0275 M, and the initial hydrochloric acid concentration varied from 0.004 to 0.015 M. All of the reactions were run at a constant ionic strength of 0.10 M by adding appropriate amounts of potassium chloride. All solutions used in the kinetic runs were thermostated in the constant temperature bath to  $\pm 0.01^\circ\text{C}$ . The concentrations were adjusted so that the half-life of the component in the lower concentration was attained in 10-15 minutes. There were two half-lives in the longest run, and the usual run was halted after one half-life.

An excellent fit of the data to the rate equation

$$-d[\text{dimethylamineborane}]/dt = k[\text{dimethylamineborane}][\text{H}^+]$$

was obtained over the range of half-life, temperature, and solvent composition studied. The second order rate constants,  $k$ , were determined from the slope of the straight line relation of  $\log [\text{dimethylamineborane}]/[\text{H}^+]$  and the time. The method of least squares was used to optimize the fit. The activation energy was then determined from the Arrhenius equation,  $\ln k = A(\exp)-\Delta E^\ddagger/RT$ , where  $\Delta E^\ddagger$  is the activation energy,  $A$  is the pre-exponential factor,  $k$  is the second order rate constant, and  $T$  is the absolute temperature. The activation energy was calculated by a least squares treatment of  $\log k$  versus  $1/T$ .

The decomposition of dimethylamineborane in pure water occurred at a negligible rate. A detailed discussion of the proposed mechanism of solvolysis appears in a later section.

The acid hydrolysis of monomethylamineborane in water. The acid hydrolysis of monomethylamineborane in aqueous solutions proceeds to completion analogous to the dimethylamineborane hydrolysis according to the overall equation



The method of analysis of the monomethylamineborane hydrolysis was the same as for the dimethylamineborane hydrolysis.

The reaction was studied over the temperature range of 27.5 to 35.9°C. The initial monomethylamineborane concentration varied from 0.0025 to 0.0070  $M$ , and the initial hydrochloric acid concentration varied from 0.0030 to 0.0062  $M$ . The ionic strength was adjusted to 0.10  $M$  with potassium chloride. Each run covered at least one half-life of the component in the lower concentration.

Monomethylamineborane is more sensitive to moisture than the dimethylamineborane, and consequently, samples of the former were stored in the dry box. In a typical run, a sample of monomethylamineborane was removed from the dry box, dissolved in 50 ml. of 0.10 M potassium chloride, and the initial concentration of the amineborane was determined by measuring the reducing power of the solution by the iodate method. A known volume and concentration of hydrochloric acid was then added, and the initial concentrations of both components were determined from dilution factors. No decomposition of monomethylamineborane in pure water was detected over the approximately ten minute time interval utilized in the measurements.

The data obtained were treated in the same manner as that in the dimethylamineborane hydrolysis.

The acid hydrolysis of di- and trimethylamineborane in 1-propanol-water solutions. The hydrolysis proceeds in the same manner as that indicated for the preceding two amineboranes. The method of analysis differed from that in pure water, in that the concentration of the amineborane was followed by measuring the loss in reducing power by the iodate method.

The reaction with trimethylamineborane in the mixed 1-propanol-water solvent was studied over the temperature range of 31.8 to 44.4°C. The initial trimethylamineborane concentration varied from 0.370 to 0.710 M, and the initial hydrochloric acid concentration varied from 0.818 to 1.02 M. The solvent contained 50.6 per cent of 1-propanol by volume. The longest run covered approximately two half-lives, and the usual run covered one half-life.

The reaction with dimethylamineborane in the mixed solvent was studied over the temperature range of 4.5 to 14.6°C. The initial dimethylamineborane concentration varied from 0.425 to 0.454 M, and the initial hydrochloric acid concentration was 0.818 M. The volume ratio of 1-propanol to water was constant throughout the experiments. Each run covered at least one half-life of the amineborane.

It was found that when the reaction was carried out in an open vessel and with large reaction rates, the hydrogen gas evolved would carry out considerable amounts of the solvent, and preferentially the 1-propanol. This proved to be a serious source of error. This effect was minimized by running the reactions in a closed tube connected to a mercury bubbler which maintained a slight positive pressure on the solution, but which allowed the hydrogen to escape with much smaller amounts of the solvent. At high concentrations of amineborane and hydrochloric acid, solvent evaporation restricted the reaction conditions to a relatively narrow range of concentrations and temperatures.

In a typical run, a weighed amount of the amineborane was dissolved in the 1-propanol-water azeotrope, which contained 75.85 per cent 1-propanol by volume. The initial concentration of the amineborane was found by measuring the reducing power of the solution by the iodate method. A known amount of this solution was then pipetted into the reaction tube, and a known volume and concentration of hydrochloric acid was added. The volume ratio of the azeotrope to the hydrochloric acid solution was two, so that the volume ratio of 1-propanol to water in the final solution was 1.02. Aliquots of the reacting solution were removed at different time intervals, and the instantaneous concentration of the amineborane was found by the iodate method. The instantaneous acid

concentration could then be determined from the stoichiometry of the reaction.

No ionic strength adjustments were made. The solutions used in the trimethylamineborane hydrolysis were thermostated to  $\pm 0.01^{\circ}\text{C}$ ., and those used in the dimethylamineborane hydrolysis were thermostated to  $\pm 0.1^{\circ}\text{C}$ . The data obtained were treated in the same manner as that of the hydrolysis in pure water. Vigorous stirring of the solution before removing the aliquots reduced the interference of the hydrogen gas evolution with pipetting.

Attempts were made to study the trimethylamineborane reaction as a pseudo-first order reaction, in which the amineborane concentration was approximately 0.02 M, and the hydrochloric acid concentration was 1.0 M. Consistent and reproducible data could not be obtained, and the behavior of these reactions will be discussed in a later section.

The distribution coefficient of monomethylamineborane between benzene and water. A weighed amount of monomethylamineborane was dissolved in a known volume of water, and this solution was shaken with an equal volume of benzene. All of the solutions were thermostated to  $\pm 0.1^{\circ}\text{C}$ . Twenty to thirty minutes were allowed for equilibrium to be reached, and then aliquots were removed from both the organic and aqueous phases and titrated by the iodate method.

Precision of the data was relatively poor, and the experiment was abandoned in favor of direct solubility measurements in water. The reasons for the initial undertaking of this experiment and for the poor results are outlined in the discussion section.

The solubility of monomethylamineborane in benzene. The solubility was studied over the temperature range of 5.9 to 21.5 $^{\circ}\text{C}$ . A saturated

solution with a large excess of solid was prepared at room temperature. The temperature was held constant to  $\pm 0.1^{\circ}\text{C}$ . in a Dewar flask. Aliquots were pipetted out at several temperatures through a small glass fritted filter tube, which was attached to the pipet by means of a lubricated loop of tygon tubing. The concentration of the amineborane was then determined by measuring the reducing power of an aliquot by the iodate method. A straight line was obtained from a plot of  $\log$  (monomethylamineborane concentration) versus  $1/\text{temperature}$ , and the heat of solution was calculated from the least squares slope of this line. The solubility of the monomethylamineborane at the freezing point of the benzene solution was determined by extrapolation from this plot, and this particular concentration was then utilized in calculations involved in the cryoscopic study.

The cryoscopy of monomethylamineborane-benzene solutions. The freezing point depressions in benzene were determined at various concentrations of monomethylamineborane. The apparatus consisted of a double-walled, glass wool insulated vessel, a Beckman thermometer, and a magnetic stirring mechanism operated by a relay timer, as shown in the figure on the following page.

The thermometer was calibrated at the freezing point of pure benzene. In order to correct for the effect of supercooling, the temperature versus time curve was extrapolated through the supercooling region in all instances. The intercept of the extrapolated line and the initial portion of the curve was taken as the freezing point of the solution. Temperature differences were measured to  $\pm 0.005^{\circ}\text{C}$ .

In a typical run, 8-10 ml. of a monomethylamineborane-benzene solution were placed in the freezing point apparatus. The concentration of

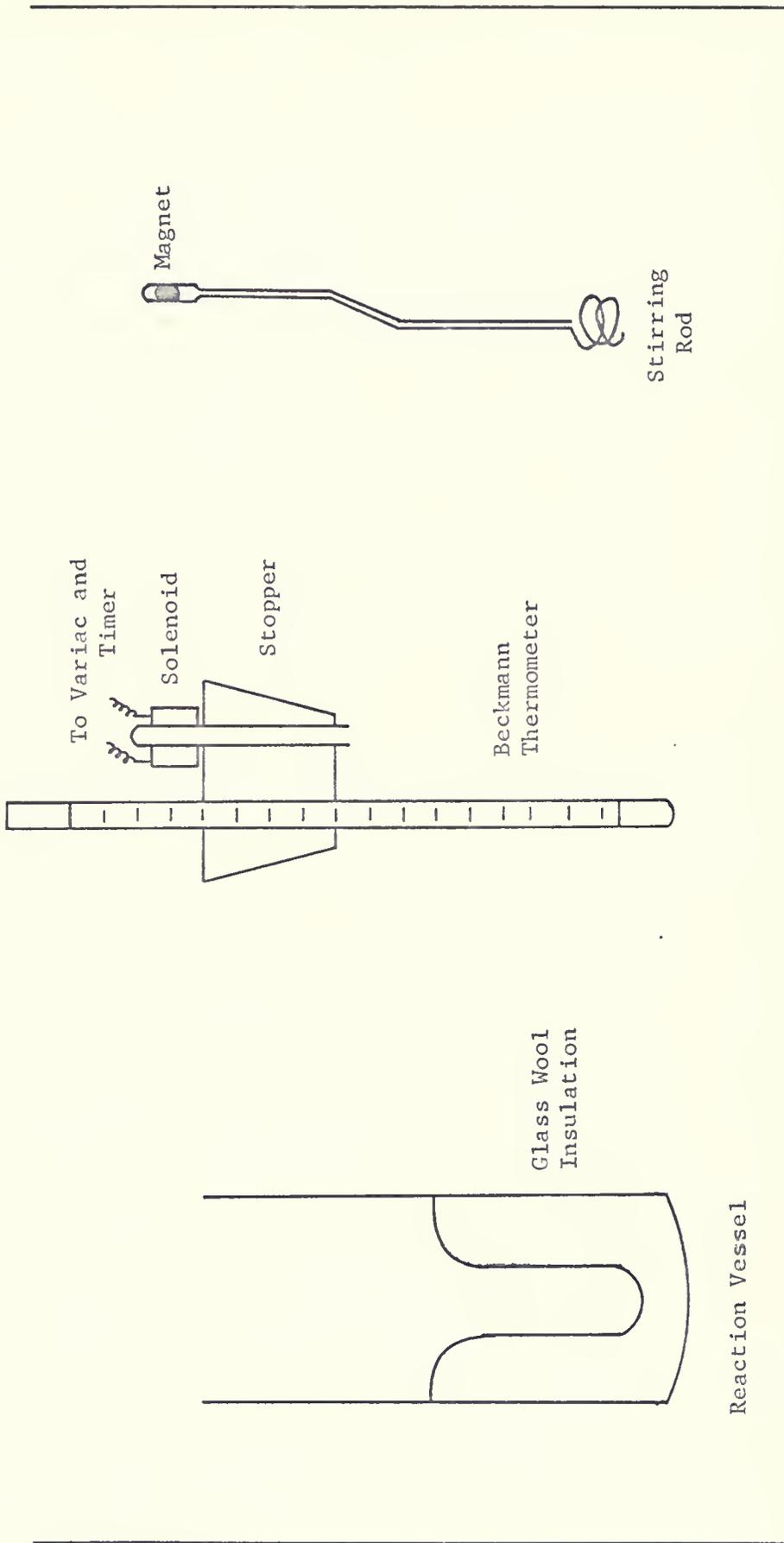


Fig. 1. Cryoscopic Apparatus

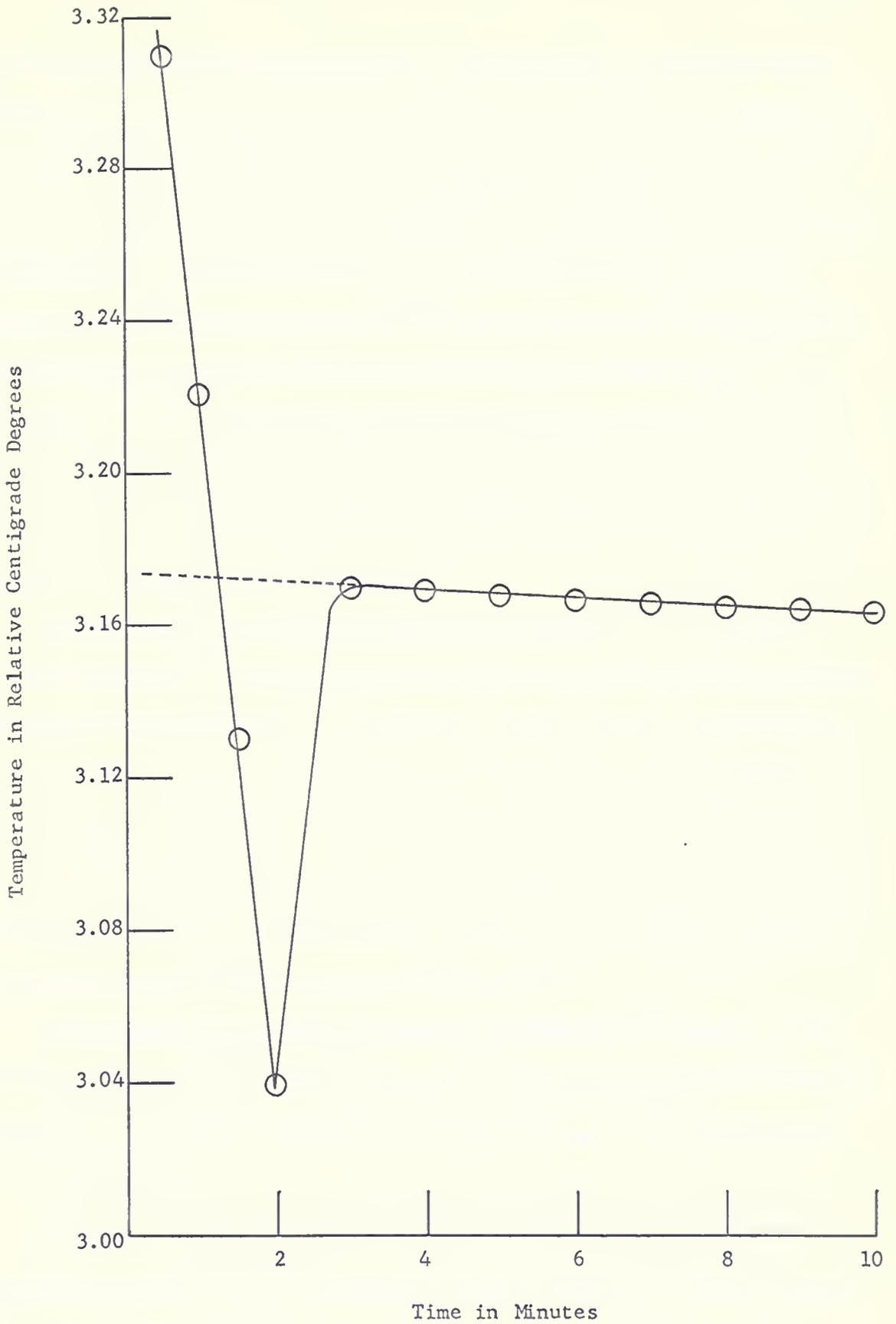


Fig. 2. Temperature vs. Time Plot for Monomethylamineborane in Benzene with Extrapolation to Correct for Supercooling

the solution was then determined by the iodate method from the reducing equivalents of an aliquot. The molality of the solution was then approximated by dividing the molarity by the density of benzene at 25°C. The density of benzene at 25°C. was calculated to be 0.874 g./ml. from a linear interpolation of the densities at 20°C. and 30°C.<sup>21</sup> The van't Hoff factor,  $i$ , was determined from the ratio of the expected freezing point depression,  $\Delta T_e$ , to the observed freezing point depression,  $\Delta T_o$ ; i.e.,  $i = \Delta T_e / \Delta T_o$ . The expected freezing point depression can be calculated from the expression  $\Delta T_e = K_f \cdot \text{molality}$ , where  $K_f$  is the cryoscopic constant for benzene and has the value of 5.12.<sup>15</sup> These  $i$  values were then compared to those in the literature.<sup>46</sup>

The solubility of trimethylamineborane in water. A saturated, aqueous solution of trimethylamineborane was prepared at room temperature. Aliquots were removed over the temperature range of 0-33°C. by means of a glass fritted filter tube attached to a 1 ml. pipet. The temperature was held constant to  $\pm 0.1^\circ\text{C}$ . The reducing equivalents contained in the aliquots were then determined by the iodate method. The heat of solution was calculated from the least squares slope of a plot of log (trimethylamineborane concentration) versus 1/temperature.

The solubility of mono- and dimethylamineborane in water. Since these compounds were vastly more soluble in water than was the trimethylamineborane, a slightly different procedure was used in order to economize on reagents.

Saturated, aqueous solutions of the amineboranes were prepared at temperatures below 20°C. A 0.10 ml. capacity Hamilton microliter syringe with a small styrofoam ball attached to the orifice of the needle tip

was used to remove 0.05 to 0.085 ml. aliquots from the solutions. Dimethylamineborane was studied over the temperature range of 0-20°C., and monomethylamineborane was studied over the temperature range of 0-13°C. The reducing equivalents contained in the aliquots were then determined by the iodate method. The heats of solution of these amineboranes were determined in the same manner as the heat of solution of trimethylamineborane.

### CHAPTER III

#### EXPERIMENTAL RESULTS

The data compiled from the acid hydrolysis of the methylamineboranes are listed in Table 2 through Table 21. Following Table 3 for monomethylamineborane in water, Table 11 for dimethylamineborane in water, Table 14 for trimethylamineborane in 50 per cent 1-propanol-water, and Table 20 for dimethylamineborane in 50 per cent 1-propanol-water, are plots indicative of the treatment given to each kinetic run. At the end of the pertinent tables, a summary of the kinetic data for each amineborane hydrolysis is given, along with the Arrhenius plots and parameters.

The solubility curves for each of the methylamineboranes are presented at the end of the kinetic data.

The results of the cryoscopic work on monomethylamineborane in benzene and the distribution coefficient data appear in the discussion section.

Tables of comparison of data, or tables containing specific data from the literature, are presented in the discussion to which they refer. A table of the list of symbols and abbreviations used throughout the thesis is presented on the following page.

TABLE 1  
LIST OF SYMBOLS AND ABBREVIATIONS

Symbols	Definitions
MMAB	Monomethylamineborane
DMAB	Dimethylamineborane
TMAB	Trimethylamineborane
$\Delta T_e$	Expected freezing point depression
$\Delta T_o$	Experimentally observed freezing point depression
$i$	van't Hoff factor
$^{\circ}\text{K.}$	Degrees Kelvin
$\Delta E^{\ddagger}$	Activation energy in kcal./mole
$T$	Absolute temperature
$k$	Second order rate constant in liter/mole/time
$t$	Time
$\mu$	Ionic strength in moles/liter
$[ ]$	Concentration in moles/liter
$[ ]_o$	Initial concentration in moles/liter
$\underline{M}$	Molarity in moles/liter
$\underline{m}$	Molality in moles of solute/1000 g. of solvent
$R$	Gas constant in cal./mole/deg.
$A$	Defined by $\ln k = A - B/T$
$B$	Defined by $\ln k = A - B/T$
$\Delta H_h$	Heat of hydration in kcal./mole
$\Delta H_s$	Heat of solution in kcal./mole

TABLE 1 - Continued

Symbols	Definitions
$\Delta H_v$	Heat of vaporization in kcal./mole
K	An equilibrium constant
50% 1-propanol-water	A solution containing 50.6% of 1-propanol by volume

TABLE 2  
KINETIC DATA FOR MMAB IN WATER AT 27.55°C.

$[H^+] \times 10^3$	$[MMAB] \times 10^3$	$\log [MMAB]/[H^+]$	Time, min.
6.026	6.132	0.0078	0
3.793	3.899	0.0120	4
2.692	2.798	0.0166	8
2.079	2.185	0.0216	12
1.687	1.793	0.0265	16
	k = 25.57 liter/mole/min.		
6.012	5.129	-0.0690	0
4.853	3.970	-0.0872	2
4.036	3.153	-0.1072	4
3.467	2.584	-0.1277	6
3.048	2.165	-0.1576	8
	k = 26.33 liter/mole/min.		
4.410	6.673	0.2074	0
3.119	5.652	0.2582	2
2.394	4.927	0.3135	4
1.884	4.417	0.3700	6
1.514	4.047	0.4270	8
	k = 25.20 liter/mole/min.		

TABLE 3  
KINETIC DATA FOR MMAB IN WATER AT 30.70°C.

$[\text{H}^+] \times 10^3$	$[\text{MMAB}] \times 10^3$	$\log [\text{MMAB}]/[\text{H}^+]$	Time, min.
6.000	7.896	0.1193	0
4.853	6.749	0.1433	1
3.990	5.886	0.1688	2
3.304	5.200	0.1970	3
2.786	4.682	0.2256	4
2.399	4.295	0.2529	5
2.070	3.966	0.2824	6
1.815	3.711	0.3107	7
1.603	3.499	0.3391	8
1.419	3.315	0.3685	9
$k = 33.91$ liter/mole/min.			
4.083	6.830	0.2235	0
3.357	6.104	0.2596	1
2.780	5.527	0.2984	2
2.317	5.064	0.3397	3
1.954	4.701	0.3813	4
1.671	4.418	0.4223	5
1.429	4.176	0.4657	6
$k = 33.98$ liter/mole/min.			

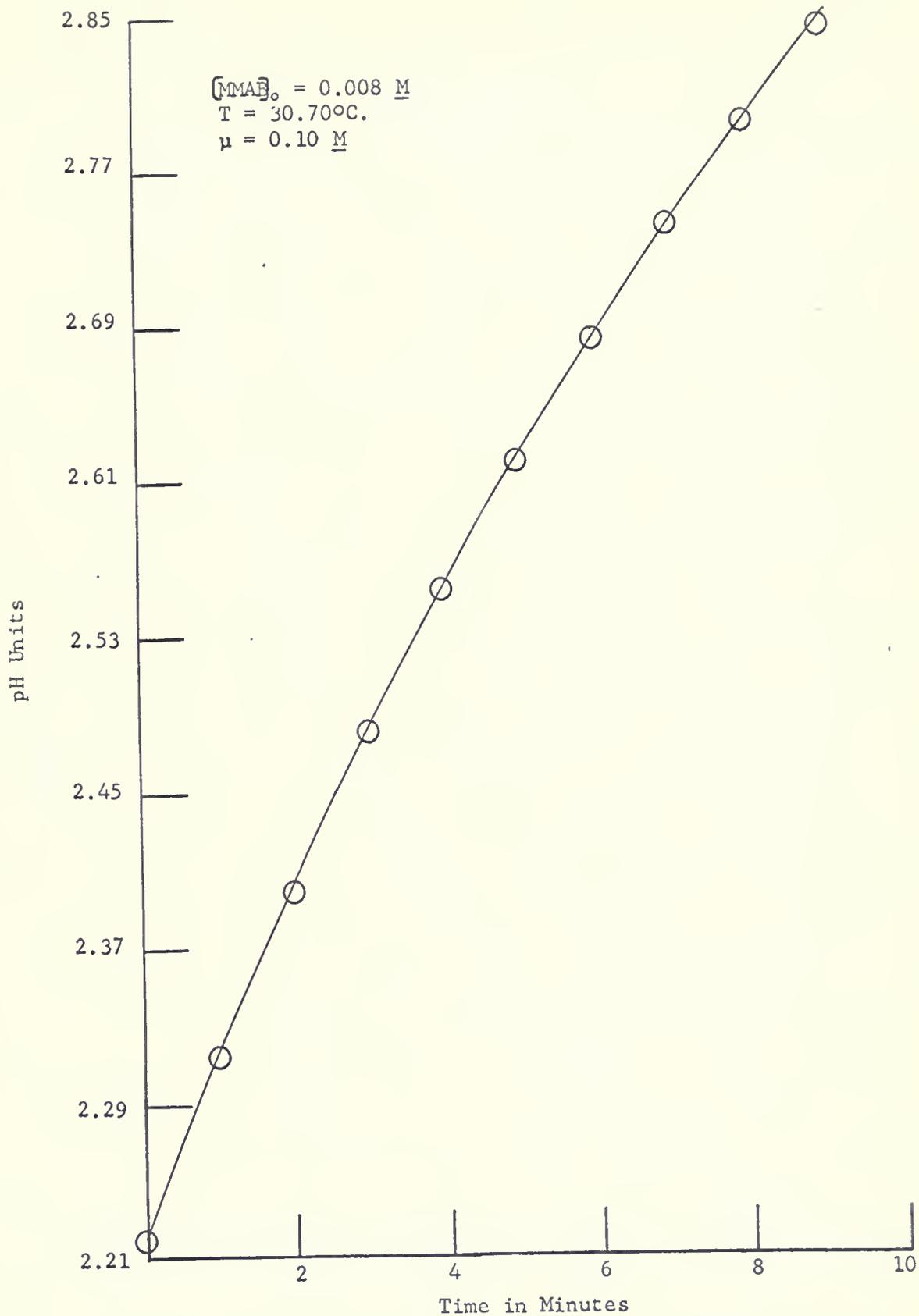


Fig. 3. pH vs. Time Plot for Monomethylamineborane (MMAB) in Water

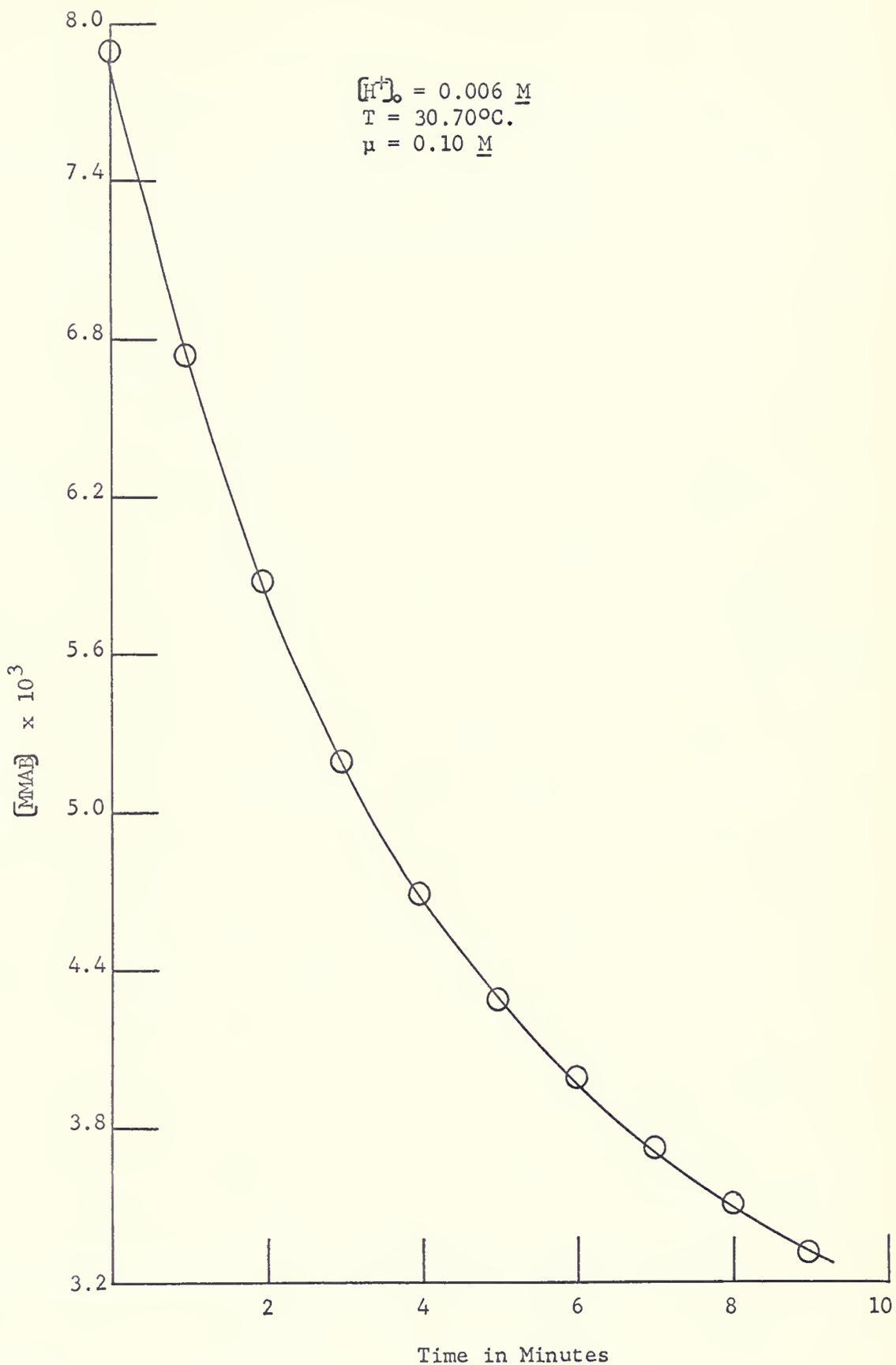


Fig. 4. Concentration vs. Time Plot for Monomethylamineborane (MMAB) in Water

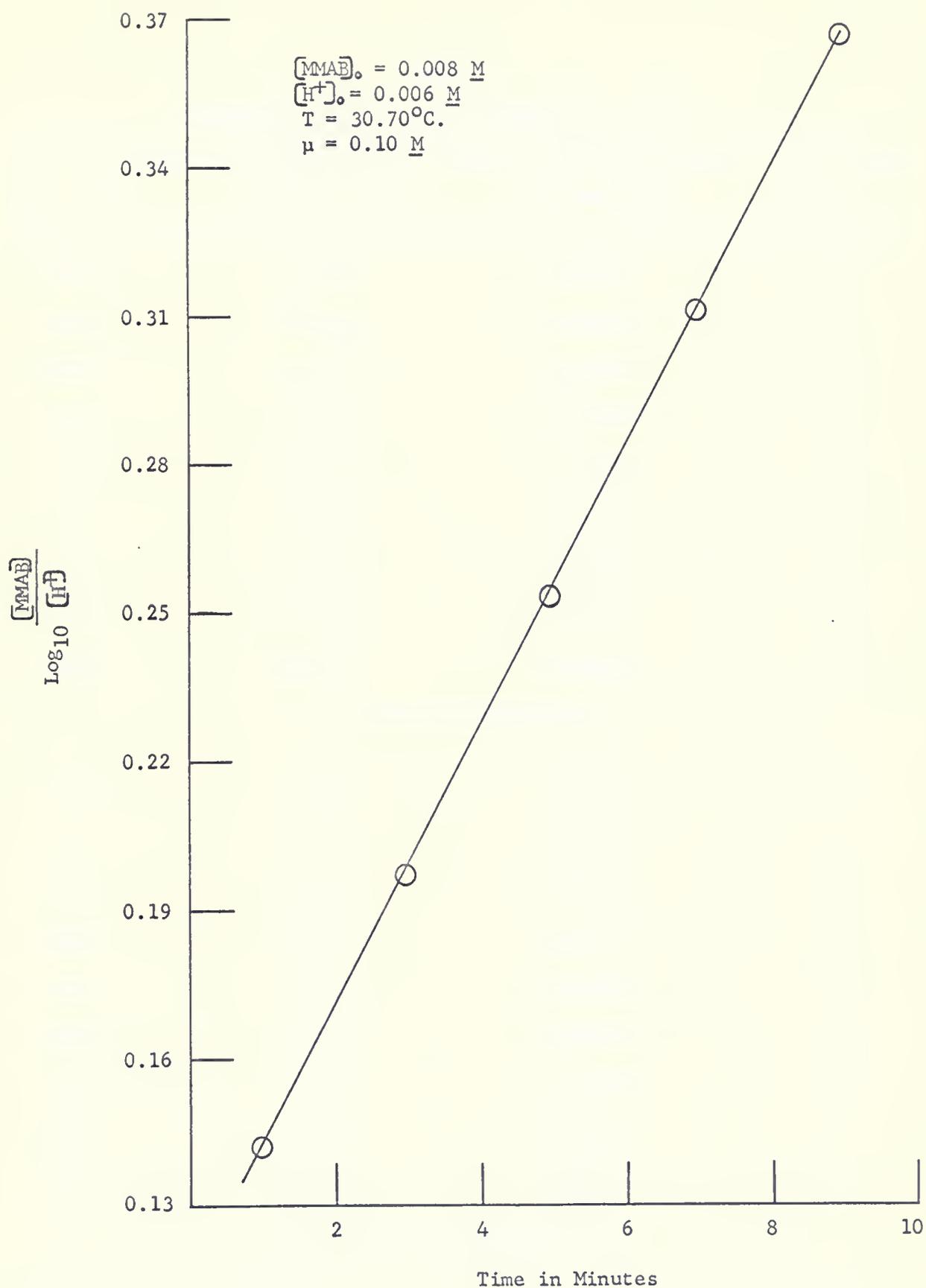


Fig. 5. Second Order Rate Plot for Monomethylamineborane (MMAB) in Water

TABLE 4  
KINETIC DATA FOR MMAB IN WATER AT 31.94°C.

$[H^+] \times 10^3$	$[MMAB] \times 10^3$	$\log [MMAB]/[H^+]$	Time, min.
3.140	4.971	0.1995	0
2.673	4.504	0.2266	1
2.286	4.117	0.2555	2
1.954	3.785	0.2871	3
1.698	3.529	0.3177	4
1.493	3.324	0.3475	5
1.318	3.149	0.3782	6
1.159	2.990	0.4116	7
1.040	2.871	0.4411	8
$k = 38.30$ liter/mole/min.			
3.162	4.878	0.1884	0
2.716	4.432	0.2127	1
2.328	4.044	0.2398	2
2.000	3.716	0.2691	3
1.742	3.458	0.2978	4
1.531	3.247	0.3265	5
1.349	3.065	0.3564	6
1.202	2.918	0.3853	7
1.072	2.788	0.4151	8
$k = 38.36$ liter/mole/min.			

TABLE 5  
KINETIC DATA FOR MMAB IN WATER AT 35.94°C.

$[H^+] \times 10^3$	$[MMAB] \times 10^3$	$\log [MMAB]/[H^+]$	Time, min.
6.166	2.799	-0.3430	0
5.495	2.128	-0.4119	1
5.012	1.645	-0.4839	2
4.624	1.257	-0.5659	3
4.364	0.997	-0.6411	4
4.140	0.773	-0.7289	5
3.990	0.623	-0.8066	6
3.855	0.488	-0.8976	7
3.767	0.400	-0.9739	8
3.698	0.331	-1.0482	9
k = 54.55 liter/mole/min.			
4.169	2.506	-0.2210	0
3.715	2.052	-0.2577	1
3.365	1.702	-0.2960	2
3.076	1.413	-0.3378	3
2.851	1.188	-0.3802	4
2.692	1.029	-0.4177	5
2.547	0.884	-0.4595	6
2.432	0.769	-0.5000	7
2.328	0.665	-0.5441	8
2.259	0.605	-0.5722	9
k = 55.29 liter/mole/min.			

TABLE 6  
SUMMARY OF KINETIC DATA FOR MMAB IN WATER

$k, \text{l.mole}^{-1}\text{min.}^{-1}$	Standard deviation	$\log k$	$1/T, 10^3 \times \text{°K.}^{-1}$
25.70	0.47	1.410	3.326
33.95	0.05	1.531	3.292
38.33	0.04	1.584	3.278
54.92	0.05	1.740	3.236

$$\Delta E^\ddagger = 15.81 \text{ kcal./mole}$$

Arrhenius parameters from  $\log k = A - B/T$ :  $k$  in  $\text{l.mole}^{-1}\text{sec.}^{-1}$

$$A = 11.14$$

$$B = 3,457$$

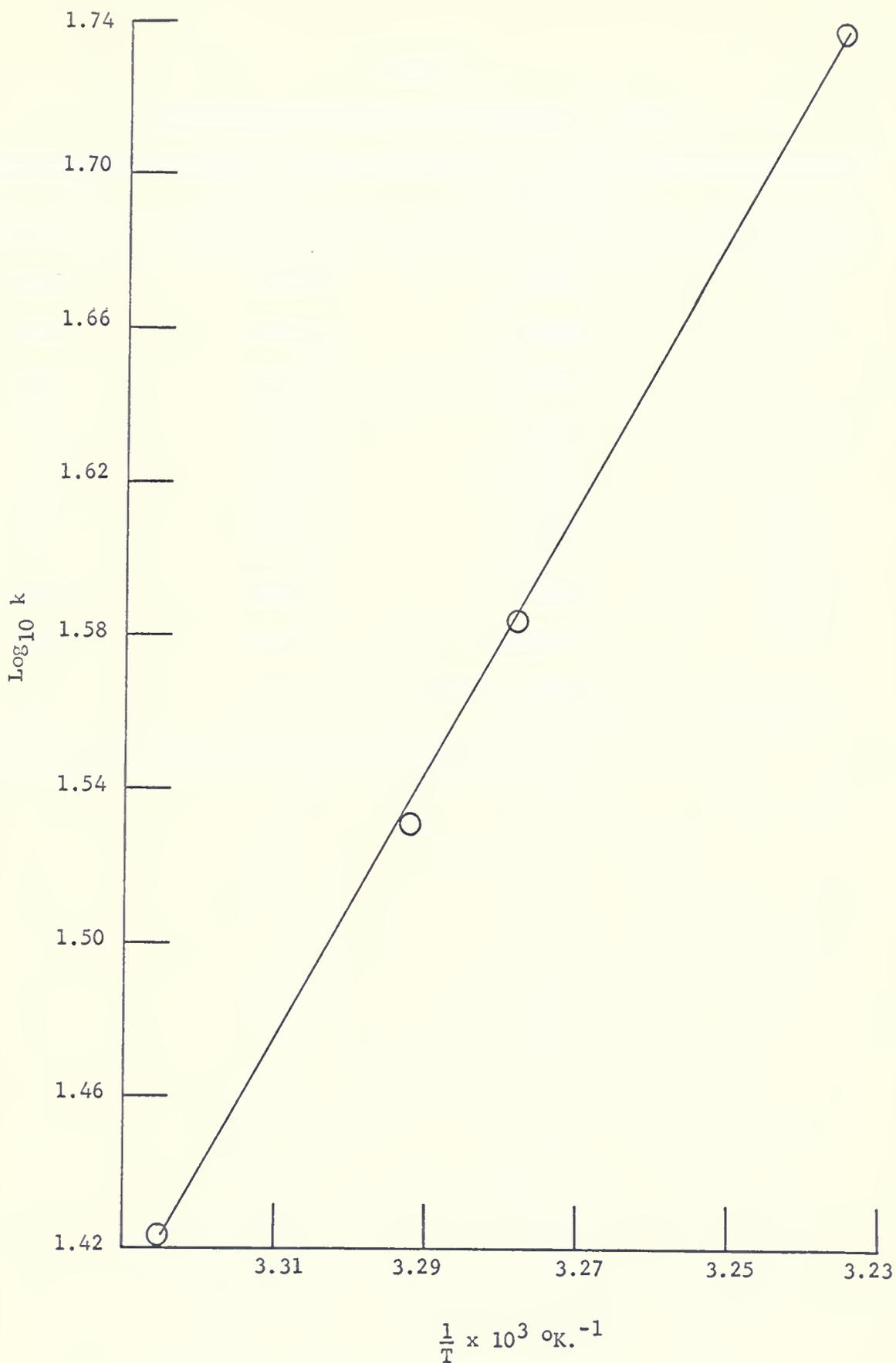


Fig. 6. Arrhenius Plot for the Acid Hydrolysis of Monomethylamineborane in Water

TABLE 7  
KINETIC DATA FOR DMAB IN WATER AT 36.08°C.

$[H^+]$ $\times 10^2$	[DMAB] $\times 10^2$	$\log [DMAB]/[H^+]$	Time, min.
1.589	2.759	0.2396	0*
1.400	2.570	0.2639	2*
1.268	2.438	0.2840	4
1.183	2.353	0.2986	6
1.109	2.279	0.3128	8
1.038	2.208	0.3278	10
0.975	2.145	0.3424	12
0.918	2.088	0.3568	14

$k = 1.439$  liter/mole/min.

\*These points omitted from the least squares fit.

TABLE 8  
KINETIC DATA FOR DMAB IN WATER AT 40.34°C.

$[H^+] \times 10^3$	$[DMAB] \times 10^2$	$\log [DMAB]/[H^+]$	Time, min.
9.772	1.903	0.2894	0
8.974	1.823	0.3077	2
8.260	1.752	0.3263	4
7.621	1.688	0.3452	6
7.063	1.632	0.3636	8
6.546	1.580	0.3827	10
6.109	1.537	0.4005	12
k = 2.309 liter/mole/min.			
9.885	1.879	0.2790	0
9.099	1.799	0.2960	2
8.375	1.727	0.3143	4
7.727	1.662	0.3326	6
7.161	1.606	0.3506	8
6.622	1.552	0.3698	10
6.138	1.503	0.3890	12
k = 2.390 liter/mole/min.			
9.908	1.873	0.2767	0
9.141	1.797	0.2934	2
8.453	1.728	0.3105	4
7.816	1.664	0.3282	6

TABLE 8 - Continued

$[\text{H}^+] \times 10^3$	$[\text{DMAB}] \times 10^2$	$\log [\text{DMAB}] / [\text{H}^+]$	Time, min.
7.228	1.605	0.3466	8
6.683	1.551	0.3655	10
6.180	1.500	0.3852	12

$k = 2.366$  liter/mole/min.

TABLE 9  
KINETIC DATA FOR DMAB IN WATER AT 42.79°C.

$[H^+] \times 10^3$	$[DMAB] \times 10^2$	$\log [DMAB]/[H^+]$	Time, min.
10.28	1.434	0.1446	0
9.506	1.357	0.1544	2
8.770	1.283	0.1652	4
8.110	1.217	0.1764	6
7.482	1.154	0.1884	8
6.966	1.103	0.1995	10
6.457	1.052	0.2119	12
k = 3.244 liter/mole/min.			
10.47	1.457	0.1436	0
9.660	1.376	0.1535	2
8.912	1.301	0.1644	4
8.222	1.232	0.1758	6
7.568	1.167	0.1881	8
6.998	1.110	0.2003	10
6.501	1.060	0.2124	12
k = 3.289 liter/mole/min.			
10.59	1.642	0.1903	0
9.660	1.549	0.2049	2
8.810	1.464	0.2206	4
8.035	1.386	0.2368	6

TABLE 9 - Continued

$[H^+]$ $\times 10^3$	$[DMAB]$ $\times 10^2$	$\log [DMAB]/[H^+]$	Time, min.
7.345	1.317	0.2538	8
6.730	1.256	0.2709	10
6.209	1.204	0.2874	12
k = 3.250 liter/mole/min.			

TABLE 10  
KINETIC DATA FOR DMAB IN WATER AT 44.95°C.

$[H^+] \times 10^3$	$[DMAB] \times 10^3$	$\log [DMAB]/[H^+]$	Time, min.
4.027	9.897	0.3906	0
3.767	9.637	0.4079	2
3.507	9.377	0.4272	4
3.273	9.143	0.4461	6
3.048	8.928	0.4667	8
2.851	8.721	0.4856	10
2.673	8.543	0.5046	12
$k = 3.771$ liter/mole/min.			
4.027	9.124	0.3553	0
3.758	8.855	0.3722	2
3.057	8.604	0.3897	4
3.311	8.408	0.4047	6
3.112	8.209	0.4213	8
2.917	8.014	0.4389	10
2.748	7.845	0.4556	12
$k = 3.769$ liter/mole/min.			
4.027	8.058	0.3012	0
3.793	7.824	0.3145	2
3.597	7.628	0.3265	4
3.404	7.435	0.3390	6

TABLE 10 - Continued

$[H^+]$ $\times 10^3$	[DMAB] $\times 10^3$	$\log [DMAB]/[H^+]$	Time, min.
3.221	7.252	0.3524	8
3.041	7.072	0.3665	10
2.877	6.990	0.3804	12

$k = 3.756$  liter/mole/min.

TABLE 11  
KINETIC DATA FOR DMAB IN WATER AT 50.27°C.

$[H^+] \times 10^3$	$[DMAB] \times 10^3$	$\log [DMAB]/[H^+]$	Time, min.
4.808	8.403	0.2425	0
4.345	7.940	0.2617	2
3.954	7.549	0.2808	4
3.614	7.209	0.2999	6
3.296	6.891	0.3204	8
3.013	6.608	0.3410	10
2.754	6.349	0.3637	12
2.547	6.142	0.3822	14
$k = 6.419$ liter/mole/min.			
4.989	9.314	0.2711	0
4.477	8.802	0.2936	2
4.018	8.343	0.3172	4
3.606	7.931	0.3422	6
3.258	7.583	0.3699	8
2.965	7.290	0.3908	10
2.698	7.023	0.4155	12
2.460	6.785	0.4406	14
$k = 6.474$ liter/mole/min.			
4.955	8.027	0.2095	0
4.519	7.591	0.2253	2
4.112	7.184	0.2423	4

TABLE 11 - Continued

$[\text{H}^+] \times 10^3$	$[\text{DMAB}] \times 10^3$	$\log [\text{DMAB}]/[\text{H}^+]$	Time, min.
3.741	6.813	0.2603	6
3.444	6.516	0.2769	8
3.170	6.242	0.2942	10
2.917	5.989	0.3126	12

$k = 6.459 \text{ liter/mole/min.}$

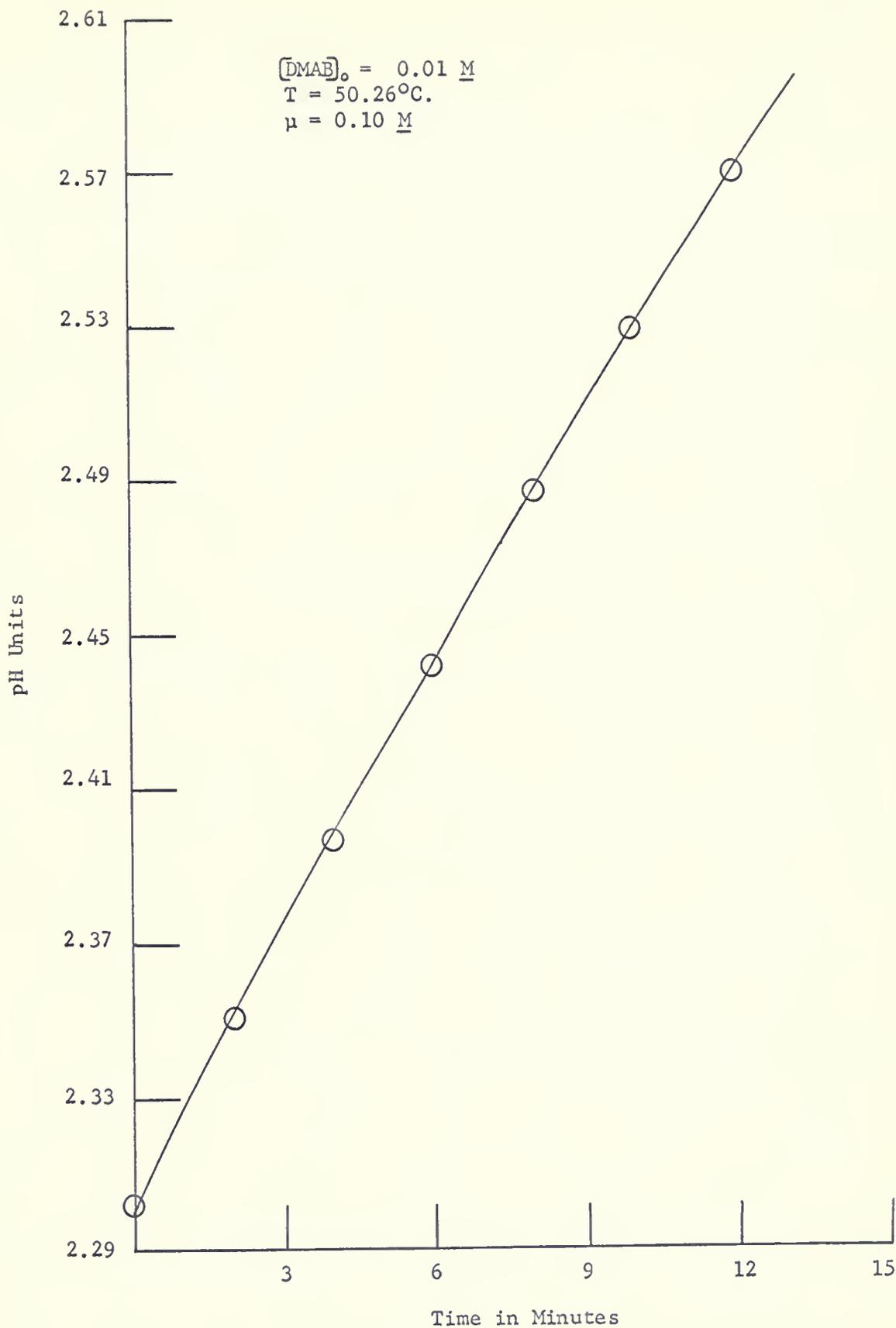


Fig. 7. pH vs. Time Plot for Dimethylamineborane (DMAB) in Water

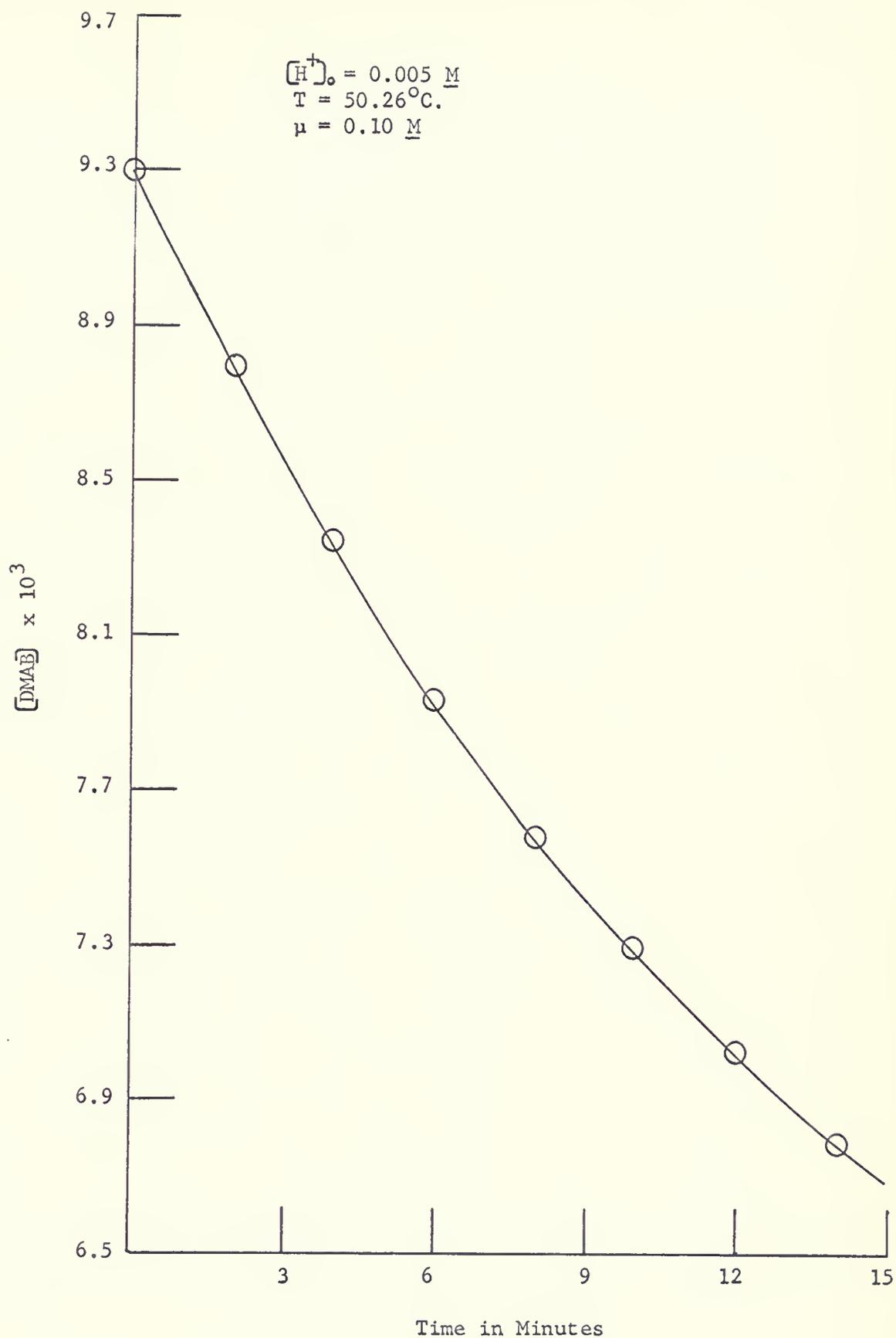


Fig. 8. Concentration vs. Time Plot for Dimethylamineborane (DMAB) in Water

TABLE 12  
SUMMARY OF KINETIC DATA FOR DMAB IN WATER

$k, \text{l.mole}^{-1}\text{min.}^{-1}$	Standard deviation	$\log k$	$1/T, 10^3 \times \text{°K.}^{-1}$
1.439	-	0.1581	3.234
2.355	0.07	0.3700	3.190
3.261	0.03	0.5132	3.165
3.765	0.01	0.5758	3.143
6.451	0.04	0.8096	3.092

$$\Delta E^\ddagger = 21.21 \text{ kcal./mole}$$

Arrhenius parameters from  $\log k = A - B/T$ :  $k$  in  $\text{l.mole}^{-1}\text{sec.}^{-1}$

$$A = 13.38$$

$$B = 4,637$$

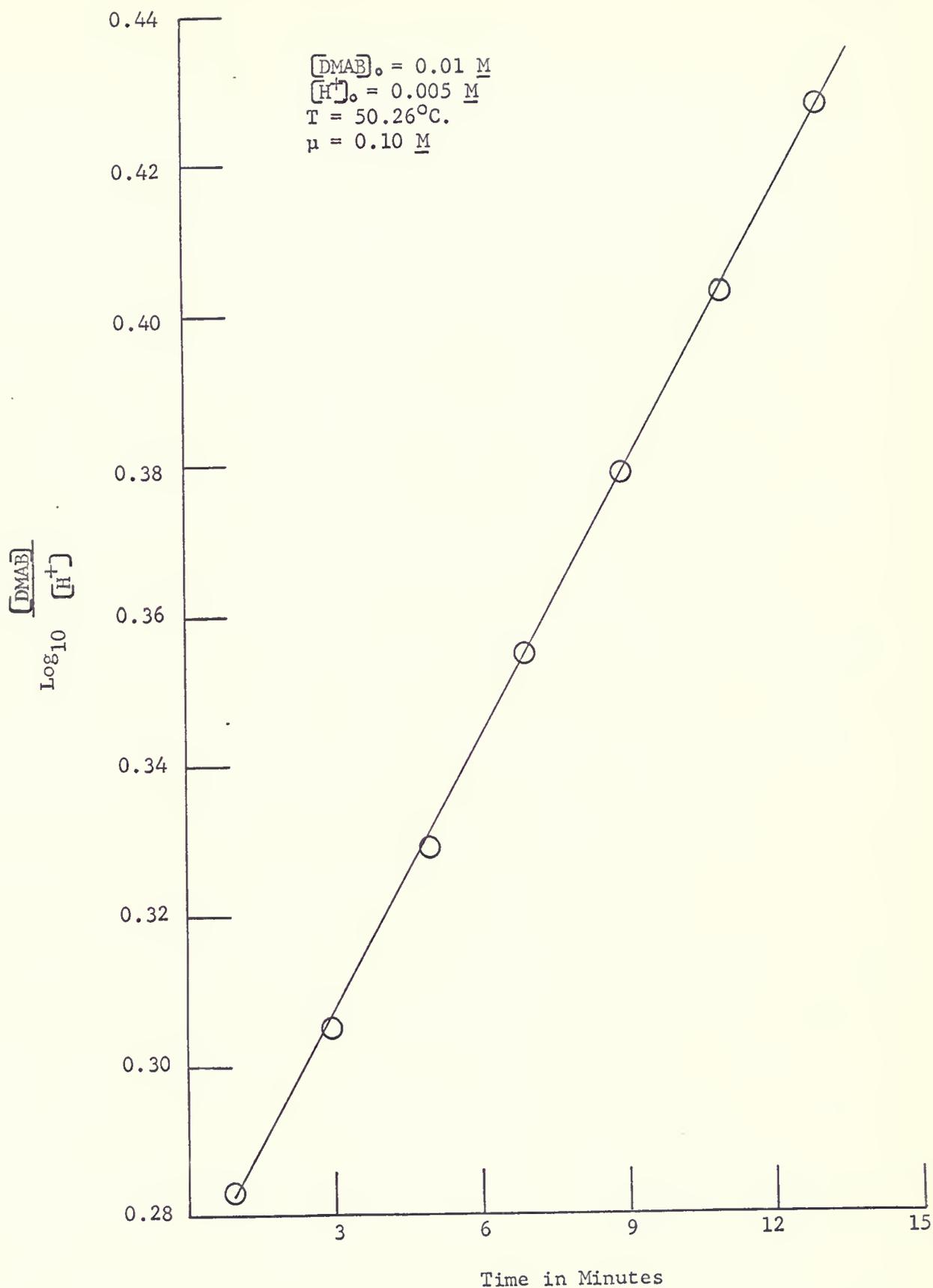


Fig. 9. Second Order Rate Plot for Dimethylamineborane (DMAB) in Water

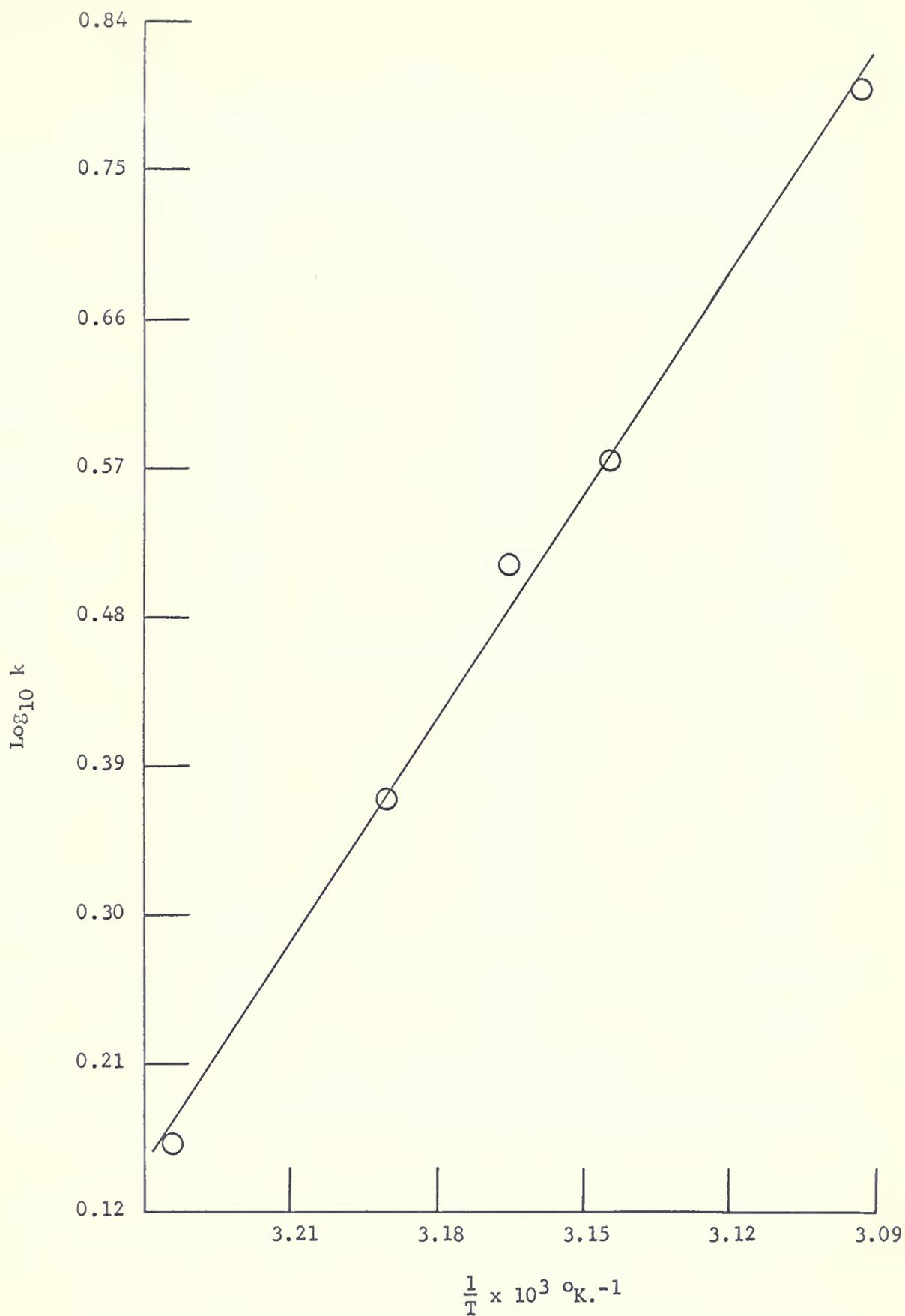


Fig. 10. Arrhenius Plot for the Acid Hydrolysis of Dimethylamineborane in Water

TABLE 13  
 KINETIC DATA FOR TMAB IN 50 PER CENT 1-PROPANOL-WATER  
 AT 31.83°C.

$[H^+]$	[TMAB]	$\log [H^+] / [TMAB]$	Time, min.
1.022	0.706	0.161	0
0.930	0.614	0.180	60
0.840	0.524	0.205	120
0.744	0.428	0.240	255
0.705	0.389	0.258	315
0.699	0.353	0.278	375
0.647	0.331	0.291	426
$k = 2.2 \times 10^{-3}$ liter/mole/min.			
1.022	0.574	0.250	0
0.946	0.498	0.279	60
0.879	0.431	0.309	117
0.811	0.363	0.349	210
0.772	0.324	0.377	267
0.741	0.293	0.403	325
0.711	0.263	0.432	382
$k = 2.42 \times 10^{-3}$ liter/mole/min.			

TABLE 14

KINETIC DATA FOR TMAB IN 50 PER CENT 1-PROPANOL-WATER AT 35.85°C.

[H <sup>+</sup> ]	[TMAB]	log [H <sup>+</sup> ]/[TMAB]	Time, min.
1.022	0.514	0.298	0
0.910	0.402	0.355	60
0.828	0.320	0.413	121
0.730	0.222	0.517	233
0.694	0.186	0.572	301
0.649	0.141	0.663	407
$k = 4.05 \times 10^{-3}$ liter/mole/min.			
1.022	0.659	0.191	0
0.951	0.588	0.209	30
0.827	0.466	0.250	90
0.755	0.392	0.285	150
0.668	0.305	0.340	240
0.604	0.240	0.400	308
$k = 4.20 \times 10^{-3}$ liter/mole/min.			

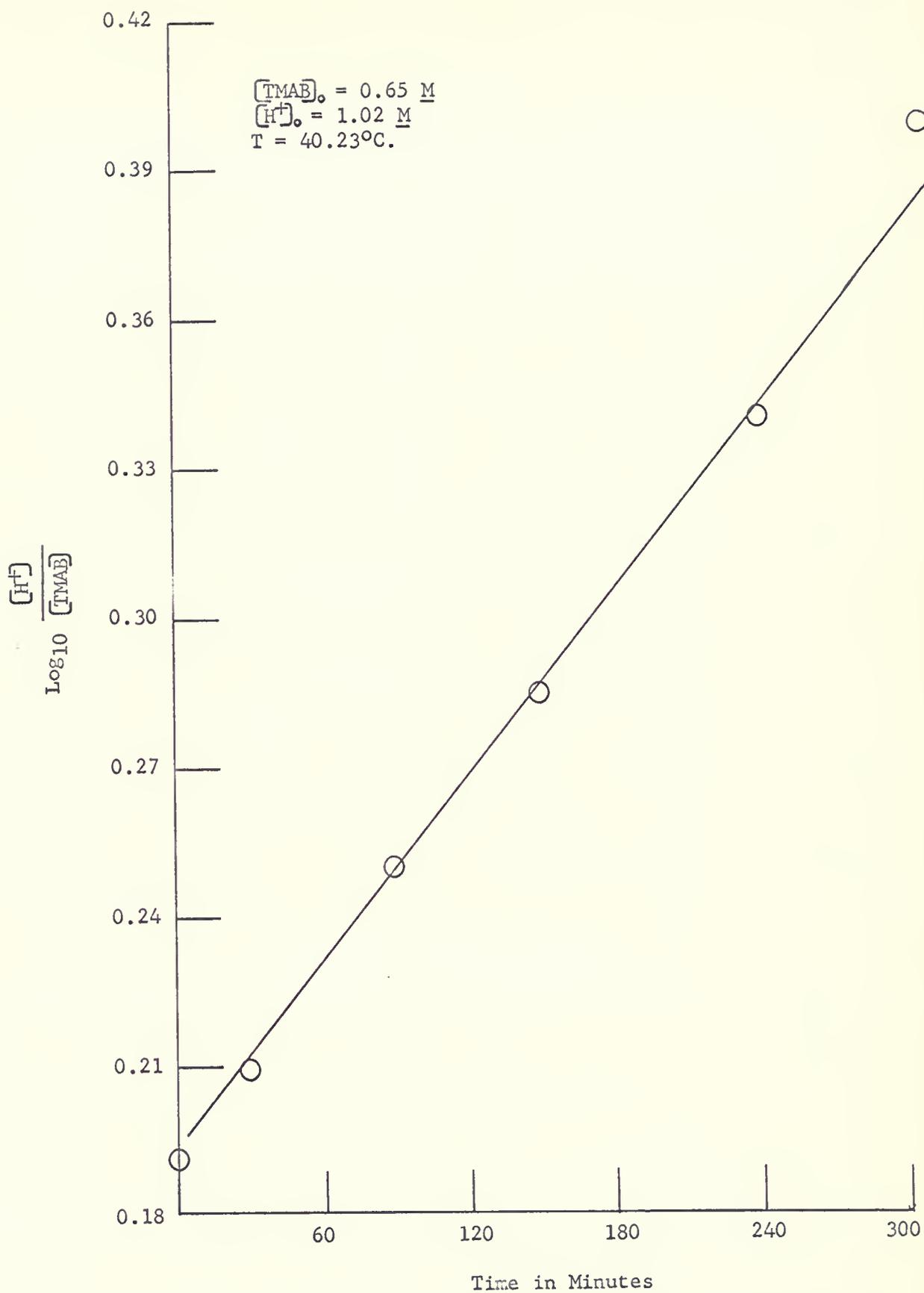


Fig. 11. Second Order Rate Plot for Trimethylamineborane (TMAB) in 50 Per Cent 1-Propanol-Water

TABLE 15

KINETIC DATA FOR TMAB IN 50 PER CENT 1-PROPANOL-WATER AT 40.23°C.

[H <sup>+</sup> ]	[TMAB]	log [H <sup>+</sup> ]/[TMAB]	Time, min.
1.022	0.653	0.195	0
0.914	0.541	0.228	30
0.825	0.456	0.257	57
0.760	0.391	0.289	86
0.696	0.327	0.328	123
0.657	0.288	0.358	150
0.616	0.247	0.397	186
k = 6.77 x 10 <sup>-3</sup> liter/mole/min.			
0.818	0.371	0.343	0
0.756	0.309	0.389	35
0.719	0.272	0.422	61
0.681	0.234	0.464	92
0.651	0.204	0.504	124
0.626	0.179	0.544	151
0.605	0.158	0.583	182
k = 6.81 x 10 <sup>-3</sup> liter/mole/min.			

TABLE 16  
 KINETIC DATA FOR TAMB IN 50 PER CENT 1-PROPANOL-WATER  
 AT 44.38°C.

[H <sup>+</sup> ]	[TMAB]	log [H <sup>+</sup> ]/[TMAB]	Time, min.
0.818	0.422	0.287	0
0.719	0.323	0.348	31
0.659	0.236	0.399	58
0.613	0.217	0.451	84
0.568	0.172	0.519	120
0.540	0.144	0.574	151
0.522	0.126	0.617	174

k = 1.10 x 10<sup>-2</sup> liter/mole/min.

TABLE 17

SUMMARY OF KINETIC DATA FOR TMAB IN 50 PER CENT 1-PROPANOL-WATER

$k, \text{l.mole}^{-1}\text{min.}^{-1}$	Standard deviation	$\log k$	$1/T, 10^3 \times \text{°K.}^{-1}$
$2.31 \times 10^{-3}$	0.11	-2.635	3.279
$4.13 \times 10^{-3}$	0.08	-2.384	3.236
$6.79 \times 10^{-3}$	0.02	-2.168	3.191
$1.10 \times 10^{-2}$	-	-1.959	3.149

$$\Delta E^\ddagger = 23.4 \text{ kcal./mole}$$

Arrhenius parameters from  $\log k = A - B/T$ .  $k$  in  $\text{l.mole}^{-1}\text{sec.}^{-1}$

$$A = 12.30$$

$$B = 5,110$$

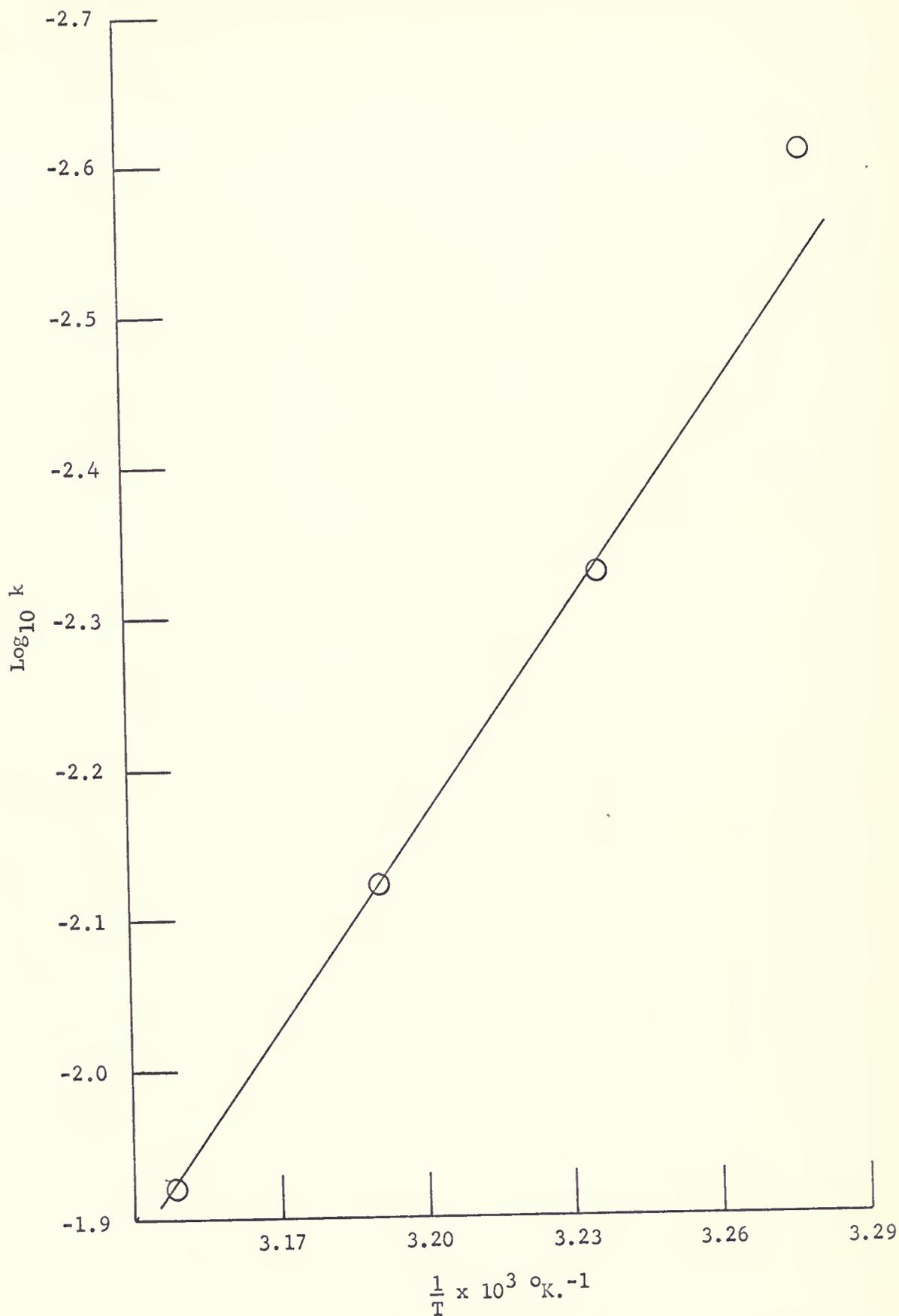


Fig. 12. Arrhenius Plot for the Acid Hydrolysis of Trimethylamineborane in 50 Per Cent 1-Propanol-Water

TABLE 18

KINETIC DATA FOR DMAB IN 50 PER CENT 1-PROPANOL-WATER  
AT 6.5°C.

$[H^+]$	[DMAB]	$\log [H^+]/[DMAB]$	Time, min.
0.818	0.425	0.284	0.0
0.769	0.376	0.311	20.0
0.729	0.336	0.336	41.5
0.685	0.292	0.370	63.5
0.649	0.256	0.404	85.0
0.595	0.202	0.469	122.5

$k = 8.81 \times 10^{-3}$  liter/mole/min.

TABLE 19  
KINETIC DATA FOR DMAB IN 50 PER CENT 1-PROPANOL-WATER  
AT 10.5°C.

[H <sup>+</sup> ]	[DMAB]	log [H <sup>+</sup> ]/[DMAB]	Time, min.
0.818	0.425	0.284	0.0
0.764	0.371	0.314	15.5
0.705	0.312	0.354	31.0
0.656	0.263	0.397	49.0
0.599	0.206	0.463	70.0
0.571	0.178	0.506	85.0

$k = 1.55 \times 10^{-2}$  liter/mole/min.

TABLE 20  
KINETIC DATA FOR DMAB IN 50 PER CENT 1-PROPANOL-WATER  
AT 14.6°C.

[H <sup>+</sup> ]	[DMAB]	log [H <sup>+</sup> ]/[DMAB]	Time, min.
0.818	0.454	0.256	0.0
0.744	0.380	0.292	11.0
0.661	0.297	0.348	25.0
0.589	0.225	0.418	40.0
0.549	0.185	0.472	50.0
0.518	0.154	0.527	60.0

$k = 2.87 \times 10^{-2}$  liter/mole/min.

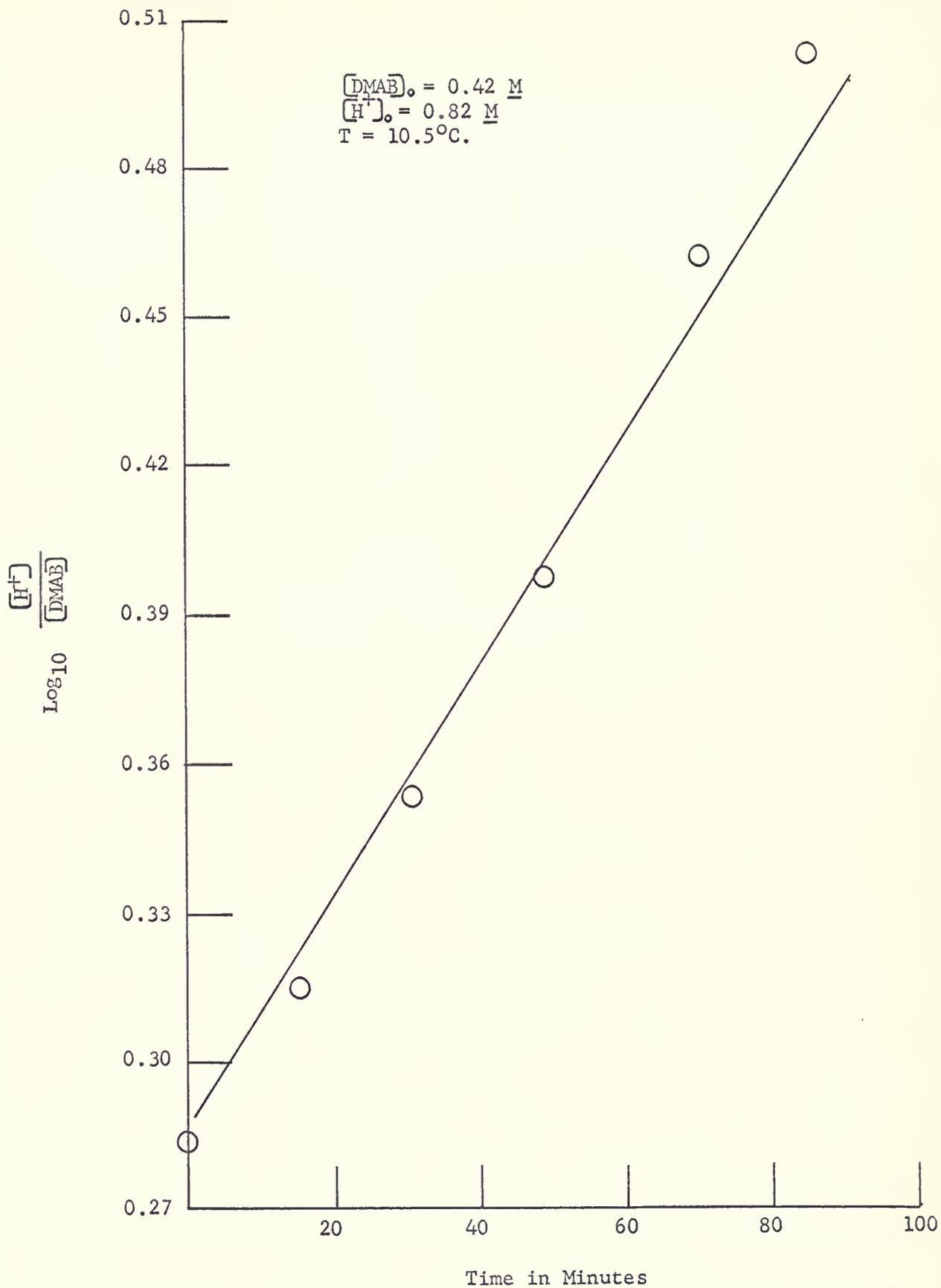


Fig. 13. Second Order Rate Plot for Dimethylamineborane (DMAB) in 50 Per Cent 1-Propanol-Water

TABLE 21

SUMMARY OF THE KINETIC DATA FOR DMAB IN 50 PER CENT 1-PROPANOL-  
WATER

$k, \text{l.mole}^{-1}\text{min.}^{-1}$	$\log k$	$1/T, 10^3 \times \text{°K.}^{-1}$
$8.81 \times 10^{-3}$	-2.055	3.575
$1.55 \times 10^{-2}$	-1.810	3.525
$2.87 \times 10^{-2}$	-1.542	3.475

$$\Delta E^\ddagger = 22.0 \text{ kcal./mole}$$

Arrhenius parameters from  $\log k = A - B/T$ :  $k$  in  $\text{l.mole}^{-1}\text{sec.}^{-1}$

$$A = 13.64$$

$$B = 4,890$$

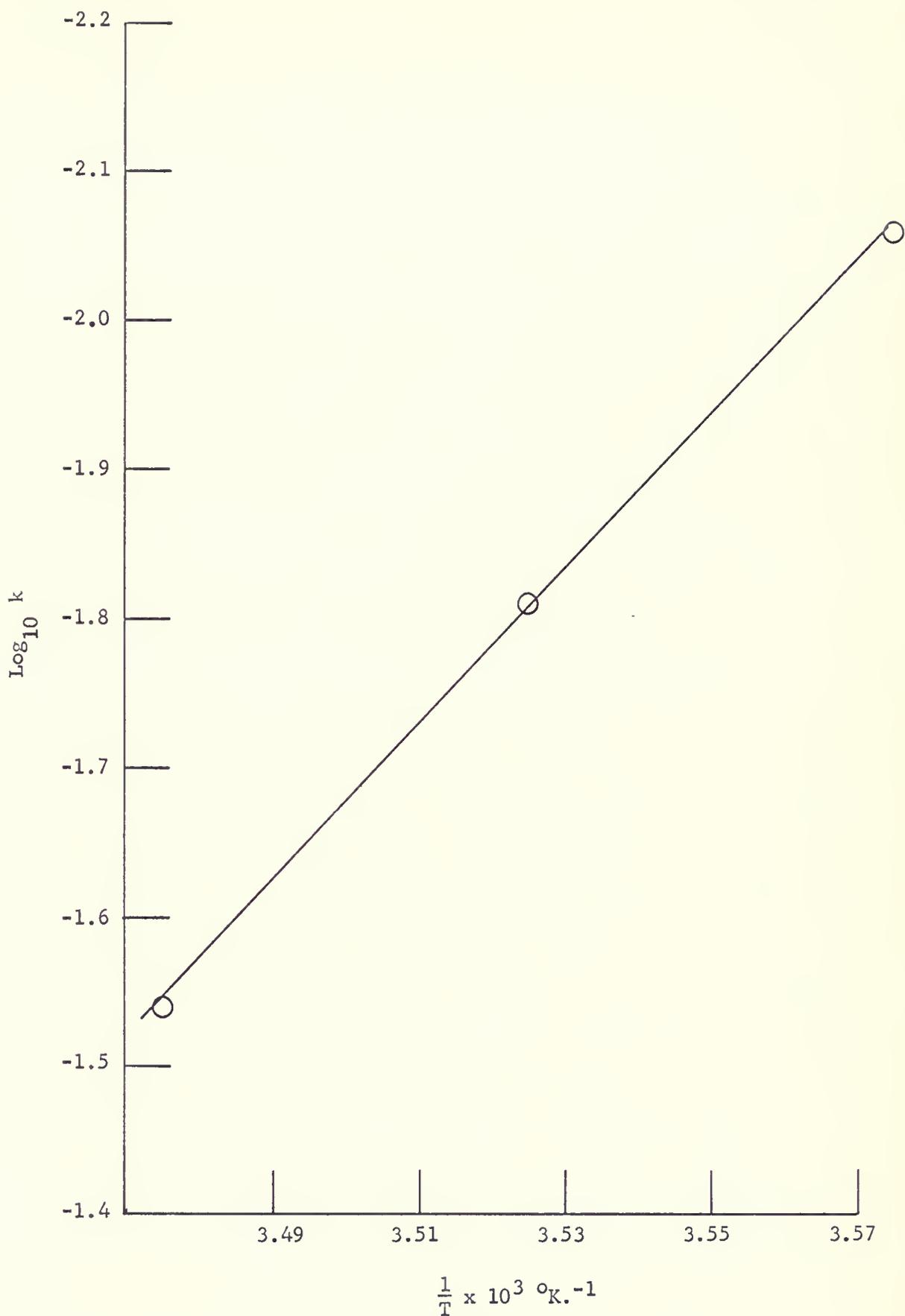


Fig. 14. Arrhenius Plot for the Acid Hydrolysis of Dimethylamineborane in 50 Per Cent 1-Propanol-Water

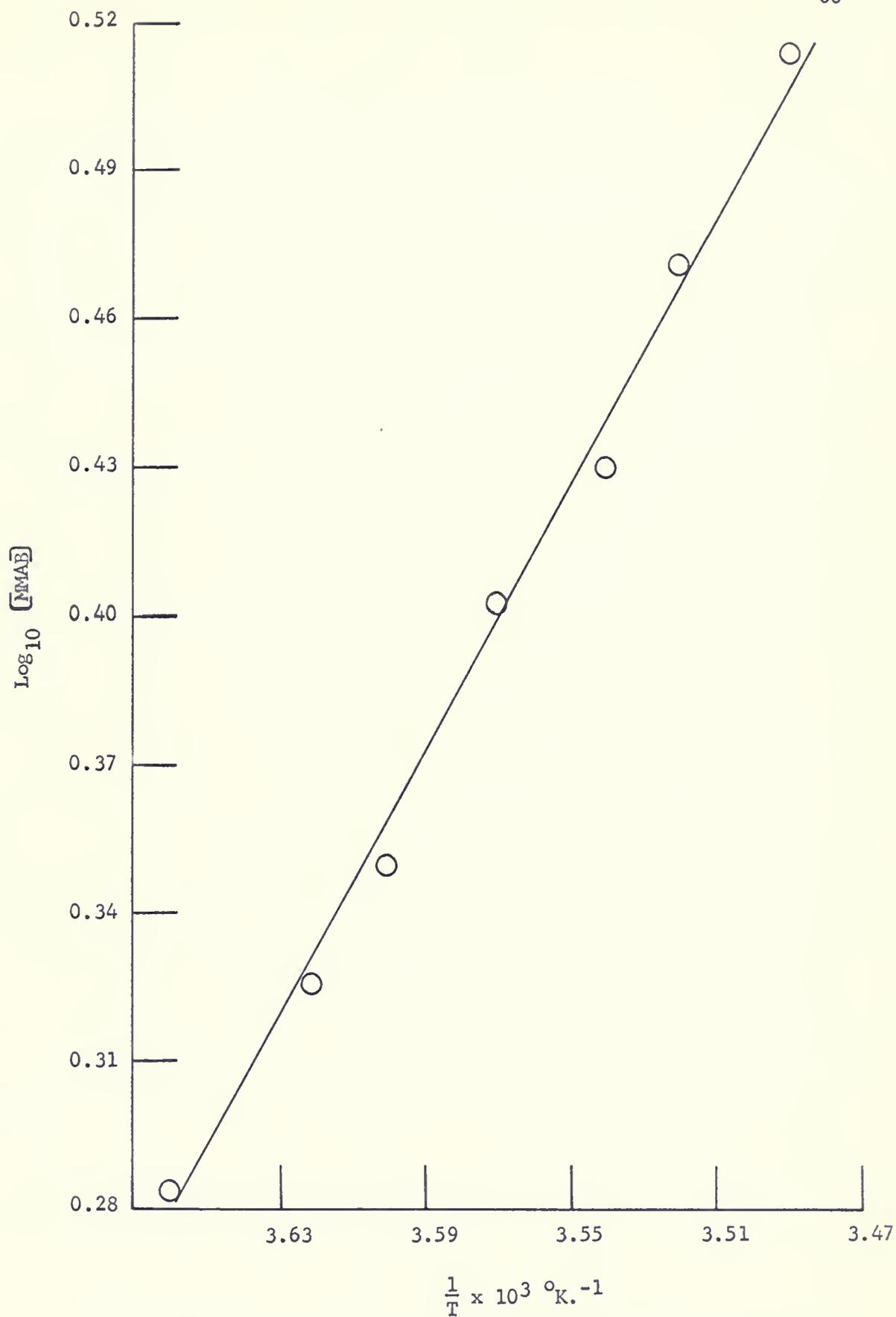


Fig. 15. Solubility of Methylamineborane (MMAB) in Water

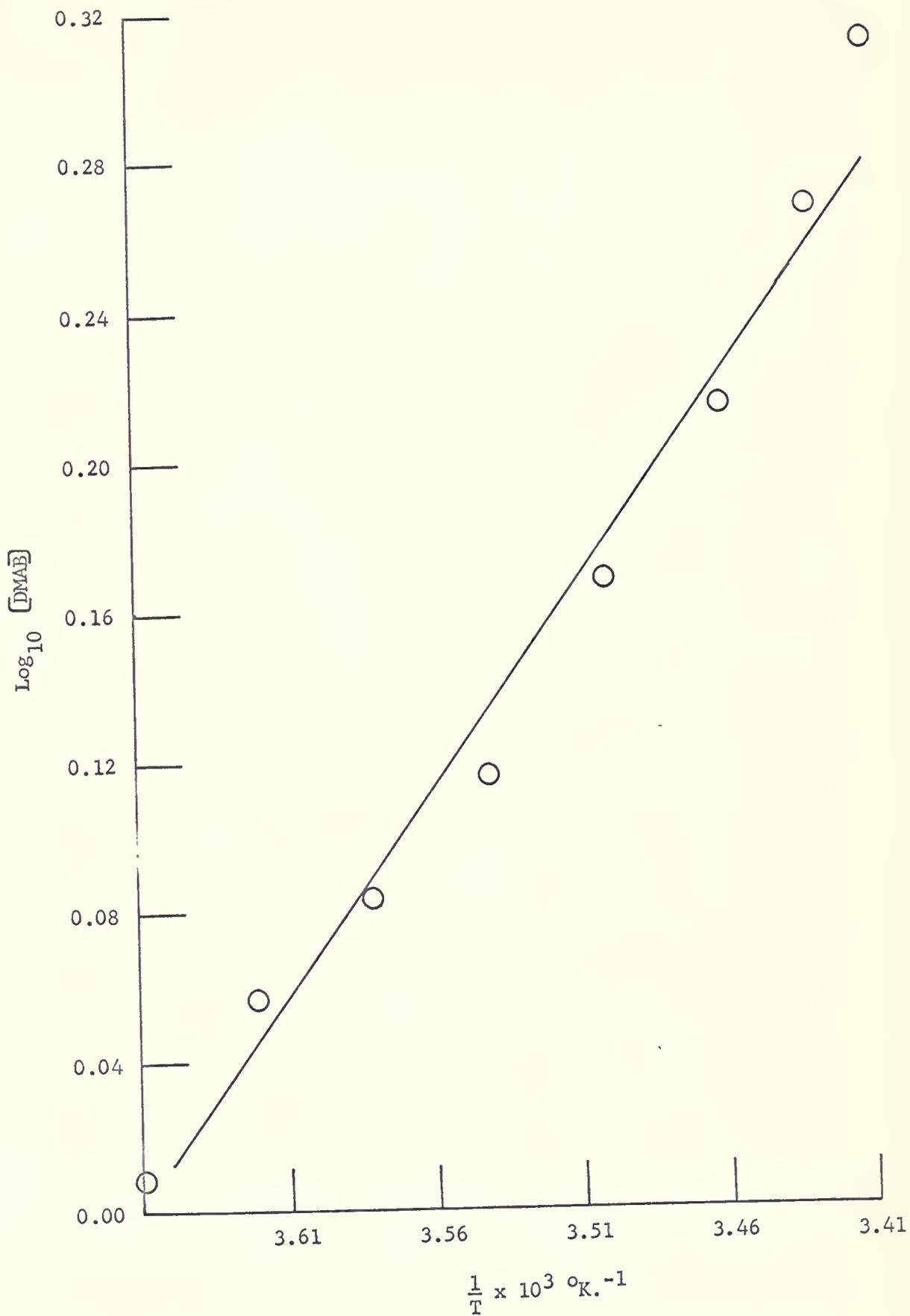


Fig. 16. Solubility of Dimethylamineborane (DMAB) in Water

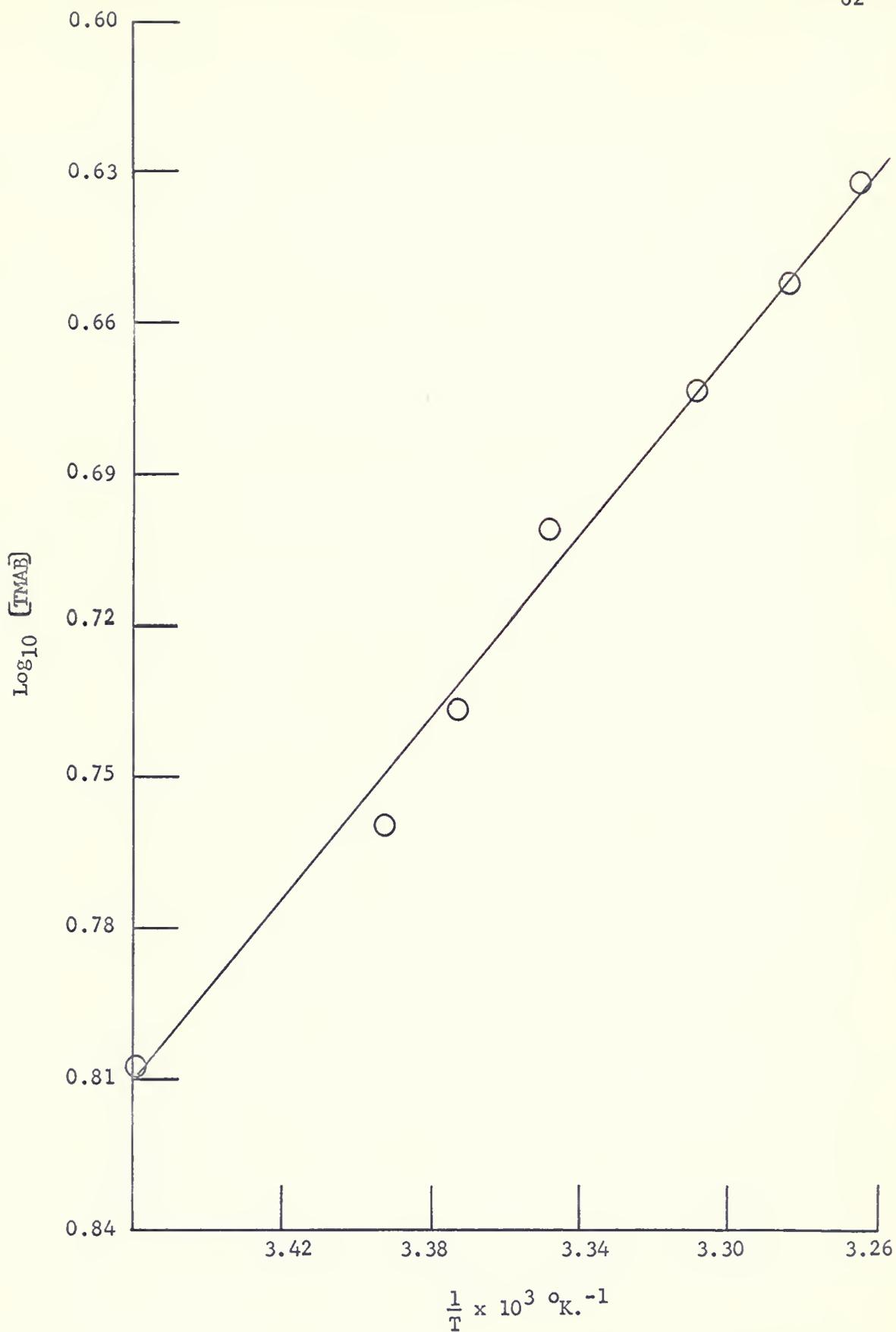


Fig. 17. Solubility of Trimethylamineborane (TMAB) in Water



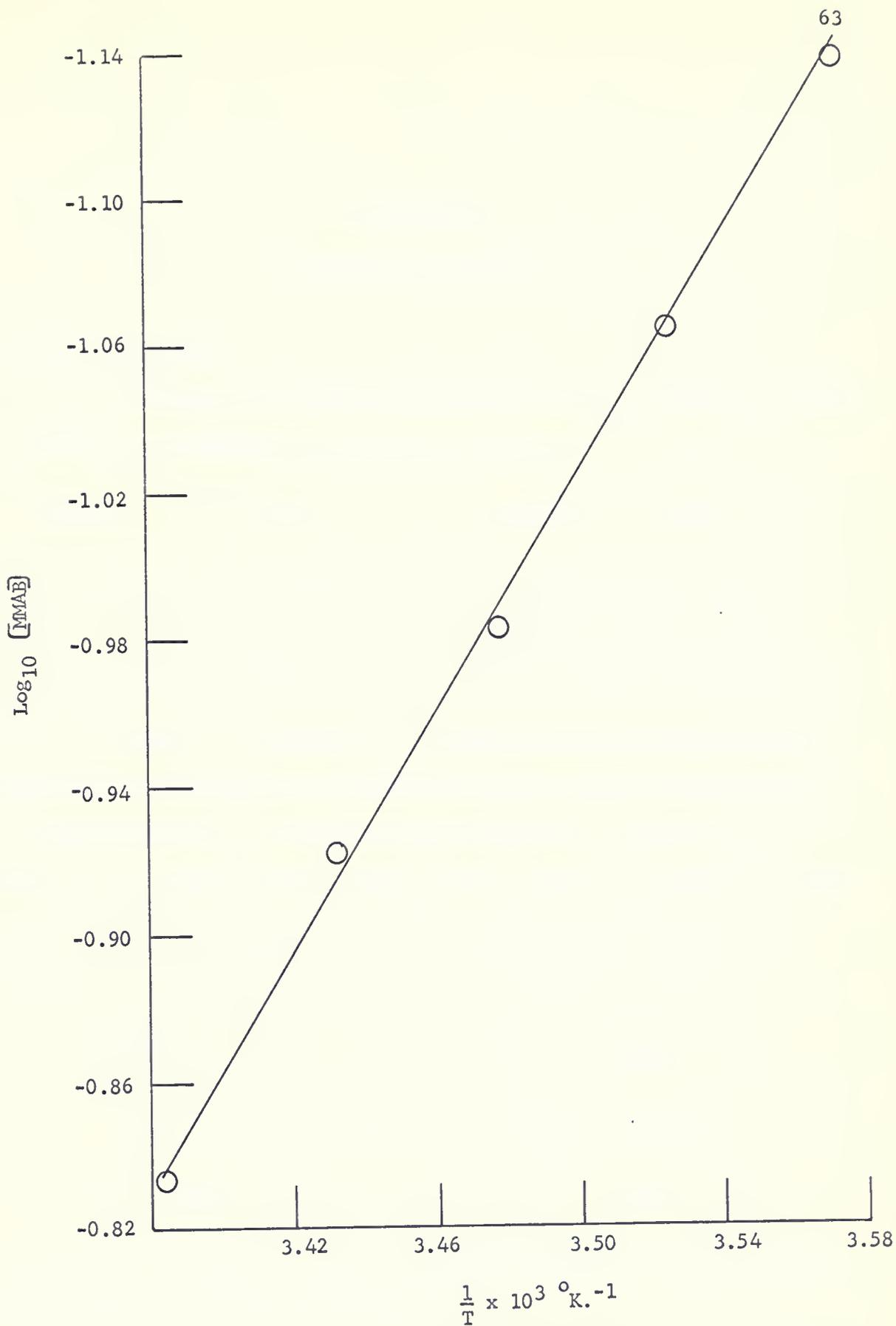


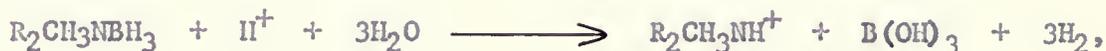
Fig. 18. Solubility of Methylamineborane (MMAB) in Benzene

## CHAPTER IV

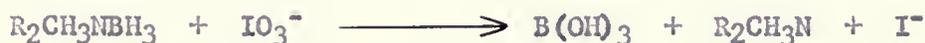
### DISCUSSION OF RESULTS

#### A. Aqueous kinetics

The reaction of the methylamineboranes in acidic solution proceeds to completion according to the overall equation



where R is CH<sub>3</sub> or H. The reaction can be studied by several modes of analysis. The H<sup>+</sup> concentration can be followed by measuring the instantaneous pH of the solution, or by quenching with base and back titrating. The amount of hydrogen gas evolved can be followed by manometric techniques, taking into account the solubility of the gas in solution. The reducing power of the solution can be followed by quenching the reaction with excess iodate, converting the iodate to iodine with excess acid and potassium iodide, and then back titrating the iodine with arsenite. The following set of reactions describes this method:



This method of analysis of boranes was first reported by Lyttle, Jensen, and Struck<sup>42</sup> for the borohydride group.

The stoichiometry of the reaction was established by a combination of two methods. The hydrogen ion, boric acid, and methylammonium ion concentrations were determined by a potentiometric titration with  $\text{OH}^-$ , as aliquots were removed during different stages of the reaction. The instantaneous reducing power of the solution was simultaneously determined by the iodate method. The experimentally determined stoichiometry agreed with the overall equation for the acid hydrolysis indicated above. These results also agree with Ryschkewitsch's<sup>57</sup> study of the acid hydrolysis of trimethylamineborane, in which the author concludes that there is no build-up of B-H intermediates.

In this work the aqueous hydrolyses were followed by measuring the instantaneous pH of the solutions. The excellent fit of the data to second order kinetics, the agreement with the proposed stoichiometry, and the conclusions of other investigators<sup>34,57</sup> appear to preclude the formation of any oxidizable B-H intermediates that could be detected by our methods.

The general rate equation is given by

$$-d[\text{R}_2\text{CH}_3\text{NBH}_3]/dt = k[\text{R}_2\text{CH}_3\text{NBH}_3][\text{H}^+], \quad (1)$$

where  $k$  is the second order rate constant,  $t$  is the time, and the brackets indicate molar concentrations. Expressing (1) in terms of the initial concentrations and the amount reacted after some time,  $t$ ;  $a$  and  $b$ , and  $x$ , respectively, we have

$$dx/dt = k(a-x)(b-x). \quad (2)$$

Separating the variables, integrating, and imposing the boundary condition that  $x$  is zero when  $t$  is zero, the resulting equation is

$$kt = \frac{1}{(a-b)} \ln \frac{b(a-x)}{a(b-x)} . \quad (3)$$

A plot of  $\log (a-x)/(b-x)$  versus time should thus be linear with a slope equal to  $k(a-b)/2.303$ . The linear plots obtained from our data are confirmation that the reaction is first order in amineborane concentration and first order in hydrogen ion concentration. This is the same conclusion reached by Kelly, Marchelli, and Giusto<sup>39</sup> in their investigation of the hydrolysis of several amineboranes.

In a somewhat analogous manner to the treatment of the hydrolysis of trimethylamineborane by Ryschkewitsch,<sup>57</sup> there appear to be several possible mechanisms consistent with the data. Besides the solvated proton, the acids water, methylammonium ion, and boric acid could conceivably react with the amineboranes according to the following equations:



The reactions of the amineboranes with water, methylammonium ion, or boric acid can be eliminated from consideration because of their comparatively slow reaction rates with respect to the rate of the reaction with hydrogen ion in the time and concentration ranges studied.

There are two possible equilibria that could produce a  $BH_3$  species; a displacement,



or a dissociation,



The  $\text{BH}_3$  fragment could then be attacked by the acids listed in equations (4a)-(4d):



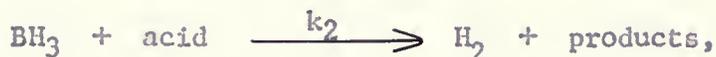
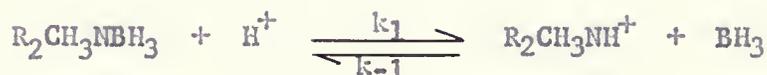
Another alternative is the direct attack of the solvated proton on the B-H bond of the amineborane,



Hawthorne and Lewis<sup>34</sup> have reported this type of mechanism in their study of the hydrolysis of pyridine diphenylborane in acetonitrile. The most direct approach would be a study of the isotope effect in the hydrolysis of the amineboranes and their deuterated analogs, i.e.,  $\text{R}_2\text{CH}_3\text{NBH}_3$  and  $\text{R}_2\text{CH}_3\text{NBD}_3$ . However, Davis *et al.*<sup>17</sup> found that trimethylamineborane undergoes a rapid and quantitative exchange of the boron hydrides with heavy water,  $\text{D}_2\text{O}$ . Therefore, nothing would be gained by running the deuterated compound in aqueous solutions if the rate of deuteration greatly exceeded the rate of hydrolysis. Ryschkevitch and Birnbaum<sup>58</sup> studied the kinetics of pyridineborane in 1-propanol and in 1-propanol-water solutions, and the authors conclude that the reaction probably proceeds by loss of the

amine rather than  $H^+$  in the slow step. Kelly, Marchelli, and Giusto<sup>39</sup> studied the solvolysis of several amineboranes and proposed that the mechanism involved a rate determining attack of the solvated proton on the amineborane, in which a proton is being transferred to the nitrogen atom concurrent with a loosening of the B-N bond, followed by a rapid solvolysis of the borane fragment. A borane cation of the type  $(R_3N)_2BH_2^+$  has been reported by Miller and Muertertities<sup>45</sup> and found to be very stable toward acid attack. We would suspect that the borane cation in equation (8) would be coordinated to the solvent water to form the analogous species  $(R_2CH_3N)(H_2O)BH_2^+$ . On the basis of the evidence in the literature cited above, we would thus eliminate equation (8) from consideration as a possible mechanism.

First order kinetics in the acid concentration could result from a rapid displacement equilibrium, followed by the slow reaction of the borane fragment with a protonic species, equations (7b)-(7d). We would like to show how this process can be eliminated from consideration. If we assume the reaction proceeds by



where  $k_1$  and  $k_{-1}$  are the forward and reverse rate constants for the rapid displacement equilibria, and  $k_2$  is the rate constant of the slow step, then the rate expression would be given by  $\text{rate} = k_2 [BH_3] [\text{acid}]$ . The  $BH_3$  concentration can be related to the equilibrium constant,  $K$ , of the displacement equilibrium by

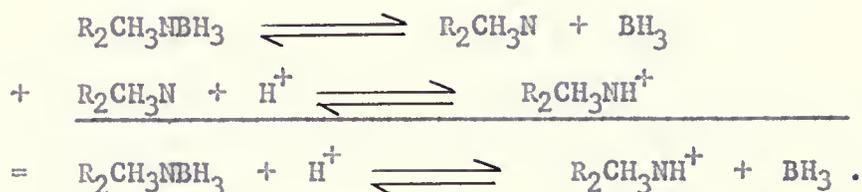
$$K = \frac{[\text{BH}_3] [\text{R}_2\text{CH}_3\text{NH}^+]}{[\text{R}_2\text{CH}_3\text{NBH}_3] [\text{H}^+]}$$

Solving for the  $\text{BH}_3$  concentration in terms of  $K$  and substituting this in the rate expression, we arrive at the new rate expression

$$\text{rate} = \frac{k_2 K [\text{R}_2\text{CH}_3\text{NBH}_3] [\text{H}^+] [\text{acid}]}{[\text{R}_2\text{CH}_3\text{NH}^+]}$$
 (9)

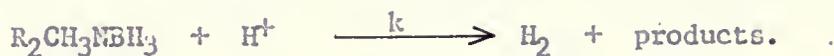
It can be seen immediately why (7a) is eliminated. If the acid is  $\text{H}^+$ , and this is substituted in (9) for the acid, then this will give a rate expression that is second order in hydrogen ion, which is contrary to our observed data. However, substituting water, methylammonium ion, or boric acid for the acid in (9) would present a rate expression that is first order in hydrogen ion. The rate would also be inversely proportional to the methylammonium concentration, as readily seen from equation (9). Therefore the addition of the methylammonium ion to the solution should retard the rate, if this is the correct mechanism. This would be true of course only for (7b) or (7d), which contain water and boric acid as the attacking acids. Actually, the rate of the trimethylamineborane hydrolysis is increased by the addition of trimethylammonium ion according to Ryschkewitsch's<sup>57</sup> study, and we would assume an analogous effect for the other two adducts. Thus, we have so far eliminated a rapid displacement equilibrium followed by a slow solvolysis of the borane fragment by hydrogen ion, water, or boric acid. We would also like to eliminate from consideration the equilibrium followed by the slow reaction of the borane fragment with methylammonium ion, for the following reasons. If step (7c) is analogous to reaction with hydrogen ion, and if the

reactivity increases with the acid strength, then both steps would be competing and (7a) should be faster. Therefore, as long as the equilibrium is maintained, step (7a) would produce second order kinetics in a hydrogen ion. This has already been eliminated as being contrary to our results. Therefore, a rapid displacement equilibrium followed by the slow reaction of a borane fragment in steps (7a) through (7d) has been eliminated from consideration as a possible mechanism. The dissociation equilibrium (6), can also be eliminated, because the displacement equilibrium (5), is a combination of (6) and the rapid proton transfer equilibrium to the methylammonium ion,

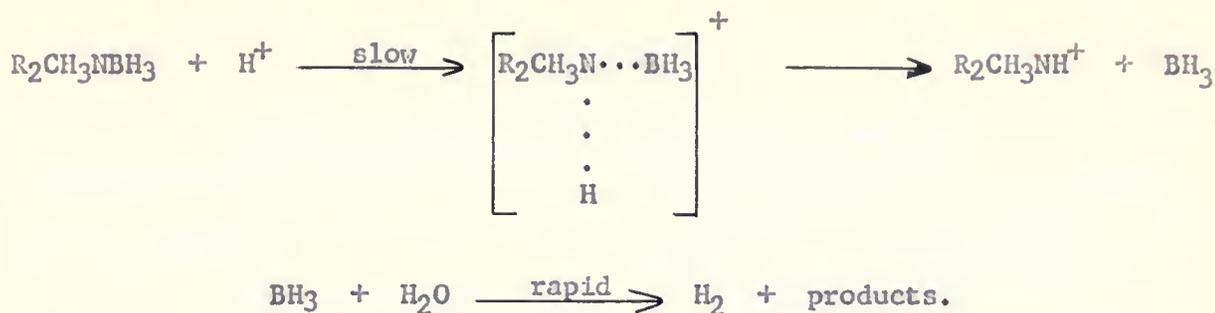


This, of course, has been eliminated as indicated above.

However, if step (7a) were so fast that equilibrium is not maintained, then step (4a) would represent the reaction, i.e.,



Thus, first order kinetics in amineborane concentration and first order kinetics in hydrogen ion concentration would be observed from the protonation of the nitrogen atom of the amineborane, concurrent with B-N bond breakage, followed by a rapid solvolysis of the borane intermediate. The reaction, including the transition state, can be conceived as



This type of transition state is also in agreement with the ionic strength dependence of the trimethylamineborane hydrolysis studied by Ryschkewitsch,<sup>57</sup> and that proposed by Kelly, Marchelli, and Giusto<sup>39</sup> in their study. The latter authors base their hypothesis on the influence of substituents on the aniline ring in  $\text{C}_6\text{H}_5\text{NH}_2\text{BH}_3$  and on dielectric effects from using mixed solvents.

The activation energies and the Arrhenius parameters calculated for the methylamineboranes are listed in Table 22 on the next page. On the basis of the proposed transition state and the rate determining protonation of the amineborane, there are several factors which may be helpful in explaining the trend in activation energies. These factors include any influences which weaken or strengthen the B-N bond, steric and inductive effects, and the stabilization of the transition state and reactants by the solvent.

A study of the heat of the reaction



could be an indication of the relative B-N bond strengths of the adducts. McCoy and Bauer<sup>44</sup> have calorimetrically determined the heat of reaction for the gaseous reactants to give the solid adducts. At the time of their study, the heats of vaporization of the methylamineboranes had not been determined. Values for the gaseous heats of reaction were obtained by

TABLE 22  
THE ACID HYDROLYSIS OF THE METHYLAMINEBORANES

Methylamineborane	A	B	$\Delta E^\ddagger$ , kcal./mole	Temp. range, °C.
Water				
Methyl	11.14	3,457	15.81	26.5-55.0
Dimethyl	13.38	4,637	21.21	36.0-50.0
Trimethyl <sup>62</sup>	14.74	5,623	25.73	35.0-44.0
50 Per Cent 1-Propanol-Water				
Dimethyl	13.6	4,890	22.0	6.5-14.6
Trimethyl	12.3	5,110	23.4	31.8-44.4

Arrhenius parameters for the second order rate constants and activation energies:

$$\log k = A - B/T; k \text{ in } \text{l.mole}^{-1}\text{sec.}^{-1}$$

$$A = \log A'$$

$$B = \Delta E^\ddagger (1000)/2.303 R$$

adding the heats of vaporization found by Parry *et al.*<sup>50</sup> to the values for the solid adducts obtained by McCoy and Bauer. These values are listed in Table 24 on page 82. The heat of dissociation of diborane enters into the heat of reaction, but this will be true for each methylamineborane and will not affect the trend in these heats. It is seen that the trimethylamineborane has the highest heat of reaction and would, on this basis, be expected to have the highest activation energy. Analogous arguments apply to the two other methylamineboranes, and the trend in activation energies should parallel the trends in the absolute values of the heats of formation of the amineboranes.

This same trend would also be predicted on the basis of inductive effects. The trimethylamineborane would be expected to have the nitrogen atom with the highest electron density compared to the other two methylamineboranes, and would be expected to have the strongest B-N bond. The stronger the B-N bond in the transition state, the more difficult it would be to break this bond, and hence the activation energy should increase with bond strength. Since the heats of reaction of the methylamines with diborane is also a measure of the relative bond strengths, McCoy and Bauer's work also indicates an increase in bond strength from methyl- to trimethylamineborane, when their data has been adjusted to the gas phase. However, some data on the interaction of methylamines and Lewis acids do not exhibit this trend. Instead the trend appears to be dimethylamine > monomethylamine  $\approx$  trimethylamine. This is true of Brown, Bartholomay, and Taylor's<sup>8</sup> study of the gaseous dissociation of the methylaminetrimethylboranes; Bauer's<sup>27</sup> work on the methylamines and borontrifluoride; and the data quoted by Braude and Nachod<sup>6</sup> on the heats of reaction of the methylamines and borontrifluoride in nitrobenzene. However, these reactions do

not involve the same substituents on the boron atom, are subject to solvent effects in the case of the nitrobenzene measurements, and consequently make strict comparisons difficult. Also, when the solid adduct is formed from gaseous reactants, different Lewis acids will be subject to different lattice effects which influence the heats of vaporization.

In all of these cases, and in our case as well, there is only a difference of a few kilocalories per mole for the heats of reaction of the methylamines with the boranes. One can conclude that an explanation of the trends in activation energies based only on the B-N bond strengths or on inductive effects is inconclusive, but that these factors necessarily influence the activation energies. Bauer<sup>27</sup> also agrees that heats of association and the activation energies of the methylamineboranes should be only roughly related.

Assuming the first step in the mechanism, the slow or rate determining step, is the protonation of the nitrogen atom of the amineborane, then there appear to be two important factors to consider. Sterically, it would be expected that trimethylamineborane would be least susceptible to an attack by a solvated proton. Conversely, the monomethylamineborane would be the most readily attacked of the three amineboranes. Therefore the monomethylamineborane might be expected to react faster than the dimethylamineborane, etc. This does agree with the observed rates of hydrolysis for the amineboranes.

One would also expect the solvent to influence this first step, depending on the effective acidity of the solvated proton in different media.

On the basis of electronic effects, the nitrogen atom in the monomethylamineborane would be expected to have the lowest electron density of the three amineboranes. Therefore on the basis of attraction for the solvated proton, the monomethylamineborane would react the slowest. However, the steric, electronic, and inductive effects may be minor compared to other factors such as hydrogen bonding and dielectric effects, which are discussed below.

In considering solvent effects, a hypothetical energy diagram can be constructed showing the energies involved in going from the solvent phase to the gas phase. This diagram is illustrated on the following page. Attention will be focused on the reactants and the transition states; the transition state is assumed to be a loosely bound methylammonium ion and a borane fragment. Once the B-N bond is loosened, the borane fragment undergoes rapid solvolysis to the final products.

In the solvation process, the energy terms involved are the heats of hydration,  $\Delta H_h$ , of each species of reactants and transition states and the activation energies of the gaseous and solvated transition states. In the series of the methylamineboranes, the heat of hydration of the proton will be the same in all cases and should not affect the overall energy differences. The borane fragment is present in each transition state and one would expect that the borane portion of the transition state would have an interaction energy with the solvent environment which is independent of the amine portion, even though the energy of formation of each transition state from the gaseous reactants would be related to the B-N bond strength.

Briegleb<sup>7</sup> has found the heats of hydration of methyl-, dimethyl-, and trimethylamine to be -10.4, -11.0, and -11.4 kcal./mole, respectively.

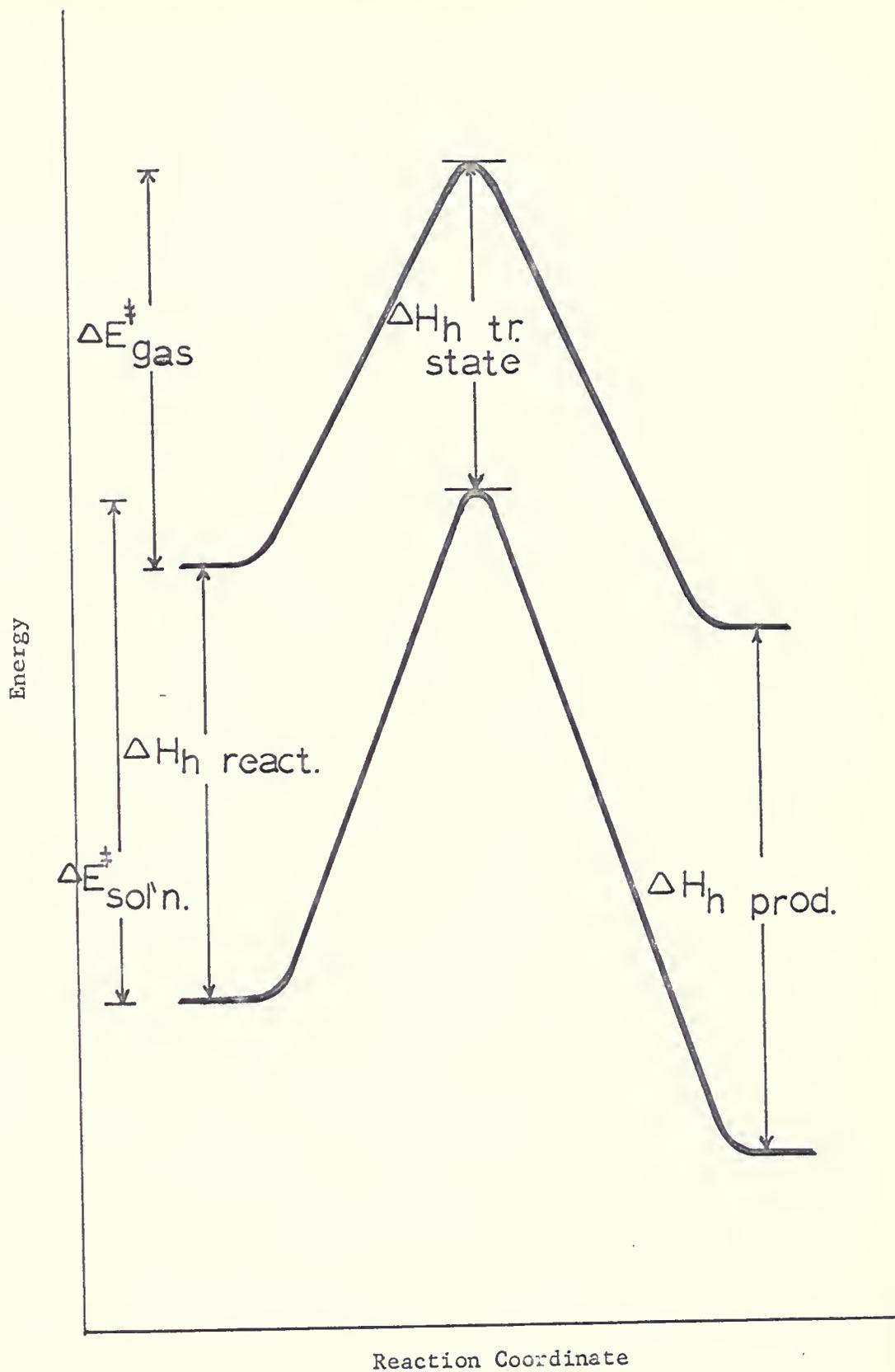
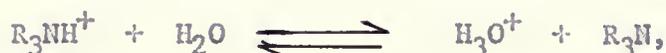


Fig. 19. Reaction Path in the Aqueous (Lower Curve) and in the Gas Phase (Upper Curve)

Therefore, as a first approximation, one would not expect the heats of hydration of the methylamineboranes to differ by much. This is fairly well substantiated by the experimental data obtained from the heats of solution of the amineboranes listed in Table 23 on page 80, and from the heats of vaporization found by Parry et al.<sup>50</sup> The heats of solution were determined from the least squares slope of a plot of log [methylamineborane] versus 1/temperature for the saturated solutions. The heats of hydration were then calculated by subtracting the heats of vaporization from the heats of solution. The temperature ranges of the solubility measurements do not coincide with the temperature ranges of the kinetic data, but only a rough estimate was desired. The curvatures in the solubility curves of the di- and monomethylamineborane (Figures 15 and 16 on pages 60 and 61, respectively) may be due to changes in the degree of association of the molecules. Such behavior has been reported by Noth and Beyer<sup>46</sup> for the methylamineboranes. The values calculated for the heats of hydration of tri-, di-, and monomethylamineborane are -9.1, -12.9, and -12.5 kcal./mole, respectively. Since the heats of solution were calculated from the slope of a log (concentration) versus 1/temperature plot, and since the curvature observed in the di- and monomethylamineborane curves is toward a more rapid increase in the saturation concentration than expected, then one might predict even higher values for the heats of solution of these two adducts in the temperature range of the kinetics, i.e., 25-50°C. This in turn would lead to lower negative heats of hydration of these two amineboranes, since the heats of hydration were calculated from the differences between the heats of solution and the heats of vaporization. Therefore the differences in the

heats of hydration of the methylamineboranes may even be closer together than our data indicate.

It seems that the factor affecting the differences in activation energies to the greatest extent is the heat of hydration of the transition state. If protonation occurs with the concurrent loosening of the B-N bond to form loosely bound methylammonium ion and  $\text{BH}_3$ , then it seems logical to discuss the differences in the heats of hydration of the transition state on the basis of the differences in the heats of hydration of the methylammonium ions, assuming a fairly constant contribution from the  $\text{BH}_3$  part of the molecule. Trotman-Dickenson<sup>65</sup> has postulated that in the equilibrium



the degree of stabilization depends on the number of hydrogen bonds capable of being formed, and on the aqueous ionization constants of the amines. The author states that the effect of methyl substitution, although increasing the base strength inductively, is more than compensated for by the loss of hydrogen bonding; and that the amines will be stabilized to approximately the same extent owing to solvation, but that the amine ions will be stabilized much more, and to different degrees owing to hydrogen bonding. Hall's<sup>33</sup> study of the correlation of the base strengths of the amines confirms Trotman-Dickenson's theory. Pearson and Vogelsong<sup>51</sup> have estimated the heats of hydration of the methylammonium ions to be -71, -63, and -55 kcal/mole for the methyl-, dimethyl-, and trimethylammonium ions, respectively. These values were calculated from a modified Born equation and from the lattice energies of the hydrochlorides and tetramethylammonium chloride. It is seen that there is a

decrease of approximately 8 kilocalories per mole in the heat of hydration when methyl is substituted for hydrogen on the nitrogen atom. Therefore, one might expect that a transition state involving a loosely bound methylammonium ion to a borane fragment is subject to somewhat analogous effects. The monomethylamineborane transition state, capable of forming the greatest number of hydrogen bonds of the three methylamineboranes, would be the most stabilized. Thus, the expected trend in activation energies would be the same as that experimentally observed, for the differences in the stabilization of the transition states are much greater than the differences in the stabilization of the amineboranes.

It is proposed then, that a major factor in the observed trend in activation energies of the methylamineboranes is the stabilization of the transition state by the solvent water. It would be interesting to determine the activation energies of several series of amineboranes, such as the ethyl- or n-propylamineboranes, to test the hypothesis, and to evaluate the consequences of possible steric effects which have been previously discussed. A discussion of the activation energies in a mixed solvent is undertaken in Part B of this section.

Summarizing the factors contributing to the observed trend in activation energies, it is proposed that steric effects play a relatively minor role, that the activation energies follow the trend expected from the B-N bond strengths, but that in addition a most important effect is the stabilization of the methylammonium ion part of the transition state by hydrogen bonding in the aqueous solvent.

#### B. Kinetics in the 50 per cent 1-propanol-water mixed solvent

The kinetics of trimethylamineborane in 1-propanol-water were considerably different at large trimethylamineborane concentrations than

TABLE 23

## SELECTED PHYSICAL VALUES FOR THE METHYLAMINEBORANES AND THE METHYLAMMONIUM IONS

Methylamine- borane or methylammonium ion	$\Delta H_{\text{formation, gas}}$ for methyl- amineboranes <sup>a</sup> in kcal./mole	$\Delta H_v$ for the methylamine- boranes in kcal./mole <sup>50</sup>	$\Delta E^{\ddagger}$ for the methylamine- boranes in kcal./mole	$\Delta H_{\text{sol'n}}$ for the methylamine- boranes in H <sub>2</sub> O in kcal./mole	$\Delta H_n$ for the methylamine- boranes in kcal./mole <sup>b</sup>	$\Delta H_h$ for the methylammon- ium ions in kcal./mole <sup>51</sup>
Methyl	-12.3	18.8	15.81	6.3	-12.5	-71
Dimethyl	-14.0	18.5	21.21	5.6	-12.9	-63
Trimethyl	-17.7	13.6	25.73 <sup>62</sup>	4.5	-9.1	-55

<sup>a</sup>See page 71.<sup>b</sup>See page 77.

those at low concentrations, and the kinetics for these two cases will be discussed separately.

Trimethyl- and dimethylamineborane concentrations greater than 0.300 M. The kinetic data for the acid hydrolysis of tri- and dimethylamineborane show a linear fit to the second order rate expression previously discussed. Dimethylamineborane kinetics were not investigated at low concentrations, but the trimethylamineborane kinetics do not obey the second order rate expression at concentrations around 0.02 M.

The 1-propanol-water azeotrope used in the experiments contains 71.7 per cent 1-propanol and 28.3 per cent water, by weight,<sup>43</sup> as prepared in Part A of the experimental section. The volume ratio of the azeotrope contains 75.8 per cent 1-propanol by volume, as calculated from the room temperature densities of water and 1-propanol. In each experiment two volumes of the azeotrope were mixed with one volume of the aqueous acid (giving a mixture of 50.6 per cent 1-propanol by volume) and throughout this paper this mixture will be referred to as 50 per cent 1-propanol-water.

A comparison of the rate constants found in the mixed solvent with the rate constants found in the pure water is listed in Table 24 on the following page, and shows the rates to be slower in the mixed solvent. This is similar to the behavior found by Ryschkewitsch<sup>57</sup> in the acid hydrolysis of trimethylamineborane in 20 per cent dioxane-water solutions, and that reported by Kelly, Marchelli, and Giusto<sup>39</sup> in their investigation of the hydrolysis rates of several amineboranes in 50 per cent dioxane-water solutions. Ryschkewitsch and Birnbaum,<sup>58</sup> however, found an increase in the rate of solvolysis of pyridineborane in 1-propanol-water solutions compared to the rate in pure water. These authors used the solvents

TABLE 24

COMPARISON OF THE SECOND ORDER RATE CONSTANTS OF DI- AND TRIMETHYLAMINEBORANE IN WATER AND IN 50 PER CENT 1-PROPANOL-WATER

Methylamine- borane	k in water*	k in 50 per cent 1-propanol-water	Temperature, °C.
Dimethyl	$6.50 \times 10^{-4}$	$1.47 \times 10^{-4}$	6.5
	$1.10 \times 10^{-3}$	$2.58 \times 10^{-4}$	10.5
	$1.91 \times 10^{-3}$	$4.78 \times 10^{-4}$	14.6
Trimethyl	$1.87 \times 10^{-4}$	$3.87 \times 10^{-5}$	31.83
	$3.24 \times 10^{-4}$	$6.88 \times 10^{-5}$	35.85
	$5.83 \times 10^{-4}$	$1.13 \times 10^{-4}$	40.23
	$1.00 \times 10^{-3}$	$1.84 \times 10^{-4}$	44.38

k in liter/mole/sec.

\*These values were calculated at the temperatures indicated from the relation  $\log k = A - B/T$ , where the parameters A and B are given in Table 22 on page 72.

themselves as the hydrolyzing acids, and this is probably why the behavior is different from the other cases listed above. The pyridineborane solvolysis involves the dissociation of the adduct into pyridine and a borane fragment as the rate determining step, whereas our data indicate the rate determining step in the acid hydrolysis is the protonation of the nitrogen atom of the amineborane.

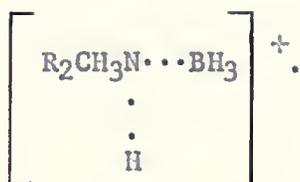
The decrease in rates in the mixed solvents may be caused by a decrease in the pre-exponential factor, A. This factor can be related to the entropy of activation, but definite conclusions based on entropy considerations would be difficult from the present state of our knowledge of the liquid state. The differences in the activation energies in 1-propanol-water and in water only will be discussed on the basis of dielectric and hydrogen bonding effects.

The effect of stabilizing the transition state more than the ground state by hydrogen bonding has been discussed earlier in this section. It was postulated that the trend in activation energies observed in the acid hydrolysis of methylamineboranes can largely be ascribed to the differences in the heats of hydration of the methylammonium ion portion of the transition state caused by hydrogen bonding, the heats of hydration of the methylamine adducts contributing little. On this basis, the transition states of the amineboranes would be stabilized more than the amineboranes themselves by hydrogen bonding with the solvent. Therefore as the hydrogen bonding power of the solvent is reduced, one would predict a higher activation energy for each methylamineborane due to the relative destabilization of the transition states in the mixed solvent. Thus, in the acid hydrolysis of di- and trimethylamineborane in 50 per cent 1-propanol-water, we would expect a higher activation energy in the mixed

solvent for both compounds than in water only. Moreover, the dimethylamineborane transition state should be affected to a relatively greater degree than the trimethylamineborane transition state by changes in the hydrogen bonding power of the solvent. The activation energies obtained in this investigation are listed in Table 22 on page 72, and it is seen that although the activation energy for dimethylamineborane in the mixed solvent is higher than in pure water, the activation energy of the trimethylamineborane is lower in the mixed solvent than in water.

We interpret these data to be the result of two opposing trends. Decreasing the hydrogen bonding power of the solvent tends to increase the activation energy, with the sensitivity increasing from trimethyl- to monomethylamineborane. However, decreasing the dielectric constant of the solvent would tend to decrease the activation energy. This is due to the relatively greater destabilization of the ground state compared to the transition state when the dielectric constant of the solvent is decreased. Now, the dilution of water with 1-propanol reduces both the hydrogen bonding power of the medium and the dielectric constant. Reducing the dielectric constant would then destabilize the ground state relative to the transition state and lead to a lower activation energy.

The acid hydrolysis of the amineboranes can be imagined as the reaction between a small, positively charged, solvated proton and the solvated amineborane dipole to form the larger, positively charged, solvated transition state,



We can assume that the positive charge on the transition state is more diffuse than that on the solvated proton, and consequently the solvated proton will be destabilized more than the transition state by a reduction of the dielectric constant of the solvent. Moreover, we might expect this destabilization to be fairly constant throughout the methylamineborane series because of the relatively small differences in the sizes of the methylamineboranes and their postulated transition states.

The observed trend in activation energies in the mixed solvent can now be rationalized on the basis of whether the dielectric effect or the hydrogen bonding effect is predominant. The trimethylamineborane transition state is affected less by hydrogen bonding changes in the solvent than the dimethylamineborane transition state, and therefore the effect of changing the dielectric constant of the solvent might be the controlling factor in determining the activation energy. Thus, in the 50 per cent 1-propanol-water solution the hydrogen bonding power of the solvent is reduced, but this is more than compensated for by the concurrent reduction in the dielectric constant of the solvent. The dimethylamineborane transition state, being affected to a relatively greater extent by the decrease in hydrogen bonding power, could have a higher activation energy in the mixed solvent than in pure water. In the case of the dimethylamineborane, it is assumed that the dielectric effect is of the same order as the trimethylamineborane, but that the larger influence of the loss of hydrogen bonding power leads to an increase in the activation energy in the mixed solvent over water. We would therefore predict an even larger difference between the activation energies of monomethylamineborane in the mixed solvent and in water than the difference in activation energies of dimethylamineborane in the same media.

Trimethylamineborane concentrations below 0.02 M. Originally, it was decided to run the kinetics of trimethylamineborane in 50 per cent 1-propanol-water as a pseudo-first order reaction using a large excess of hydrochloric acid and following the reaction by the loss of reducing power of the solution. However, reproducible data could not be obtained. The unexpected behavior of these solutions will be discussed along with the implications of each experiment. A brief summary of these reactions is listed in Table 25 on the following page.

The upper curve in Figure 20 on page 83 is the pseudo-first order plot of reducing strength versus time for the hydrolysis of approximately 0.02 M trimethylamineborane and 1.0 M hydrochloric acid in 50 per cent 1-propanol-water at 31.4°C. This type of deviation from linearity could be caused by the build-up of intermediates of the type  $\text{BH}_2\text{OR}$  and  $\text{BH}(\text{OR})_2$ , or  $\text{R}_2\text{CH}_3\text{NBH}_2\text{OR}$  and  $\text{R}_2\text{CH}_3\text{NBH}(\text{OR})_2$ . If these intermediates were present, then an analysis of the reducing power of the solution would erroneously attribute these reducing equivalents to unreacted trimethylamineborane. From the results of the experiments outlined below, we would like to eliminate the possibility of intermediate build-up.

If we assume that the mechanism of the reaction involves the loosening of a B-N bond in the transition state to form the ammonium ion and a borane fragment, and that the borane fragment then forms intermediates with the solvent, then the other methylamineboranes as well as diborane would be expected to form the same intermediates. These  $\text{BH}_2\text{OR}$  and  $\text{BH}(\text{OR})_2$  intermediates would also be expected to have the same reaction rates, regardless of the Lewis base to which the borane fragment was originally attached. Solutions of dimethylamineborane and diborane with with approximately the same initial concentrations as those used in the

TABLE 25

SUMMARY OF THE EFFECTS PRODUCED BY VARYING CONDITIONS IN THE  
ACID HYDROLYSIS OF TMAB AT LOW CONCENTRATIONS IN  
50 PER CENT 1-PROPANOL-WATER

Condition varied	Effect on rate
Added solid TMAB to spent solution	Marked decrease
Added allyl alcohol to fresh solution	No change
Added allyl alcohol to spent solution	No change
Added trimethylammonium ion and boric acid to fresh solution	No change
Used alcohol distilled from a spent solution	Slightly accelerated
Used alcohol solution in which trimethylammonium ion, boric acid, and hydrochloric acid had sat for twelve hours	No change

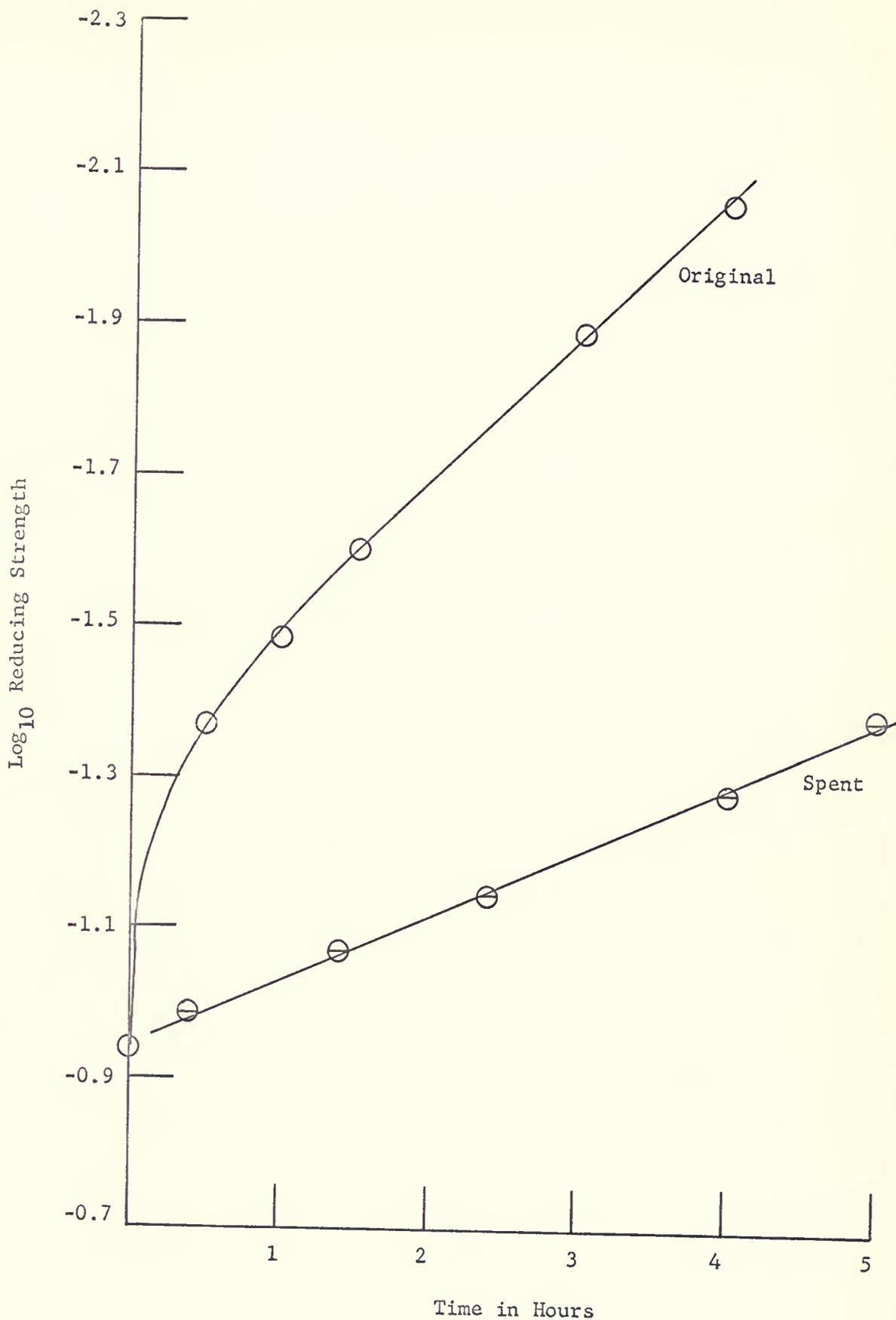


Fig. 20. Pseudo-First Order Rate Plot for Trimethylamineborane in 50 Per Cent 1-Propanol-Water for 0.02 M TMAB

trimethylamineborane hydrolysis were prepared. The reactions with these two compounds were very rapid, and over 90 per cent of the reaction exhibited no tendency to slow to a rate comparable to that of the trimethylamineborane. We therefore concluded that if our mechanism is operative in the acid hydrolysis of trimethylamineborane in 1-propanol-water solution, there was no build-up of oxidizable intermediates of the type  $\text{BH}_2\text{OR}$  and  $\text{BH}(\text{OR})_2$ .

If the intermediates were of the type  $\text{R}_2\text{CH}_3\text{NBH}_2\text{OR}$  and  $\text{R}_2\text{CH}_3\text{NBH}(\text{OR})_2$ , then the stoichiometry would be different from that originally proposed; i.e.,



Aliquots were removed from an acid hydrolysis in 1-propanol-water of similar concentrations to the original experiment with trimethylamineborane, and these aliquots were simultaneously analyzed for reducing power by the iodate method and for boric acid, hydrogen ion, and trimethylammonium ion by a potentiometric titration. This analysis showed that for each six equivalents of amineborane used, one mole of hydrogen ion was used, one mole of boric acid was produced, and one mole of trimethylammonium ion was produced. This appears to confirm the stoichiometry originally proposed for the acid hydrolysis. We therefore eliminated a build-up of this kind of intermediate as an explanation of the behavior exhibited by dilute trimethylamineborane hydrolysis in alcohol solutions.

The lower curve in Figure 20 on page 88 was obtained from the data when solid trimethylamineborane was again added to the solution originally used to obtain the upper curve, and in which reaction had gone to

completion. The rate was now markedly slower and fitted pseudo-first order kinetics. This could indicate a retardation of the rate by one of the products of the hydrolysis. A solution approximately 0.02 molar in trimethylammonium ion and boric acid was prepared in 50 per cent 1-propanol-water. Solid trimethylamineborane was added to this solution; no loss in reducing power was observed over a five hour period. This indicates that the trimethylamineborane itself does not react with the products of the hydrolysis. A 50 per cent 1-propanol-water solution was made 1.0 M in hydrochloric acid and 0.02 M in boric acid and trimethylammonium ion. Solid trimethylamineborane was added to the solution; the kinetic behavior of this reaction was the same as the behavior of the reaction in a fresh solution without addition of reaction products. This evidence appears to eliminate the possibility of rate retardation by a product of the hydrolysis.

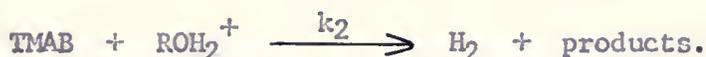
Another possibility of rate retardation was that the hydrogen ion concentration was being depleted by an equilibrium which was slow to be established relative to the half-life of the reaction. A 50 per cent 1-propanol-water solution was made 1.0 M in hydrogen ion and allowed to stand overnight. Solid trimethylamineborane was again introduced, but the behavior did not change. No change in the behavior was observed when solid trimethylamineborane was added to a 50 per cent 1-propanol-water solution containing 1.0 M hydrochloric acid, and 0.02 M in trimethylammonium ion and boric acid. It was concluded that the hydrogen ion concentration was not being depleted in the initial stages of the reaction by an equilibrium.

If there were an equilibrium between the acid and the alcohol and a competition of these two acids for the amineborane, a second order

rate expression would result anyway. Consider the equilibrium constant

$$K_{\text{eq}} = \frac{[\text{ROH}_2^+][\text{H}_2\text{O}]}{[\text{ROH}][\text{H}_3\text{O}^+]},$$

where R is the n-propyl group. Assuming the  $[\text{H}_2\text{O}]/[\text{ROH}] = 1/K^1$  ratio remains constant, then  $[\text{ROH}_2^+]$  equals  $K'[\text{H}_3\text{O}^+]$ . The two competing rates are given by the equations



The rate expression is then given by

$$\text{rate} = k_1[\text{TMAB}][\text{H}_3\text{O}^+] + k_2[\text{TMAB}][\text{ROH}_2^+].$$

Substituting the  $[\text{ROH}_2^+]$  in the rate expression, we arrive at

$$\text{rate} = k_1[\text{TMAB}][\text{H}_3\text{O}^+] + k_2K'[\text{TMAB}][\text{H}_3\text{O}^+],$$

or factoring,

$$\text{rate} = [\text{TMAB}][\text{H}_3\text{O}^+](k_1 + K'k_2).$$

Since  $(k_1 + K'k_2)$  is also a constant, this type of equilibrium should also give second order kinetics. Therefore this line of reasoning cannot explain the type of behavior observed.

Attempts were made to determine the initial rates of the reaction while varying one concentration and keeping the other constant. However, reproducible results could not be obtained.

The next possibility investigated was that an impurity in the alcohol might be accelerating or retarding the rate of the reaction. It was

found that the rate constant of the linear lower curve in Figure 20 is about  $0.0034 \text{ min.}^{-1}$ . Converting this pseudo-first order rate constant,  $k_1$ , to the second order rate constant,  $k_2$ , by the relations

$$\text{rate} = k_1 [\text{TMAB}] \text{ and}$$

$$k_1 = k_2 [\text{H}^+],$$

we get  $5.6 \times 10^{-5}$  liter/mole/sec. as the second order rate constant. This is the same order of magnitude as the rate constant calculated for the hydrolysis of the amineborane at higher concentrations in 50 per cent 1-propanol-water at a comparable temperature. Therefore, it was assumed that there was an initial acceleration of the rate rather than a subsequent retardation.

To eliminate a small impurity which might react rapidly with the amineborane, reagent grade 1-propanol was treated with hydrochloric acid and trimethylamineborane. When the gas evolution had ceased, the solution was neutralized with potassium hydroxide and then distilled. The azeotrope previously mentioned was collected. The rate curve in solutions made with this alcohol was very similar, but not identical, with the original rate curve. The hydrolysis of the spent solutions behaved the same way as the spent solutions in the lower curve of Figure 20.

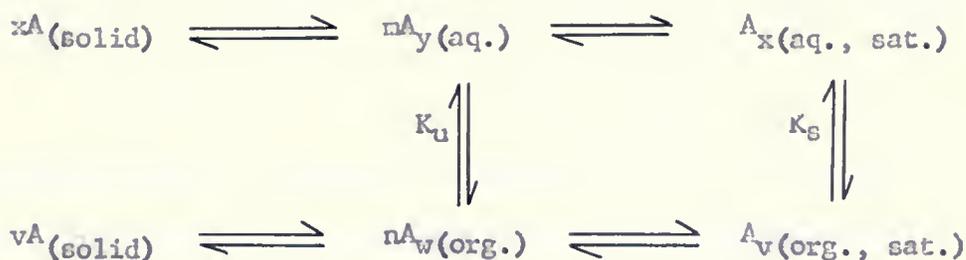
According to the literature<sup>43</sup> allyl alcohol might be a possible contaminant, but the addition of allyl alcohol had no effect on the behavior of the hydrolysis in spent solutions or in fresh solutions. Reagent grade 1-propanol was dried over calcium sulfate and then distilled. A vapor phase chromatograph showed only one peak which indicates a rather pure solution. Hydrolysis in spent and fresh solutions of this alcohol showed the same behavior as previous experiments. It should be pointed

out that at the lower concentrations of trimethylamineborane used, an impurity concentration of only about 0.5 per cent could cause the observed behavior. As the initial concentration of trimethylamineborane is increased, the initial fast portion of the reaction extends over increasingly smaller percentages of reaction until, finally, at larger trimethylamineborane concentrations the fast rate portion is no longer observed, and the reaction behaves according to a simple second order rate law.

From these observations it is concluded that an entirely different mechanism is operative, or that an impurity is being regenerated in the alcohol distillation. As discussed in the first part, the kinetics of trimethylamineborane in 50 per cent 1-propanol-water solutions behave as expected at higher concentrations.

### C. The distribution coefficient of monomethylamineborane between water and benzene

Because of the high solubility of monomethylamineborane in water and the rather cumbersome preparative procedures, it was decided to determine the heat of solution of the adduct in water by an indirect method. Consider the equilibria below, where the  $K$ 's are the distribution coefficients,  $y$  and  $x$  are the degrees of association in unsaturated and saturated aqueous solutions, respectively, and  $w$  and  $v$ , in the benzene, respectively.



The distribution coefficient at saturation is

$$K_S = \frac{[A_x]_{\text{aq.}, \text{ sat.}}}{[A_v]_{\text{org.}, \text{ sat.}}},$$

and at unsaturation is

$$K_U = \frac{[A_y]_{\text{aq.}}^m}{[A_w]_{\text{org.}}^n}.$$

Assuming that  $K_U = K_S$ , and taking the logarithm of the equation, we have

$$m \ln [A_y]_{\text{aq.}} - n \ln [A_w]_{\text{org.}} = \ln [A_x]_{\text{aq.}, \text{ sat.}} - \ln [A_v]_{\text{org.}, \text{ sat.}} \quad (1)$$

Differentiating the equation with respect to  $1/T$  where  $T$  is the temperature, we get

$$\begin{aligned} \frac{dm}{d(1/T)} \ln [A_y]_{\text{aq.}} + m \frac{d \ln [A_y]_{\text{aq.}}}{d(1/T)} - \frac{dn}{d(1/T)} \ln [A_w]_{\text{org.}} - n \frac{d \ln [A_w]_{\text{org.}}}{d(1/T)} \\ = \frac{d \ln [A_x]_{\text{aq.}, \text{ sat.}}}{d(1/T)} - \frac{d \ln [A_v]_{\text{org.}, \text{ sat.}}}{d(1/T)} \end{aligned} \quad (2)$$

Assume that  $m$  and  $n$  are not temperature dependent, so that  $\frac{dm}{d(1/T)}$  and  $\frac{dn}{d(1/T)}$  are zero, then

$$m \frac{d \ln [A_y]_{\text{aq.}}}{d(1/T)} - n \frac{d \ln [A_w]_{\text{org.}}}{d(1/T)} = \frac{d \ln [A_x]_{\text{aq.}, \text{ sat.}}}{d(1/T)} - \frac{d \ln [A_v]_{\text{org.}, \text{ sat.}}}{d(1/T)} \quad (3)$$

The right hand terms of the equation can be related to the heats of solution by the procedure outlined below for the aqueous case.



$$K_{\text{eq.}} = \frac{[\text{A}_x]_{\text{aq., sat.}}, \text{ assume } [\text{A}(\text{s})]^x = 1}{[\text{A}(\text{s})]^x}$$

$$\therefore K_{\text{eq.}} = [\text{A}_x]_{\text{aq., sat.}}$$

$$\Delta G = -RT \ln K_{\text{eq.}} = -RT \ln [\text{A}_x]_{\text{aq., sat.}}$$

$$\Delta H - T \Delta S = -RT \ln [\text{A}_x]_{\text{aq., sat.}}$$

Differentiate with respect to  $1/T$ , assuming  $\Delta S \neq f(T)$ , although  $\Delta S$  is probably a function of  $T$ .

$$\Delta H_{\text{aq.}} = -R \frac{d \ln [\text{A}_x]_{\text{aq., sat.}}}{d(1/T)}$$

The heat of solution in benzene can be found by an analogous procedure. Substituting the heats of solution for the terms in the right hand side of equation (3), we arrive at

$$m \frac{d \ln [\text{A}_y]_{\text{aq.}}}{d(1/T)} - n \frac{d \ln [\text{A}_w]_{\text{org.}}}{d(1/T)} = \frac{-\Delta H_{\text{aq.}}}{R} + \frac{\Delta H_{\text{org.}}}{R} \quad (4)$$

Assume that over the given temperature range, the degrees of association change in such a way that the ratio  $m/n = 1$  is essentially maintained. Therefore, the equation becomes on rearrangement

$$\Delta H_{\text{aq.}} = \Delta H_{\text{org.}} - Rm \frac{d \ln \frac{[\text{A}_y]_{\text{aq.}}}{[\text{A}_w]_{\text{org.}}}}{d(1/T)}$$

$$\text{or } \Delta H_{\text{aq.}} = \Delta H_{\text{org.}} - Rm \frac{d \ln K_d}{d(1/T)} \quad (5)$$

It is seen that the heat of solution of monomethylamineborane can be approximated from the heat of solution in benzene and the slope of  $\ln K_{11}$  versus  $1/\text{temperature}$ .

We therefore obtained the solubility curve of monomethylamineborane in benzene, shown in Figure 18 on page 63. The heat of solution calculated from the least squares slope of the line was 7.32 kcal./mole. This experiment also led to the cryoscopic experiment which is discussed in part D.

The distribution coefficients were calculated for several temperatures assuming that  $m = n = 1$ . These data are listed in Table 26 on the following page. The plot of the  $\log K_{11}$  versus  $1/\text{temperature}$  is shown in Figure 21 on page 98. It can be seen that the precision was rather poor. The average  $K_{11}$  value for each temperature was calculated, and a straight line was drawn through these average points. The value of  $-R \, d \log K_{11}/d(1/T)$  was calculated to be -1.01 kcal./mole from the least squares slope of the line. Adding this value to the 7.32 kcal./mole found for the heat of solution in benzene, we arrived at an approximate value of 6.31 kcal./mole for the heat of solution of monomethylamineborane in water.

Due to the lack of precision of the data and the assumptions we made, it was decided to use a more direct approach. Noth and Beyer's<sup>46</sup> data indicated considerable and varying degrees of association of the amineborane in water and benzene, and we were reluctant to trust our approximation.

The heat of solution of monomethylamineborane in water was determined directly by using microtechniques; the solubility curve is shown in Figure 15 on page 60. The heat of solution calculated from the least

TABLE 26  
DISTRIBUTION COEFFICIENT FOR MMAB IN BENZENE AND WATER

Distribution coefficient, $K_u$	$\log K_u$	$\log K_u$ , avg.	$1/T, 10^3 \times ^\circ K.^{-1}$
46.47	1.6672		
45.56	1.6586	1.6600	3.322
45.11	1.6543		
45.44	1.6574		
47.74	1.6790	1.6797	3.381
50.42	1.7026		
48.70	1.6875		
48.70	1.6875	1.6863	3.434
48.31	1.6840		
49.38	1.6936		
49.42	1.6939	1.6971	3.482
50.55			
51.52	1.7120		
50.44	1.7028	1.7059	3.531
50.46	1.7030		
54.96	1.7400		
51.88	1.7150	1.7238	3.595
52.05	1.7164		



squares slope of the line is 6.26 kcal./mole. This apparent agreement between the two methods implies that our assumptions may not be too bad, and that the degrees of association,  $m$  and  $n$ , are close to unity. The association of monomethylamineborane in benzene is greater than the association in water, according to Noth and Beyer, and since the concentration in water is 40-50 times greater than that in the benzene, both  $m$  and  $n$  may have been approximately equal to one. Our data also seem to indicate that the ratio and the degrees of association themselves do not change very much with a change in temperature.

#### D. The cryoscopy of monomethylamineborane in benzene.

As mentioned above in part C, we had occasion to determine the solubility of monomethylamineborane in benzene at various temperatures. However, cryoscopic data obtained by Noth and Beyer<sup>46</sup> on the association of the alkylamines in benzene implied that monomethylamineborane had a much higher solubility in benzene than we had observed by direct measurement. We therefore decided to repeat their experiment on the association of the monomethylamineborane in benzene.

The van't Hoff factors,  $i$ , were calculated from the expression  $m \cdot K_f / \Delta T_0$ , where  $m$  is the molality in grams of solute per 1000 gm. of solvent,  $K_f$  is the cryoscopic constant for benzene, and  $\Delta T_0$  is the experimentally observed freezing point depression in degrees Centigrade. Noth and Beyer list  $i$  values up to 2.15, corresponding to a molality of .107. Our data indicated that the solubility of monomethylamineborane in benzene near the freezing point of the solution was around 0.08 molal. The molarity determined at room temperature was converted to molality by dividing the molarity by the density of benzene at 25°C. The density at this temperature was calculated from a linear interpolation of the

densities of benzene at 20 and 30°C.<sup>1</sup> The value calculated was 0.874 g./ml. It was thought that we could confirm our solubility curve if we observed no change in the freezing point depression of solutions greater than 0.08 molal. The data obtained are listed in Table 27 on the following page, and these data appear to verify the fact that the solution is indeed saturated above concentrations around 0.08 molal. To determine the molality of the solution at saturation, the observed freezing point depression was subtracted from the freezing point of pure benzene. The freezing point of the saturated solution was calculated to be 5.25°C. The concentration of the saturated solution was then found from the solubility curve in Figure 18 on page 63, by extrapolation at this temperature, to be 0.0774 molal. The  $i$  values calculated from this molality and the constant freezing point depression value found above this concentration, gave a maximum  $i$  value of 1.40. A comparison of the  $i$  values found in this work and those found by Nöth and Beyer are listed in Table 27, as well as  $i$  values calculated using our data and neglecting the saturation. A comparison of these various  $i$  values versus molality plots is illustrated in Figure 22 on page 102.

The sources of error which would lead to high  $i$  values in Nöth's work or low values for the observed freezing point depressions are difficult to assay and highly speculative. Any error due to an impurity in the monomethylamineborane would depend on the type and molecular weight of the impurity. Less obvious and less likely sources of error also include the possibility of supersaturated solutions, compound hydrolysis, an inaccurate thermometer, and varying degrees of water contamination of the benzene.

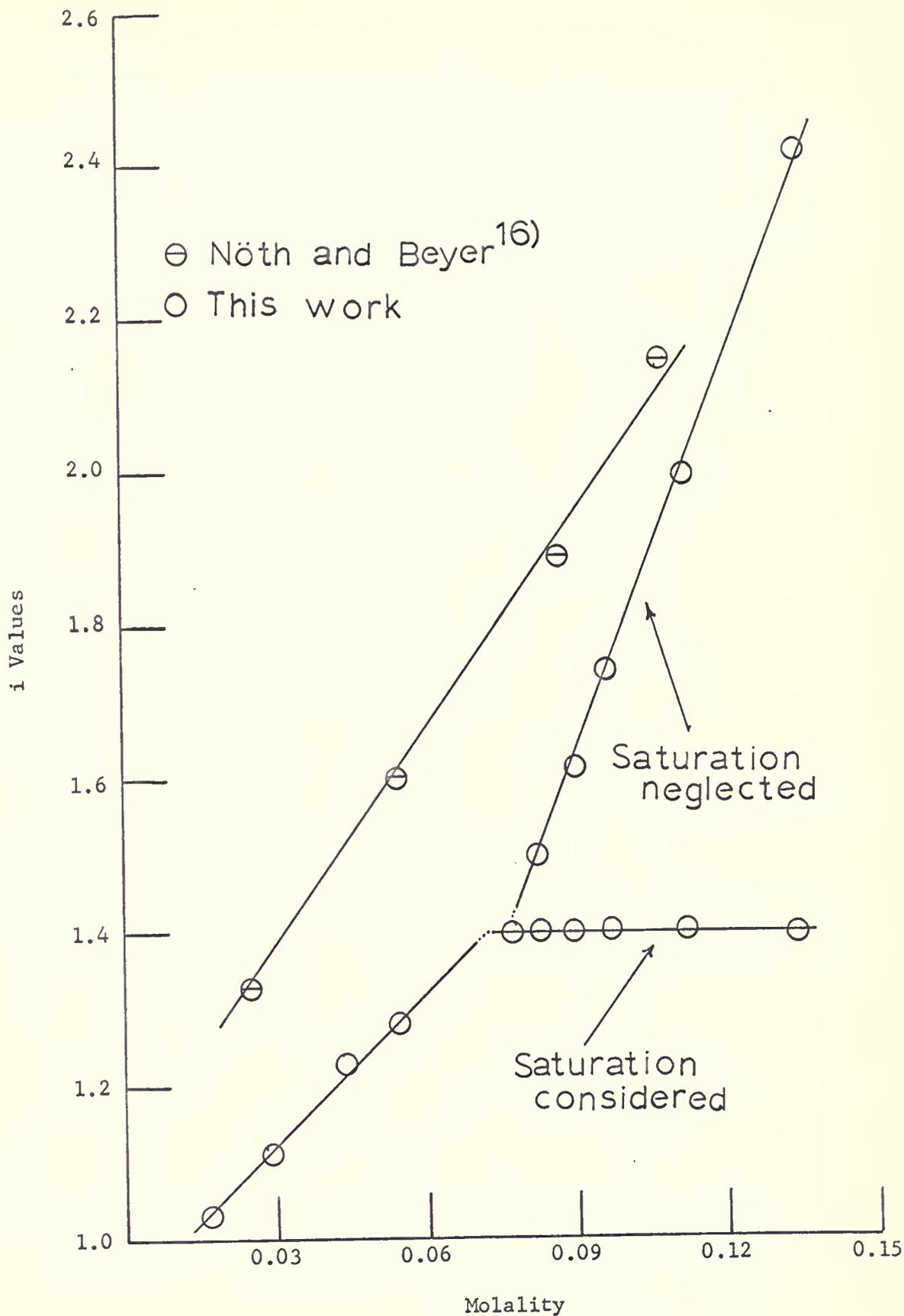
TABLE 27

## CRYOSCOPIC DATA FOR MONOMETHYLAMINEBORANE IN BENZENE

Molality at 25°C. <sup>a</sup>	Expected fr. pt. depress. neglect- ing saturation	Observed fr. pt. depress.	i This work	i Noth & Beyer <sup>b</sup>
0.0167	0.084	0.081	1.03	-
0.0286	0.146	0.132	1.11	1.52
0.0439	0.226	0.183	1.23	1.50
0.0551	0.282	0.221	1.28	1.63
0.0834	0.427	0.282	1.51	1.89
0.0399	0.460	0.284	1.62	1.94
0.0974	0.499	0.285	1.75	2.05
0.112	0.573	0.285	2.01	2.20
0.134	0.686	0.283	2.42	-
Saturation concentration- 0.0774	0.396	0.284 (Avg.)	1.40	-

<sup>a</sup>Linear interpolation from densities of benzene at 20 and 30°C.<sup>21</sup>

<sup>b</sup>Values extrapolated from graph on page 931 of Chem. Ber., 93 (1960).

Fig. 22. Plot of  $i$  Values vs. Molality for MMAB in Benzene

If the  $i$  values were calculated on the basis of the molality at room temperature, without suspecting that a saturated solution was present, high  $i$  values would be obtained, but a constant freezing point depression should have been observed for the higher concentrated solutions. This behavior is not indicated in Noth's study.

The most probable error, in our opinion, is the lack of experimental points in the saturated region. According to Noth's plot of  $i$  versus molality, only four experimental points are indicated. Two of these points are below the saturation concentration, one is above, and one is very near our calculated saturation concentration value. Therefore it is very possible that the freezing point depression of the two latter points were different. If only one point were taken in the region of saturation, and if the molality of this solution were calculated by a weighed amount of solid added, then the expected freezing point depression would be too high. This in turn would lead to an abnormally high  $i$  value for this point. The  $i$  versus  $m$  curve for the monomethylamineborane in benzene would then be different from the curve given and might show the same behavior as the other monoalkylamineboranes, although actual measurements in this region would be impossible to obtain. Noth and Beyer's  $i$  values are slightly higher than ours, but we believe the significant point to be made, is that our data show that  $i$  values for the association of monomethylamineborane in solutions above approximately 0.08 molal cannot be experimentally determined.

In an article on the dipole moments of the methylamineboranes in benzene,<sup>47</sup> the authors mention an unexpectedly low dipole moment difference between the monomethylamineborane and the other amineboranes,

compared to their data on the association phenomena. Our results indicate that the association of monomethylamineborane in benzene is less than that found by Nöth, and therefore this discrepancy between the dipole moment data and the association data reported by Nöth may not, in fact, exist.

## CHAPTER V

### SUMMARY

The kinetics of the acid hydrolysis of mono- and dimethylamineborane have been studied in water, and the acid hydrolysis of di- and trimethylamineborane has been studied in an aqueous solution containing 50.6 per cent 1-propanol by volume. The activation energies for each case were determined from the slopes of the Arrhenius plots.

The heats of hydration of mono-, di-, and trimethylamineborane were calculated from experimentally determined heats of solution and literature values for the heats of vaporization. The heat of solution for monomethylamineborane was determined directly from the solubility curve in water, and indirectly from the distribution coefficients in water and benzene and the solubility curve in benzene.

The freezing point depressions of monomethylamineborane in benzene were determined at several concentrations. Van't Hoff factors were then calculated and compared to values in the literature.

The results obtained show that the acid hydrolyses in both media are first order in amineborane concentration and first order in acid concentration. The activation energies in water are 21.2 and 15.8 kcal./mole for di- and monomethylamineborane, respectively. The activation energies in the mixed solvent are 22.0 and 23.4 kcal./mole for di- and trimethylamineborane, respectively. The trends exhibited by the activation energies in the two media have been rationalized on the basis of changes in the dielectric constant of the media, changes in the

hydrogen bonding power of the media, and differences in the hydrogen bonding capabilities of the transition states compared to the amineboranes themselves.

The heats of hydration of mono-, di-, and trimethylamineborane are -12.5, -12.9, and -9.1 kcal./mole, respectively. It is proposed that the relatively greater changes in the heats of hydration of the transition states compared to the ground states are a major factor in the activation energy trends.

The freezing point depression data indicate that the monomethylamineborane-benzene solution is saturated at concentrations above 0.08 molal, at the freezing point of the solution. It was concluded that the van't Hoff factors for monomethylamineborane in benzene, which are given in the literature, have been erroneously reported.

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## BIOGRAPHICAL SKETCH

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 8, 1964

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