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STUDIES OF RACEMIZATION RATES

IN DIMETHYL SULFOXIDE

by

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Petroleum Refining engineering.

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ABSTRACT

This thesis is a study of the rates of racemization of the ester dimethyl α -bromosuccinate in the solvent dimethyl sulfoxide. For a comparison with existing work, a brief study with acetone as the solvent was also included. Tetraethylammoniumbromide salt was used as the source of bromide ions which acted as a catalyst for the racemization. Reaction rate constants in dimethyl sulfoxide were determined at 25.00°C and 35.00°C, with two series of tests being made at each temperature. One series was at a constant ester concentration with the salt concentration being varied over a 10-fold range; the other series was at constant salt concentration with ester concentration being varied over a 10-fold range. Of the duplicate tests that were made, an accuracy of $\pm 0.64\%$ in the pseudo first-order rate constant was obtained.

A positive ester effect was obtained; there was an increase in the reaction rate with increased ester concentration at constant salt concentration. Comparison on a Debye-Hückel

basis, the logarithm of the reaction rate constant versus the reciprocal of the solvent dielectric constant squared, showed that reaction rates in dimethyl sulfoxide are higher than would be expected on this basis alone. That tetraethylammoniumbromide is not totally ionized in dimethyl sulfoxide was shown by the fact that the reaction rate was not proportional to salt concentration, but was lower than expected at the high salt concentrations.

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INTRODUCTION

The study of racemization rates in dimethyl sulfoxide was undertaken to broaden the scope of an investigation by Morgan (1). His work dealt with solvents in the intermediate dielectric range ($D=20-35$) whereas this work dealt with dimethyl sulfoxide ($D=46.6$).

The reaction that took place in the dimethyl sulfoxide (DMS) was the racemization of optically active dimethyl α -bromosuccinate (it will simply be called succinate). Succinate racemizes via an S_N2 reaction (2,3) with a bromide ion, and an inversion takes place with each substitution. Tetraethylammoniumbromide (TeaBr) is the source of bromide ions.

In this investigation, a brief series of racemization runs was made in acetone. To show the validity of the work being done in this laboratory, it was felt that the work in acetone would establish a comparison with the acetone study by Morgan (1) before starting an investigation on a pre-

viously unstudied solvent.

Dimethyl sulfoxide was chosen because not only was its dielectric constant in the desired range, but it has no hydrogen bonding, which can completely mask the other liquid phenomena that are sought.

The salt TeaBr was used because of its large cation. Olson, Frashier, and Spieth (4) attributed the total rate of racemization of succinate with LiBr in acetone to the sum of the reaction rates of succinate with a bromide ion and of succinate with the associated LiBr. Even though it has since been shown (5) that these data could be determined to be solely ascribed to the bromide ion concentration, it was felt that the large steric effect displayed by the TeaBr molecule would be more promising in eliminating the molecular catalysis. Morgan's data (1) with TeaBr showed that the molecule TeaBr did not react.

Racemization rate tests were made at two temperatures, 25.00° and 35.00°; and at each temperature, two separate series were run. One series was at a constant TeaBr concentration, 14.28 mM., with the succinate concentration being varied over the range 0.065-0.78 M. The other series was at a constant succinate concentration, 0.26 M., with the TeaBr concentration being varied over the range 3.86-30.65 mM. at 35.00° and 7.36-58.9 mM. at 25.00°. It was necessary to

make runs at the two temperatures to make possible the calculation of the enthalpy of activation. Also it was desired to examine the trend of ester or salt effects to determine whether they increased or diminished with increasing temperature. Olson and collaborators (4) discerned an ester effect; the reaction rate dropped off with increasing ester concentration which they explained as TeaBr absorption on the ester molecule. Most of Morgan's work (3) substantiated this, but two of his systems in acetonitrile showed a positive ester effect; the rate increased with increased ester concentration. This fact defied explanation by the above absorption theory; therefore it was felt that this area would be fruitful for further study.

EXPERIMENTAL PROCEDURES AND APPARATUS

Experimentally, three problems had to be met and solved; preparation of materials that were anhydrous and pure, the transferring and making of solutions of these materials under conditions that would preserve this purity, and measurement of the rates of racemization of the resulting solutions.

Preparation of Dimethyl Bromosuccinate

In all, four batches of succinate were prepared, each by the following procedure (1). The main reactant for the preparation was l-asparagine. Thirty-five grams of asparagine was refluxed for 2 hours with 150 ml. of saturated aqueous hydrogen bromide in a 500-ml round-bottomed flask equipped with a water-cooled condenser and heated with a Glas-Col heating jacket. The mixture then stood for 3 hours while it cooled to room temperature, at which time 93 g of sodium bromide and 100 g of water were added, and the resulting mixture was transferred to a 1-l beaker immersed in an ice bath. Once the

mixture had attained 5°C , a solution of 35g of sodium nitrite in 55 ml of water was added very slowly through a dropping funnel. This drop-by-drop addition required a period of 2 hours to keep the temperature below 6.5° . An electric stirrer was used to keep the solution agitated. Since bromine was evolved during this step, a hood was required.

Ten minutes after the last addition of the sodium nitrite-water solution, 15 ml of concentrated sulfuric acid in 75 ml of water was added. Four other extractions were performed to remove the bromoacid from the water phase; the first extraction was with 200 ml of ether, and the other three each consisted of 100 ml with a 2-1 separatory funnel being used for the extractions. The solution of bromoacid and ether was placed in a 7-in. evaporating dish on an electric hotplate to boil away the ether. The temperature was kept slightly below boiling, and the vapors entered the hood. For recrystallization, the brownish crystals of acid were then dissolved in 125 ml of acetone; 150 ml of thiophene free benzene was added; and the solution was allowed to evaporate overnight to about 15 ml. The bromine-colored crystals were rinsed in a small sintered glass filter and inserted into the top of the filter was a one-hole stopper connected to a rubber hose from a low-pressure air supply to force liquid through the crystal bed and filter. This recrystallization removed most of the color from the

crystals, and only a light brown color remained.

Into a reflux apparatus similar to that of the first step were placed the recrystallized acid crystals, 300 ml of methyl alcohol, and 3.6 ml of concentrated sulfuric acid. Esterification took place in the 2 hours that this solution was refluxed. After 480 ml of water was added, the ester was extracted with four portions of ether; the first extraction consisted of 300 ml of ether while the other three were 100 ml each. The ether and extracted ester solution were placed in a 7-in. evaporating dish and kept under a hood for a period of several days. The small amount of water phase that was present was removed with an eye dropper.

At this point, two batches of succinate were combined in an ester still as shown in Figure VII. Water and ether bubbled off first and were discarded, while, due to the small amount of ester that was produced, the ester was collected in the feed flask for the molecular still. The bulk of the ester was collected at 41° under 28μ pressure.

Two molecular distillations were made in a Arthur F. Smith, Model 50-2, Rota-Film molecular still. The first was for topping the ester and took place under mild conditions, 100μ and 31° (skin temperature). Twenty percent overhead was taken and discarded. The bottoms were recharged, and the second molecular distillation with conditions of 95μ and 38° gave an

overhead product which consisted of about 80% of the second charge. This amounted to about 30 ml for the two batches, and it was collected directly into the 125-ml glass-stoppered flask that was used for its storage.

Purification and Drying of Solvents

Acetone. --Four liters of acetone were fractionated on a Glenco 70-plate (50 theoretical plates) vacuum-jacketed bubble-cap distillation column with an overhead temperature of 50° at 618 mm Hg and a reflux ratio of 3 to 1. Retained was a constant boiling heart-cut while a 100-ml forecut and a 100-ml bottoms were discarded.

To the heart-cut were added potassium permanganate and potassium hydroxide pellets, and this was allowed to stand for two weeks. More KMnO_4 was added periodically until the pink color existed for several hours. Acetone was decanted from the KOH and the MnO_2 that was produced and recharged to the distillation column, and again a small forecut was discarded, and at 3:1 reflux ratio, a constant-boiling heart-cut retained. A considerable bottoms product was left when the bottoms temperature started going much higher (18°) than the overhead temperature. Apparently acetone polymerization had occurred. This heart-cut was stored over Drierite in a stoppered flask.

The acetone was further dried by vaporizing it through Drierite in a 24- by 1½-in. glass column that was wound with heating wire. To regenerate the Drierite, air was passed through the column and a voltage applied across the heating wire sufficient to keep the out-going air temperature at 130-140°. To carry out this drying, about 1 l of acetone was placed in a 2-l round-bottomed flask equipped with a capillary tube to eliminate bumping. (Air admitted through the capillary was dried in a CaCl₂ tube). Acetone vapors passed up through the Drierite and condensed in a 500-ml storage bottle immersed in a dry ice-acetone bath (temperature approx. -78°F). Vacuum was pulled on the bottle with a small vacuum pump protected by a dry ice-acetone trap. The level of vacuum pulled was sufficient to vaporize the acetone (even through the pressure drop created by the column) so that it would not condense in the apparatus leading to the receiver.

When the drying run was started, vacuum was pulled before the dry ice-acetone bath was placed around the receiver, which allowed the system to be flushed free from air and moisture before condensation occurred in the receiver. A small amount of acetone was lost to the cold trap. Acetone dried in this manner was used for racemization rate runs; however the rates encountered were considerably lower than those found by Morgan, who also used acetone dried with P₂O₅. Therefore, for the

rates reported herein, the following procedure was added.

Dry P_2O_5 powder was dusted on $\frac{1}{4}$ -in. glass helices and placed in a 24- by 1-in. glass column with glass wool on either end to hold the helices in place and keep the P_2O_5 from blowing through. This column was placed vertically in series with the Drierite column, and the acetone vapors passed down through the Drierite column and up through the P_2O_5 column. The P_2O_5 showed no apparent moisture pickup, but did turn a buff color from acetone condensation. The vapors were condensed in a manner similar to that described in the Drierite drying and the receiver was the flask that was used for the solvent storage, thus eliminating one solvent transfer.

Dimethyl Sulfoxide. -- Three pints of Baker "Reagent" grade dimethyl sulfoxide (DMS) were fractionated on a small, glass bubble-cap column. The distillation was carried out under vacuum and the product was condensed in a 500-ml round-bottomed flask immersed in a dry ice-acetone bath. The column contained 10 plates and was equipped with a partial condenser; heating wire wrapped around the condenser and connected to a Varic permitted adjustment of the reflux ratio to 2. Heat was supplied to the reboiler with a Glas-Col heating jacket, and a small forecut and bottoms were discarded.

This heart-cut was stored over calcium oxide for 2 weeks, and then the entire slurry was fractionated on the same column. However, because much bumping occurred with the CaO present, the DMS was decanted with the CaO being discarded. The DMS was then successfully distilled at approximately 60 torr and 115°C and was stored over CaO for 2 days and decanted. Then it was vaporized through the Drierite drying tube and condensed in its own storage flask in a dry ice-acetone bath (the process being similar to the analogous step in acetone purification).

The distilled product was treated with several grams of calcium hydride, CaH_2 . Hydrogen gas bubbled off, indicating a reaction with the water that must have still been present. This product was allowed to stand for 10 days.

The final distillation isolated a heart-cut after discarding about 25 ml from each end of a 1000-ml batch. The distillation took place at approximately 82°C and 15 torr, and several crystals of CaH_2 were added to the final product to remove contamination picked up during storage. No hydrogen was evolved. All DMS for the ensuing experiments was removed when needed with a hypodermic syringe.

Purification of Tetraethylammoniumbromide

Eastman TeaBr was available, and the only steps used in the purification were its recrystallization from absolute ethanol and drying under high vacuum at elevated temperatures.

To produce the absolute ethanol, about 350 ml of an azeotropic solution of water and ethanol was first vaporized through a Drierite drying column. The condensed product was distilled at atmospheric pressure from magnesium amalgam, which had been produced from a heated mixture of 5 g of magnesium in 10 ml of mercury. This anhydrous ethanol was considered pure enough for the TeaBr recrystallization.

One hundred milliliters of anhydrous ethanol was slowly added to 70 g of TeaBr in a 500 ml flask equipped with a Claisen distillation head and dropping funnel, the whole apparatus being protected by a CaCl_2 drying tube. Gentle refluxing, with the Claisen head acting as a condenser, followed each addition of ethanol. The solution was filtered rapidly through a 1-in. sintered-glass filter, and a vacuum was pulled on the outlet side of the filter with a water aspirator through a CaCl_2 bottle. The liquor flask was immersed in a dry ice-acetone bath and, with constant shaking, the TeaBr recrystallized into small crystals. The

salt was collected on a 4-in. sintered-glass filter, connected similarly to the 1-in. filter above. For 2 hours, dry carbon dioxide gas passed through the cake from a tank to a 4-in. rubber stopper on top of the filter.

The salt was placed in a weighing bottle and put into the salt drying oven in which a vacuum down to 0.01 m μ and a temperature of 83° was attained, and the salt remained in this atmosphere for 24 hours. Any temperature above this caused considerable sublimation. There was a 0.6% weight loss, but a portion of this was sublimation of the salt and subsequent deposition on the oven walls. Throughout this drying, the cover of the weighing bottle was ajar, but a slight tapping on the oven wall knocked the cover in place after the vacuum was broken with dry air, and the bottle was safely carried to and stored in a desiccator. All salt was redried just prior to its use.

Preparation of Salt Stock Solutions

Salt stock solutions were made and stored in volumetric flasks, 100 ml flasks for acetone and 25 ml for DMS. The volumetric flask, without its stopper, was first dried in the salt drying oven shown in Figure VII. The conditions applied were vacuum of 0.01 m μ and a temperature of 83°, the same as for salt drying, and drying usually lasted over

night. After dry air was admitted to the oven from a CaCl_2 drying bottle and the flask was cool, the flask was removed and the stopper replaced and weighed immediately. This gave the tare weight of the flask.

An approximate amount of salt was spooned with a spatula from its weighing bottle storage case into the flask. With the stopper removed, the same drying procedure was performed on the salt in the flask as was performed on the empty flask preceding this. This drying continued for at least 24 hours. Before removing the flask from the oven, the connection between the oven and the vacuum manifold was broken, and the stopper was replaced on the flask with a pair of long forceps. This then was weighed; the difference between it and the tare weight was the amount of TeaBr in the standard solution.

Solvent was added to the flask by means of hypodermic syringes, the largest of which had a 100-ml capacity. Care was taken to give minimal contact between surrounding air and solvent, so at all times during solvent or reactant transfer, a stream of dry air from a CaCl_2 bottle was blown over the neck of the opened bottle or flask so that dry air would be drawn into the solvent storage bottle when solvent was removed. After filling the volumetric flask to the required level, it was brought down to the required temperature,

20° and topped up to the calibration line.

To preclude any error in the making of the standard salt solutions, at least two solutions were made from each solvent. Equivalent reaction mixtures were made up from each of the salt solutions, taking into account the differences in salt concentration. To show the proper precision, and hence probably accuracy, the reaction rate constant had to be within experimental error. In each solvent, they differed by 1% or less.

The standard salt solution was stored in the stoppered volumetric flask until used.

Experimental Procedures

Preparation and Handling of Reaction Mixtures.--The avoidance of water in reaction mixtures was of prime importance. Therefore, in the transfer of all materials, it was necessary to avoid contact with moist air. Although a dry box is often used in combating problems such as this, it was not employed here because of the several substances that went into each reaction mixture and because of the rapidity necessary in the additions.

The alternate technique that was developed involved the use of hypodermic syringes for the transfer of liquids. Long hypodermic needles or short needles fastened to teflon

tubing reached to the bottom of storage flasks. Dry air from the CaCl_2 bottle was directed horizontally over the mouth of the flask from which solvent was being added or extracted. All syringes were thoroughly dried before use, so that the only contact of the liquid with air came at the tip of the hypodermic needle, and it was usually possible to knock this small drop off before transfer was completed. The following gives the detailed procedure for making up the reaction mixtures.

All reaction mixtures were made in 5-ml volumetric flasks which were first washed, rinsed with acetone, and dried with dry air. The dry air used here and in subsequent steps was the dry air from the CaCl_2 bottle. The flask used was allowed to stand with its unlubricated stopper in place. The neck of the salt stock solution flask was placed in the stream of dry air and the stopper removed. To achieve the highest accuracy possible, the syringe used to withdraw salt stock solutions was the smallest possible to hold the required amount of solution. A portion of solution, slightly more than the amount required, was withdrawn, and the stopper from the salt solution flask was lubricated and replaced. The dry-air hose was lowered to the height of the 5-ml reaction flask, the neck placed in the stream of dry air, and the stopper removed. This stopper was not lubricated.

Salt stock solution was carefully forced out of the syringe into a tissue paper until only the required amount remained. A piece of tissue paper was used to dry the needle and to knock the last droplet of liquid off its tip, and the solution was then added to the reaction flask. The unlubricated stopper was replaced and the flask set aside.

With the dry air hose adjusted for the height of the solvent storage flask, another dry 5-ml syringe was used to withdraw slightly less than 5 ml of solvent. The solvent flask was removed after its relubricated stopper was replaced. A portion of this solvent was added, enough to bring the level in the reaction flask up to about 4 ml, after due precautions were taken to insure dryness. (Procedures similar to those described above were used for the transfer of all liquids). This portion of solvent was added to the reaction mixture flask before the addition of ester as the more concentrated stock salt solution would racemize an appreciable portion of the ester before polarimeter readings could be observed.

Succinate was added to the flask in a like fashion. For a majority of the reaction runs made, a 0.25-ml syringe was used for the succinate addition, thus good precision was possible here. To bring the reaction flask up to 5 ml, another small portion of solvent was added. For this, the

same syringe and solvent that was remaining were used; only a small portion was expelled and the needle dried before the addition to the reaction flask.

No attempt was made to make the 5-ml reaction solutions at 20°, which is the standard for the volumetric flask. Instead, all liquids were taken to be at the same initial temperature, namely, room temperature which was generally 25-28°. It was assumed that this would produce a solution that was the same molarity in both ester and salt as if all additions were made at 20°. This is tantamount to saying that the difference in coefficient of volumetric expansion between the three addents is negligible. Over this narrow temperature range, the error introduced would be minute.

With the reaction solution completed, the stopper was replaced, and the flask was shaken 3 or 4 times, which resulted in a slight but negligible leakage, since the stopper was unlubricated. Almost immediately, the stopper was removed and the solution withdrawn into a clean 5-ml syringe. This was done adjacent to the polarimeter and not in a dry air stream, so slight moisture contact was possible here. With the needle removed, the syringe was inserted into a needle head that was imbedded into the sample cell which had been previously cleaned, dried, and filled with dry air. The reaction mixture completely filled the sample cell, pushing

the dry air out the top vent which was connected to 3 ft of small-bore teflon tubing. Enough reaction mixture was added to expel a few drops through this top vent. The tubing was left in place throughout the racemization, thus allowing for expansion and contraction effects due to temperature change while giving a very long diffusion path to prevent the influx of moisture from the atmosphere.

Measurement of Optical Rotation.—A Bendix Automatic Polarimeter, type 143a, was used to measure the rates of racemization of the optically active succinate. The sample cell had a 1-cm bore and a path length of 5 cm. It was water jacketed for temperature control, and the ends were covered with double layers of optical glass separated by a dead-air space to provide resistance to heat transfer. Full-scale deflection on the polarimeter is 0.5° , and since both positive and negative deflections can be measured, a 1.0° span is available for usage. This instrument has a resolution of $\pm 0.0001^{\circ}$, with the measured angle being represented by an electric amperage output. The accuracy of the instrument was limited, however, since the output current was fed into a Taylor strip chart recorder. The 5-in. chart from the recorder was divided into 100 one-volt divisions. Since the recorder has 250Ω resistance and a full-scale deflection current of 4 ma, a variable resistance set at approximately

93.5 Ω was placed parallel with the recorder. With the zero point set at mid-scale on the recorder, full-scale deflection current from the polarimeter gave full-scale deflection on the recorder.

Many of the racemic mixtures that were made contained enough succinate so that the optical rotation between the initial rotation and the end point of the racemized mixture was more than the 1° total deflection. This problem was solved by use of the recorder. When a reaction solution was added to the sample cell, the zero point of the polarimeter was adjusted so that the initial rotation was slightly less than the -0.5° ; this produced a reading of 100 v on the recorder. The adjustment of the zero point takes approximately 10 sec. Later in the run, as the bottom of chart, 0 v, was approached, the zero point was reset to again give a rotation of -0.5° . The gap in time was covered by an extension of chart-recorder lines so that the jump in the resetting of the zero point could be measured. This figure was necessary to determine the total change in optical rotation. The maximum rotation measured was about 3° for the solutions 0.78 M in succinate, and the minimum was 0.25° for 0.065 M. For the latter, the variable resistance was adjusted so that the 0.25° span on the recorder still produced a 100-v deflection on the chart recorder.

Two drive motors were available for the chart recorder, 1 in. per minute and 1 in. per hour. The fastest motor was used for all but the slowest runs; those in which 55-60% racemization took longer than 90 minutes.

Temperature Control.--The sample cell was constructed so that it was surrounded by a water-jacket (Figure VII), and a steady stream of cooling water passed through the jacket to keep the cell at the required temperature.

Figure VII shows a schematic diagram of the cooling-water circulation system. Cooling water came from a constant temperature bath which held about 8 gal and temperature control was accomplished with the aid of a Philadelphia Scientific Glass Thermostat, type CE-712, which turned off or on a 3-kw heating element in the water. An additional 2-kw element was available when the heat loss to surroundings was greater than that which could be supplied by the controlled element, but this was never needed.

From the bath, the water passed through a vacuum-jacketed transfer line to the sample cell. Then, leaving this, it went through rubber tubing to a small Eastern centrifugal pump which pumped the water back into the bath.

During the middle of the summer, the ambient temperature was oftentimes over the bath temperature when runs were made at 25°. Also the cooling water picked up heat from the

circulating pump, which for this reason was cautiously placed between the cell and the bath, and not before the cell in the cooling water path. Since temperature control was accomplished by use of a heating element, except for the influx of heat from the element, it was necessary to have a net heat loss in the system rather than a heat gain. To eliminate this problem, between the circulating pump and the bath, two parallel paths were constructed. One was merely the direct hose previously described; the other passed through a 3-ft section of $\frac{1}{4}$ " O.D. copper tubing which was imbedded close to the bottom of a 5-gal can with only the ends of the tubing sticking through holes in the side of the can. Solder filled the extra space in the holes and kept the water and ice which was contained above from leaking out. Heat was transferred from the cooling water to the water-ice mixture in the 5-gal can thus removing enough sensible heat from the cooling water to allow the temperature to be controlled with a heating element. A pinch clamp controlled the amount of cooling water that was to flow through each of the two parallel paths.

Temperature measurement in the bath was with an ASTM 56c Bomb Calorimeter Thermometer, No. 7A 9567, marketed by BKH-Braun-SS Co. With the aid of a magnifying lens, the temperature could be read to 0.01° . Due to the influx of cold water, the heat gain from the surroundings, and slight (about 0.002°)

hysteresis in the thermostat, there was a slight but regular variance in the temperature of the bath. The 24.96° temperature was actually taken to be an average of the span 24.93° to 24.99°.

RESULTS

Experimental Results

Reaction rate constants were determined for the racemization of succinate in two solvents, acetone and DMS. In acetone, all runs were made at 24.96° , and using the enthalpy of activation of 18.9 kcal as calculated by Morgan (1), the results were transformed to reaction rate constants at 25.00° . All runs in this series were made at an ester concentration of 0.26 M with only the salt concentration being varied. The runs reported fall in the same range as those by Morgan and are given in Table 1 and are plotted in Figure 1.

In DMS, reaction rate constants were determined at 24.96° and 34.92° for wide ranges of concentration of TeaBr and succinate. With the value for the enthalpy of activation, as was calculated from the reaction rate constants at each temperature extrapolated to zero ester concentration, the reaction rate constants at the even temperature of 35° and 25° were calculated. Tables 2 and 3 give these values.

One of the primary purposes for conducting this experiment was to examine the effect of varying the ester concentration upon the reaction rate. At each temperature, a salt concentration of 14.28 mM was used with various ester concentrations, and the reaction rate extrapolated down to zero ester concentration, k_0 , as shown in Figure III as k_0/k versus ester concentration. Table 4 gives a summary of the ester concentration effect.

As can be seen from the slight curvature of lines of k versus salt concentration in Figure II, the salt, Teab_r, is not completely ionized in DMS. In using a method advanced by Morgan (1), the second-order reaction rate constants were calculated as given in Table 5, but due to the fact that the data was for quite high salt concentrations, the method gave only approximate ionization constants. Table 6 gives the ionization constants, and Figures IV and V present the graphical calculations.

Calculations for enthalpy of activation are presented in Table 7.

Comparison of Results

For any experimental work to have merit in itself, there must be some basis for comparison with existing knowledge or facts. This was primarily a study of reaction rates in DMS,

but included also was a brief study using acetone as the solvent for comparison with the work of Morgan (1).

For the racemization rates in acetone, acetone was prepared by two different procedures. Morgan (1) used both Drierite and P_2O_5 in the drying of acetone for his work. However, he believed there was no evidence of water removal with the P_2O_5 , so it was felt that Drierite alone might be sufficient. In preliminary results not reported in this thesis, acetone prepared in this manner was used for reaction studies. The rates were only about one half as high as those reported by Morgan. Since water is known (4) to have a large hindering effect on the kinetics of this reaction, it was felt that P_2O_5 drying was also needed. So the added drying took place as described under the heading Acetone Purification on all acetone runs reported herein. Thus acetone used in these runs was dried identically to that of Morgan's. A comparison of equivalent runs is given in Figure I. It was discouraging that the results reported here were as much lower than Morgan's as they were (they averaged about 15% lower). This leads to the conclusion that the acetone used in this work contained some moisture. However, it might be argued that the discrepancy in results was caused in some error in technique or malfunction of apparatus. This is possible but unlikely since there are only a few sources of error that could be translated.

The chart recorder speed was compared to an electric clock for periods up to two hours, and it agreed to a small fraction of 1%. If there were impurities in the TeaBr (inert materials that would contribute to the weight) or moisture in either the TeaBr or succinate, since these materials were used in all runs, it would lead to low results that would carry over to results from the DMS runs.

Fortunately, the conclusions that are being advanced from the DMS results are not influenced by a constant error on the low side. Conclusions concerning ester effects, ionization constants, and salt effects deal with the internal consistency of the results only, and with nothing absolute. The only topic influenced by absolute values of reaction rates is the testing of the validity of the Debye-Hückel theory, as shown in Figure VI. It can be seen from this plot that the value for the reaction rate in DMS is higher than what would be expected on the basis of a Debye-Hückel comparison with data from Morgan (1) on various solvents. Thus, if there is an error in the DMS data, the actual reaction rate is higher yet, and the same conclusion is made, that the Debye-Hückel theory predicts a lower value than it should for DMS.

Precautionary steps had to be taken to insure that another type of error did not arise, namely, mistakes in the

concentration of standard salt solutions. To combat this, each standard solution was checked against another standard solution, as discussed under the heading "Preparation of Standard Salt Solutions". For example, under acetone racemization runs, runs S12 and S14 were equivalent, except that they were made from different standard salt solutions. The results were 6.48 and 6.41 respectively, which gives an average deviation of only 0.53%. Actually, this percentage of error includes all errors in the experiment, although it is doubtful that this precision could always be counted upon.

The following pairs are equivalent runs in DMS at 25.00°; D11-D25, D13-D18, and D19-D21, and they give an average deviation from their respective means of 0.64%. It was difficult to get the same precision with DMS as it was with acetone, basically because of the slight tendency of the DMS to react with bromide ions. This will be discussed in the next section.

DISCUSSION OF RESULTS

At the start of work on this thesis, it was noticed from a literature investigation that several experimenters reported the reaction of halide ions with DMS. Many reported this as a very explosive reaction, although none had specifically used TeaBr as the bromide ion source. For this reason, extreme care was taken in making and testing the first solutions of TeaBr in DMS. Small additions of TeaBr gave no indication of reaction for periods of several weeks, and the same result was found as concentrations were increased. A solution of unknown concentration of TeaBr in DMS was used for a reaction rate test. The result compared within experimental error with an equivalent test run two weeks later on the same base solution. This was taken to show that there was no reaction between the DMS and the bromide ion in the solution, at least not enough to deplete the bromide ion concentration an appreciable extent. Runs D11 and D25, equivalent runs at 25.00°, were run eight days apart, yet again the results are within experimental error. Therefore,

if there was a reaction, it must have been slow. But all reported data was taken over a period of ten days, so a slow reaction would have little effect on the internal consistency of the data. If bromide ions had reacted between the time the standard solution was made and when the rate test was run, the apparent reaction rate would be lower than that for the pre-supposed bromide ion concentration. But, as was shown under Comparison of Results, the conclusions that are drawn in this thesis are in no way impaired by an error in this direction.

It is possible that no reaction took place between DMS and bromide ions because of the high purity of the solvent and salt. If this was a reaction catalyzed by moisture or other impurities, this might explain why a reaction did not take place here and evidence was found that would support this viewpoint. On runs of a long duration (low salt concentration), green, water-soluble solids were in the sample cell at the end. Evidently the succinate, which was probably the least pure of all additions, was able to catalyze, through itself or its impurities, the reaction in question. Although it is not known to what degree this could change reaction rate constants, it could only lower it from the actual. Before further experimentation in DMS, this reaction should be investigated.

Ester Concentration Effects

Olson and collaborators (4) found a negative ester effect in the system acetone-succinate-LiBr. This they attributed to the absorption of bromide ions on the surface of ester molecules, thus depleting the solution of active catalyst particles. In solvents of low dielectric constant such as acetone, an association is possible between the bromide ion and the dipolar succinate molecule. They used an adsorption equation to correlate their data. Morgan's data (1) substantiated this observation, using TeabBr instead of LiBr. However, his data on two other systems showed curious results. Acetonitrile and TeabBr at 25°, with two other esters, methyl α -bromoisocaproate and dimethyl α -bromoglutarate, showed a positive ester effect. The reaction rate increased with increased ester concentration. He was aware of the possibility that these two new esters, which were prepared and purified for the first time for his thesis, may not have had the purity attained in the succinate. Also the positive ester effect was not noticed in the succinate, but rather a negative one. Since Morgan's data on ester effect was sparse (only two ester concentrations with each system) and since this phenomenon could not be explained by the previous adsorption theory, it was felt that this would be a fruitful area for further study.

It is for the reasons outlined above that this project was

reactivated. Though acetonitrile was not used, it was still decided to investigate thoroughly the ester effect. Curiously enough, a positive ester effect was again observed. This at least shows the possibility that Morgan's data may be valid.

The data on ester effects is plotted and extrapolated to zero ester concentration using the adsorption type (straight line) relationship, even though this equation is not theoretically justified. The scatter of the data is enough to prevent a determination of the best relationship.

Ionization Constant for TeaBr and Second-Order Reaction Rates

Morgan's method for the calculation of ionization constants from reaction rate data is presented in Appendix I. The equations given are derived in his thesis. The ionization constants for TeaBr in DMS are calculated in Figures 4 and 5, and range higher than Morgan's results for TeaBr by a factor of 5.4 at 25° and 7.5 at 35°. This is to be expected because of the higher dielectric constant exhibited by DMS. But this calculation mentioned above was merely based on the equation listed as approximate; the ionization constant is based on the second derivative of the reaction rate constant with respect to salt concentration at zero salt concentration. But as mentioned in the introduction to this section, a foreign reaction was noticed to have taken place in the slow runs (the ones near

zero salt concentration). Therefore, the added uncertainty connected with these results casts a shadow of doubt on the ionization constants and it is quite possible that these results are accurate to within only a factor of two. The value thus calculated is the value being reported. The more accurate equation for the ionization constant (Equation (3) of Appendix I) proved to be of limited applicability. Equation (2) is meant to be an approximation, while this one produces an accurate value. But this equation, based on the reaction rate data, yielded results that showed that the ionization constant increases fairly rapidly with increasing salt concentration. It is a point of conjecture whether this is so, or whether the points at low concentration were off enough to give the contradictory results.

The second-order reaction rate constant was calculated in much the same manner as the ionization constant. In fact, calculation of k_1 , the second-order constant, was one step in the calculation of the ionization constant. This calculation is also based on an extrapolation to zero salt concentration, but since only the first derivative is involved, the result is more accurately known, probably to within 10%.

It was the second-order rate constant that was used for a comparison with previous work. Morgan's reaction rate data for acetonitrile, acetone, and nitromethane is shown in Figure 5.

Compared with it, are the results from this work. The data are plotted as suggested by Amis (6), on a Debye-Hückel basis and it can be seen that the results from this work fall much higher than would be expected on the basis of dielectric constant alone. In this case, other specific solvent effects become more important. Even though the value of the second-order reaction rate constant from this work is somewhat in question, the above conclusion can still be drawn with confidence, because, if the ionization constant were taken to be infinite, which means the highest concentration of bromide ions possible for a given salt addition, and hence the lowest second-order reaction rate constant, the rate constant would still be high enough to make the same conclusion.

Note on the Ester Concentration Effects

Figure III shows the positive ester effect that was observed in DMS. Previous work (4) explained a negative ester effect as absorption of bromide ions on the ester molecules, but this theory cannot be used for the positive ester effect. However, as is shown in Figure VI, the reaction rate is inversely proportional to the square of the dielectric constant. If the dielectric constant of the reaction medium (solvent and reactants) decreases with increasing ester concentration, this would account for the increased reaction rate and hence the

positive ester effect.

To examine if this proposed theory is correct, it would be necessary to know the dielectric constant of the succinate. This theory is dependent upon the dielectric constant of the succinate being lower than that of the solvent. Morgan (1) found a positive ester effect in acetonitrile ($D=35$), so if the dielectric constant of the succinate was lower than 35, it could explain his data also.

CONCLUSIONS AND RECOMMENDATIONS

The following are lists of recommendations and conclusions.

Conclusions

1. In comparison to Morgan's rates for acetone, acetonitrile, and nitromethane, the Debye-Hückel theory does not hold for the racemization of succinate in DMS as the rate is higher than predicted.
2. A positive ester effect was present; a higher concentration of succinate led to a higher reaction constant.
3. The salt, TeabBr, is not totally ionized in DMS, although the ionization constant is high. The ionization constant increases with increasing salt concentration.

Recommendations

1. Reactions in another solvent which also does not have hydrogen bonding and is in the same dielectric range as DMS ($D=40-50$) should be studied for its effect on reaction rates.

2. Controlled additions of water would show the delicate dependence of the reaction rate upon water.
3. A standard solution of TeaBr in DMS should be made and used for equivalent reaction rate tests spaced over long periods of time (1-2 months). This would test for reaction of the bromide ion with DMS.
4. The ester concentration effects should be studied at another TeaBr concentration level.

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APPENDIX

APPENDIX I

Calculations for Bromide Ion Rate Constants

Calculation of the rate constant was done from the output of the Taylor Chart Recorder. Results from the chart were transferred for numerous intervals to another sheet; the end-point rotation was subtracted; and the result was plotted on semi-log paper (time being the linear coordinate). The best straight line was passed through the data points. When, on occasion, the data points showed slight curvature, the end point value was varied to make the semi-log plot a straight line.

The slope of this straight line is $\Delta \ln \theta / \Delta t$ or $\ln(\theta_2/\theta_1)/(t_2-t_1)$, but the inversion of one molecule of ester not only removes its contribution to the original optical activity of the solution; it also forms another molecule with a negative of the original contribution. Thus reaction of one acts as though the activity of two were destroyed. For this reason, the slope presented above must be divided by a factor of two for it to represent the pseudo-first-order rate constant. Hence, $k = \ln(\theta_2/\theta_1)/2(t_2-t_1)$.

The following is a list of equations taken directly from the work by Morgan (1). They are used to calculate second-order rate constants and ionization constants for TeabR as

shown in Figures IV and V.

$$k_1 = \lim(dk/dc) \quad c=0 \quad (1)$$

$$K_{\text{approx}} = 2k_1 / \lim(-d^2k/dc^2) \quad c=0 \quad (2)$$

$$(dk/dc)/k_1 = 1/(1+4c/K)^{\frac{1}{2}} \quad (3)$$

APPENDIX IITABLE I

Summary of (TeaBr) and (Succinate) Effects in
Acetone at 25.00°

<u>RUN</u>	<u>TeaBr</u> <u>(mM)</u>	<u>k_{xpt}</u> <u>(1/10³ min.)</u>	<u>SUCCINATE</u> <u>(M)</u>
S9	2.22	9.23	0.26
S10	4.85	18.77	0.26
S11	0.585	2.89	0.26
S12	1.45	6.48	0.26
S13	5.03	18.79	0.26
S14	1.45	6.41	0.26
S15	3.5	13.80	0.26

TABLE 2

Summary of (TeaBr) and (Succinate) Effects inDMS at 35.00°

<u>RUN</u>	<u>TeaBr (mM)</u>	<u>k_{xpt} (1/10³ min.)</u>	<u>k_o (1/10³ min.)</u>	<u>SUCCINATE (M)</u>
D11	14.28	22.40		0.52
D12	14.28	23.97		0.78
D17	14.28	19.97		0.13
D21	14.28	20.40		0.065
D23	14.28	22.40		0.39
D25	14.28	22.93		0.52
D26	14.28	21.12	19.8	0.26
D28	30.65	41.10	38.6	0.26
D30	24.50	33.90	31.8	0.26
D33	7.36	11.55	10.84	0.26
D35	3.86	5.40	5.07	0.26

TABLE 3Summary of (TeaBr) and (Succinate) Effects inDMS at 25.00°

<u>RUN</u>	<u>TeaBr (mM)</u>	<u>k_{xpt} ($1/10^3$ min.)</u>	<u>k_o ($1/10^3$ min.)</u>	<u>SUCCINATE (M)</u>
D11	14.28	8.62		0.52
D12	14.28	9.11		0.78
D13	14.28	7.63		0.13
D18	14.28	7.65		0.13
D19	14.28	7.52		0.065
D21	14.28	7.34		0.065
D24	14.28	7.94		0.39
D25	14.28	8.52		0.52
D26	14.28	7.87	7.31	0.26
D27	58.9	30.20	28.05	0.26
D28	30.65	16.35	15.18	0.26
D29	7.36	4.40	4.09	0.26
D31	45.4	24.00	22.3	0.26

TABLE 4Ester Concentration Effect Constants

$$k = k_0 / (1 + b(\text{succinate}))$$

where (succinate) is succinate molarity

<u>Temperature</u>	<u>b</u>
35°	-0.24
25°	-0.28

TABLE 5Second-Order Rate Constants

<u>Temperature</u>	<u>k_{01}</u>
35°	1.57
25°	0.533

TABLE 6Ionization ConstantsFor TeabBr in DMS

<u>Temperature</u>	<u>K</u>
35°	59.8x10 ⁻³
25°	90 x10 ⁻³

TABLE 7Enthalpy of Activation

$$\Delta H^* = 19.7 \text{ kcal.}$$

$$\Delta \ln k_{01} = \Delta(1/T) (\Delta H^*/R)$$

$$T_2 - T_1 = 10^\circ \Delta(1/T) = -0.000109 = -0.109 \times 10^{-3}$$

$$\Delta H^* = -(1.987 \times 10^{-3} / 0.109 \times 10^{-3}) \Delta \ln k_{01}$$

$$\Delta H^* = -18.2 \Delta \ln k_{01} \text{ kcal.}$$

APPENDIX III

TABLE 8

Properties of the Solvents (7, 8, 9, 12)

	<u>Acetone</u>	<u>DMS</u>
D-25°	20.7	46.6.
ΔH_{25°	765° cal/g mole	12,600 cal/g mole (10)
Normal Boiling Point	56.2°C	189°C (11)
Vapor Pressure	282.5mm-30°C	0.853mm-30°C (11)
Density	0.7793g/ml-30°C	1.0956g/ml-25° (11)
Refractive Index		1.4768 (11)
N_D at 25°		1.47753 (This work)
Melting Point		18.5°C (11)
		18.5°C (This work)

TABLE 9Properties of Succinate (1)

Boiling Point	53-56°/50 μ	(From Morgan)
	41°/128 μ	(This work)
Density (dry)	1.46 \pm 0.01 g./ml.	
Density (exposed to room air)	1.512 @ 25°	

TABLE 10List of Symbols and Abbreviations

b	Ester concentration effect constant
c	Salt concentration
D	Dielectric constant
ΔH^*	Enthalpy of activation
K	Equilibrium constant
k	Pseudo first-order rate constant
k_1	Second order rate constant
k_0	Pseudo first-order rate constant extrapolated to zero ester concentration
k_{01}	Second order rate constant extrapolated to zero ester concentration
kw	Kilowatt
M	Molarity
mM	Millimolarity
R	Gas constant
S	Acetone
t	Time in minutes
θ	Angular reading
μ	Micron
Ω	Ohms
DMS	Dimethyl Sulfoxide

kcal	Kilocalories
Succinate	Dimethyl α -bromosuccinate
TeaBr	Tetraethylammoniumbromide

APPENDIX IV

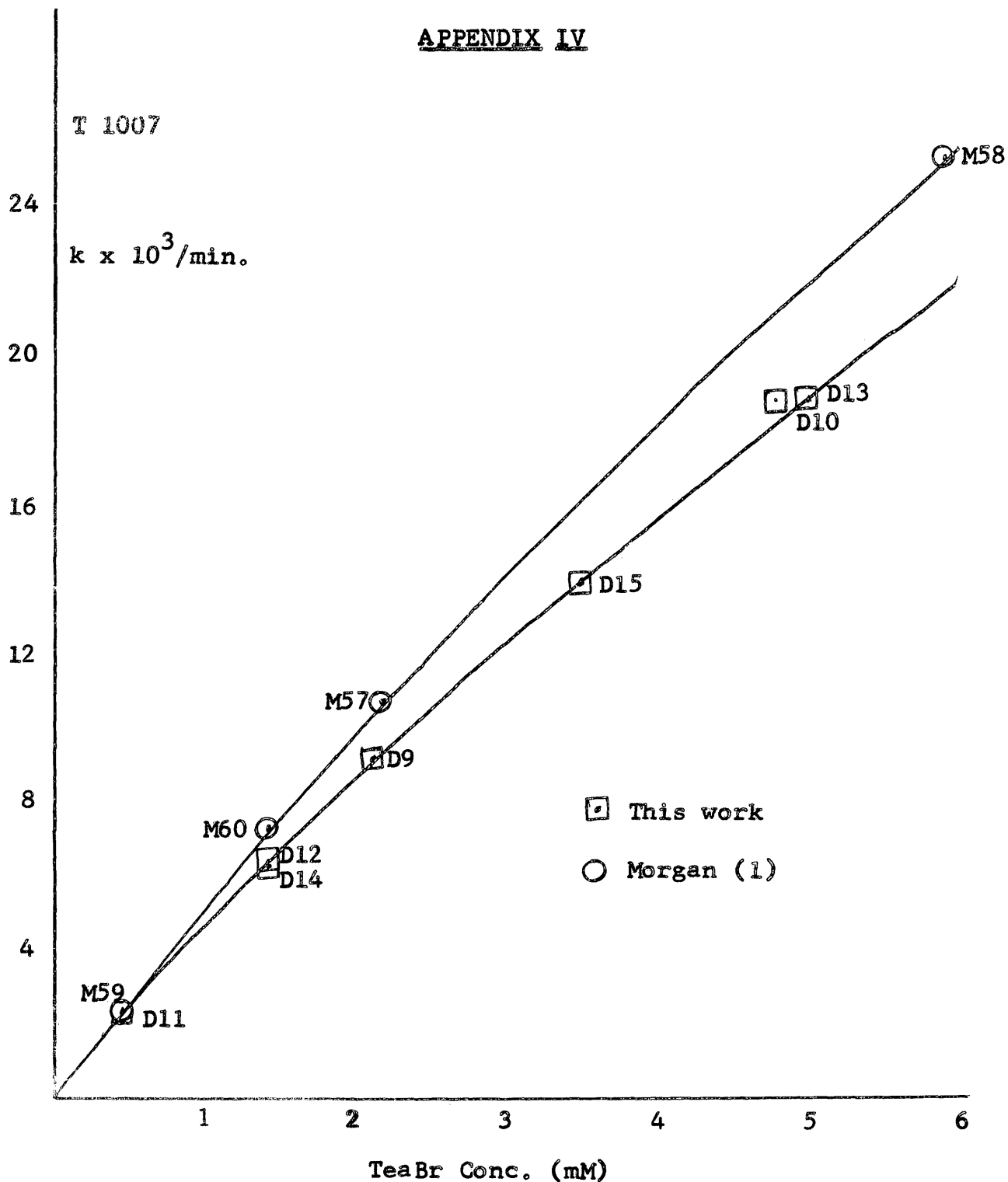


Figure I. Pseudo First-Order Rate Constants in Acetone vs. TeaBr Concentration. Temp. 25°, points not corrected for ester effects. Data from Table I.

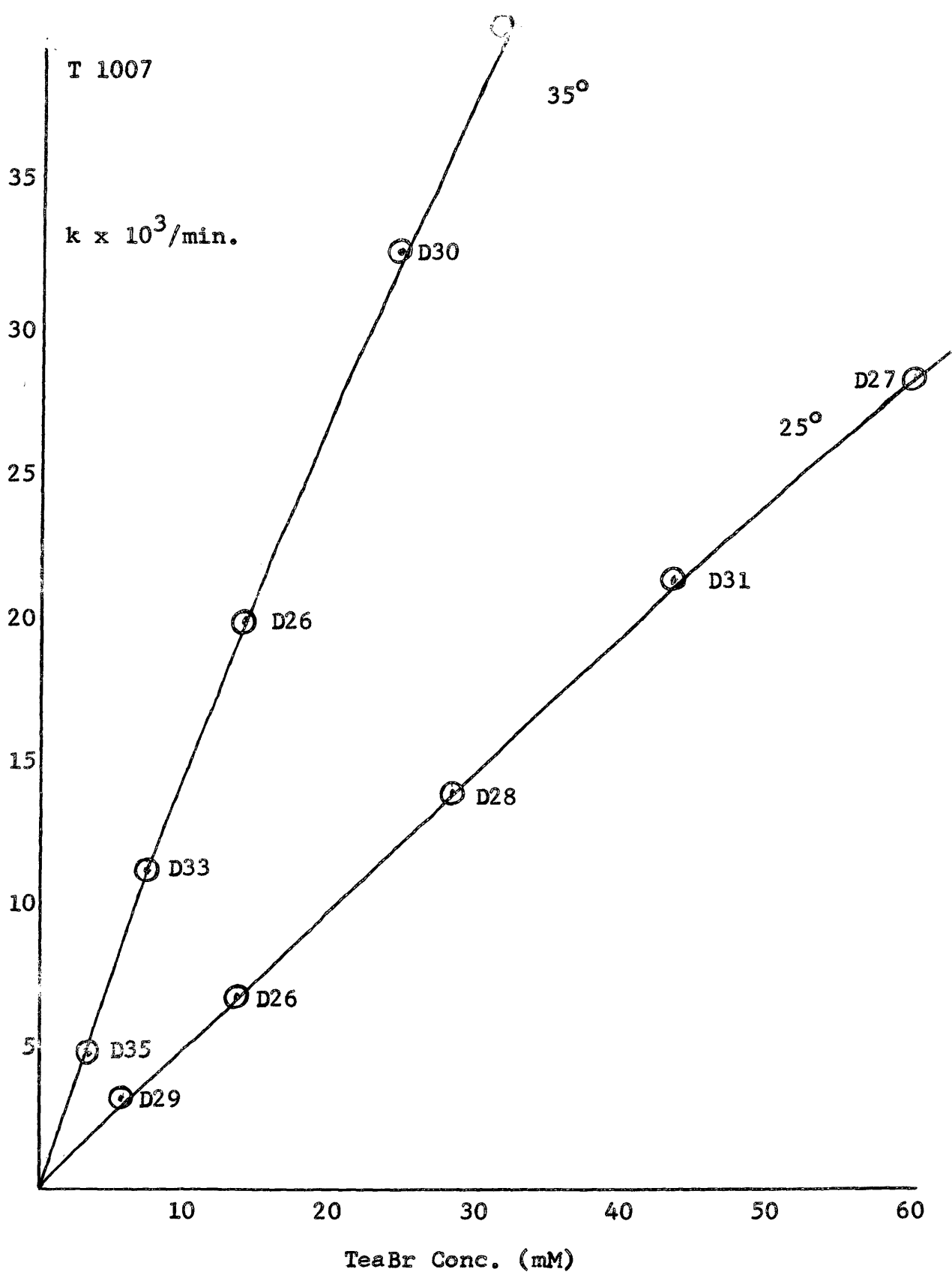


Figure II. Pseudo First-Order Rate Constants Corrected for Ester Effects vs. TeaBr Concentration. Data from Tables 2 and 3.

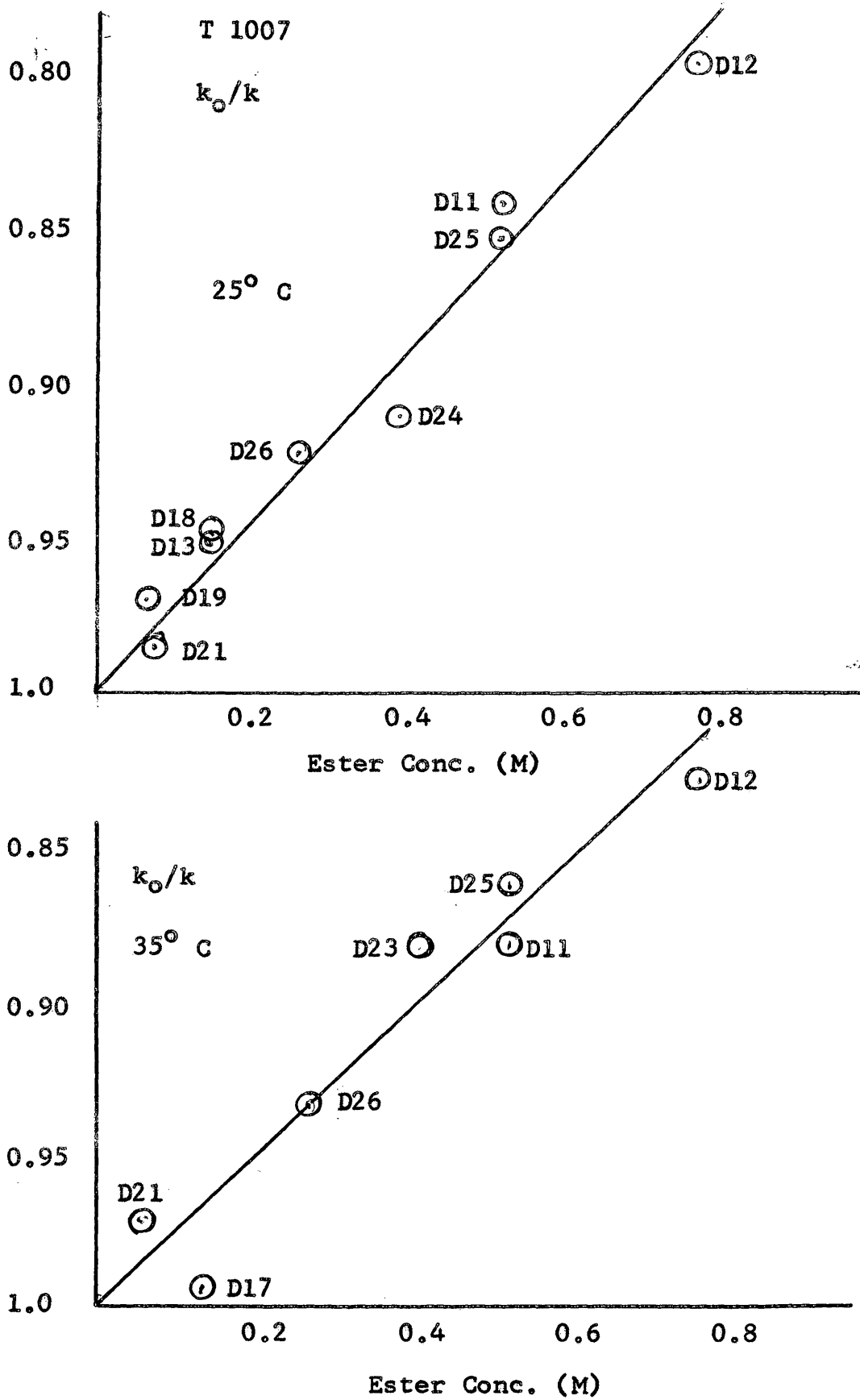


Figure III. Ester Concentration Effect on Rate Constant.

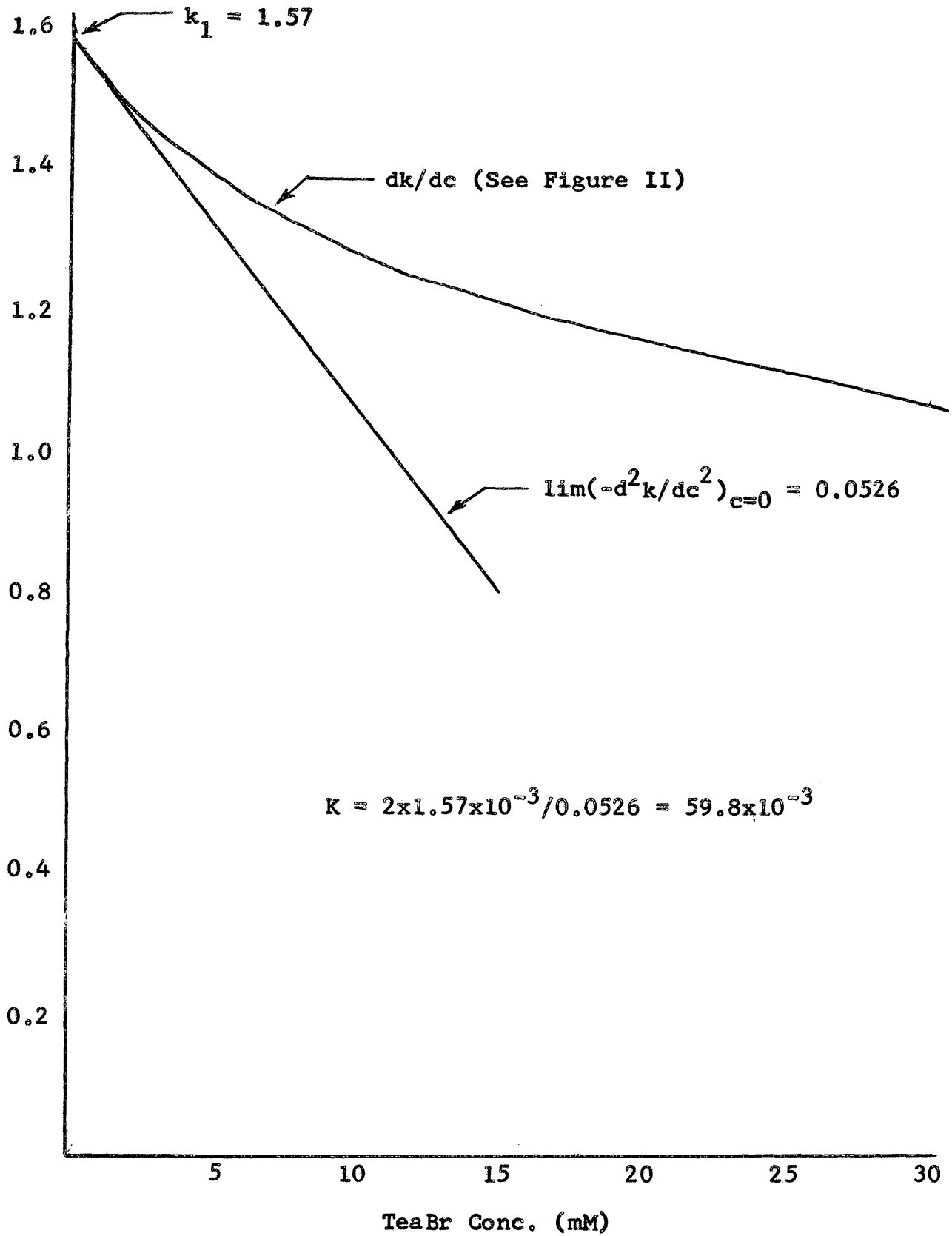


Figure IV. Graphical Solution for Ionization Constants at 35°. See Appendix I.

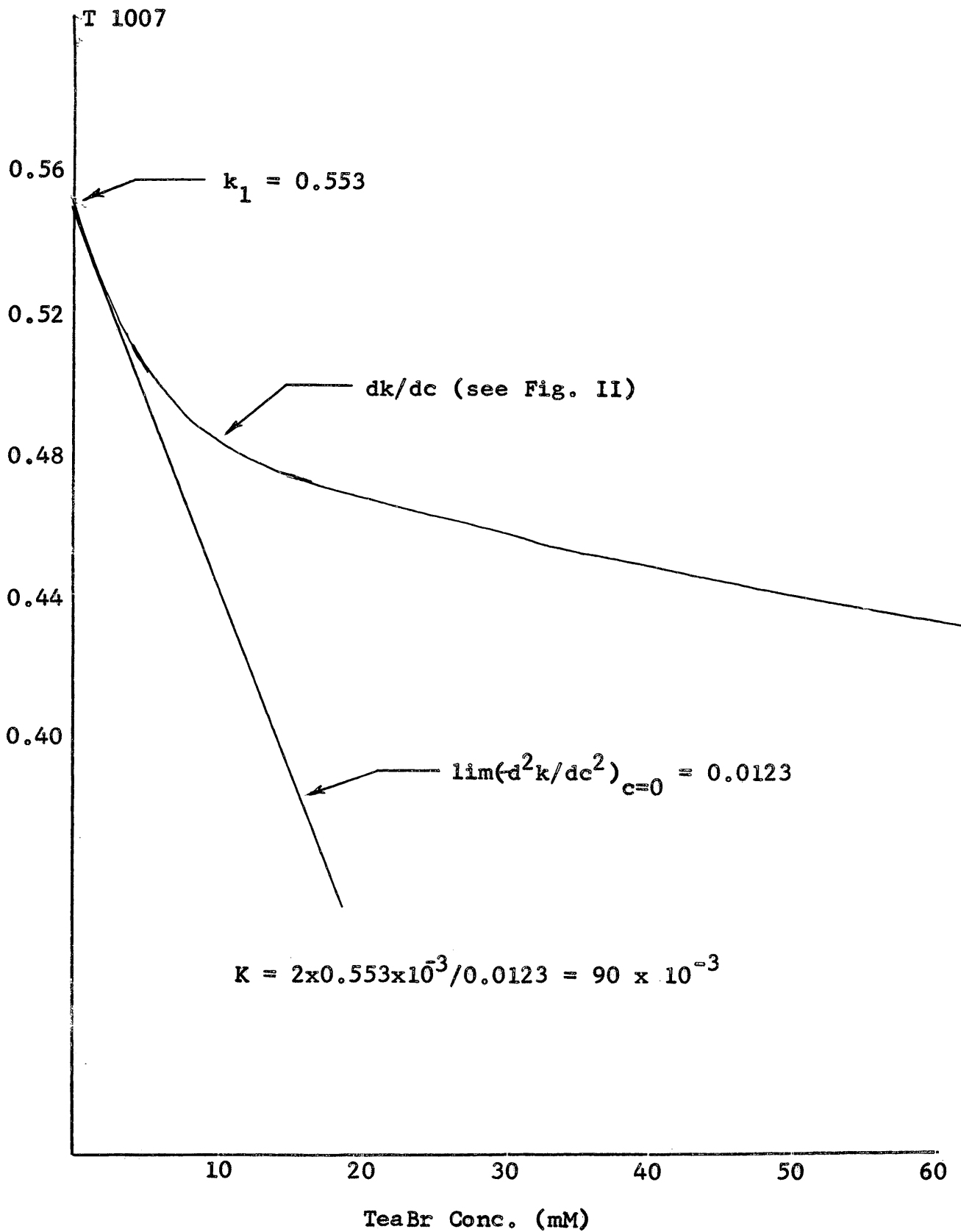


Figure V. Graphical Solution for Ionization Constants at 25°. See Appendix I.

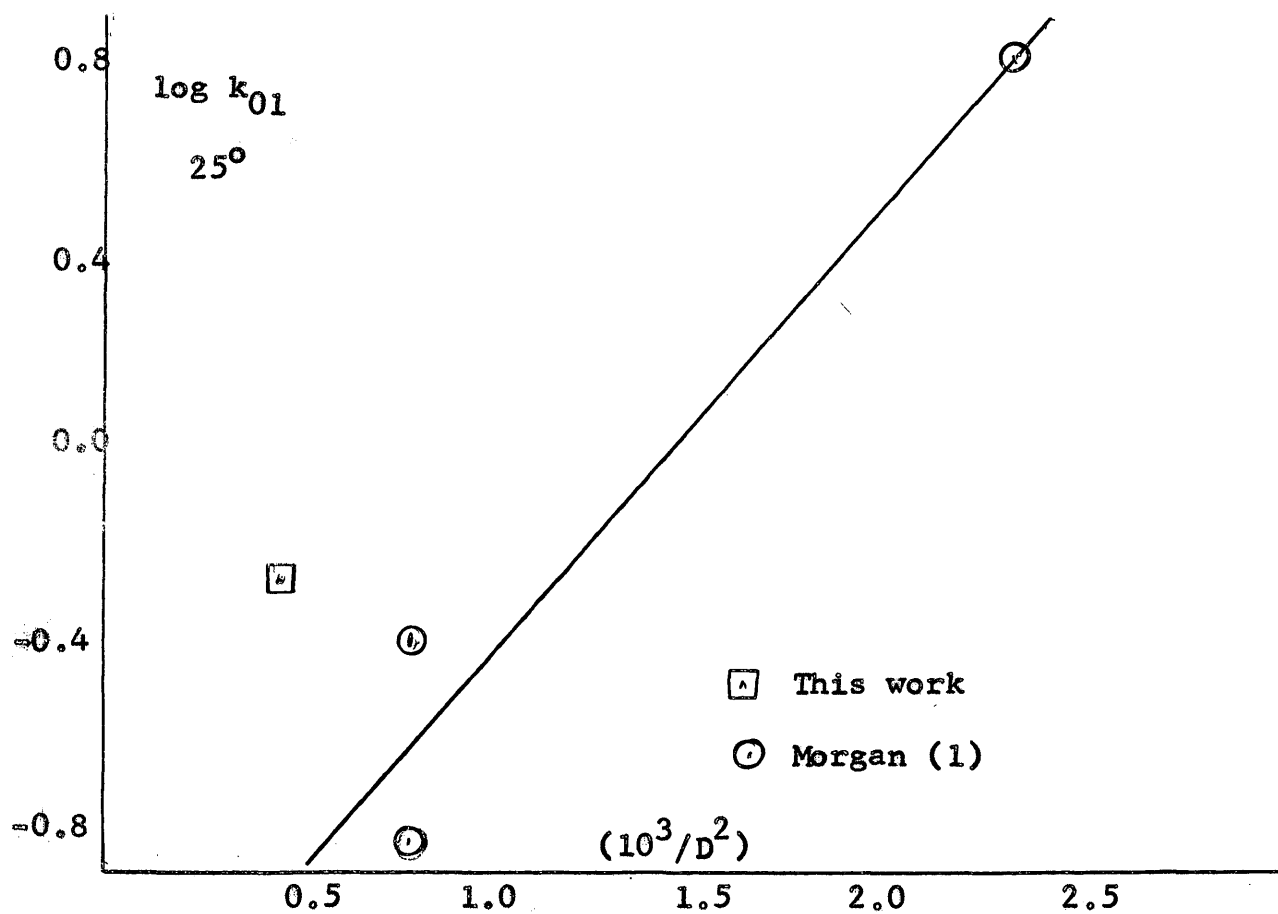
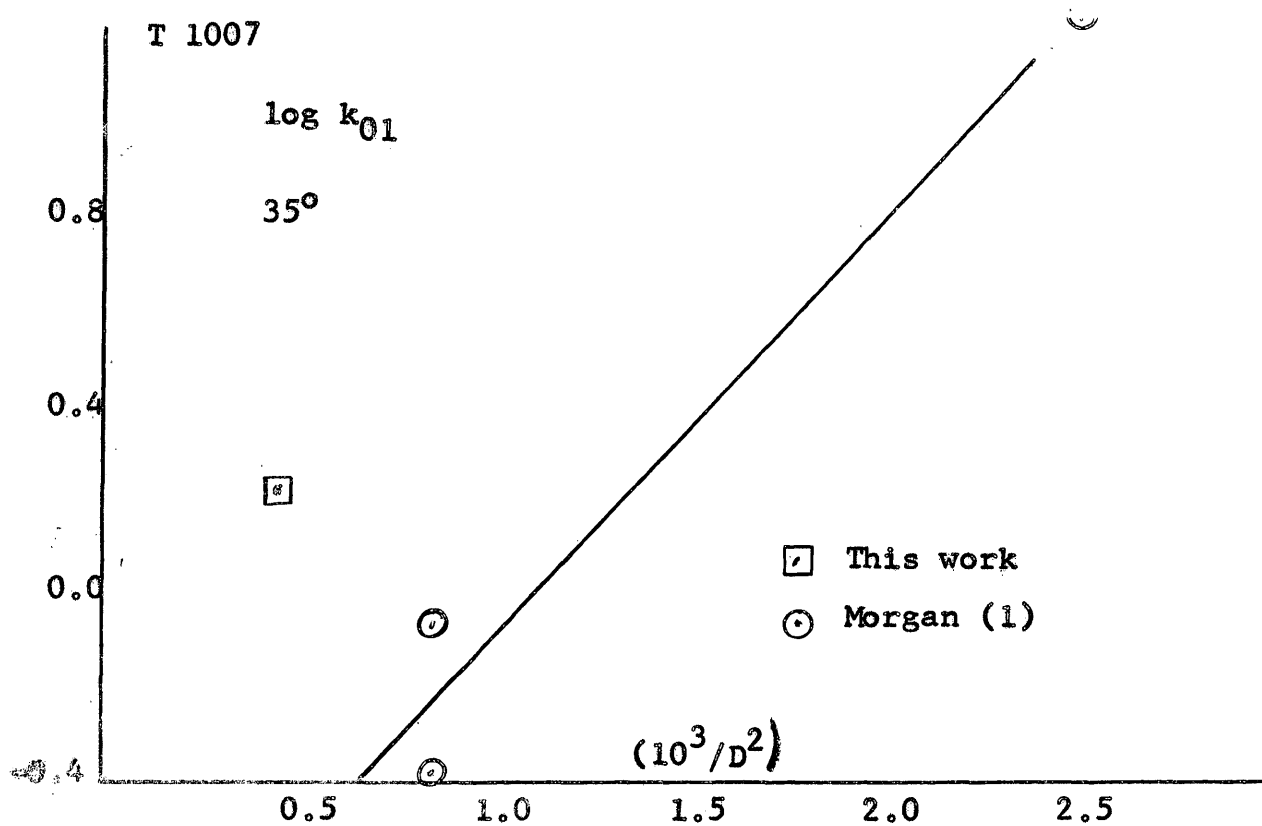
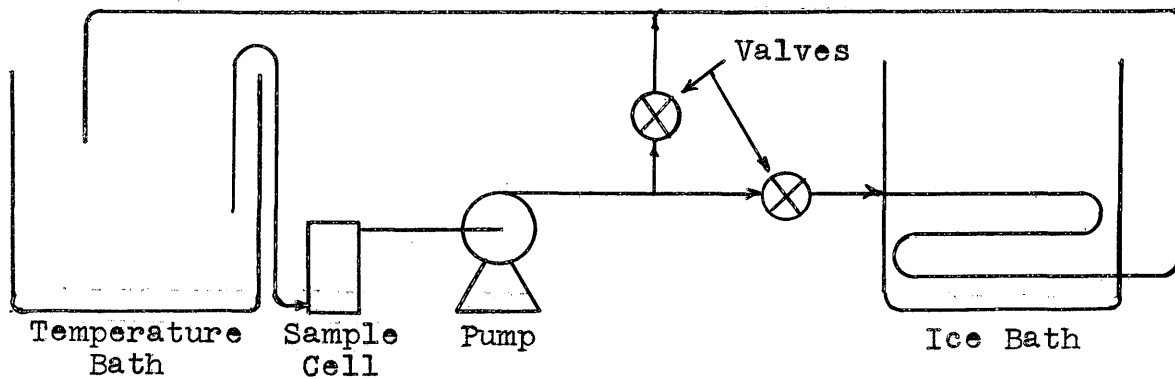
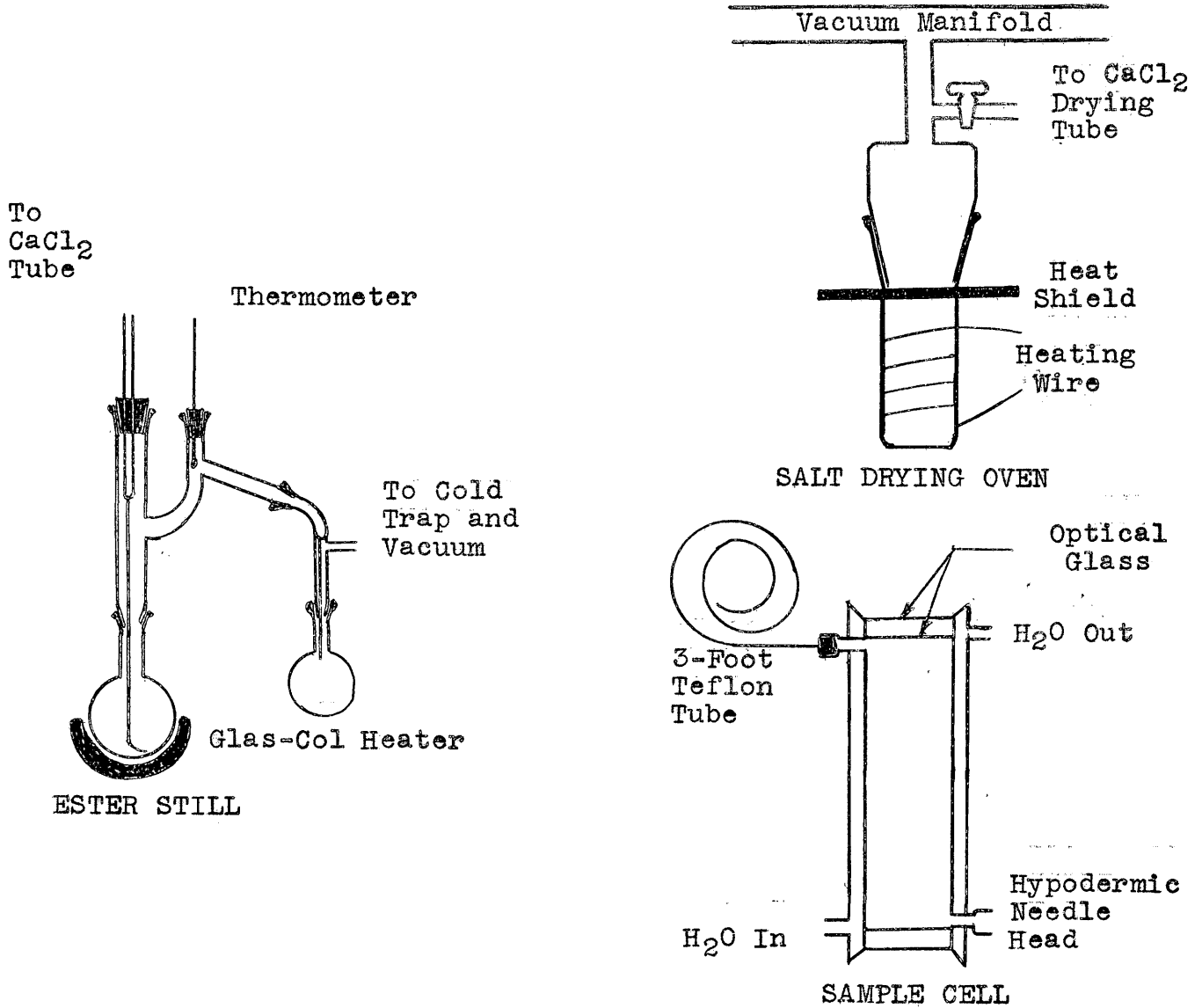


Figure VI. Debye-Hückel Comparison.



SCHEMATIC DIAGRAM OF THE WATER CIRCULATION PATH

Figure VII. Experimental Apparatus