THE KINETICS AND ENERGY OF ACTIVATION OF THE

ALKALINE HYDROLYSIS OF MONOETHYL MALONATE ION

By

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I. INTRODUCTION

This thesis is concerned with the theory of reaction kinetics in solution. Certain theoretical concepts are examined in their application to kinetic data obtained for a particular reaction. The data covers varying conditions of ionic strength, dielectric constant and temperature.

It was desired to study a reaction between ions of similar charge. It was considered advantageous to choose ions of unit charge to avoid complications that might ensue with polyvalent ions. The reaction would have to be straightforward (isolated) and capable of being followed without difficulty.

The reaction chosen for kinetic observation was,

$$C_2H_5O_2CCH_2COO^{-1} + OH^{-1} \longrightarrow CH_2(COO)_2^{-2} + C_2H_5OH \qquad (1)$$
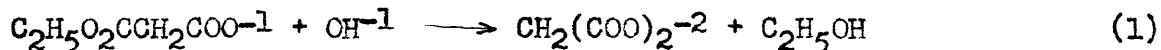
where the co-ions for the ethyl malonate and hydroxyl ions were potassium and sodium, respectively. The mechanism of the alkaline hydrolysis of an ester has been explicitly elucidated[1]. It involves an attack by hydroxyl ion on the ester linkage with polarization of the carbonyl group and attachment to the carbonyl carbon. Simultaneously or subsequently the bond to the alkyloxy group is weakened and broken. Kinetically the reaction is second order between ester and hydroxyl ion. For the reaction given in (1) the ester group is part of an anion and the reaction is thus between two ions each of unit negative charge.

This reaction has been studied previously[2,3] and found to be without complications. There are no side reactions, the monoethyl malonic acid does not disproportionate or decompose at ordinary temperatures and the reaction is second order. The result of alkaline hydrolysis of an ester is to leave the carboxylic group as an anion and not as the molecular acid.

The molecule is removed from equilibrum and alkaline hydrolysis is thus irreversible. The rate of reaction can easily be observed by ordinary acid-base titration of the remaining hydroxyl ion.

Other reactions between ions of similar charge have been studied[4,5], and extensive work has been carried out on the ammonium cyanate reaction[6] and others which are reactions between ions of opposite charge. In the main the results are in accord with theory.

Theory predicts that the reaction (1) should show a positive primary salt effect, i.e., the rate constant should increase with ionic strength. Westheimer, Jones and Lad[3] showed this was so, but their work was at only one temperature and in two different dielectric media giving no information as to the energy of activation and very little as to the effect of dielectric constant. Neither of the references cited give sufficient data for an accurate calculation of the rate constant at zero ionic strength.

In this work the reaction velocity has been studied at four temperatures in two isocomposition media, water and 27.57 weight percent dioxane in water; and in three isodielectric media corresponding to dielectric constants of 50, 55 and 60, in which the percentages of dioxane and water were varied to maintain the dielectric constant fixed as the temperature was changed. Observations were also made at 25° C. in three isodielectric mixtures of tertiary butyl alcohol-water corresponding to dielectric constants of 50, 55 and 60 to see if specific solvent interactions effected the results.

II. THEORETICAL DISCUSSION

Evaluation of the Rate Constant

A reaction between two specie is said to be second order when the rate of reaction is proportional to the product of the first power of the concentrations of each of the reactants.

$$\frac{dx}{dt} = k\, C_A C_B \tag{2}$$

If the two species A and B are present in equal concentrations and if they react in a one to one ratio, equation (2) can be integrated to,

$$\frac{1}{C_2} - \frac{1}{C_1} = k\,(t_2 - t_1) \tag{3}$$

The proportionality constant, k, is termed the reaction rate constant and for a second order reaction has the dimensions of concentration^{-1} time^{-1}.

In practice it is found that k is not a true constant but varies with the ionic strength of the solution. The effect is known as a primary salt effect and its explanation is based on the Bronsted theory of reaction in solution[7]. The Bronsted theory postulates that the reacting particles form an intermediate complex which may either decompose reversibly to regenerate the reactants or may decompose to give the reaction products.

$$A + B \rightleftharpoons X \longrightarrow C + D \tag{4}$$

The formation of the complex is an equilibrum process for which an equilibrum constant may be formulated according to the mass action law,

$$K = \frac{a_X}{a_A a_B} \tag{5}$$

or introducing the activity coefficient,

$$K = \frac{C_X}{C_A C_B} \cdot \frac{f_X}{f_A f_B} \tag{6}$$

According to the Bronsted theory, the rate of reaction will be proportional to the concentration of the intermediate complex,

$$\frac{dx}{dt} = k'C_X = k'KC_A C_B \frac{f_A f_B}{f_X} \tag{7}$$

For $k'K$ the symbol k_0 is given,

$$\frac{dx}{dt} = k_0 C_A C_B \frac{f_A f_B}{f_X} \tag{8}$$

By comparison with equation (2) it can be seen,

$$k = k_0 \frac{f_A f_B}{f_X} \tag{9}$$

The term $\frac{f_A f_B}{f_X}$ may be considered a correction factor to the classical rate equation making the proportionality constant independent of ionic strength, and k_0 may then be defined as the reaction rate constant at zero ionic strength.

Where the reaction is between ions the evaluation of this correction term is dependent on the Debye-Huckel treatment of activity coefficients in solution[8] which leads to an expression,

$$-\ln f_i = \frac{z_i^2 A\sqrt{u}}{1 + Ba_i \sqrt{u}} \tag{10}$$

where the terms A and B are defined by the equations,

$$A = \frac{\epsilon^3}{DkT} \sqrt{\frac{2\pi N}{1000 DkT}}$$

$$B = \sqrt{\frac{8\pi N \epsilon^2}{1000 DkT}}$$

For the general reaction,

$$A^{zA} + B^{zB} \rightleftharpoons Z^{zA+zB} \tag{11}$$

we can evaluate the correction term in the Bronsted equation (9) by use of the Debye-Huckel equation (10),

$$\ln \frac{f_A f_B}{f_X} = \frac{2z_A z_B A \sqrt{u}}{1 + Ba_i \sqrt{u}} \tag{12}$$

or,

$$\frac{f_A f_B}{f_X} = e^{\frac{2z_A z_B A \sqrt{u}}{1 + Ba_i \sqrt{u}}} \tag{13}$$

Inserting this expression in our original equation (9) and taking logarithms,

$$\ln k = \ln k_o + \frac{2z_A z_B A \sqrt{u}}{1 + Ba_i \sqrt{u}} \tag{14}$$

Converting to Briggsian logarithms,

$$\log k = \log k_o + \frac{2z_A z_B A' \sqrt{u}}{1 + Ba_i \sqrt{u}} \tag{15}$$

where $A' = A/2.303$

Evaluating this expression employing the latest values of the physical constants,[23] and considering that for the reaction studied here $z_A = z_B = -1$, equation (15) becomes,

$$\log k = \log k_o + \frac{\dfrac{3.647 \times 10^6 \sqrt{u}}{(DT)^{3/2}}}{1 + \dfrac{5.028 \times 10^9 a_i \sqrt{u}}{(DT)^{\frac{1}{2}}}} \tag{16}$$

on rearrangement,

$$\log k_o = \log k - \frac{3.647 \times 10^6 \sqrt{u}}{(DT)^{3/2} + 5.028 \times 10^9 a_i DT \sqrt{u}} \tag{17}$$

The significance of a_i in the Debye-Huckel equation is that of mean distance of approach of the ions, or it is often referred to as the average effective ionic diameter. Its exact physical significance cannot be expressed precisely. It is on the order of magnitude of ionic diameters as determined by other methods. In practice a value of a_i may be arbitrarily assigned, or as in this work it may be treated as an adjustable parameter.

In very dilute solution where u is small the second term in the denominator of equation (10) becomes insignificant and the equation assumes the form designated as the Debye-Huckel limiting law,

$$-\ln f_i = \frac{z_i^2\ A\sqrt{u}}{(DT)^{3/2}} \tag{18}$$

in which case equation (17) becomes,

$$\log k_o = \log k - \frac{3.647\ \text{X}10^6 \sqrt{u}}{(DT)^{3/2}} \tag{19}$$

From equation (19) a plot of log k versus $\sqrt{u}$ in dilute solution should give a straight line of slope $3.647\ \text{X}10^6 / (DT)^{3/2}$

Since the reaction rate varies with the ionic strength it becomes important to know the ionic strength corresponding to any value of k to permit the evaluation of k_o. For the reaction in equation (1) the ionic strength will be a function of the original concentrations and the amount reacted. Considering ester and alkali present initially in equal concentrations, C, and letting the amount reacted equal x,

$$u = \tfrac{1}{2}\left[(C-x)_{\text{ethyl malonate}^-} + C_{K^+} + (C-x)_{OH^-} + C_{Na^+} + 4x_{\text{malonate}-2}\right]$$

or summing up terms,

$$u = 2C + x \tag{20}$$

The ionic strength and thus k should increase as the reaction proceeds. The effect of this increase is such that if $C = 0.0150$ ($u = 0.0300$), at fifty percent reaction ($u = 0.0375$) the logarithm of k will increase by 0.0125 or if we let k equal 1.00 initially, then k at fifty percent reaction should be equal to 1.03.

In the presence of added uni-univalent neutral electrolyte, e.g. NaCl, in concentration S,

$$u = 2C + S + x \qquad (21)$$

Effect of Dielectric Constant

From the Debye-Huckel development Scatchard[9] has derived an expression for the effect of the dielectric constant of the medium on the reaction rate constant at zero ionic strength,

$$\ln k_o{}^* - \ln k_o = \frac{\epsilon^2 z_A z_B}{kTr} \left[\frac{1}{D^*} - \frac{1}{D} \right] \qquad (22)$$

where * refers to some reference solvent. Differentiation of (22) with respect to dielectric constant at constant temperature yields,

$$\left(\frac{\partial \log k_o}{\partial D} \right)_T = \frac{\epsilon^2 z_A z_B}{2.303r \ k \ D^2 T} \qquad (23)$$

Equation (23) predicts an increase in the reaction rate constant with increasing dielectric constant for a reaction between ions of like sign. From (23) may be derived,

$$\left(\frac{\partial \log k_o}{\partial 1/D} \right)_T = - \frac{\epsilon^2 z_A z_B}{2.303r \ kT} \qquad (24)$$

A plot of log k_o against $1/D$ should thus result in a straight line with negative slope if z_A and z_B are of the same sign with,

$$r = \frac{\epsilon^2 z_A z_B}{2.303 \ kT \ (slope)} \tag{25}$$

The significance of r in these equations is that of the radius of the complex. It may further be described as the distance to which two ions must approach in order to react. While there need be no exact equality between r and a_i, the distance of closest approach, they should certainly be on the same order of magnitude.

Effect of Temperature

To account for the effect of temperature on the rate of a chemical reaction Arrhenius proposed the equation,

$$k = Ze^{-E/RT} \tag{26}$$

Where E is the energy of activation and Z is termed the frequency factor. Z has the dimensions of frequency and is given the significance of the number of molecules colliding in unit time. Thus the reaction rate is equal to the rate of collision multiplied by the fraction of molecules having the necessary energy, E, to react. Z can be calculated from kinetic theory,

$$Z = \frac{N}{1000} \ \sigma^2 \left[8\pi RT \left(\frac{1}{M_A} + \frac{1}{M_B} \right) \right]^{1/2} \tag{27}$$

where σ is the mean collision diameter. Since Z is proportional to the square root of the temperature it changes only slightly with temperature. Over a small temperature range Z can be treated as a constant. If rate constants at two temperatures be substituted in the logarithmic form of equation (26) and the two resulting expressions are subtracted,

$$\log \frac{k_2}{k_1} = \frac{E}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \tag{28}$$

from which the activation energy can be readily calculated.

While the kinetic theory has been quite successful in application to gas reactions, the theory is inadequate to account for the many slow reactions found in solution. The "English school" has introduced the concept of the probability or steric factor, P,

$$k = PZe^{-E/RT} \tag{29}$$

which while very convenient as a correction factor adds little to the argument.

Not till Eyring developed from a thermodynamic formulation an absolute theory of reaction rates[10] could a fundamental exposition of the frequency factor be given. From the Eyring theory,

$$k = \frac{RT}{Nh} e^{S/R} e^{-E/RT} \tag{30}$$

where S is the entropy of activation. Comparison with equation (26) shows that,

$$Z = \frac{RT}{Nh} e^{S/R} \tag{31}$$

or on substituting the value of Z, equation (27),

$$\frac{RT}{Nh} e^{S/R} = \frac{N}{1000} \sigma^2 \left[8\pi RT \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right]^{1/2} \tag{32}$$

Equation (32) may be used to calculate S if σ is assumed or available from other types of data (e.g. from viscosity measurements,) or may be evaluated from experimental values of Z.

The free energy of activation may be calculated by the thermodynamic equation,

$$F = E - TS \tag{33}$$

where the energy of activation has been set equal to the heat of activation since the change in volume in solution reactions is practically zero.

The "True" Activation Energy in Solution

It has been shown that the ionic strength affects the reaction rate constant (and thus the activation energy), and the consequences of changing independently the dielectric constant and temperature have been considered. Historically, the activation energies were always measured in isocomposition media. Since the dielectric constant of a solution as well as the rate of reaction will change with temperature, the reaction rate will be seen to be a function of both variables. Svirbely and Warner[6] first considered the problem of activation energy in isodielectric media.

Avoiding the ionic strength effect by considering rate constants at zero ionic strength, i.e. k_o's, it is assumed that the dielectric constant and temperature are the only other important effects,

$$\ln k_o = f\,(D,T)$$

or,

$$\frac{d \ln k_o}{d\,T} = \left(\frac{\partial \ln k_o}{\partial\,T}\right)_D + \left(\frac{\partial \ln k_o}{\partial D}\right)_T \frac{dD}{dT} \qquad (34)$$

Multiplying by $2.303RT^2$

$$E^o{}_{F.C.} = E^o{}_{F.D.} + 2.303RT^2\left(\frac{\partial \log k_o}{\partial D}\right)_T \frac{dD}{dT} \qquad (35)$$

where $E^o{}_{F.C.}$ is the activation energy in solution of fixed composition, and $E^o{}_{F.D.}$ is the activation energy in isodielectric media, both energies being derived from rate constants at zero ionic strength. $E^o{}_{F.D.}$ represents a pure temperature effect and may be considered the "true" activation energy. Experimentally, fixed dielectric media can be realized by varying the composition to maintain the constancy of dielectric at each

temperature of measurement.

Since $\dfrac{\partial \log k_o}{\partial D}$ is positive for reactions between ions of like charge, and $\dfrac{dD}{dT}$ is negative for most solvents, equation (35) predicts for such a reaction,

$$E^{o}_{F.D.} \; \rangle \; E^{o}_{F.C.}$$

The term $\dfrac{\partial \log k_o}{\partial D}$ may be evaluated by measurement of k_o in various dielectric media at constant temperature. For most solvents and solvent mixtures the relation of dielectric constant to temperature may be expressed in the form[11],

$$D = ae^{-bT} \tag{36}$$

where a and b are empirically determined constants. Hence,

$$\dfrac{dD}{dT} = -bD \tag{37}$$

It is to be emphasized that the above equations relate to k_o's. The effect of ionic strength on the activation energy can now be considered independently. Differentiating equation (17) with respect to temperature and multiplying by $2.303\ RT^2$,

$$E_u = E^o - 8.398 \times 10^6 \sqrt{u}\ \ RT^2$$

$$\left(\dfrac{3/2\ (DT)^{\frac{1}{2}} + 5.028 \times 10^9\ a_i \sqrt{u}}{(DT)^{3/2} + 5.028 \times 10^9\ a_i \sqrt{u}\ \ DT} \right) \left(D + T\ \dfrac{dD}{dT} \right) \tag{38}$$

where E_u is the activation energy at some finite value of the ionic strength. From equation (37) the expression enclosed in the second brackets of equation (38) can be shown to be equal to $D(1-bT)$. If isodielectric media are considered $\dfrac{dD}{dT}$ is, of course, zero and the last term in the

brackets drops out.

Amis[12] has considered the problem of the change of activation energy in changing dielectric media at constant temperature. From the Born equation it can be derived,

$$\Delta E = - \frac{z_1 z_2 \epsilon^2}{D_1 D_2 r} \Delta D \qquad (39)$$

where ΔE is the change in activation energy and ΔD the difference in dielectric constants. From equation (39) for reactions between ions of like charge there will be an increase in activation energy when the dielectric constant is lowered. This effect readily follows from Coulomb's Law: for ions of like charge the lower the dielectric constant the greater the repulsion and hence the greater the energy of activation.

Units of the Rate Constant

Scatchard[13] has pointed out that in a mixture of non polar molecules the activity coefficients are proportional to the mol fractions and not to the volume concentrations. Consideration of this factor has improved the correlation of the data for the thiosulfate-bromoacetate reaction[5]. Svirbely and Peterson attempted its application to the ammonium cyanate reaction with little advantage[14].

The relation of rate constant on a mol fraction (k_N) and volume concentration (k_C) basis for a second-order reaction taking place in a pure solvent can be shown to be,

$$k_N = \left(\frac{1000 \ d}{M} \right) k_C \qquad (40)$$

where d is the density and M the molecular weight. For mixed solvents the relationship is

$$k_N = \left(\frac{1000 \ \Sigma n}{V} \right) k_C \qquad (41)$$

where $\sum n$ is the total number of moles of solvent, V the volume of the solution in milliliters. The conversion factors for the solutions used in this study have been calculated and are given in the Appendix.

REAGENTS AND APPARATUS

1. Reagents

The potassium salt of the monoethyl ester of malonic acid was

prepared from the diethyl ester according to the equation:

$$CH_2(CO_2C_2H_5)_2 \; + \; KOH \; \rightarrow \; \begin{matrix} CO_2C_2H_5 \\ | \\ CH_2 \\ | \\ CO_2K \end{matrix} \; + \; C_2H_5OH \qquad (42)$$
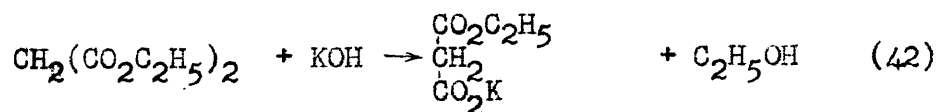
The method first employed was that of Walker[15]. A technical grade

of diethyl malonate was fractionally distilled under reduced pressure and

a middle cut reserved. This portion had a refractive index, n_D^{25}, equal to

1.4122. One mole of the purified diethyl ester was dissolved in three

times its volume of ethanol. One mole of potassium hydroxide, also in

alcoholic solution, was added slowly with stirring to the diethyl ester

solution. The potassium salt separated out immediately in the form of

large white flakes. The semisolid mass was digested for twenty-four hours

at 70°C. and allowed to cool. The salt was filtered off and washed with

ether to remove any traces of the diethyl ester.

The fact that the dipotassium salt of malonic acid is insoluble in

absolute ethanol while the potassium salt of the monoethyl ester is

readily soluble affords a means of purification. Alcohol was added to

the crude product until about 90% had dissolved. The remaining 10% was

discarded. Ether was added to the mother liquor to precipitate out the

monopotassium salt with the first fraction of crystals being rejected.

The purified salt was filtered off, washed with ether and dried at 50°C.

The purity of the salt was determined by the method of saponifica-

tion analysis. Analyses were carried out by saponification of one-half

of a gram of salt with sodium hydroxide in about ten percent excess at

50°C. for three days. The excess alkali was backtitrated with standard hydrochloric acid. The results in terms of percent of theoretical varied from 98 to 99%.

The method of Walker, as outlined above, attempts the separation of a less soluble compound from one that is more soluble. Thus the desired material cannot be obtained pure by fractional crystallization. It can only be hoped that the major part of the impurity will either not be dissolved by the alcohol, or will separate out in the first crop of crystals on addition of ether. It is not too surprising, then, that the final product still contained one to two percent of the less soluble impurity.

An attempt was made, without success, to find a solvent or a mixture of solvents in which the order of solubilities would be reversed, i.e., in which the mono-potassium salt would be less soluble.

Finally, it was found that solution of the salt in absolute ethanol and fractional precipitation with ether with the first 50% of material to crystallize discarded, resulted in a product that was 100% ± 0.1% of theory as determined by saponification analysis.

In an attempt to avoid the formation of any of the dipotassium salt the method as described above was modified so that one mole of the diethyl ester was reacted with only four-tenths of a mole of potassium hydroxide. This product was found to be pure after the first crystallization.

Dioxane was purified by the method of Fieser[16]. Commercial dioxane was refluxed with hydrochloric acid while passing through a slow stream of nitrogen gas. Potassium hydroxide pellets were added till a water layer no longer formed. The dioxane was dried with sodium metal and

finally distilled through a three foot helix-packed column equivalent to about nine theoretical plates. A middle cut boiling at 100.8°C. and having a refractive index, n_D^{20}, equal to 1.4219 was reserved.

Tertiary butyl alcohol was purified from Eastman's best-grade by drying with anhydrous calcium sulphate and fractionally distilling. A middle cut boiling at 82.2°C. was collected for use.

Boiled, distilled water was used in making up all solutions. Sodium hydroxide used in the preparation of standard solutions was carbonate free. Alkali solutions were standardized against a National Bureau of Standards standard sample of potassium acid phthalate.

2. Apparatus

The rate measurements were carried out in a water thermostat with stirrer and heating coil controlled by a mercury thermoregulator. The bath temperature was constant to ± 0.015°C. For operating at temperatures below that of the room, a large can was placed inside the thermostat bath and the cooling coil of a portable refrigerating unit was placed inside the can. A bimetallic thermoregulator governing the refrigeration unit was used to hold the water in the can several degrees below the temperature in the bath, with the more sensitive mercury thermoregulator and heating coil still controlling the temperature in the bath itself.

The thermometer used was of a total immersion type divided in tenths of a degree. The temperature could be read to the nearest hundredth of a degree with the aid of a magnifying glass. The thermometer was calibrated against a similar one that had been certified by the National Bureau of Standards.

A stopwatch that was calibrated against the National Bureau of Standards time signals was used to observe the times of sampling.

A 20 ml., jacketed pipette was used for withdrawing samples. Water from the bath was circulated through the jacket to keep the sample at the reaction temperature till its discharge from the pipette. All pipettes and burettes were calibrated.

The reactions were carried out in 300 ml. glass stoppered flasks. As a precautionary measure, Erlenmeyers of alkali resistant glass (Corning #928) were usually used though there was no indication of any consequential attack on pyrex Erlenmeyers by the dilute alkali solutions. The titration flasks were 125 ml. glass stoppered pyrex Erlenmeyers. All flasks were provided with side arms and an atmosphere of nitrogen was kept over the

solutions to prevent absorption of carbon dioxide.

Standard alkali solutions in stock bottles and in burettes were protected from atmospheric carbon dioxide by Ascarite tubes. An automatic, delivery arrangement permitted direct transfer from stock bottle to burette.

EXPERIMENTAL METHOD AND DATA

The method of preparing reaction mixtures was to first weigh out a sample of potassium ethyl malonate in a small vial. The volume of standard sodium hydroxide calculated to contain an equivalent amount of alkali was then measured out by burette into the reaction vessel. If it was desired to lower the initial concentration, the mixture was diluted with water added by pipette. In those experiments where a high ionic strength was required, sodium chloride was weighed out in a small vial and added to the reaction mixture.

When a mixed solvent was employed, the appropriate volume of organic solvent was added by burette to bring the mixture to the desired dielectric constant. From a knowledge of the volume of water present, and the densities of water and organic solvent, the volume of solvent could be calculated from Table 1. This table represents interpolated data of Akerlof for dioxane[17] and tertiary butyl-alcohol[11].

In Table 2 are given dielectric constants at various temperatures for the 27.57 weight percent dioxane in water isocomposition mixture employed.

The density of dioxane was measured as 1.030 at 25°C. The density at other temperatures was calculated from the data of Hovorka and co-workers[18]. The density of tertiary butyl alcohol was taken as 0.7810 at 25°C.[19]

Table 1

Weight Percentages of Organic Solvents in Water Corresponding to Specified Dielectric Constants at Various Temperatures

Dioxane-water

Dielectric Constant	50	55	60
Temperature, °C.			
5.37	37.87	32.73	27.57
15.01	35.11	29.75	24.33
25.08	32.11	26.49	20.85
34.94	29.06	23.21	17.39

Tertiary butanol-water

25.08	33.01	27.25	21.47

Table 2

Dielectric Constants of 27.57 weight percent Dioxane in Water at Various Temperatures

Temperature, °C	5.37	15.01	25.08	34.94
Dielectric constant	60	57.01	54.04	51.28

After preparation of the reaction mixture, the reaction flask was placed in the thermostat and allowed to reach temperature equilibrium. The reaction was initiated by dropping into the reaction vessel the vial containing the potassium ethyl malonate. The vessel was swirled to hasten solution of the salt.

At suitable time intervals samples were withdrawn by a pipette and analyzed for remaining alkali. As the reaction proceeded the time interval between samples was lengthened to allow for more nearly equal decrements of normality. The mean of the initial and final times for discharge of pipette was recorded to the nearest second as the time of sampling.

The reaction was stopped by releasing the sample into an excess of standard hydrochloric acid. The HCl was weighed out from a weight pipette to the nearest milligram. The weight was corrected to vacuo and converted to volume assuming the density to be the same as that of water. Since the HCl was standardized by a similar procedure making the same assumption, no error was introduced by the fact that the density would actually be slightly different from that of water. The solution was backtitrated with standard sodium hydroxide to an end point at a pH of 9.0. The end point was observed by use of a mixed indicator of phenolphthalein and thymol blue[20].

The backtitration procedure involves the titration of HCl in the presence of potassium ethyl malonate and of dipotassium malonate and of dipotassium malonate. A substantial portion of the excess hydrogen ion will be tied up in molecular form in the weak acids: monoethyl malonic acid, malonic acid and monohydrogen malonate ion. The latter is the weakest acid having an ionization constant of 2.0×10^{-6}[21] in water at 25°C.

In order to attain the true equivalence point and recover all the excess HCl it is necessary to titrate to the pH corresponding to that of the salt of the weakest acid present. The expression giving the pH of the salt of a weak acid is,

$$(H^+) = \sqrt{\frac{K_w K_A}{c}}$$

where K_w is the ionization constant of water, K_A the ionization constant of the weak acid, and c the salt concentration.

In a particular kinetic run the amount of monohydrogen malonate ion will increase as the reaction goes towards completion. Moreover, experiments were carried out over a range of initial concentrations. Though no one indicator would therefore be perfectly suited for the titration of all samples, the use of the mixed indicator described above changing at pH equal to 9.0 was determined as being adequate and most suitable.

In Table 3 is given a sample of the complete data for a run. The volume of dioxane was calculated from Table 1. The initial normality was calculated assuming volume additivity of the water in dioxane. This value was used only for calculation of ionic strengths. It was not employed for calculation of rate constant, since a finite time was required for solution of the salt and zero time for the run was uncertain.

Table 3

Dioxane—water
D = 60
T = 25.30° C. (uncorrected)
T = 25.08° C. (corrected)

Sample weight = 0.3395 gms.
Vol. 0.04253 N NaOH = 46.90 ml.
Vol. water = 61.98 ml.
Vol. dioxane = 27.61 ml.

Normality, initial = 0.01459

u, initial = 0.02918

Sample number	1	2	3	4
Sample volume	19.97	19.97	19.97	19.97
Time (minutes and seconds)	15 24	29 59	56 38	117 36
Time, corrected	15 23	29 57	56 35	117 30
Time, decimal (minutes)	15.38	29.95	56.58	117.50
Vol. of .02843 N HCl to kill reaction	8.926	8.208	7.583	5.899
Backtitration with final	29.08	31.63	37.38	43.78
.00785 N NaOH initial	27.88	29.08	31.63	37.38
Volume NaOH, uncorrected	1.20	2.55	5.75	6.40
Burette correction	—	—	−0.02	—
Blank correction	−0.22	−0.22	−0.23	−0.23
Volume NaOH, corrected	0.98	2.33	5.50	6.17
Equivalent Vol. .02843 N HCl	0.270	0.643	1.518	1.703
Vol. HCl neutralized by sample	8.656	7.565	6.065	4.196
Normality of sample	.01232	.01071	.008634	.005973
$(\text{Normality})^{-1}$	81.15	93.40	115.82	167.40
$\Delta(\text{Normality})^{-1}$		12.25	22.42	51.58
Δ Time		14.57	26.63	60.92
k		0.841	0.842	0.847
u	.03145	.03306	.03514	.03780
u (mean)		.03226	.03410	.03647
k_0		0.522	0.518	0.515

The sodium hydroxide used in back-titration was more dilute than the HCl, 0.01 ml. of alkali being equivalent to 0.0036 ml. of the HCl. The volume of alkali, corrected by a blank depending on the final total volume of the solution, was converted to ml. of the HCl normality. This figure subtracted from the original HCl volume gave the volume neutralized by the sample and together with the HCl normality and sample volume permitted calculation of the sample normality.

The k's were calculated by equation (3) for each pair of consecutive samples. The ionic strength was calculated by equation (20) from the initial normality and the normality of the sample. Since each value of k corresponds to an ionic strength range, the mean value of ionic strength for two consecutive samples was employed in equation (17) for calculation of k_o's. This calculation is discussed more in detail after Table 25.

In Tables 4 through 25 are recorded time, concentration and ionic strength data for all experiments and calculated values of k and k_o. Data are given for water, and for water-dioxane mixtures of 27.57 weight percent and dielectric constants of 60, 55 and 50 at four temperatures; and also for tertiary butyl alcohol-water mixtures of dielectric constants of 60, 55 and 50 at one temperature. For each set of conditions at least two runs were made. Units of time are in minutes and of k and k_o in minutes^{-1} (moles / liter)$^{-1}$. The temperatures given in round figures correspond to exact temperatures of 5.37°, 15.01°, 25.03° and 34.94°C.

Table 4

Water $D = 86.12$ $T = 5°C$

Run #1   Initial normality $= 0.01499$

Time	Normality	$\sqrt{u}$ mean	k	k_o
5.25	0.01436			
23.08	.01342	0.1763	0.274	0.200
59.72	.01184	.1798	.271	.197
141.72	.009357	.1853	.273	.197
				.198

Run #2   Initial normality $= 0.01656$

31.03	.01430			
63.48	.01265	.1903	.281	.202
129.08	.01026	.1955	.282	.201
192.07	.008643	.2005	.289	.205
				.203

Run #3   Initial normality $= 0.01507$ NaCl normality $= 0.1709$

8.55	.01411			
32.10	.01258	.4503	.364	.200
83.03	.01019	.4524	.366	.201
241.53	.006376	.4558	.370	.202
				.201

Run #4   Initial normality $= 0.01588$ NaCl normality $= 0.3278$

5.93	.01506			
33.05	.01298	.6011	.393	.195
76.05	.01064	.6030	.393	.195
139.10	.008402	.6050	.397	.196
				.195

k_o mean $= 0.199$

Table 5

Dioxane-water   D = 60   T= 5°C

Run #1   Initial normality = 0.01541

Time	Normality	$\sqrt{u}$ mean	k	k_0
16.43	0.01473			
41.97	.01372	0.1789	0.195	0.1159
90.83	.01215	.1825	.193	.1138
173.07	.01018	.1873	.193	.1127
				.1141

Run #2   Initial normality = 0.01478

81.42	.01008			
135.43	.009122	.1864	.192	.1124
200.50	.008170	.1889	.196	.1141
284.00	.007185	.1915	.201	.1161
				.1142

k_0 mean = 0.1142

Table 6

Dioxane-water   D = 55   T = 5°C

Run #1   Initial normality = 0.01663

19.50	.01573			
54.75	.01436	.1867	.178	.0971
114.82	.01244	.1910	.179	.0967
205.55	.01030	.1962	.184	.0981
				.0973

Run #2   Initial normality = 0.01783

13.38	.01719			
39.58	.01592	.1922	.178	.0956
172.27	.01157	.1994	.178	.0941
281.40	.009407	.2074	.183	.0946
				.0948

k_0 mean = 0.0963

Table 7

Dioxane-water   D = 50   T = 5°C

Run #1   Initial normality = 0.01550

Time	Normality	$\sqrt{u}$ mean	k	k_0
13.37	0.01494			
102.50	.01234	0.1813	0.159	0.0811
189.60	.01052	.1872	.161	.0806
307.28	.008748	.1920	.164	.0809
				.0809

Run #2   Initial normality = 0.01820

Time	Normality	$\sqrt{u}$ mean	k	k_0
9.25	.01779			
40.25	.01630	.1938	.165	.0813
98.85	.01405	.1986	.167	.0814
185.48	.01169	.2043	.166	.0794
				.0807

k_0 mean = 0.0808

Table 8

Water   D = 82.29   T = 15°C

Run #1   Initial normality = 0.01838

Time	Normality	$\sqrt{u}$ mean	k	k_0
20.27	.01485			
34.05	.01327	.2026	.582	.409
56.63	.01133	.2069	.571	.399
88.62	.009365	.2116	.579	.402
				.403

Run #2   Initial normality = 0.01911

Time	Normality	$\sqrt{u}$ mean	k	k_0
26.57	.01466			
49.73	.01226	.2096	.577	.402
78.77	.01015	.2148	.585	.404
125.42	.007948	.2197	.584	.401
				.402

k_0 mean = 0.403

Table 9

Dioxane-water   D= 60   T = 15°C

Run #1   Initial normality = 0.01548

Time	Normality	$\sqrt{u}$ mean	k	k_o
9.13	0.01436			
21.87	.01379	0.1792	0.411	0.250
42.40	.01235	.1827	.412	.249
89.28	.01003	.1877	.400	.239
				.246

Run #2   Initial normality = 0.01486

Time	Normality	$\sqrt{u}$ mean	k	k_o
10.93	.01399			
26.05	.01289	.1764	.405	.248
45.85	.01166	.1797	.414	.251
88.45	.009743	.1840	.395	.238
				.243

k_o mean = 0.244

Table 10

Dioxane-water   D = 55   T = 15°C

Run #1   Initial normality = 0.01616

Time	Normality	$\sqrt{u}$ mean	k	k_o
10.33	.01526			
24.03	.01414	.1838	.378	.213
54.02	.01219	.1879	.379	.212
116.10	.009463	.1940	.380	.210
				.212

Run #2   Initial normality = 0.02225

Time	Normality	$\sqrt{u}$ mean	k	k_o
10.87	.02027			
36.42	.01679	.2196	.401	.209
75.15	.01333	.2273	.399	.205
122.45	.01063	.2339	.404	.205
				.206

k_o mean = 0.209

Table 11

Dioxane—water

$$D = 50 \quad T = 15\,°C$$

Run #1   Initial normality = 0.01451

Time	Normality	$\sqrt{u}$ mean	k	k_o
28.27	0.01277			
63.15	.01107	0.1778	0.336	0.178
107.55	.009430	.1824	.341	.178
168.38	.007942	.1866	.336	<u>.174</u>
				.177

Run #2   Initial normality = 0.01534

Time	Normality	$\sqrt{u}$ mean	k	k_o
23.18	.01312			
63.05	.01134	.1838	.342	.178
114.33	.009446	.1887	.345	.178
176.75	.007861	.1933	.342	<u>.174</u>
				.177

k_o mean = 0.177

Table 12

Dioxane—water

$$D = 57.01 \qquad T = 15\,°C$$
(27.57 weight percent)

Run #1   Initial normality = 0.01410

Time	Normality	$\sqrt{u}$ mean	k	k_o
17.32	.01290			
79.92	.009876	.1758	.379	.224
140.33	.008041	.1826	.384	.223
207.93	.006646	.1869	.386	<u>.222</u>
				.222

Run #2   Initial normality = 0.01612

Time	Normality	$\sqrt{u}$ mean	k	k_o
16.97	.01458			
40.60	.01285	.1861	.392	.226
80.50	.01069	.1913	.393	.224
140.28	.008576	.1968	.386	<u>.218</u>
				.223

k_o mean = 0.222

Table 13

Water $D = 78.47$ $T = 25°C$

Run #1 Initial normality $= 0.01466$

Time	Normality	$\sqrt{u \text{ mean}}$	k	k_o
6.18	0.01252			
13.17	.01140	0.1789	1.120	0.807
28.72	.009438	.1831	1.135	.813
57.37	.007238	.1888	1.144	.813
				.811

Run #2 Initial normality $= 0.01431$

Time	Normality	$\sqrt{u \text{ mean}}$	k	k_o
17.37	.01272			
41.65	.009454	.1785	1.118	.806
73.07	.007057	.1862	1.143	.816
185.83	.003716	.1937	1.130	.798
				.807

Run #3 Initial normality $= 0.02123$ NaCl normality $= 0.06795$

Time	Normality	$\sqrt{u \text{ mean}}$	k	k_o
5.50	.01798			
11.70	.01561	.3388	1.366	.814
25.42	.01207	.3432	1.368	.811
58.77	.007801	.3488	1.359	.802
				.809

Run #4 Initial normality $= 0.02083$ NaCl normality $= 0.1543$

Time	Normality	$\sqrt{u \text{ mean}}$	k	k_o
6.02	.01740			
16.16	.01375	.4485	1.504	.812
31.25	.01050	.4518	1.491	.803
57.07	.007455	.4557	1.507	.809
				.808

Table 13 (continued)

Run #5 Initial normality = 0.02085   NaCl normality = 0.2942

Time	Normality	$\sqrt{u}$ mean	k	k_o
14.10	0.01393			
31.27	.01003	0.5872	1.63	0.796
50.13	.007655	.5898	1.64	.801
83.97	.005363	.5918	1.65	.805
				.801

Run #6 Initial normality = 0.02076   NaCl normality = 0.3795

10.12	.01506			
18.25	.01243	.6542	1.72	.809
52.03	.007211	.6573	1.72	.809
83.32	.005189	.6601	1.73	.809
				.809

k_o mean = 0.807

Table 14

Dioxane-water   D = 60   T = 25°C

Run #1 Initial normality = 0.01459

15.38	.01232			
29.95	.01071	.1796	0.841	.522
56.58	.008634	.1847	.842	.518
117.50	.005973	.1909	.847	.515
				.518

Run #2 Initial normality = 0.03250

21.48	.01259			
36.95	.01082	.1925	.840	.509
63.03	.008728	.1972	.850	.510
97.05	.006973	.2022	.848	.504
				.508

k_o mean = 0.513

Table 15

Dioxane-water   D = 55   T = 25°C

Run #1   Initial normality - 0.01555

Time	Normality	$\sqrt{u\ mean}$	k	k_o
27.32	0.01195			
49.37	.009867	0.1891	0.781	0.447
77.45	.008127	.1940	.786	.445
169.62	.005144	.2000	.775	<u>.434</u>
				.442

Run #2   Initial normality = 0.01491

36.55	.01047			
57.63	.008942	.1871	.775	.446
97.48	.007006	.1917	.776	.442
156.70	.005310	.1963	.770	<u>.434</u>
				.441

k_o mean = 0.441

Table 16

Dioxane-water $D = 50$ $T = 25°C$

Run #1 Initial normality = 0.01353

Time	Normality	$\sqrt{u \text{ mean}}$	k	k_o
23.18	.01115			
40.13	.009876	.1733	.684	.177
94.37	.007221	.1790	.686	.373
140.32	.005874	.1845	.691	.371
				.374

Run #2 Initial normality = 0.01375

38.03	.01009			
70.43	.008196	.1792	.682	.371
108.10	.006762	.1838	.687	.369
180.32	.005075	.1879	.681	.362
				.367

Run #3 Initial normality = 0.02189

19.95	0.01639			
35.88	.01363	0.2250	0.776	0.378
64.42	.01049	.2316	.769	.370
99.57	.008160	.2374	.775	.368
				.372

Run #4 Initial normality = 0.02208 NaCl normality = 0.06429

15.12	.01627			
54.45	.01005	.3411	.967	.378
88.33	.007564	.3427	.965	.376
148.95	.005245	.3523	.964	.370
				.375

k_o mean = 0.374

Table 17

Dioxane-water   D = 54.04   T = 25 °C
                                                      (27.57 weight percent)

Run #1 Initial normality = 0.01606

Time	Normality	$\sqrt{u\ mean}$	k	k_o
9.55	.01425			
27.28	.01191	.1872	.775	.440
59.18	.009232	.1938	.764	.427
158.38	.005433	.1995	.764	.422
				.430

Run #2 Initial normality = 0.01415

15.28	.01253			
33.38	.01071	.1756	.750	.437
66.68	.008438	.1813	.754	.434
164.85	.005172	.1864	.752	.428
				.433

k_o mean = 0.431

Table 18

Water   D = 74.90   T = 35 °C

Run #1 Initial normality = 0.01579

Time	Normality	$\sqrt{u\ mean}$	k	k_o
4.12	0.01355			
14.42	.01040	0.1881	2.18	1.54
28.67	.007846	.1956	2.19	1.54
59.00	.005177	.2021	2.17	1.50
				1.53

Run #2 Initial normality = 0.02383

5.40	.01917			
16.73	.01265	.2357	2.37	1.57
54.52	.006003	.2493	2.32	1.51
99.08	.003690	.2581	2.34	1.51
				1.53

k_o mean = 1.53

Table 19

Dioxane-water			D = 60	T = 35°C

Run # 1   Initial normality = 0.01678

Time	Normality	$\sqrt{u\ mean}$	k	k_o
15.45	.01139			
31.38	.008765	.2005	1.65	1.007
73.27	.005425	.2079	1.68	1.009
141.53	.003373	.2143	1.64	0.996
				1.004

Run #2   Initial normality = 0.01891

18.22	.01190			
36.90	.008647	.2156	1.69	1.004
72.90	.005647	.2227	1.71	1.001
132.13	.003602	.2283	1.70	0.998
				1.001

k_o mean = 1.002

Table 20

Dioxane-water			D = 55	T = 35°C

Run #1   Initial normality = 0.01584

18.92	0.01084			
35.33	.008526	0.1945	1.52	0.884
60.77	.006426	.2001	1.51	.865
93.10	.004879	.2045	1.53	.869
				.872

Run #2   Initial normality = 0.02101

7.18	.01686			
19.38	.01253	.2199	1.62	.891
33.73	.009755	.2278	1.64	.890
52.15	.007552	.2332	1.63	.873
				.882

k_o mean = 0.877

Table 21

Dioxane-water $\qquad$ D = 50 T = 35 °C

Run #1 Initial normality = 0.01393

Time	Normality	$\sqrt{u\ \text{mean}}$	k	k_o
19.65	.01011			
39.30	.007932	.1810	1.381	.767
73.72	.005787	.1868	1.358	.744
115.30	.004342	.1916	1.383	.749
				.753

Run #2 Initial normality = 0.02173

7.28	.01747			
21.18	.01276	.2237	1.52	.766
35.55	.009960	.2320	1.53	.760
56.40	.007576	.2375	1.52	.742
				.756

k_o mean = 0.755

Table 22

Dioxane-water $\qquad$ D = 51.28 T = 35 °C
(27.57 weight percent)

Run #1 Initial normality = 0.01575

20.33	0.01063			
43.13	.007843	.1950	1.47	0.804
72.18	.005923	.2009	1.42	.771
102.73	.004674	.2043	1.48	.794
				.790

Run #2 Initial normality = 0.01779

22.15	.01114			
44.37	.008089	.2091	1.52	.810
74.07	.005973	.2152	1.47	.774
105.50	.004665	.2192	1.49	.778
				.789

k_o mean = 0.789

Table 23

Butanol-water $\qquad$ D = 60 $\quad$ T = 25°C

Run #1 Initial normality = 0.01621

Time	Normality	$\sqrt{u}$ mean	k	k_o
8.65	0.01449			
30.88	.01118	0.1392	0.921	0.553
66.68	.008127	.1974	.938	.553
145.58	.005104	.2050	.924	.537
				.548

Run #2 Initial normality = 0.01685

6.57	.01542			
29.33	.01161	.1925	.934	.556
64.75	.008388	.2013	.934	.546
143.75	.005185	.2082	.932	.538
				.547

k_o mean = 0.547

Table 24

Butanol-water $\qquad$ D = 55 $\quad$ T = 25°C

Run #1 Initial normality = 0.01727

10.28	.01495			
30.70	.01178	.1960	.881	.487
59.17	.009098	.2033	.880	.479
102.97	.006678	.2096	.909	.488
				.485

Run #2 Initial normality = 0.01699

12.65	.01427			
30.70	.01163	.1950	.882	.489
61.65	.008812	.2031	.888	.483
105.52	.006570	.2080	.883	.475
				.482

k_o mean = 0.484

Table 25

Butanol-water   D = 50   T = 25°C

Run #1 Initial normality = 0.01530

Time	Normality	$\sqrt{u}$ mean	k	k_o
9.30	0.01379			
31.97	.01082	0.1833	0.878	0.462
60.05	.008531	.1903	.882	.456
93.45	.006821	.1955	.880	.449
				.456

Run #2 Initial normality = 0.01811

11.40	.01540			
36.60	.01140	.2023	.906	.454
63.15	.008968	.2101	.895	.440
99.78	.006917	.2154	.903	.438
				.444

Run #3 Initial normality = 0.01510   NaCl normality = 0.1421

8.68	.01229			
29.38	.009109	.4202	1.37	.447
55.00	.006871	.4235	1.40	.452
97.68	.004943	.4260	1.33	.429
				.442

Run #4 Initial normality = 0.01539   NaCl normality = 0.2853

8.15	.01282			
28.47	.008855	.5662	1.72	.459
53.20	.006502	.5690	1.65	.440
99.30	.004308	.5711	1.70	.451
				.450

k_o mean = 0.448

CALCULATIONS AND DISCUSSION

The calculation of k^o's from values of k may be made by equation (17)
or (19) depending on experimental conditions. The latter could not be
used here for the concentrations were beyond the range where the Debye-
Huckel limiting law would be expected to apply. Equation (17) involves
the term a_i for which no independent information is available. Conseque-
ntly, by trial and error a value of a_i was determined which gave from k
values over a large ionic strength range the most consistent values of k_o.
The data of Table 13 has been condensed in the form of average values of
k and $\sqrt{u}$ for each run and the effect of varying a_i is shown in Table 26.

Table 26

Effect of a_i on k_o Values

Run	k mean	$\sqrt{u}$ mean	a_i (in A^o) 4.4	4.6	4.8	5.0	5.2
1	1.133	0.1836	0.804	0.808	0.811	0.814	0.816
2	1.130	.1861	.799	.802	.806	.809	.812
3	1.364	.3436	.797	.803	.809	.815	.821
4	1.50	.4520	.791	.800	.809	.817	.825
5	1.64	.5896	.778	.789	.801	.812	.823
6	1.72	.6572	.782	.795	.809	.821	.834

A value for a_i equal to 4.8 A^o is thus found to fit the data and give
most consistent values for k_o. The data of Table 26 is for water at 25°C.
a similar treatment was carried out for the data of Tables 4 and 16 which
represent water at 5°C and dioxane-water dielectric constant equal to 50
at 25°C., respectively. In both cases the same value of a_i, i.e., 4.8 A^o
to the nearest two-tenths of an Angstrom, was found to best fulfill the

above criterion. For tertiary butyl alcohol-water (Table 25) the best value of a_i was found to be 4.3 A°.

In Figure 1 the data are shown graphically. The positive primary salt effect shown in these graphs is characteristic of a reaction between like charged ions, and substantiates the reaction mechanism given. It is evident that it would have been impossible to accurately determine k_o by graphical means because of the distance of extrapolation involved. The calculated values of k_o are wholly consistent with an extrapolation from k values. The limiting slopes equal to $\frac{3.647 \text{ X } 10^6}{(DT)^{3/2}}$ have been drawn in at the k_o points and it can be seen that the limiting law equation (19) is applicable for only a very small ionic strength range.

The behavior observed of the a_i parameter is not peculiar: the constancy with temperature and dielectric constant for a given solvent pair has been found in conductance and equilibrium work[22], and the change in the value of a_i with a different solvent has also been noted. In view of the constancy of a_i it is likely that the Debye-Huckel equation holds down to dielectric constant 50 in dioxane-water solutions. The fact that k's over a wide ionic strength range lead to the same k_o value within experimental error justifies confidence in the method of calculation and in the reliability of the value itself.

The value of a_i equal to 4.8 A° was used for all the water and dioxane-water data for the calculation of k_o. In Table 27 are summarized all the k_o values taken from Tables 4 through 25. In Table 28 the k_o's have been converted to mol fraction units through application of equations (40) and (41) and the conversion factors given in the Appendix.
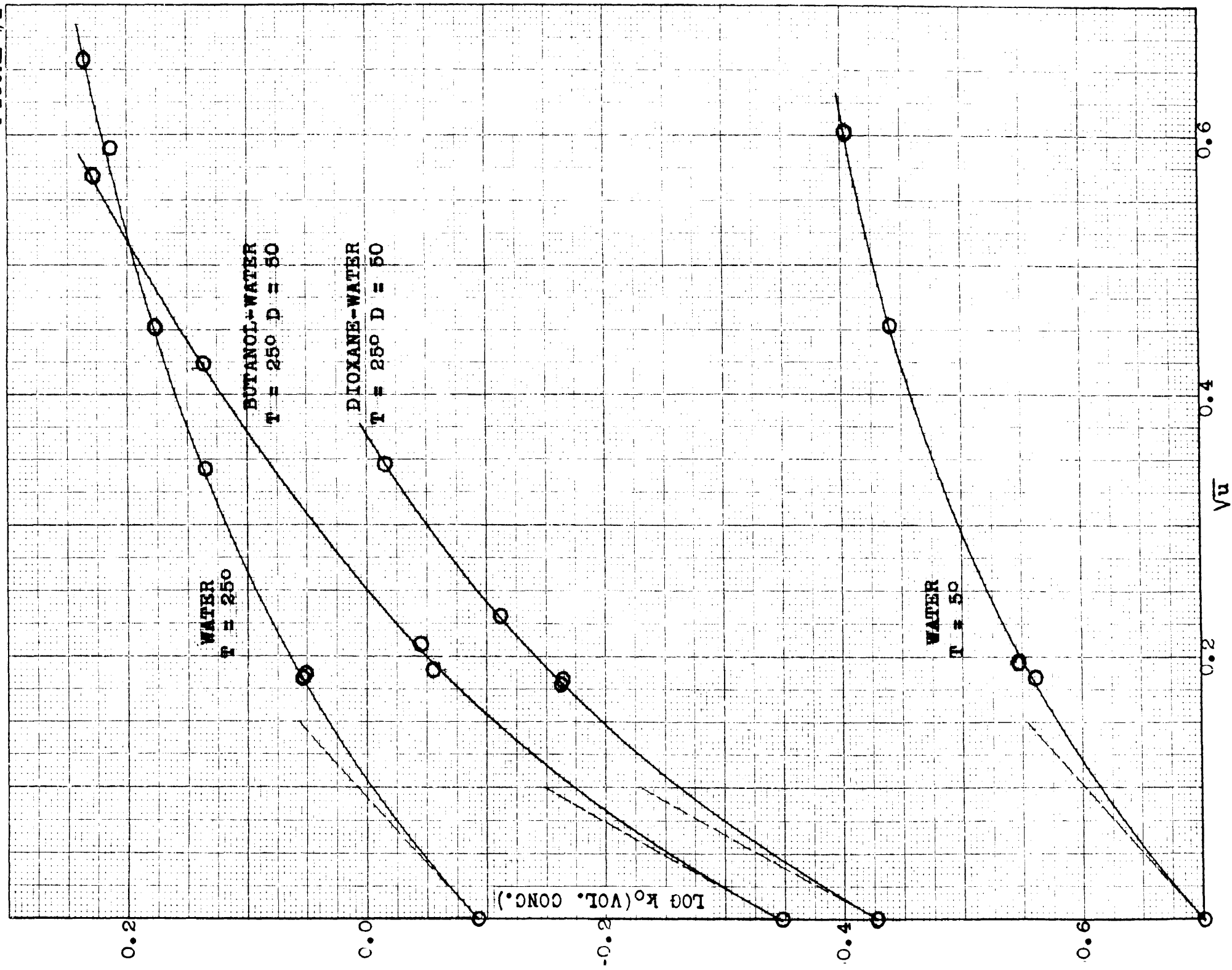
FIGURE #1

Table 27

Rate Constants (volume concentration) at u = 0

| Temperature, °C | Dioxane-water | | | | Butanol-water |
	5	15	25	35	25
Solvent					
H_2O	0.199	0.403	0.807	1.53	
60	.1142	.244	.513	1.002	0.547
55	.0963	.209	.441	0.877	.484
50	.0808	.177	.374	.755	.448
27.57 wt. %	.1142	.222	.431	.789	

Table 28

Rate Constants (mol fraction) at u = 0

| Temperature, °C. | Dioxane-water | | | | Butanol-water |
	5	15	25	35	25
Solvent					
H_2O	11.04	22.3	44.7	84.3	
60	5.00	11.01	24.1	47.9	23.9
55	4.00	8.95	19.7	39.8	19.8
50	3.18	7.17	15.6	32.4	17.0
27.57 wt. %	5.00	9.71	18.8	34.3	

There is no agreement between k_o's for dioxane-water and butanol-water when the units of k_o are in volume concentration. On a mol fraction basis, the values at dielectric constant 60 and 55 agree within experimental error. At dielectric 50, it is believed that it is the butanol-water mixture which is showing the deviation. This point will be considered later in the discussion of the relation of k_o to dielectric constant. It is concluded that mol fraction k_o's are preferable to volume concentration for the comparison of rate constants in different solvent media.

The alkaline hydrolysis of potassium ethyl malonate is a true second-order reaction. This conclusion is reached as a result of the constancy of k_o values; and as a result of other work, not tabulated here, in which the ratio of reactants was varied. Experiments were carried out in which the ester/alkali ratio was two to one, and two to three. The k_o values obtained were in agreement with those experiments where the ratio was one to one. The results are not included here because the form of the integrated equation when the concentrations of reactants are not equal leads to values for the rate constant of a lesser degree of accuracy.

In Table 29 are given values of activation energies calculated by equation (28) from the volume concentration k_o's of Table 27. In Table 30 are given activation energies from the mol fraction k_o's of Table 28.

Table 29

Activation Energies (in Kcals.) from Volume Concentration k_0's

Temperature interval, °C.	5-15	15-25	25-35	Mean
Solvent				
H_2O	11.67	11.77	11.82	11.75
60	12.55	12.60	12.40	12.52
55	12.81	12.66	12.73	12.73
50	12.97	12.68	13.00	12.88
27.57 wt. %	11.03	11.22	11.19	11.15

Table 30

Activation Energies (in Kcals.) from Mol Fraction k_0's

Temperature interval, °C.	5-15	15-25	25-35	Mean
Solvent				
H_2O	11.63	11.79	11.74	11.72
60	13.05	13.28	12.72	13.02
55	13.32	13.38	13.02	13.24
50	13.45	13.18	13.53	13.39
27.57 wt. %	10.98	11.21	11.12	11.10

The activation energy measured in isodielectric media should be constant over a temperature range if the premise expressed in equation (34) is correct. For the dielectrics 60, 55 and 50 the variation is taken to represent experimental error and the energies are averaged for each dielectric. A discussion of errors is given in the Appendix. For isocomposition media we would expect some increase in the activation energy with increasing temperature because the dielectric constant is decreasing. For water the trend is present for energies calculated from volume concentration k_o's, but disappears when the units of k_o are changed to mol fraction. For the 27.57 weight percent mixture in neither case is there an increase. Since the values are the same within experimental error, as judged by the deviations in the isodielectric data, the energies for the isocomposition media have been averaged. It is concluded that the activation energy is constant within the precision of the measurement, over the temperature range investigated.

Conversion of k_o values from volume concentration to mol fraction units is seen to have little effect on the activation energies for isocomposition media. However, there is a considerable difference for isodielectric media. This is because the conversion factors for the isocomposition media change with temperature only to the extent that the densities change. For isodielectric media, the composition and thus the conversion factor changes markedly with temperature.

From the k_o's of Table 27 values of k at $\sqrt{u}$ equal to 0.2 have been calculated by equation (17) and are listed in Table 31. For a few cases, the calculated value was checked with a graphical value obtained from a log k versus $\sqrt{u}$ plot, with good agreement. Since the k_o values were calculated from k values in the neighborhood of $\sqrt{u}$ equal to 0.2, the

calculation of k from k_o is merely a reversal of the original procedure. Agreement is to be expected, and there was nothing to be gained by checking all the calculated k values against those obtained by a graphical means.

Table 31

Rate Constants (volume concentration) at $\sqrt{u} = 0.2$ in Dioxane-water

Temperature, °C.	5	15	25	35
Solvent				
H_2O	0.281	0.572	1.153	2.20
60	.201	.419	0.859	1.64
55	.182	.384	.788	1.53
50	.167	.354	.725	1.421
27.57 wt. %	.201	.397	.781	1.454

From these values of k at $\sqrt{u}$ equal to 0.2 activation energies were calculated by equation (28) and are given in Table 32.

Table 32

Activation Energies (in Kcals) at $\sqrt{u} = 0.2$
Based on Volume Concentration k's

Temperature interval, °C.	5-15	15-25	25-35
Solvent			
H_2O	11.76	11.88	11.94
60	12.13	12.18	11.98
55	12.34	12.18	12.26
50	12.43	12.15	12.47
27.57 wt. %	11.25	11.48	11.50

The term $E^O - E_{\sqrt{u} = 0.2}$ was obtained by subtraction of $E^O_{\sqrt{u} = 0.2}$

values, Table 32, from E^O values, Table 29, and the differences are

listed in Table 33 designated as experimental values. By means of equa-

tion (38) $E^O - E_{\sqrt{u} = 0.2}$ could be evaluated directly and the results

are given in Table 33 as calculated values.

Table 33

Differences between Activation Energies (in calories) at $u = 0$ and $\sqrt{u} = 0.2$

Temperature interval, °C

Solvent	5-15		15-25		25-35	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
H_2O	-90	-90	-110	-110	-120	-130
60	420	420	420	420	420	420
55	470	480	480	470	470	470
50	540	540	530	530	530	530
27.57 wt. %	-220	-220	-260	-260	-310	-300

The agreement is excellent without exception. This is not too

surprising when it is considered that both sets of results are based on

equation (17) and merely involve slightly different paths.
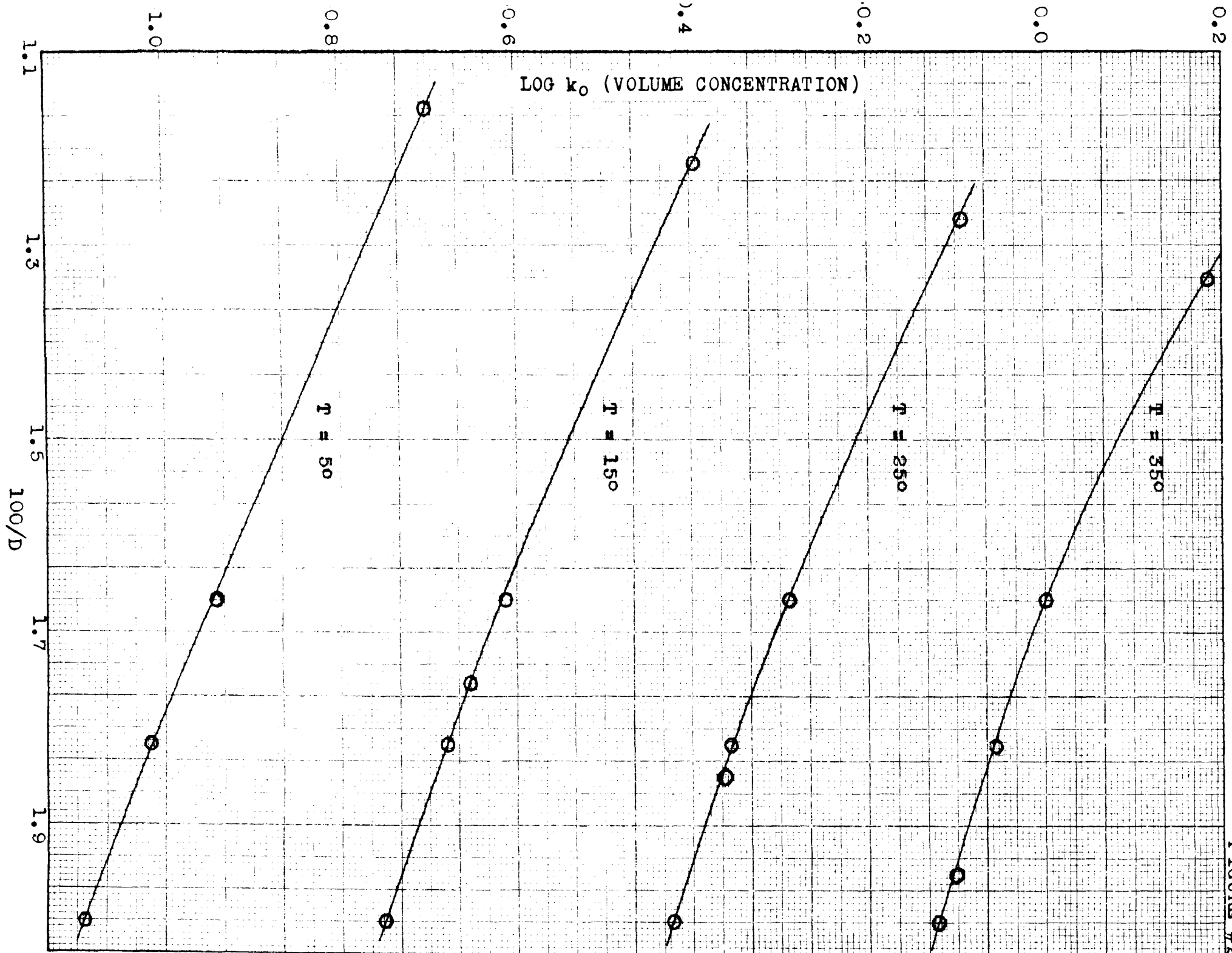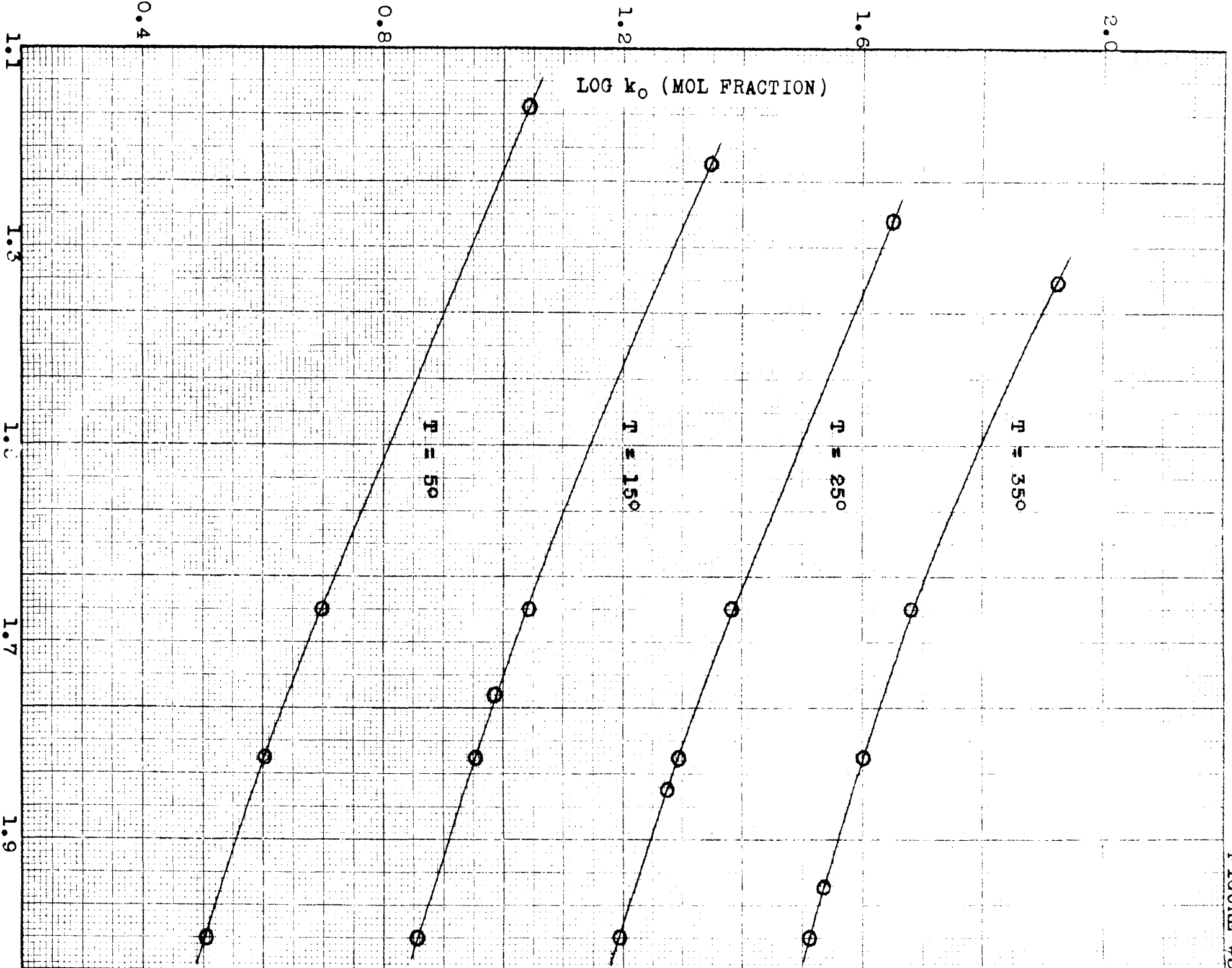
FIGURE #2

LOG k_O (MOL FRACTION)

T = 5°

T = 15°

T = 25°

T = 35°

FIGURE #3

In Figures 2 and 3 are graphed log k_o against 1/D values on a volume concentration and mol fraction scale, respectively. From equation (25) and the slopes of the curves at the points corresponding to the dielectric constants of water and 27.57 weight percent dioxane in water the radius of the complex was calculated. The results are given in Table 34.

Table 34

Radius of the Intermediate Complex

Solvent	Temp., °C.	Volume Concentration slope X 10^2	r(A°)	Mol Fraction slope X 10^2	r(A°)
H$_2$O	5	-0.565	4.61	-0.891	2.92
	15	-0.581	4.33	-0.889	2.83
	25	-0.606	4.01	-0.939	2.59
	35	-0.820	2.87	-1.21	1.95
27.57 wt. %	5	-0.447	5.83	-0.600	4.34
	15	-0.427	5.90	-0.547	4.60
	25	-0.411	5.92	-0.534	4.56
	35	-0.346	6.81	-0.479	4.91

The order of magnitude of the radii are what might be expected, though two or three Angstroms seems rather small considering that the large ethyl malonate ion is one of the reactants. The mode of change of the radii with temperature is anomalous in that for both volume and mol fraction k_o's the radii decrease with increasing temperature for water, but increase with increasing temperature for the 27.57 weight percent mixture. By equation (25) r is inversely proportional to the temperature; however, the magnitude of the decrease in r is far larger than that accounted for by the temperature

decrease. The change in slope of $\left(\dfrac{\partial \log k_o}{\partial 1/D}\right)_T$ is essentially responsible

for the decrease in radius.

From theory we expect a plot of $\log k_o$ against $1/D$ to be linear. The lines connecting the points at dielectrics 50, 55 and 60 are relatively straight. When the lines are extended to include the water data considerable curvature is introduced. Such behavior is not compatible with the concept of salting out for we would expect the more polar water molecules to be attracted to the ions rather than the dioxane. Any change in the nature of the solvation should take place at low dielectrics. The deviation of the dielectric 50 value for butanol-water may represent this effect.

The salting-out postulate, so often advanced to explain deviations from theory, is not tenable in this case, though no other interpretation can be offered to explain the curvature in the $\log k_o$ versus $1/D$ plots.

In Figures 4 and 5 are plotted activation energies, from volume concentration and mol fraction data, against $1/D$ for the three isodielectric media. In accordance with expectation the energies increase with decreasing dielectric constant. The two methods of calculating k_o's result in plots of the same slope. From the slope and by equation (39) the radius of the complex can be calculated equal to 3.0 A^o. Since each of the energies are uncertain by $\pm$ 150 calories and since the range of dielectric constant is only ten, the exact magnitude of the slope and thus of the radius has little significance.
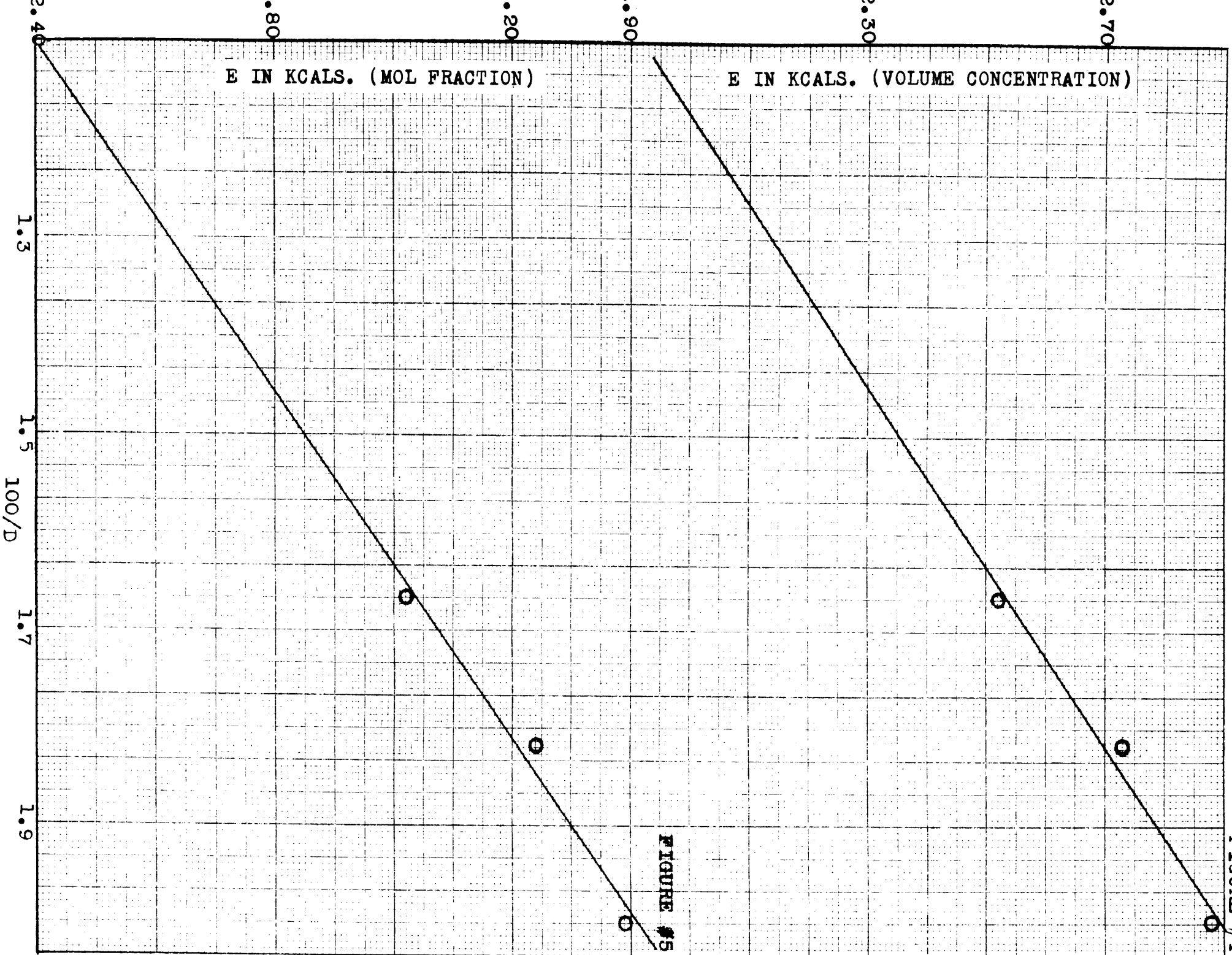
E IN KCALS. (MOL FRACTION)

E IN KCALS. (VOLUME CONCENTRATION)

100/D

FIGURE #5

FIGURE #4

In attempting to check the validity of equation (35) as applied to the preceeding data the following procedure was used.

$$E^{o}_{F.C.} = E^{o}_{F.D.} + 2.303 \ RT^2 \left(\frac{\partial \log k_o}{\partial D} \right)_T \frac{dD}{dT} \tag{35}$$

From equations (23) and (24) it can be shown that,

$$\left(\frac{\partial \log k_o}{\partial D} \right)_T = -\frac{1}{D^2} \left(\frac{\partial \log k_o}{\partial 1/D} \right)_T \tag{43}$$

From Figures 2 and 3 the value of $\left(\frac{\partial \log k_o}{\partial 1/D} \right)_T$ was obtained at a dielectric constant corresponding to that of the fixed composition media. By means of equation (43), $\left(\frac{\partial \log k_o}{\partial D} \right)_T$ could be calculated. The term $2.303 RT^2$ $\left(\frac{\partial \log k_o}{\partial D} \right)_T \frac{dD}{dT}$ could then be calculated at any specified temperature. This gives an experimental method of obtaining the value of $E^{o}_{F.C.} - E^{o}_{F.D.}$ which is called $\left(E^{o}_{F.C.} - E^{o}_{F.D.} \right)_{Calc.}$ in Table 35.

It seems necessary, in using equation (35), that any comparisons for an isocomposition medium should be made at a dielectric value obtained from studies made in isodielectric media at the same dielectric value. In the case of water as the fixed composition media, this corresponds to an extrapolation of the data in Figures 4 and 5 to a dielectric value of the same magnitude as actually exists in water at the temperature where the comparison is to be made. For the 27.57 weight percent mixture the desired values could be interpolated from the experimental. The above procedure on being carried out gives the values $E^{o}_{F.D.}$, Graph. listed in Table 35. $E^{o}_{F.C.}$, Calc. can now be obtained by subtraction of $\left(E^{o}_{F.C.} - E^{o}_{F.D.} \right)_{Calc.}$ from $E^{o}_{F.C.}$, Graph.

It should be pointed out that this procedure is based on the assumption that even though the isocomposition media showed no change in activation energy within experimental error over the temperature range

investigated, it is considered that there would have been a change observed if the precision was better, or if the temperature range was greater.

For clarity a definite example will be given. For water at $5\,^\circ$C. (dielectric constant 86.12) the value of $\left(\frac{\partial \log k_o}{\partial 1/D}\right)_T$ was determined from Figure 2 at an abscissa value of 1/86.12. The term $E^o_{F.C.} - E^o_{F.D.}$ was calculated by equation (35) as equal to - 1.10 Kcals. $E^o_{F.D.}$ from Figure 4 at 1/D equal to 1/86.12 was read as 11.98. The calculated value of $E^o_{F.C.}$ was then 11.98 less 1.10, or 10.88 Kcals. The complete results are given in Table 35. The data for mol fraction k_o's have been treated similarly and the results are tabulated in Table 36.

Table 35

Comparison of Calculated and Experimental $E^o_{F.C.}$ Values (in Kcals.) from Volume Concentration Data.

Solvent	Temp. $^\circ$C	$E^o_{F.C.} - E^o_{F.D.}$ Calc.	$E^o_{F.D.}$ Graph.	$E^o_{F.C.}$ Calc.	$E^o_{F.C.}$ Exp.
Water	5	-1.10	11.98	10.88	
	15	-1.28	12.04	10.76	
	25	-1.48	12.11	10.63	11.75
	35	-2.24	12.18	9.94	
27.57 wt %	5	-1.40	12.53	11.13	
	15	-1.51	12.64	11.13	
	25	-1.64	12.74	11.10	11.15
	35	-1.55	12.84	11.29	

Table 36

Comparison of Calculated and Experimental $E^o_{F.C.}$ Values (in Kcals.) from Mol Fraction Data

Solvent	Temp. °C	$E^o_{F.C.} - E^o_{F.D.}$ Calc.	$E^o_{F.D.}$ Graph.	$E^o_{F.C.}$ Calc.	$E^o_{F.C.}$ Exp.
Water	5	-1.73	12.47	10.74	
	15	-1.93	12.53	10.60	
	25	-2.29	12.59	10.30	11.72
	35	-3.32	12.66	9.34	
27.57 wt%	5	-1.89	13.04	11.15	
	15	-1.93	13.13	11.20	
	25	-2.13	13.24	11.11	11.10
	35	-2.15	13.35	11.20	

The agreement between the values of $E^o_{F.C.}$ is excellent for the 27.57 weight percent dioxane in water mixture. For the water solutions the experimental values are higher than the calculated by a minimum of a thousand calories. One important difference in the method of calculation for the two media might seem to be the evaluation of $E^o_{F.D.}$ As previously pointed out the values for the 27.57 weight percent mixture could be obtained, essentially, by interpolation; for water it was necessary to extrapolate the data over a considerable dielectric constant range. Since an uncertainty of ± 150 calories has been assigned to the experimental $E^o_{F.D.}$ values, extrapolation of the data could conceivably lead to an error as great as three or four hundred calories at the higher dielectrics. That the error approaches a thousand calories seems, however, out of the question. There is the possibility that the $E^o_{F.D.}$ versus 1/D plot is not a linear function, but the curvature indicated by the plotted points is in the opposite direction to account for the discrepancy of $E^o_{F.C.}$ values.

It seemed worthwhile to consider that the slope of $\left(\frac{\partial \log k_0}{\partial 1/D}\right)_T$ is

linear and to calculate $E^{o}_{F.C.}$ for water assuming that the slope observed

for the lower dielectrics was the true value. This assumption may be

justified as a result of the good agreement for the 27.57 weight percent

mixtures, and as previously pointed out, because of the increased curva-

ture of the $\left(\frac{\partial \log k_0}{\partial 1/D}\right)_T$ function as it was extended to include the water

data. The slopes at the 27.57 weight percent points were used in equation

(35) to calculate $E^{o}_{F.C.}$ for water. The results are given in Table 37.

Table 37

Comparison of Calculated and Experimental $E^{o}_{F.C.}$ Values (in Kcals.) for
Water

Volume concentration

Temp., °C.	$E^{o}_{F.C.} - E^{o}_{F.D.}$ Calc.	$E^{o}_{F.D.}$ Graph.	$E^{o}_{F.C.}$ Calc.	$E^{o}_{F.C.}$ Exp.
5	0.87	11.98	11.11	
15	0.93	12.04	11.11	
25	1.00	12.11	11.18	11.75
35	0.95	12.18	11.23	

Mol fraction

5	1.17	12.47	11.30	
15	1.19	12.53	11.34	
25	1.30	12.59	11.29	11.72
35	1.31	12.66	11.35	

The values are now found to differ by six hundred calories for the volume concentration data and four hundred calories for the mol fraction data. Considering the uncertainty of the $E^o{}_{F.D.}$ values and an uncertainty of $\pm$ 150 calories in $E^o{}_{F.C.}$, the differences may be within experimental error. The correlation cannot, however, be regarded as conclusive until an explanation can be found for the curvature of the $\left(\dfrac{\partial \log k_0}{\partial 1/D}\right)_T$ function. The results do indicate that the slope in the region of the lower dielectrics is more consistent with equation (35) and that mol fraction k_0's give slightly better agreement.

In Table 38 are tabulated values of P, σ, ΔS and ΔF calculated by equations (29) (31) (32) and (33).

Table 38

Medium	P ($\times 10^3$)	σ (A^o)	ΔS(e.u.)	ΔF(cals.)
Water	1.5	0.172	-19.53	17,570
D = 60	3.5	.262	-17.86	17,840
D = 55	4.3	.291	-17.45	17,930
D = 50	4.7	.304	-17.28	18,080
27.57 wt. %	2.9	.239	-18.22	16,580

The values for the isocomposition media are not of significance for they are not based on "true" activation energies. For the isodielectric media the entropies have large negative values, which might be expected in view of the fact that the reaction is between ions of like charge and the complexity of the activated complex molecule. Since the entropy has a large negative value collision theory is not applicable, the probability factor is less than unity, and the collision diameters are smaller than physically reasonable.

SUMMARY

1. The kinetics of the alkaline hydrolysis of potassium ethyl malonate has been studied over the temperature range 5° to 35° C., in ten degree intervals. Measurements were made in two isocomposition media, water and 27.57 weight percent dioxane in water, and in three isodielectric media corresponding to dielectric constants of 50, 55, and 60. Observations were also made in tertiary butanol-water at dielectric constants of 50, 55 and 60 at 25° C.

2. A positive primary salt effect has been found, which is in accord with the mechanism postulated for the reaction.

3. The distance of closest approach of the Debye-Huckel equation has been found to be equal to 4.8 A° in water at 5° and at 25° C., and in dioxane-water at dielectric 50 at 25° C. In tertiary butanol-water at dielectric 50, the value has been found to be 4.3 A°.

4. Mol fraction units of the reaction rate constant are shown to be preferable for comparison of rate constants in different media.

5. The energy of activation in isodielectric media increases with decreasing dielectric constant. In isocomposition media the activation energies were constant within experimental error over the temperature range investigated.

6. The validity of the equation giving the change of E with ionic strength was investigated by comparison with experimental values, with excellent agreement.

7. Plots of log k_0 versus $1/D$ were linear in the range of low dielectric constant. Including the data for water necessitated considerable curvature of the lines. The radius of the activated complex, calculated from these plots, was of a physically reasonable order of magnitude.

8. Activation energies in fixed composition and fixed dielectric media
   have been compared by a theoretical equation. The agreement is
   excellent for the 27.57 weight percent mixture, but poor for water
   solution. The curvature of the log k_o versus $1/D$ plot is shown to
   be responsible for the discrepancy in the case of water.

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APPENDIX

1. Glossary of symbols used

A^O	$\overset{O}{A}$ngström
a_i	distance of closest approach
C	concentration
D	dielectric constant
E	energy of activation
f	activity coefficient
F	free energy of activation
h	Planck's constant
k	reaction rate constant
k_o	reaction rate constant at zero ionic strength
M	molecular weight
N	Avagadro's number
P	probability factor
r	radius of the intermediate complex
R	gas constant
S	entropy of activation
t	time
T	temperature
u	ionic strength
z	ionic charge
Z	collision number
ϵ	electronic charge
σ	mean collision diameter

2. Conversion factors for changing volume concentration k_o's to mol fraction k_o's

Temperature, °C.		5.37	15.01	25.08	34.94
Water		55.49	55.44	55.33	55.16
Dioxane-water	D = 60	43.77	45.12	46.97	47.85
	D = 55	41.56	42.80	44.67	45.38
	D = 50	39.34	40.50	41.71	42.90
	27.57 wt. %	43.77	43.73	43.65	43.53
Butanol-water	D = 60			43.73	
	D = 55			40.83	
	D = 50			38.02	

3. Discussion of Errors

Two criteria are available for judging the precision of the data. The first is the consistency of k_o values for a given set of conditions. The average deviation from the mean of k_o values is on the order of one percent. This corresponds to about 150 calories in the energy of activation. In a given run it would seem the average deviation is too severe a test from the point of view that the method of calculation of k's is such that if through an error the analysis of one sample is too high, the k calculated for the preceeding time interval will be low and for the following time interval will be high. The mean value will be more reliable than the deviation of the mean would indicate. However, the spread for duplicate runs was only slightly greater than for the individual runs.

It is difficult to estimate the errors in most of the individual operations. The time of sampling is accurate to $\pm$ 0.02 minutes and is beyond consideration as an error except for the very short runs. The HCl weighed out to the nearest milligram represents an uncertainty of one part in three thousand for the smallest sample weighed. Probably the principal sources of error lay in the sampling and back-titration.

The second criteria available is the agreement of activation energies in isodielectric media over the three temperature intervals. The deviations from the mean range from 50 to 150 calories with an average value of 110, excluding one deviation of 190 calories. It is concluded that 150 calories represents a fair estimate of the uncertainty in the activation energy.