

AN INVESTIGATION OF SOLVENT EFFECTS ON THE SAPONIFICATION
RATES OF ALIPHATIC ESTERS

THESIS

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By

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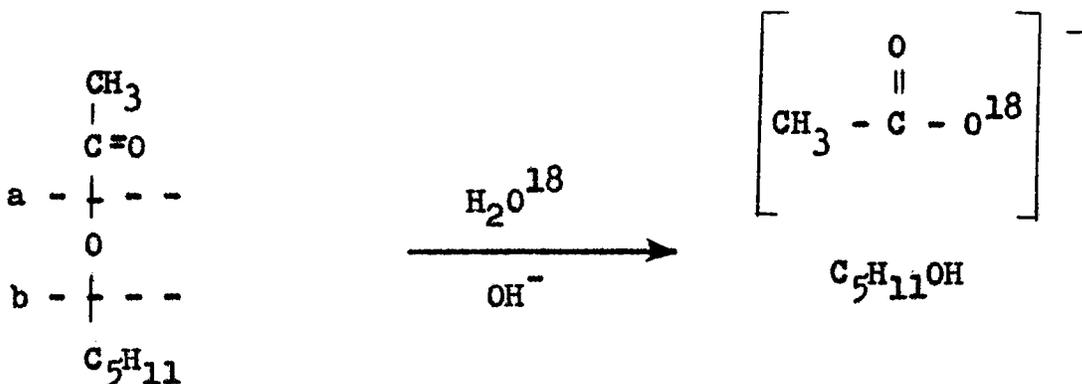
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CHAPTER I

INTRODUCTION

The basic hydrolysis of an ordinary ester has long been known to be a second-order reaction.¹ The transition state in this reaction may then be assumed to be formed from one molecule of ester and one hydroxide ion; that is, the reaction is bimolecular. Polanzi and Szabo,² using water enriched with H_2O^{18} , determined the site at which n-amyl acetate split during saponification. From the following reaction,

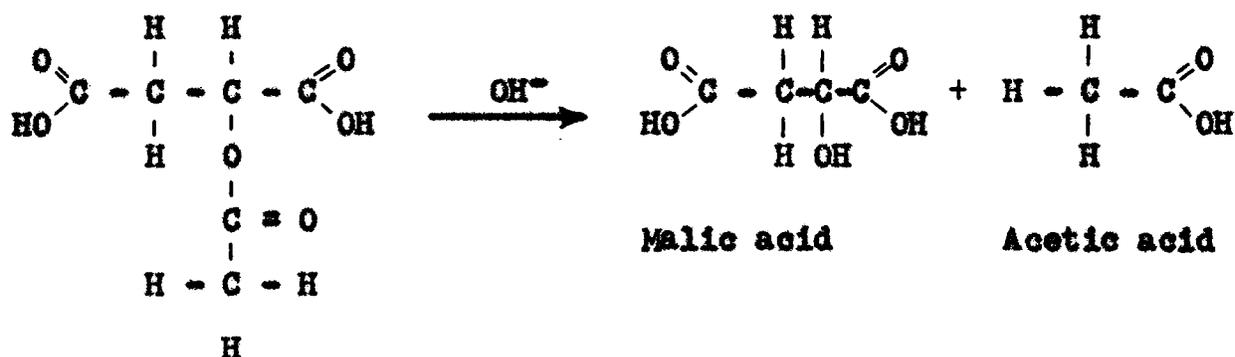


they determined that the acetate resulting from the reaction was enriched in O^{18} whereas the amyl alcohol was not. They

¹Warder, Ber., 14, 1361 (1881).

²M. Polanzi and A. L. Szabo, Trans. Faraday Soc., 30, 508 (1934).

then concluded that the ester had been split at a rather than at b. Therefore, in this particular case, acyl-oxygen cleavage had occurred. Also, Holmberg³ has shown that alkaline hydrolysis of acetoxysuccinic acid gave malic acid with retention of configuration at the asymmetric carbon atom,

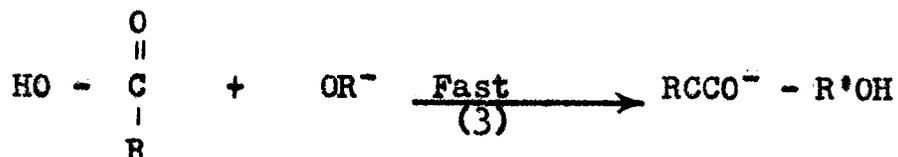
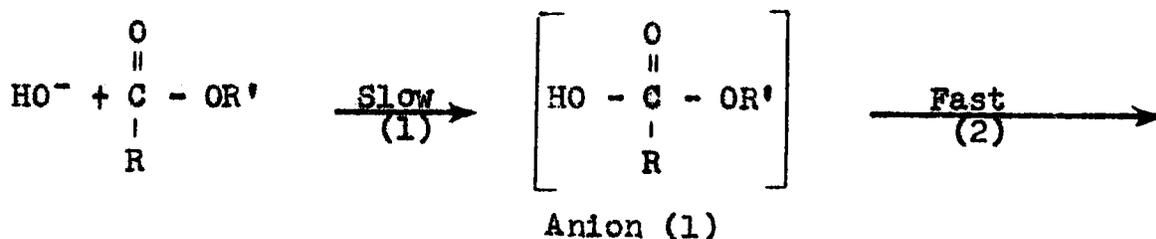


Acetoxysuccinic acid

thus clearly demonstrating acyl-oxygen fission. A mechanism consistent both with the rate law and the observed site of bond-breakage is,⁴

³B. Holmberg, *Ber.*, 45, 1997 (1912).

⁴E. S. Gould, "Mechanism and Structure in Organic Chemistry," 1959, p. 316.



The first, and probably the second, steps are reversible, but the final step is not. Thus the over-all reaction is irreversible. Bender⁵ found anion I (above) to be an intermediate rather than an activated complex. He demonstrated this by the study of the saponification of a series of various esters, each containing labeled oxygen, in ordinary water. Thus he has shown that ester saponification proceeds through a carbonyl addition mechanism. Alkaline hydrolysis, then, is a type reaction in which a negatively charged nucleophile attacks the carbonyl carbon of a neutral substrate.

Inasmuch as reactions between neutral molecules are often extremely slow and reactions between ions extremely fast (or slow, depending on the charge), one may expect that a reaction between an ion and a neutral molecule will show a

⁵M. L. Bender, J. Am. Chem. Soc., 73, 1626 (1951).

normal (neither extremely fast nor slow) type of behavior.⁶ This can be verified by approximate calculations of the energy of interaction between an ion and the dipole of a neutral polar molecule. The energy is given by equation⁷ (1),

$$\Delta F_{el} = - \frac{|Z_e| \mu \cos \theta}{D r^2} \quad (1)$$

where Z_e is the charge on the ion, μ the dipole moment of the molecule, r the distance from the center of the ion to the center of the dipole, θ the angle of approach of the ion to the line of the dipole, and D the dielectric constant of the solvent. By calculating ΔF_{el} , an estimate of the effect of the solvent on the rate of reaction between an ion and a neutral molecule may be made. Since the attraction will be somewhat greater, the rate of reaction will be larger in a medium of lower dielectric constant.

Born⁸ has formulated an equation (2) for the charging of an ion in a continuous dielectric,

$$\Delta F_{el}^{\dagger} = \frac{z^2 e^2}{2Dr} \quad (2)$$

⁶A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," 1961, p. 148.

⁷Frost and Pearson, p. 149.

⁸M. Born, Z. Physik, I, 45 (1920).

where e (charge on the electron) is a constant, 4.8×10^{-10} e.s.u. Because of the difference in radius r for the reactant ion and r_{\ddagger} (the activated complex), there is a difference in free energies which adds to the free energy of activation (ΔF_{el}^{\ddagger}).

$$\Delta F_{el}^{\ddagger} = \frac{z^2 e^2}{2D} \left(\frac{1}{r_{\ddagger}} + \frac{1}{r} \right) \quad (3)$$

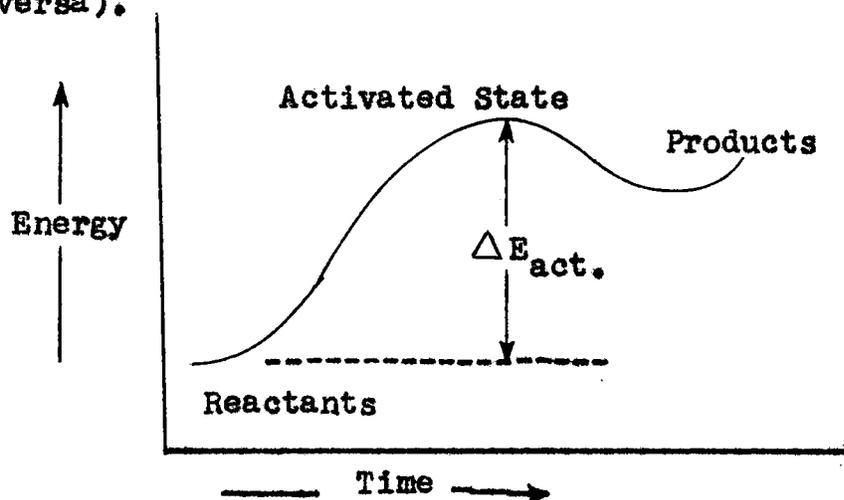
Accordingly, the rate constant may be written,

$$\ln k = \ln k_0' - \frac{Nz^2 e^2}{2DRT} \left(\frac{1}{r} - \frac{1}{r_{\ddagger}} \right) \quad (4)$$

where N is Avogadro's number (6.06×10^{23}), R is the gas constant (0.0821), T is temperature ($^{\circ}\text{K}$), and k_0' is the rate constant in a medium of infinite dielectric constant. Since r_{\ddagger} will be larger than r , the rate again should be somewhat greater in a medium of lower dielectric constant.⁹ This is an equation of straight line of slope $\frac{Nz^2 e^2}{2RT}$ in a plot of $\ln k$ vs $1/D$ if r and r_{\ddagger} are constant. Agreement would not necessarily be expected if the rate were measured in several completely different solvents. One reason is that the ionic radius is not constant but varies from solvent to solvent.

⁹K. J. Laidler and H. Eyring, Ann. N.Y. Acad. Sci., 39, 303 (1940).

In order for a change of solvent (or any other condition) to affect the rate of reaction, it must affect the reactants and transition state differently, *i.e.*, it must change the energy of activation ($E_{act.}$). This may be accomplished by solvating the reactants more readily than the transition state (or vice versa).



If the solubility of both were affected in the same way by a change in solvent, then there would be no change in the rate.

Hyne and Robertson¹⁰ presented a semiempirical equation (7) relating the solvolysis of some fifty benzenesulfonic esters to physical properties of the solvolyzing medium. They interpreted the activation energies of the solvolyses of benzenesulfonic esters in hydroxylic solvents upon the principle of a continuous spectrum of intermediate mechanisms

¹⁰J. B. Hyne and R. E. Robertson, Can. J. Chem., 34, 863 (1956).

varying between the two limits of S_n1 and S_n2 . They postulated that energy (E_e) is required to bring about charge separation in the ester undergoing scission, and that this energy must be related to dielectric constant of the surrounding medium (equation 5). Furthermore, they recognized that the bulk dielectric constant of the solvent medium is not truly representative of the localized dielectric in the immediate vicinity of the created partial charge. Some measure of success has previously been achieved with relations involving the bulk dielectric constant, however, and in the absence of a better measure of dielectric of the medium, the bulk dielectric constant (D) is employed.

$$E_e = f(D) \quad (5)$$

Also, energy (E_s) is required to remove solvent molecules from the solvent lattice to be available for their solvating role. The increase in number of solvent molecules in the solvation shell of the transition state will be a relative measure of the solvation energy which, in turn, must be related to the molecular volume (MV) of the solvent species, thus,

$$E_s = f(MV)_s \quad (6)$$

The activating energy (E_a) may then be expressed as,

$$E_a = f(D) + f(MV)_s \quad (7)$$

They conclude that equation (7) is only a generalization and not intended to be applicable in all cases.

Extensive studies of solvent effects in solvolyses have been reported,¹¹ and attempts have been made to correlate the rates with solvent composition or solvent properties such as dielectric constants. Ideally one might prefer a relationship between rates and independently determined properties of the solvent or solution, although this relationship has met with limited success.¹² To a considerable extent the limited data available have followed the generalization that anion-neutral molecule reactions proceed faster in solvents of low dielectric constant.¹³

Grunwald and Winstein¹⁴ noticed the parallel effects of solvents on the reaction rates of different compounds. They state that the reaction rates can be predicted (in some cases) by an equation similar to

$$\log (k^x/k_0^x) = (m) \log (k^s/k_0^s) \quad (8)$$

where k^x is the rate constant of the compound in solvent x ,

¹¹A. Streitwieser, Jr., Chem. Revs., 56, 571 (1956).

¹²E. M. Kosower; J. Am. Chem. Soc., 80, 3267 (1958).

¹³C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 1953, p. 347.

¹⁴E. Grunwald and S. Winstein, J. Am. Chem. Soc., 70, 846 (1948).

and k_0 is the rate constant for that compound in a standard solvent. k^s is the rate constant for a standard compound in the solvent x and k_0^s is the rate constant of the standard compound in the standard solvent. m measures the susceptibility of compound x to change in the ionizing power of the solvent. This is the equation of a straight line if solvent effects are proportional from compound to compound.

Winstein and Fainberg¹⁵ studied solvent effects on enthalpy and entropy of activation for solvolysis of t-butyl chloride. They compared the change of enthalpy and entropy of activation for t-butyl chloride with that for other substrates, and found that the various substances do not obey generalizations (nature of solvent system, substrate structure, and temperature effects), which are based solely on the nature of the solvent system.

Fuchs and Nisbet¹⁶ studied the reaction rates of substituted alpha-chlorotoluene with thiosulfate in eleven partially aqueous solvents of varying dielectric constants. Their results presented evidence of apparent disagreement with the generalization that reaction velocity increases with

¹⁵G. Winstein and A. H. Fainberg, J. Am. Chem. Soc., 79, 5937 (1957).

¹⁶R. Fuchs and A. Nisbet, J. Am. Chem. Soc., 81, 2371 (1959).

decrease in dielectric constant. They found, in most of the reactions they studied, that an increase in reaction velocity did not accompany a decrease in dielectric constant.

Work has been conducted concerning the solvent effects upon ester hydrolysis. Huang and Hsieh¹⁷ found that the reaction rate increased linearly with an increase in mole-fraction of dioxane, up to 40% dioxane with *p*-dioxane and water mixtures being used as solvents for saponification reactions. This indicated that the reaction velocity is increased by a decrease in the dielectric constant.

Nair and Anantakrishnan¹⁸ used dioxane-water and acetone-water mixtures as solvents for saponification reactions. They found that the velocity constant began to fall when the organic content of the solvent exceeded a certain value.

Kay¹⁹ determined the saponification rate constants for three aliphatic esters in varying concentrations of dioxane and water. The rate constants varied with the concentration of dioxane, and a maximum was indicated at a concentration of

¹⁷T. C. Huang and H. S. Hsieh, J. Chinese Chem. Soc., 7, 1 (1939).

¹⁸T. C. M. Nair and S. V. Anantakrishnan, Proc. Ind. Acad. Sci., 12A, 187 (1950).

¹⁹C. R. Kay, M.A. Thesis, Southwest Texas State College, August, 1964.

10% dioxene by volume. These data are in agreement with the findings of Nair and Anantakrishnan (above).

Reports in the literature with regard to solvent effects are not conclusive. After a thorough study of the literature, Hine²⁰ stated that while a number of equations have been proposed for the quantitative correlation of the rates of reaction with the nature of the solvent, none appears to have anywhere complete generality.

The saponification rates of several aliphatic esters were studied in varying organic solvent-water mixtures in order to provide more data on the effects of a solvent upon saponification. An interpretation of these data in terms of the physical properties of the solvent-water mixtures was explored.

²⁰J. Hine, "Physical Organic Chemistry," 1956, p. 83.

CHAPTER II

EXPERIMENTAL PROCEDURE

A. Method of Analysis

The classical method¹ for determining saponification rate constants is the volumetric analysis of aliquots of the reaction mixture taken at timed intervals and quenched with excess acid. This method is subject to three distinct disadvantages; (1) the uncertainty in the time of withdrawal and quenching the aliquot, (2) the chance of manipulation errors in taking the aliquot and making the analysis, and (3) the opening of the system to the atmosphere for removal of samples. This third disadvantage is of serious importance because of the reaction of the basic reaction mixture with carbon dioxide from the atmosphere.

High-frequency titrimetry² has been used to determine saponification rates. Although this method is desirable in that the reaction mixture can be completely sealed at all times,

¹F. Daniels, J. H. Matthews, J. W. Williams, P. Bender, and R. A. Alberty, "Experimental Physical Chemistry," 5th ed., 1956, p. 132.

²F. W. Jensen, G. M. Watson, and J. B. Beckhan, Anal. Chem., 23, 1770 (1951).

the lack of stability of the titrimeter over long periods of time makes this method impractical for extended reactions.

The hydrogen electrode has also been used to follow saponification reactions.³ Again the lack of stability of the system over extended periods makes it impractical for use with a wide range of rate constants.

A solution of sodium hydroxide and an ester undergoes a marked decrease in conductance with time because the poorly conducting alkanoate ion is replacing the highly conducting hydroxyl ion during the reaction. Therefore, as first proposed by Walker,⁴ a conductance bridge can be used to study the progress of the reaction. The advantages of this method are as follows: (1) the reaction mixture is sealed in a conductance cell, and (2) conductance measurements immediately reflect any change in the concentration of the reactants.

Conductance determinations were made of each ester in each of the four organic solvents at concentrations of 5, 10, and 15% solvent-water mixtures.

³C. A. Krause and R. A. Vinge, J. Am. Chem. Soc., 56, 511 (1934).

⁴J. Walker, Proc. Roy. Soc. (London), A78, 157 (1906).

B. Materials

1. Esters

Two of the esters used in this study, methyl acetate and n-butyl acetate, were purchased. The third, methyl n-butyrate, was prepared by refluxing the acid and excess alcohol with a trace of sulfuric acid as catalyst. It was then dried over magnesium sulfate and triple distilled.

All of the esters were purified by distillation. Refractive indices and boiling points were used as a criterion of purity.⁵

2. Solvent and Sodium Hydroxide Solutions

Technical-grade acetone was purified in the following manner.⁶ After being allowed to stand over anhydrous potassium carbonate for a long period of time to remove all the water, the decanted solvent was distilled in an all-glass apparatus several times.

Dimethyl sulfoxide was purified in the following manner.⁷ Approximately 1% by weight of potassium hydroxide

⁵C. D. Hodman, Ed., "Handbook of Chemistry and Physics," 43 ed., 1961.

⁶P. Walden and E. J. Birr, Z. Physik. Chem. 153A, 1 (1931).

⁷Correspondence, Crown Zellerbach Corporation, Camas, Washington, 1964.

was added to the dimethyl sulfoxide, and the mixture was heated at 120^o-130^oC. for one to two hours. After this pretreatment the dimethyl sulfoxide was distilled at reduced pressure through a 2-inch-diameter packed column having approximately 8 inches of glass-bead packing.

Methyl alcohol was purified by the method of Lund and Bjerrum.⁸ One-half gram of iodine, 5 g. of magnesium and 50-75 ml. of methyl alcohol were added to a flask provided with a reflux condenser. The flask was warmed until the iodine disappeared. An additional 900 ml. of methyl alcohol was then added, and the mixture was allowed to boil for half an hour under reflux; the product was then distilled with the exclusion of moisture and redistilled over tribromobenzoic acid to remove basic impurities.

Tetrahydrofuran was purified in the same manner⁹ as that described for *p*-dioxane. After being allowed to stand over sodium hydroxide pellets for 24 hours to remove all water, the decanted solvent was refluxed over metallic sodium for 24 hours to remove peroxides. It was then distilled from sodium, and the constant boiling middle fraction was

⁸H. Lund and J. Bjerrum, Ber. Deut. Chem. Gesell, 64, 210 (1931).

⁹A. Weissberger, "Technique of Organic Chemistry, Vol. VII, Organic Solvents," 2nd ed., 1949, p. 372.

collected. The entire distillation was conducted under a nitrogen-purged system.

The solvent mixtures used in this study were prepared by measuring a volume of solvent sufficient to make one liter of the desired concentration, then diluting to one liter with de-ionized water. This required slightly more than the theoretical amount of water because of the imperfect solution formed.

The water used was prepared by passing laboratory distilled water through a "research-grade" mixed bed ion-exchange column.¹⁰ Hancock, et al.,¹¹ found water prepared by this method to be comparable with water prepared by triple distillation from permanganate solution.

The standard sodium hydroxide solution was prepared by diluting a carbonate-free, saturated solution of sodium hydroxide. The solution was standardized against potassium acid phthalate and stored in a polyethylene bottle. The sodium hydroxide was protected against atmospheric carbon dioxide by means of a frequently changed Ascarite tube. The solution was restandardized every four weeks to check the normality of the solution.

¹⁰Illinois Water Treatment Co., Rockford, Illinois.

¹¹C. K. Hancock, E. A. Meyers, and B. J. Yager, J. Am. Chem. Soc., 83, 4211 (1961).

C. Apparatus

All saponification rate determinations were made in a constant temperature bath.¹² The bath temperature was regulated with a mercury thermoregulator,¹³ and bath temperature was maintained at $35^{\circ}\text{C.} \pm 0.015^{\circ}\text{C.}$ A Kahlsico 50°C. thermometer was kept in the bath for periodic checks on temperature variations.

An electric timer¹⁴ was used to follow the course of the reactions.

A Wheatstone bridge consisting of three decade resistance boxes¹⁵ was used to determine the resistance of the reaction mixtures. The null point was determined by the pattern on a cathode ray oscilloscope. This visual method, used in conjunction with the decade resistance boxes, allowed more accurate readings than could be obtained by using a "Magic Eye" conductance apparatus. Alternating current of one thousand cycles-per-second was provided by an oscillator.¹⁶

¹²E. H. Sargent and Co., Chicago, Cat. No. S-84805.

¹³Aloe Scientific, St. Louis, Cat. No. V79902A.

¹⁴Precision Scientific Co., Chicago, Cat. No. 69235.

¹⁵Leeds and Northrup, Philadelphia, Cat. No. 4734.

¹⁶Central Scientific Co., Chicago, Cat. No. 70029.

The conductivity cells¹⁷ used in this study were of the Jones and Bollinger¹⁸ type, i.e., the electrodes were not close to the filling tube. The cell was approximately 8 cm. in length and 2.5 cm. in diameter, and had cell constants of approximately 1.5 cm.^{-1} . The electrodes of the cell were coated with platinum black by standard procedures.

D. Procedure

Sufficient ester to make 50 ml. of 0.02 M solution was weighed on an analytical balance. To reduce evaporation, volatile esters were weighed into volumetric flasks containing a small amount of the organic solvent solution of the desired concentration. The mixture was then diluted to volume with the proper organic solvent solution. The molarity of the solution was then calculated, and 50 ml. of sodium hydroxide of the same molarity was then prepared by adding the calculated volume of 0.1 M sodium hydroxide to the correct volume of pure organic solvent, and diluting to volume with conductance water. These solutions together with a clean, dry 250-ml. volumetric flask and a conductance cell filled with conductance water were allowed to come to thermal

¹⁷Fisher Scientific Co., New York, Cat. No. 9-367.

¹⁸G. Jones and D. M. Bollinger, J. Am. Chem. Soc., 57, 280 (1935).

equilibrium for thirty minutes in the constant temperature bath. The ester solution was then poured into the larger flask, followed by the sodium hydroxide solution. The electric timer was started when one half of the base had been added. The flask was then removed from the bath and shaken quickly to insure thorough mixing of the ester and base solutions. The cell was rinsed several times with the reaction mixture, filled with the solution, replaced in the bath, and sealed with paraffin. Although the entire operation took less than a minute, readings were not started until approximately five minutes had elapsed, since the solution cooled slightly while out of the bath. Conductance readings were taken at various time intervals until 90% of the ester had saponified.

E. Data and Computations

In the study of chemical kinetics, the term rate of reaction refers to the time rate of change, dc/dt , of the concentration of some constituent of interest. The reaction rate constant, k , is a proportionality factor which relates the rate of reaction to the reactant concentrations on which it depends. The alkaline hydrolysis of an ester is a second-order reaction, i.e., the rate is dependent upon the concentration of two reactants. The reaction may be

described¹⁹ by the equation

$$dx/dt = k_2(a-x)(b-x) \quad (1)$$

where a and b are the initial concentration of ester and base, x is the decrease in concentration of each after time t , and k_2 is the second-order rate constant. However, in this study, the initial concentration of ester and of base was the same, so that equation (1) can be simplified to

$$dx/dt = k_2(a-x)^2 \quad (2)$$

Upon integration, the expression becomes

$$k_2 = 1/ta(x/a-x) \quad (3)$$

As mentioned previously, the saponification of esters was found to be proportional to the concentration of the base and of the ester, and a solution containing both will undergo a decrease in conductance with time. The number of moles per liter, x , reacting in time t is given in terms of the conductances $y_0 = 1/R_0$, $y_t = 1/R_t$ and $y_\infty = 1/R_\infty$ at times 0, t , and ∞ , respectively, by substituting into equation (3) the values $x = y_0 - y_t$ and $a = y_0 - y_\infty$ to give the following expression

¹⁹Daniels, et al., op. cit., p. 131.

$$k_2 = \frac{1}{ta} \frac{y_0 - y_t}{y_t - y_\infty} = \frac{1}{ta} \frac{1/R_0 - 1/R_t}{1/R_t - 1/R_\infty}$$

Rearranging equation (4) gives

$$1/t(1/R_0 - 1/R_t) = k_2(a/R_t - a/R_\infty) \quad (5)$$

the equation of a straight line with a slope k_2a and intercept k_2a/R_∞ . Therefore, R_∞ is not necessary for estimating the slope. The value of R_0 may be determined either by extrapolation or by using a blank solution of base of the same concentration as the reaction mixture but with no ester present.

The slope of the best straight line was estimated graphically from a plot of $1/R_t$ as abscissa versus $1/t(1/R_0 - 1/R_t)$ as ordinate. The value of k_2 was obtained by dividing the slope by the initial concentration of ester, a . As an example, the data for a saponification run on methyl acetate in 5% methanol are listed in Table I and are plotted in Figure 1.

As a general rule, three determinations were made on each ester. However, when good agreement was obtained in the first two runs, only two determinations were made. Complete experimental data from all saponification runs are listed in the Appendix. The average values of the saponification rates are listed in Table II.

TABLE I
 DATA FOR SAMPLE RUN ON METHYL ACETATE IN 5% METHANOL

Weight of ester, 0.1366 g.

Molarity of ester and base solution (100 ml.), 0.01804M

Molarity of mixture of base and ester solution, 0.00902M

t , Minutes	R , Ohms	$1/R \times 10^4$	$(1/R_0 - 1/R_t) \times 10^4$	$1/t (1/R_0 - 1/R_t) \times 10^4$
0	578	17.30		
4	785	12.75	4.68	1.150
6	856	11.69	5.61	0.934
8	912	10.96	6.34	0.793
10	963	10.39	6.91	0.691
12	1009	9.93	7.37	0.614
14	1046	9.56	7.74	0.533
16	1078	9.30	8.00	0.500
18	1103	9.06	8.24	0.458
20	1129	8.86	8.54	0.422
22	1152	8.68	8.62	0.392
24	1173	8.52	8.78	0.366

Slope = 0.17826 min.⁻¹

$k_2^{35} = 19.76 \text{ mole}^{-1} \text{ min.}^{-1}$

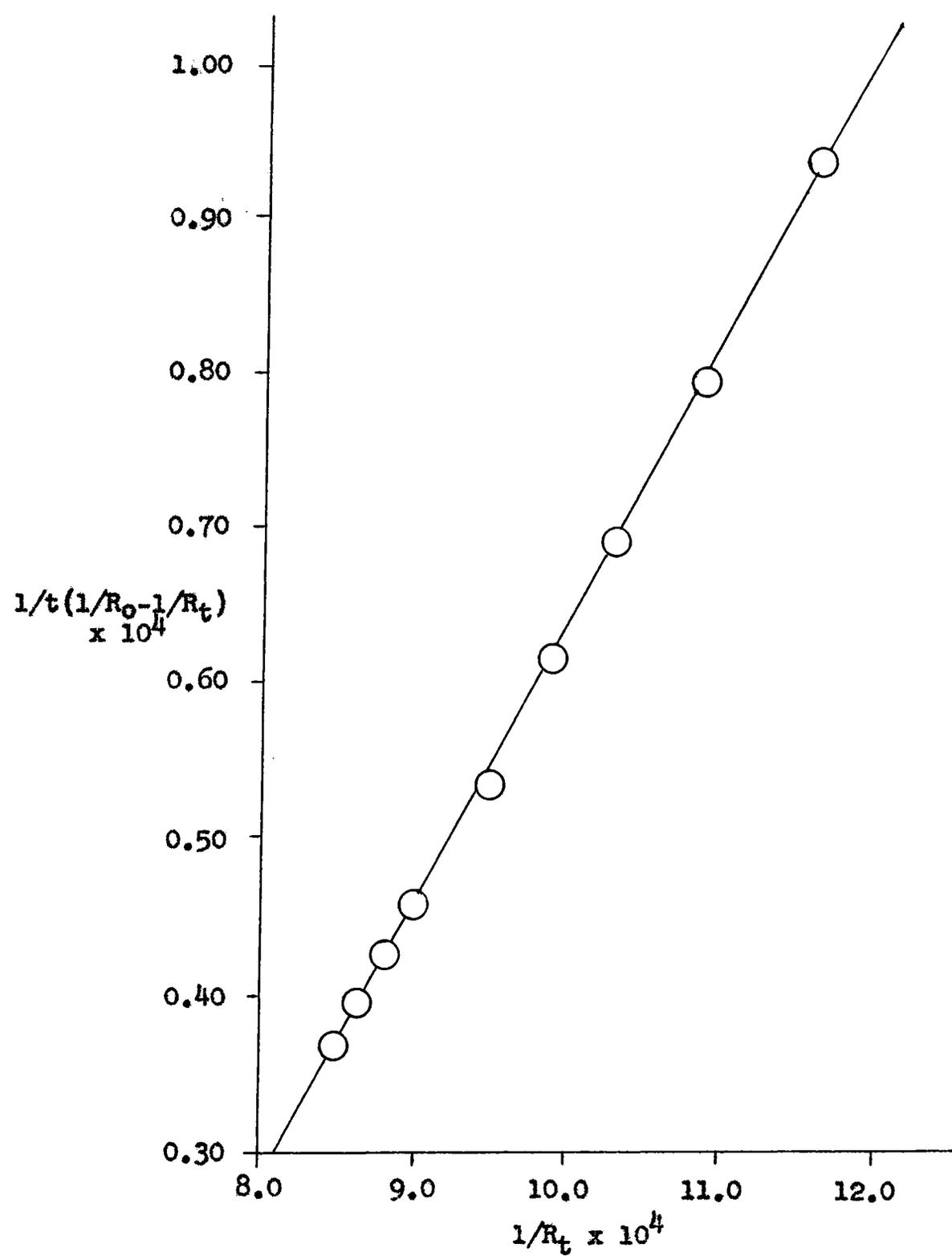


FIGURE 1

SAPONIFICATION OF METHYL ACETATE IN 5% METHANOL AT 35° C., RUN 1

TABLE II
 SAPONIFICATION RATES OF ALIPHATIC ESTERS
 IN ORGANIC SOLVENT-WATER MIXTURES AT 35° C.

Volume % Organic Solvent	k_2^{35} (l. mole ⁻¹ min. ⁻¹)		
	Methyl Acetate	<u>n</u> -Butyl Acetate	Methyl <u>n</u> -Butyrate
<u>Water</u>	21.36	7.37	9.97
<u>Acetone</u>			
5	22.37	9.15	10.59
10	23.20	8.30	9.61
15	21.03	7.91	9.11
<u>Dimethyl Sulfoxide</u>			
5	22.00	8.78	12.49
10	24.42	9.36	10.60
15	15.50	9.07	11.61
<u>Methyl Alcohol</u>			
5	19.94	----	9.73
10	18.47	----	9.47
15	17.72	----	8.42
<u>Tetrahydrofuran</u>			
5	20.36	8.15	10.72
10	21.24	9.81	9.62
15	22.05	7.15	8.40
<u>Dioxane</u> ^a			
10	25.80	10.72	8.88

^aC. B. Kay, Unpublished M. A. Thesis, Southwest Texas State College, August, 1964, p. 19.

CHAPTER III

RESULTS AND DISCUSSION

Grunwald and Winstein¹ have stated that there are (in some cases) parallel effects of solvents on the reaction rates of different compounds and these reaction rates can be predicted by the equation

$$\log (k^x/k_o^x) = m \log(k^s/k_o^s) \quad (1)$$

as described in the introduction. Since this is an equation of a straight line, a plot of $\log k_x$ versus $\log k_s$ for any type of reaction should give a straight line if solvent effects are proportional from compound to compound. A log plot of the data of Table II is shown in Figure 2, from which it may be noted that a plot of k_2^{35} of methyl n-butyrate as abscissa versus k_2^{35} of methyl acetate as ordinate is not a straight line, but rather shows considerable deviation. Thus there appears to be no proportional solvent effects. A plot was also made of the reaction rates of each of the esters studied and the same results, as in Figure 2, were obtained. The slope of the plot in Figure 2 was calculated by the method of least squares and found to be 1.183.

¹E. Grunwald and S. Winstein, J. Am. Chem. Soc., 70, 846 (1948).

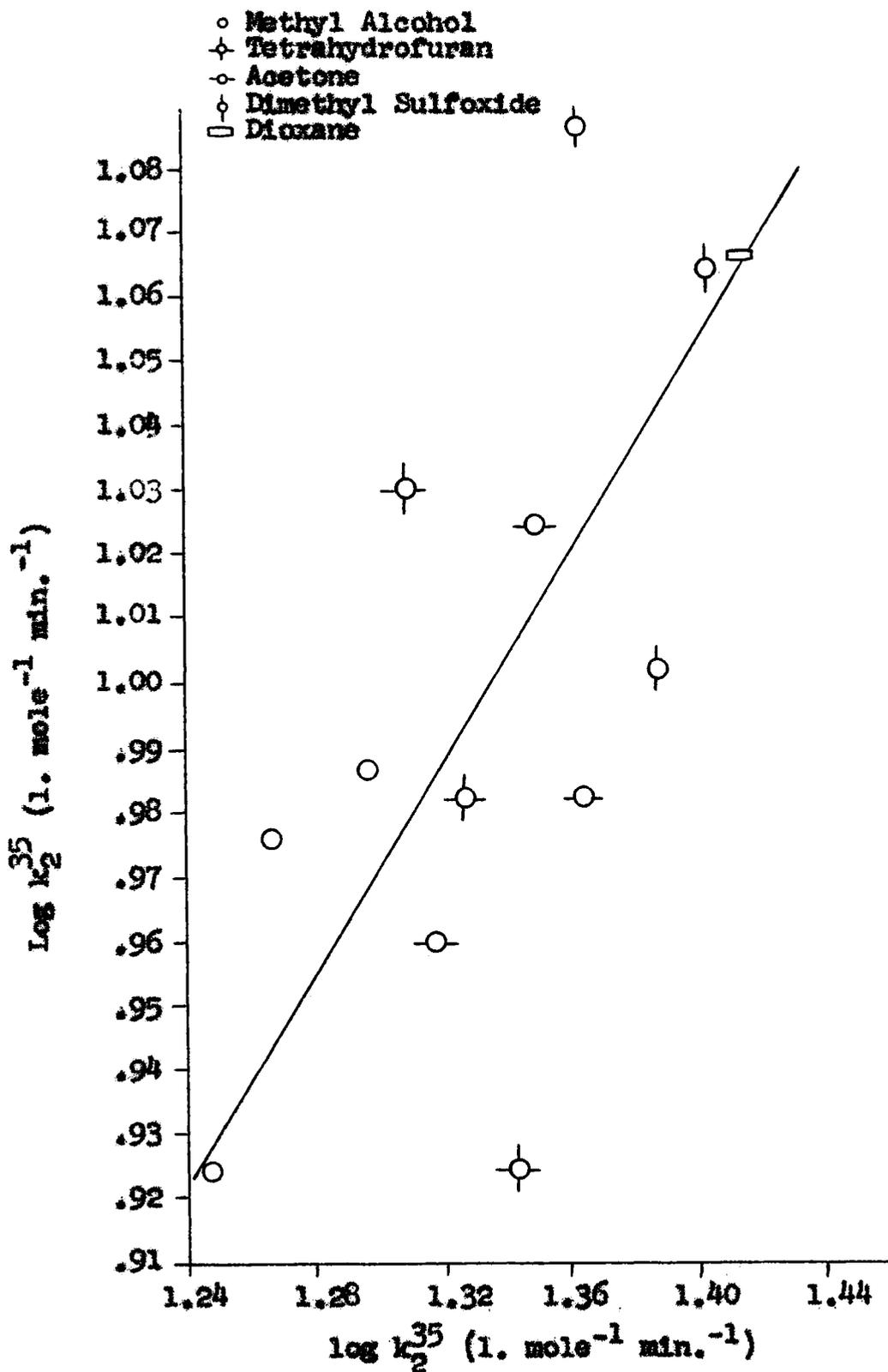


FIGURE 2

RELATIONSHIP OF SAPONIFICATION RATES OF METHYL BUTYRATE TO THE SAPONIFICATION RATES OF METHYL ACETATE

A plot of the saponification rates of the esters studied as abscissa versus the per cent of acetone as ordinate is shown in Figure 3. The plot indicates a variation in the effects upon saponification rates from ester to ester in the same solvent system. Thus the solvent does not give a uniform effect from ester to ester. The same lack of uniformity was observed upon plotting the saponification rates of the esters against the other solvents studied.

According to the equation formulated by Born,² the rate constant of a reaction may be written

$$\ln k = \ln k_0' + NZ^2e^2/2DRT (1/r - 1/r_{\dagger}) \quad (2)$$

as described by equation (4) in Chapter I. This is an equation of a straight line of slope $NZ^2e^2/2RT$ in a plot of $\ln k$ versus $1/D$ if r and r_{\dagger} are constant. Figure 4 is a plot of saponification rate of methyl acetate as abscissa versus $1/D$ of the various organic solvents as the ordinate. The "least squares" regression line is shown by the solid line, but obviously the fit is extremely poor. The dashed line parallel to the regression line fits the points corresponding to the tetrahydrofuran-water mixtures. There is little correlation for the other solvent systems.

²M. Born, Z. Physik, I, 45 (1920).

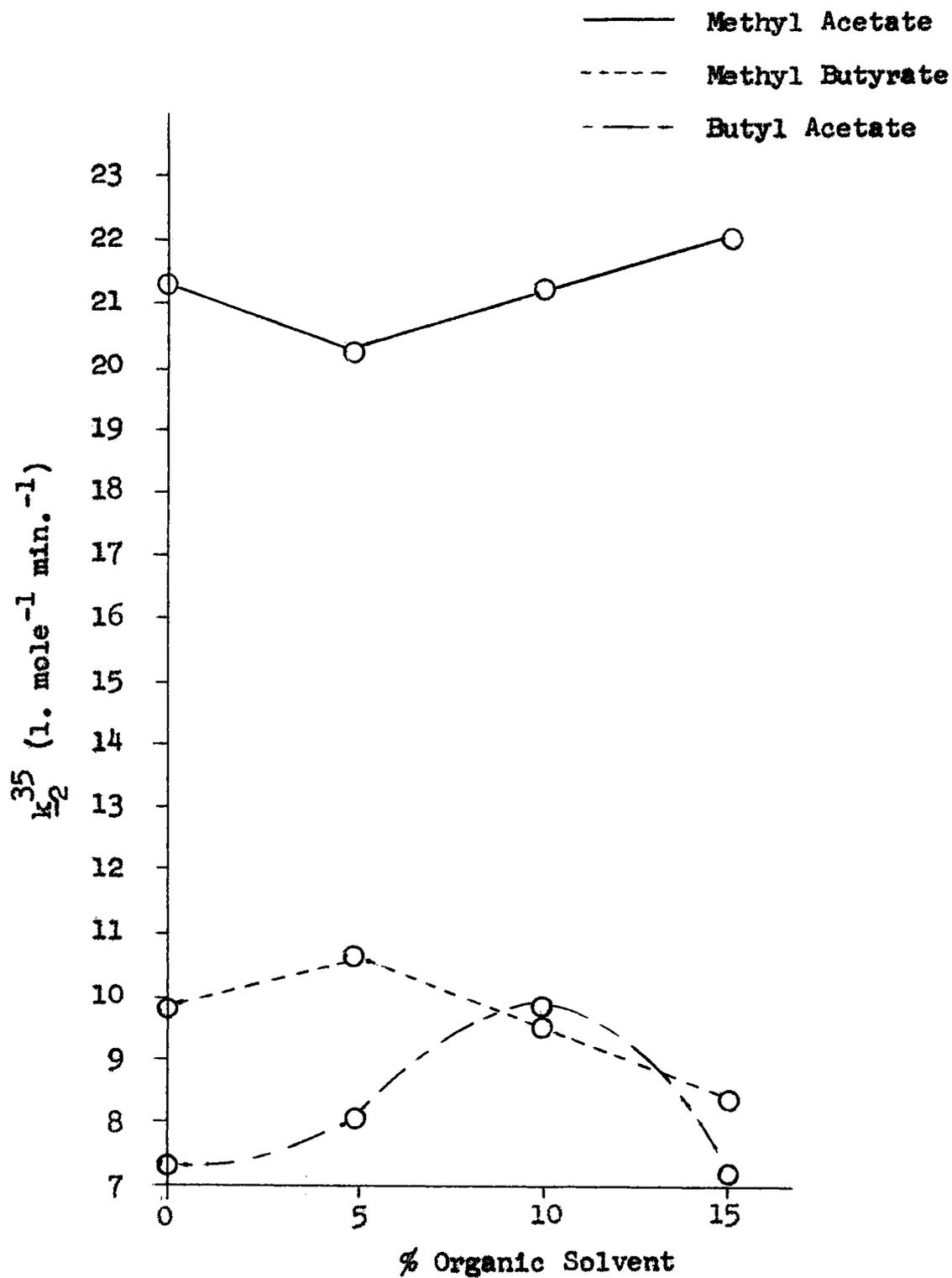


FIGURE 3

RELATIONSHIP OF SAPONIFICATION RATES OF VARIOUS ESTERS TO % ACETONE

TABLE III
DIELECTRIC CONSTANTS FOR ORGANIC SOLVENT-
WATER MIXTURES AT 35° C.

Volume % Organic Solvent	Dielectric Constant
<u>Water</u> ^a	74.97
<u>Acetone</u> ^b	
5	72.30
10	69.72
15	66.20
<u>Dioxane</u> ^a	
5	71.01
10	67.10
15	63.00
<u>Methyl Alcohol</u> ^c	
5	72.81
10	70.68
15	68.60
<u>Tetrahydrofuran</u> ^d	
5	71.84
10	68.68
15	65.18

^aFrank E. Critchfield, John A. Gibson, Jr., and James L. Hall, J. Am. Chem. Soc., 75, 1991 (1953).

^bGosta Akerlof, J. Am. Chem. Soc., 54, 4125 (1932).

^cPenrose S. Albright and Louis J. Gosting, J. Am. Chem. Soc., 68, 1061 (1946).

^dFrank E. Critchfield, John A. Gibson, Jr., and James L. Hall, J. Am. Chem. Soc. 75, 6044 (1953).

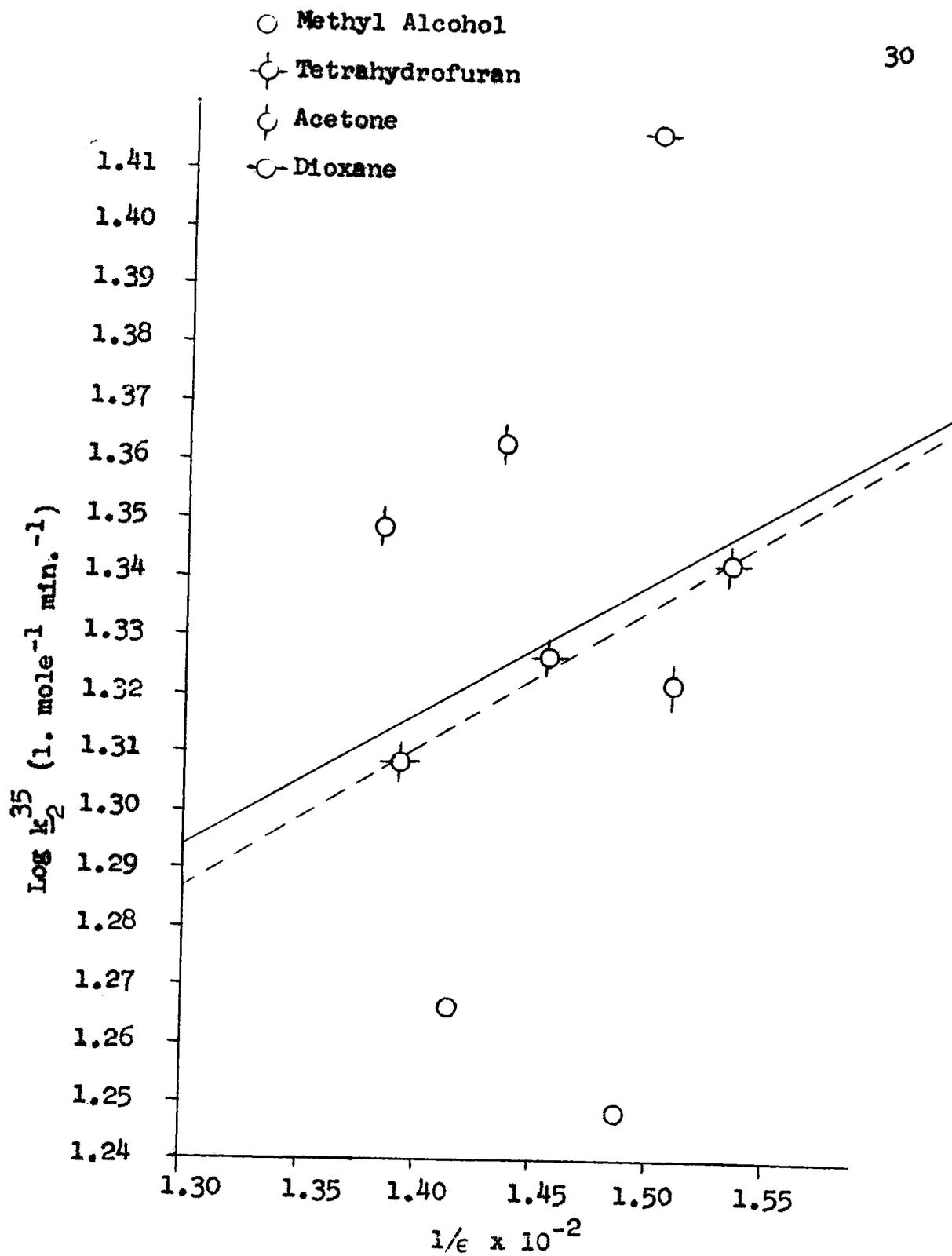


FIGURE 4

RELATIONSHIP OF SAPONIFICATION RATES OF METHYL ACETATE TO THE DIELECTRIC CONSTANT OF VARIOUS ORGANIC SOLVENTS

To a considerable extent the limited data available have followed the generalization that anion-neutral molecule reactions proceed faster in solvents of low dielectric constant.³ The slope of the straight line (obtained by the method of least squares) in Figure 4 is in general in agreement with this generalization. The slope indicates that as dielectric constant decreases, there is an increase in reaction rate. Because of the lack of uniformity of reaction rate increase with dielectric decrease, there are apparently other factors involved in effecting the reaction rate other than dielectric constant.

Bender⁴ has shown by the use of radioactively labeled oxygen that water is a reactant in ester saponification. Thus the mole fraction of water present in saponification reactions would have an influence upon the rate of reaction. A plot of saponification rates of butyl acetate versus per cent mole fraction of water is given in Figure 5. There appears to be no obvious correlation; however, if only acetone mixtures are considered, a straight line is obtained (indicated by a dashed line in Figure 5). Once again it is shown that although one particular ester in a particular

³C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 1953, p. 347.

⁴M. L. Bender, J. Am. Chem. Soc., 73, 1626 (1951).

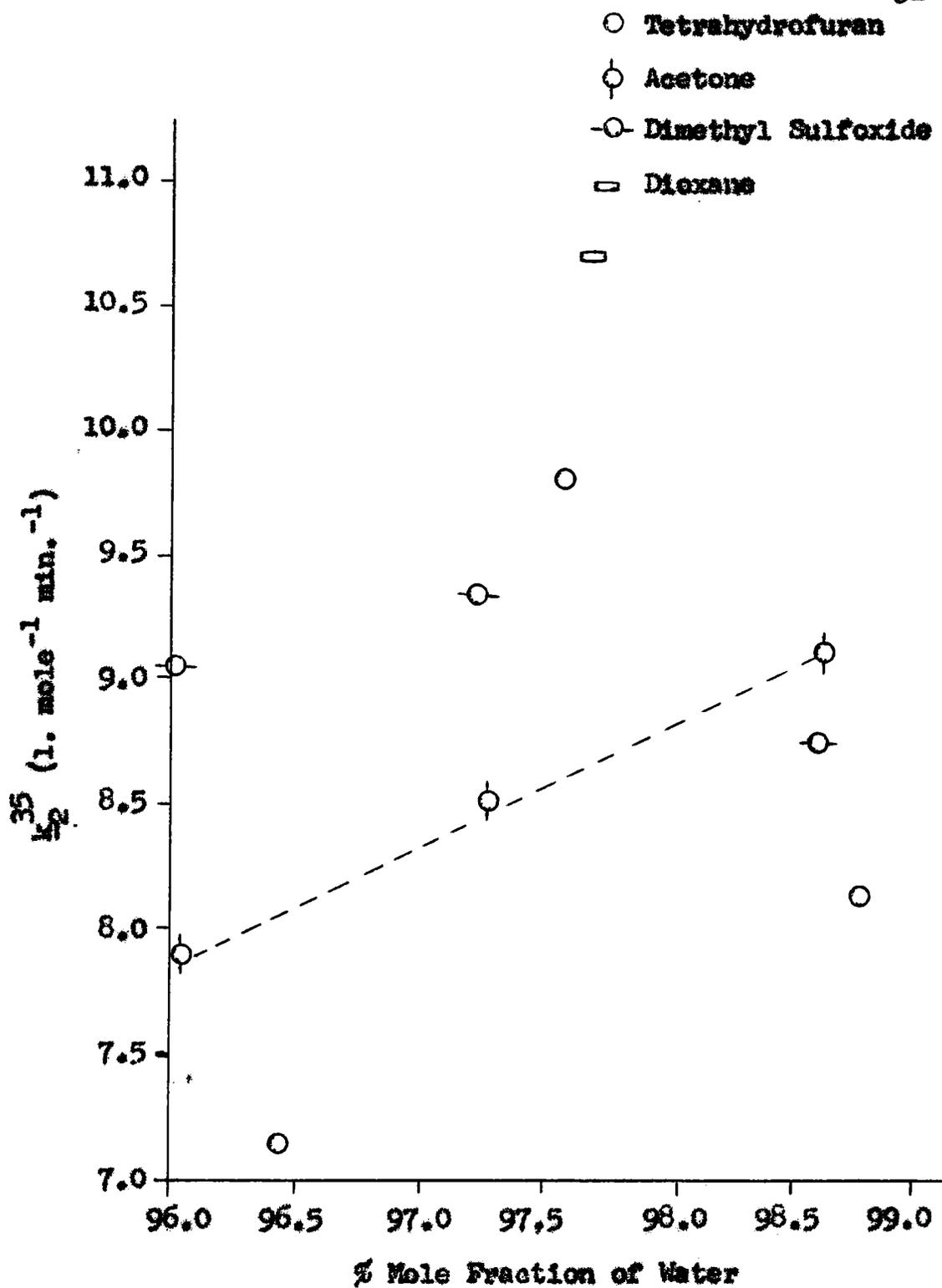


FIGURE 5

RELATIONSHIP OF SAPONIFICATION RATES OF BUTYL ACETATE TO
% MOLE FRACTION OF WATER

solvent system may follow a rule, it cannot be expected that all solvent systems will follow this same generalization.

Hine⁵ has stated that although a number of equations have been proposed for the quantitative correlation of the rates of reactions with the nature of the solvent, no simple expression appears to apply in all cases, which is in accord with the results represented here.

In this study, the saponification rates of butyl acetate in methyl alcohol were not determined because of the solvating effect (upon standing) of the methyl alcohol upon the butyl acetate. The methyl alcohol would solvate part of the butyl acetate, forming methyl acetate, thus making it impossible to determine accurately the saponification rates of butyl acetate in methyl alcohol-water mixtures.

⁵A. Hine, "Physical Organic Chemistry," 1956, p. 83.

CHAPTER IV

SUMMARY

1. Saponification rate constants were determined for three aliphatic esters in 0 - 15% organic solvent-water mixtures. Attempts were made to correlate the rate constant with physical properties of the solvent mixtures.
2. A comparison of the saponification rate of one ester to the saponification rate of another ester contained in the same organic solvent-water system was made. There appeared to be no obvious correlation, thus indicating a variation in the effects upon saponification rates from ester to ester in the same solvent system.
3. There appeared to be no obvious relationship between the mole fraction of water and the saponification rates studied.
4. Saponification rates of the esters appeared to increase with a decrease in dielectric constant of the organic solvent-water system, but there was a lack of uniformity in the comparison of dielectric constants with saponification rates. This is partially accounted for by the rather narrow range of dielectric constants exhibited by the organic-water mixtures employed.

APPENDIX

TABLE IV
SAPONIFICATION OF METHYL ACETATE IN PURE WATER

	Run 1		Run 2		Run 3	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms	
0	538	0	497	0	487	
4	746	4	707	4	700	
6	816	6	776	6	769	
8	879	8	834	8	828	
10	927	10	882	10	873	
12	966	12	920	12	910	
14	1001	14	950	14	944	
16	1032	16	980	16	970	
18	1058	18	1002	18	996	
20	1080	20	1023	20	1016	
22	1101	22	1043	22	1034	
24	1120	24	1055	24	1053	
				Run 1	Run 2	Run 3
Slope (min.^{-1})				0.50000	0.22500	0.22400
Concentration (mole l.^{-1})				0.00943	0.01043	0.01053
k_2 ($\text{l. mole}^{-1} \text{min.}^{-1}$)				21.20	21.56	21.33

TABLE V
 SAPONIFICATION OF METHYL n-BUTYRATE IN PURE WATER

Time, Min.	Run 1 Resistance in Ohms	Time, Min.	Run 2 Resistance in Ohms	Time, Min.	Run 3 Resistance in Ohms
0	430	0	460	0	460
4	532	4	571	4	572
6	579	6	618	6	618
8	623	8	661	8	662
10	658	10	699	10	699
12	692	12	734	12	734
14	721	14	762	14	763
16	747	16	790	16	789
20	789	20	837	20	836
25	833	25	884	25	882
30	869	30	921	30	919
35	896	35	953	35	950
40	920	40	979	40	976
51	960	50	1017	50	1014
60	985				
			Run 1	Run 2	Run 3
	Slope (min. ⁻¹)		0.11700	0.11247	0.11060
	Concentration (mole l. ⁻¹)		0.01257	0.01135	0.01127
	k_2 (l. mole ⁻¹ min. ⁻¹)		9.54	9.91	9.81

TABLE VI
SAPONIFICATION OF n-BUTYL ACETATE IN PURE WATER

Time, Min.	Run 1 Resistance in Ohms	Time, Min.	Run 2 Resistance in Ohms
0	550	0	550
3	609	3	599
5	647	5	636
7	682	7	675
10	734	10	727
12	764	12	757
15	803	15	796
18	842	18	834
21	873	21	863
25	910	25	900
28	933	28	923
30	946	30	936
36	983	36	973
40	1006	40	995
50	1047	50	1035
60	1078	60	1069
		Run 1	Run 2
	Slope (min. ⁻¹)	0.07200	0.06950
	Concentration (mole l. ⁻¹)	0.00955	0.00967
	k_2 (l. mole ⁻¹ min. ⁻¹)	7.55	7.18

TABLE VII
SAPONIFICATION OF METHYL ACETATE IN 5% METHYL ALCOHOL

	Run 1		Run 2		Run 3	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms	
0	578	0	600	0	576	
4	785	4	808	4	786	
6	856	6	883	6	857	
8	912	8	948	8	918	
10	963	10	1003	10	969	
12	1009	12	1046	12	1009	
14	1046	14	1086	14	1049	
16	1078	16	1118	16	1081	
18	1103	18	1148	18	1106	
20	1129	20	1176	20	1133	
22	1152	22	1195	22	1153	
24	1173	24	1216	24	1175	
				Run 1	Run 2	Run 3
				0.17826	0.18696	0.18571
				0.00902	0.00913	0.00949
				19.76	20.48	19.57

TABLE VIII
 SAPONIFICATION OF METHYL ACETATE IN 10% METHYL ALCOHOL

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	540	0	506
4	745	4	736
6	812	6	783
8	874	8	827
10	924	10	869
12	963	12	907
14	999	14	940
17	1044	16	966
18	1058	18	989
20	1080	20	1011
22	1100	22	1028
24	1117	24	1044
		Run 1	Run 2
	Slope (min.^{-1})	0.19375	0.21290
	Concentration (mole l.^{-1})	0.01056	0.01150
	k_2 ($\text{l. mole}^{-1} \text{min.}^{-1}$)	18.35	18.59

TABLE IX
SAPONIFICATION OF METHYL ACETATE IN 15% METHYL ALCOHOL

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	605	0	576
4	810	4	778
6	884	6	853
8	944	8	911
10	994	10	961
12	1035	12	1003
14	1073	15	1058
16	1105	16	1072
18	1135	18	1100
20	1159	20	1122
22	1182	22	1142
24	1198	24	1161
		Run 1	Run 2
	Slope (min.^{-1})	0.17667	0.18276
	Concentration (mole l.^{-1})	0.00985	0.01040
	k_2 ($\text{l. mole}^{-1} \text{min.}^{-1}$)	17.92	17.51

TABLE X
 SAPONIFICATION OF METHYL n-BUTYRATE IN 5% METHYL ALCOHOL

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	447	0	456
4	564	4	569
6	607	6	614
8	649	8	654
10	686	10	690
12	719	12	723
15	762	15	778
20	819	20	819
26	871	25	865
30	900	30	896
35	929	35	928
44	971	40	951
50	990	50	990
		Run 1	Run 2
Slope (min. ⁻¹)		0.11875	0.11622
Concentration (mole l. ⁻¹)		0.01222	0.01193
k_p (l. mole ⁻¹ min. ⁻¹)		9.72	9.74

TABLE XI

SAPONIFICATION OF METHYL n-BUTYRATE IN 10% METHYL ALCOHOL

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	467	0	505
4	580	4	625
6	629	6	674
8	671	8	718
10	707	10	756
12	740	12	794
15	785	15	826
20	844	20	904
25	891	25	953
30	929	30	997
35	958	35	1029
40	985	40	1060
50	1023	50	1104
		Run 1	Run 2
Slope (min.^{-1})		0.11333	0.10714
Concentration (mole l.^{-1})		0.01209	0.01120
k_2 ($\text{l. mole}^{-1} \text{min.}^{-1}$)		9.37	9.56

TABLE XII

SAPONIFICATION OF METHYL n-BUTYRATE IN 15% METHYL ALCOHOL

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	548	0	512
4	656	4	633
6	704	6	679
8	747	8	724
10	789	10	762
12	826	12	799
15	875	15	845
20	940	20	910
25	995	25	961
30	1040	31	1012
35	1075	35	1040
40	1105	40	1079
50	1157	50	1114
		Run 1	Run 2
Slope (min.^{-1})		0.09211	0.10000
Concentration (mole l.^{-1})		0.01108	0.01171
k_2 ($\text{l. mole}^{-1} \text{min.}^{-1}$)		8.30	8.54

TABLE XIII
SAPONIFICATION OF METHYL ACETATE IN 5% TETRAHYDROFURAN

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	545	0	541
4	760	4	749
6	824	6	820
8	882	8	880
10	935	10	934
12	978	12	973
14	1013	14	1008
16	1045	16	1039
18	1073	18	1066
20	1096	20	1088
22	1118	22	1108
24	1136	24	1126
		Run 1	Run 2
Slope (min.^{-1})		0.19190	0.19616
Concentration (mole l.^{-1})		0.00947	0.00959
k_2 ($\text{l. mole}^{-1} \text{min.}^{-1}$)		20.27	20.45

TABLE XIV
 SAPONIFICATION OF METHYL ACETATE IN 10% TETRAHYDROFURAN

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	595	0	563
4	817	4	786
6	898	6	861
8	959	8	923
10	1015	10	974
12	1062	12	1015
14	1099	14	1054
16	1134	16	1086
18	1158	18	1111
20	1185	20	1132
22	1206	22	1155
24	1227	24	1172
		Run 1	Run 2
	Slope (min.^{-1})	0.19391	0.20526
	Concentration (mole l.^{-1})	0.00913	0.00966
	k_2 ($\text{l. mole}^{-1} \text{min.}^{-1}$)	21.13	21.35

TABLE XV

SAPONIFICATION OF METHYL ACETATE IN 15% TETRAHYDROFURAN

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	540	0	559
5	809	4	781
6	846	6	858
8	908	8	918
10	956	10	971
12	995	12	1013
14	1030	14	1046
16	1064	16	1076
18	1085	18	1105
20	1105	20	1128
22	1124	22	1140
24	1141	24	1155
		Run 1	Run 2
Slope (min. ⁻¹)		0.22963	0.20857
Concentration (mole l. ⁻¹)		0.01048	0.00939
k_2 (l. mole ⁻¹ min. ⁻¹)		21.91	22.19

TABLE XVI
 SAPONIFICATION OF n-BUTYL ACETATE IN 5% TETRAHYDROFURAN

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	576	0	493
3	644	3	555
5	684	5	593
7	723	7	629
11	790	10	672
13	819	12	700
15	845	15	724
18	880	18	754
21	914	21	780
25	948	25	806
30	986	30	835
35	1017	35	860
40	1046	40	880
50	1087	50	911
60	1119	60	935
		Run 1	Run 2
Slope (min. ⁻¹)		0.07727	0.89474
Concentration (mole l. ⁻¹)		0.00953	0.01094
k_2 (l. mole ⁻¹ min. ⁻¹)		8.11	8.18

TABLE XVII

SAPONIFICATION OF n-BUTYL ACETATE IN 10% TETRAHYDROFURAN

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	556	0	549
3	654	4	671
5	698	5	695
7	740	7	734
10	795	10	789
12	828	12	834
15	871	15	862
18	907	18	901
22	952	21	933
25	980	25	970
31	1029	30	1010
40	1084	40	1073
50	1128	50	1116
60	1168	60	1156
		Run 1	Run 2
Slope (min. ⁻¹)		0.09531	0.09706
Concentration (mole l. ⁻¹)		0.00969	0.00993
k_2 (l. mole ⁻¹ min. ⁻¹)		9.83	9.78

TABLE XVIII

SAPONIFICATION OF n-BUTYL ACETATE IN 15% TETRAHYDROFURAN

	Run 1		Run 2		Run 3	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms	
0	612	0	662	0	600	
3	684	3	719	3	659	
6	746	5	759	5	705	
7	768	7	799	7	749	
10	823	10	856	9	785	
12	856	12	888	12	836	
15	899	15	932	15	880	
18	942	18	971	18	918	
21	976	21	1006	21	952	
25	1018	25	1047	28	1018	
30	1060	30	1089	30	1031	
35	1095	36	1127	35	1068	
40	1127	40	1155	40	1097	
50	1176	50	1205	50	1143	
60	1211	67	1264	60	1182	
			Run 1	Run 2	Run 3	
	Slope (min.^{-1})		0.72581	0.06666	0.07308	
	Concentration (mole l.^{-1})		0.00989	0.00943	0.01036	
	k_2 ($\text{l. mole}^{-1} \text{min.}^{-1}$)		7.34	7.06	7.06	

TABLE XIX

SAPONIFICATION OF METHYL n-BUTYRATE IN 5% TETRAHYDROFURAN

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	532	0	480
4	666	6	659
6	723	8	708
9	796	10	751
10	819	12	780
12	860	14	811
14	899	17	854
16	932	18	868
18	964	20	889
20	991	25	940
25	1052	30	989
30	1101	35	1012
35	1141	40	1042
40	1176	50	1086
50	1230		
		Run 1	Run 2
	Slope (min. ⁻¹)	0.10714	0.12245
	Concentration (mole l. ⁻¹)	0.01022	0.01119
	k_2 (l. mole ⁻¹ min. ⁻¹)	10.48	10.94

TABLE XX

SAPONIFICATION OF METHYL n-BUTYRATE IN 10% TETRAHYDROFURAN

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	500	0	502
4	612	4	618
6	663	6	673
8	708	8	718
10	740	10	757
12	784	12	796
14	815	14	827
16	843	16	854
18	879	18	880
21	903	20	904
25	938	25	963
30	978	30	990
36	1008	35	1026
40	1037	40	1058
50	1083	50	1098
		Run 1	Run 2
	Slope (min. ⁻¹)	0.11148	0.11176
	Concentration (mole l. ⁻¹)	0.01162	0.01157
	k_2 (l. mole ⁻¹ min. ⁻¹)	9.60	9.66

TABLE XXI

SAPONIFICATION OF METHYL n-BUTYRATE IN 15% TETRAHYDROFURAN

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	553	0	553
4	654	4	654
6	703	6	708
8	753	8	753
10	794	10	797
12	833	12	836
14	866	14	869
16	896	16	896
18	924	18	926
20	949	20	952
28	1028	25	1003
30	1046	31	1056
35	1079	35	1082
40	1109	40	1110
50	1157	50	1158
		Run 1	Run 2
Slope (min.^{-1})		0.09545	0.09714
Concentration (mole l.^{-1})		0.01144	0.01139
k_2 ($\text{l. mole}^{-1} \text{ min.}^{-1}$)		8.34	8.53

TABLE XXII
 SAPONIFICATION OF METHYL ACETATE IN 5% ACETONE

Time, Min.	Run 1 Resistance in Ohms	Time, Min.	Run 2 Resistance in Ohms	Time, Min.	Run 3 Resistance in Ohms
0	500	0	519	0	540
2	646	2	661	2	679
3	688	3	715	3	723
4	727	4	758	4	767
6	799	5	809	5	804
8	875	6	836	6	841
10	908	8	899	8	901
12	948	10	957	10	951
14	984	12	1005	12	994
16	1019	14	1035	14	1032
18	1041	16	1068	16	1068
20	1061	18	1099	18	1089
22	1079	20	1121	20	1112
24	1097	22	1141	22	1133
26	1107	24	1161	24	1154
		26	1174	26	1164
			Run 1	Run 2	Run 3
	Slope (min.^{-1})		0.24400	0.22847	0.22350
	Concentration (mole l.^{-1})		0.01072	0.01066	0.01002
	k_2 (1. mole $^{-1}$ min. $^{-1}$)		22.78	22.46	22.13

TABLE XXIII
SAPONIFICATION OF METHYL ACETATE IN 10% ACETONE

Time, Min.	Run 1 Resistance in Ohms	Time, Min.	Run 2 Resistance in Ohms	Time, Min.	Run 3 Resistance in Ohms
0	568	0	622	0	630
2	725	2	789	2	799
3	779	3	848	3	857
4	823	4	899	4	912
5	869	5	939	5	964
6	903	6	984	6	1009
8	968	8	1054	8	1082
10	1019	10	1115	10	1148
12	1069	12	1163	12	1193
14	1103	14	1207	14	1240
18	1167	16	1243	16	1284
20	1189	18	1279	18	1320
22	1211	20	1302	20	1351
24	1231	22	1330	22	1371
26	1247	24	1354	24	1390
		26	1373	26	1410
			Run 1	Run 2	Run 3
	Slope (min.^{-1})		0.23761	0.21000	0.21760
	Concentration (mole l.^{-1})		0.01024	0.00915	0.09355
	k_2 (1. mole $^{-1}$ min. $^{-1}$)		23.20	22.93	23.28

TABLE XXIV
 SAPONIFICATION OF METHYL ACETATE IN 15% ACETONE

Time, Min.	Run 1 Resistance in Ohms	Time, Min.	Run 2 Resistance in Ohms	Time, Min.	Run 3 Resistance in Ohms
0	590	0	550	0	570
2	738	2	710	5	867
3	786	3	753	6	901
4	830	4	792	8	970
5	870	5	833	10	1020
6	907	6	867	12	1060
8	970	8	926	14	1095
10	1021	10	974	16	1126
12	1059	12	1017	18	1156
14	1097	14	1051	20	1180
16	1127	16	1080	22	1200
18	1151	18	1105	24	1214
20	1172	20	1125	26	1227
22	1192	22	1144		
24	1210	24	1160		
26	1227	26	1174		
			Run 1	Run 2	Run 3
	Slope (min.^{-1})		0.22398	0.24328	0.23572
	Concentration (mole l.^{-1})		0.01087	0.01153	0.01102
	k_2 ($\text{l. mole}^{-1} \text{min.}^{-1}$)		20.60	21.10	21.39

TABLE XXV

SAPONIFICATION OF n-BUTYL ACETATE IN 5% ACETONE

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	567	0	566
2	638	2	637
4	674	4	672
6	719	6	718
8	756	8	754
10	790	10	788
15	866	15	864
21	938	21	935
25	980	25	978
30	1021	30	1020
35	1051	35	1049
40	1080	40	1078
45	1109	45	1107
51	1132	51	1130
55	1153	56	1151
60	1170	60	1070
70	1200	70	1198
		Run 1	Run 2
	Slope (min.^{-1})	0.08650	0.09487
	Concentration (mole l.^{-1})	0.00946	0.00949
	k_2 ($\text{l. mole}^{-1} \text{ min.}^{-1}$)	9.11	9.18

TABLE XXVI

SAPONIFICATION OF n-BUTYL ACETATE IN 10% ACETONE

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	578	0	577
3	667	3	668
5	707	5	711
7	747	7	750
10	807	10	809
12	839	12	841
15	883	15	886
20	949	20	951
25	999	25	1001
30	1040	30	1043
35	1073	35	1077
40	1106	40	1110
45	1130	45	1134
50	1153	50	1158
60	1191	60	1198
		Run 1	Run 2
	Slope (min. ⁻¹)	0.08640	0.08650
	Concentration (mole l. ⁻¹)	0.01033	0.01049
	k_2 (l. mole ⁻¹ min. ⁻¹)	8.34	8.25

TABLE XXVII
 SAPONIFICATION OF n-BUTYL ACETATE IN 15% ACETONE

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	671	0	671
3	766	3	760
5	807	4	804
7	852	7	848
10	910	10	907
12	947	12	943
15	996	15	993
18	1061	18	1058
20	1119	20	1116
25	1170	25	1168
30	1189	30	1187
35	1208	35	1206
40	1240	40	1239
45	1270	45	1269
50	1299	50	1299
62	1346	60	1339
		Run 1	Run 2
	Slope (min. ⁻¹)	0.07560	0.07570
	Concentration (mole l. ⁻¹)	0.00957	0.00955
	k_2 (l. mole ⁻¹ min. ⁻¹)	7.90	7.92

TABLE XXVIII

SAPONIFICATION OF METHYL n-BUTYRATE IN 5% ACETONE

Time, Min.	Run 1 Resistance in Ohms	Time, Min.	Run 2 Resistance in Ohms
0	484	0	501
4	618	4	634
6	665	6	687
8	708	8	732
10	738	10	774
12	785	12	812
14	820	14	844
16	849	16	874
20	898	20	924
25	950	25	979
30	988	30	1019
35	1022	35	1059
40	1052	40	1091
50	1096	50	1135
		Run 1	Run 2
	Slope (min. ⁻¹)	0.12049	0.11691
	Concentration (mole l. ⁻¹)	0.01137	0.01105
	k_2 (l. mole ⁻¹ min. ⁻¹)	10.60	10.58

TABLE XXIX

SAPONIFICATION OF METHYL *n*-BUTYRATE IN 10% ACETONE

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	529	0	530
4	657	4	659
6	707	6	709
8	756	8	757
10	798	10	798
12	836	12	839
14	866	14	867
16	900	16	901
20	947	20	951
25	999	25	1002
30	1042	30	1046
35	1080	35	1082
40	1111	40	1113
45	1140	50	1162
50	1160		
		Run 1	Run 2
	Slope (min. ⁻¹)	0.10870	0.10889
	Concentration (mole l. ⁻¹)	0.01136	0.01128
	k_2 (l. mole ⁻¹ min. ⁻¹)	9.57	9.65

TABLE XXX

SAPONIFICATION OF METHYL *n*-BUTYRATE IN 15% ACETONE

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	551	0	548
4	686	4	677
6	740	6	730
8	786	8	777
10	825	10	820
12	862	12	858
14	898	14	889
16	930	16	921
18	955	20	975
26	1046	25	1028
30	1077	30	1070
35	1116	35	1107
40	1146	40	1137
50	1190	55	1207
		Run 1	Run 2
Slope (min.^{-1})		0.11176	0.10882
Concentration (mole l.^{-1})		0.01195	0.01221
k_2 ($\text{l. mole}^{-1} \text{min.}^{-1}$)		9.32	8.91

TABLE XXXI

SAPONIFICATION OF METHYL ACETATE IN 5% DIMETHYL SULFOXIDE

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	512	0	518
4	750	4	752
6	818	6	823
8	877	8	879
10	927	10	930
12	970	12	971
14	1001	14	1004
16	1030	16	1033
18	1058	18	1059
20	1078	20	1080
22	1094	22	1096
24	1107	24	1110
		Run 1	Run 2
	Slope (min.^{-1})	0.24060	0.23636
	Concentration (mole l.^{-1})	0.01092	0.01075
	k_2 ($\text{l. mole}^{-1} \text{min.}^{-1}$)	22.03	21.97

TABLE XXXII

SAPONIFICATION OF METHYL ACETATE IN 10% DIMETHYL SULFOXIDE

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	580	0	550
4	853	4	825
6	934	6	899
8	998	8	969
10	1057	10	1020
12	1099	12	1061
14	1137	14	1099
16	1168	16	1130
18	1197	18	1156
20	1213	20	1176
22	1237	22	1194
24	1255	24	1213
		Run 1	Run 2
Slope (min.^{-1})		0.26087	0.27222
Concentration (mole l.^{-1})		0.01059	0.01124
k_2 ($\text{l. mole}^{-1} \text{min.}^{-1}$)		24.63	24.20

TABLE XXXIII

SAPONIFICATION OF METHYL ACETATE IN 15% DIMETHYL SULFOXIDE

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	689	0	629
4	1015	4	946
6	1105	6	1037
8	1184	8	1101
10	1247	10	1170
12	1298	12	1220
14	1342	14	1260
16	1382	16	1291
18	1411	18	1320
20	1442	20	1341
22	1464	22	1362
24	1478	24	1382
		Run 1	Run 2
	Slope (min.^{-1})	0.25217	0.27727
	Concentration (mole l.^{-1})	0.00992	0.01083
	k_2 ($\text{l. mole}^{-1} \text{min.}^{-1}$)	25.41	25.58

TABLE XXXIV

SAPONIFICATION OF n-BUTYL ACETATE IN 5% DIMETHYL SULFOXIDE

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	577	0	525
5	702	5	640
7	739	7	674
10	794	10	721
12	824	12	750
15	863	15	785
18	900	18	816
20	922	20	833
25	965	25	872
30	1004	30	904
35	1034	35	928
40	1062	40	950
52	1111	50	983
60	1133	60	1009
		Run 1	Run 2
Slope (min. ⁻¹)		0.86667	0.94286
Concentration (mole l. ⁻¹)		0.09874	0.01074
k_2 (l. mole ⁻¹ min. ⁻¹)		8.77	8.78

TABLE XXXV

SAPONIFICATION OF n-BUTYL ACETATE IN 10% DIMETHYL SULFOXIDE

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	610	0	610
3	710	3	705
5	757	5	754
7	801	7	798
10	860	10	857
12	892	12	890
15	939	15	936
18	976	18	973
21	1009	21	1005
25	1050	25	1048
30	1091	30	1089
35	1121	25	1119
40	1149	40	1148
50	1191	50	1189
60	1227	60	1225
		Run 1	Run 2
Slope (min. ⁻¹)		0.09565	0.95313
Concentration (mole l. ⁻¹)		0.01021	0.01020
k_2 (l. mole ⁻¹ min. ⁻¹)		9.38	9.34

TABLE XXXVI

SAPONIFICATION OF n-BUTYL ACETATE IN 15% DIMETHYL SULFOXIDE

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	686	0	660
5	821	5	800
7	860	7	844
10	916	10	897
12	948	12	929
15	985	15	972
18	1022	18	1008
20	1043	20	1028
25	1086	26	1079
30	1121	30	1107
35	1149	35	1135
40	1172	40	1158
50	1208	50	1197
60	1234	60	1225
		Run 1	Run 2
Slope (min. ⁻¹)		0.09090	0.09483
Concentration (mole l. ⁻¹)		0.01006	0.01042
k_2 (l. mole ⁻¹ min. ⁻¹)		9.04	9.10

TABLE XXXVII

SAPONIFICATION OF METHYL n-BUTYRATE IN 5% DIMETHYL SULFOXIDE

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	485	0	490
5	664	5	673
7	714	7	724
9	756	9	766
11	796	11	807
13	831	13	842
15	864	15	875
18	903	18	913
20	927	20	936
25	978	25	987
30	1017	30	1025
35	1049	35	1057
40	1080	40	1088
50	1122	50	1130
		Run 1	Run 2
Slope (min. ⁻¹)		0.13793	0.14048
Concentration (mole l. ⁻¹)		0.01125	0.01105
k_2 (l. mole ⁻¹ min. ⁻¹)		12.26	12.71

TABLE XXXVIII

SAPONIFICATION OF METHYL n-BUTYRATE IN 10% DIMETHYL SULFOXIDE

	Run 1		Run 2		Run 3	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms	
0	568	0	570	0	570	
4	702	4	712	4	710	
5	728	5	741	5	740	
7	785	7	797	7	795	
9	829	9	854	9	852	
11	870	11	898	11	897	
13	908	13	936	13	935	
15	939	15	968	15	968	
18	981	18	1014	18	1015	
20	1007	20	1040	20	1041	
25	1060	25	1106	25	1105	
30	1102	30	1144	30	1144	
35	1135	35	1185	35	1188	
40	1163	40	1212	40	1215	
50	1208	50	1262	50	1265	
			Run 1	Run 2	Run 3	
Slope (min. ⁻¹)			0.11739	0.12162	0.11667	
Concentration (mole l. ⁻¹)			0.01098	0.01072	0.01084	
k_2 (1. mole ⁻¹ min. ⁻¹)			10.69	11.34	10.76	

TABLE XXXIX

SAPONIFICATION OF METHYL *n*-BUTYRATE IN 15% DIMETHYL SULFOXIDE

Run 1		Run 2	
Time, Min.	Resistance in Ohms	Time, Min.	Resistance in Ohms
0	658	0	638
4	835	4	799
5	868	5	829
7	930	7	887
9	986	9	935
11	1038	11	979
13	1085	13	1021
15	1125	15	1054
18	1175	18	1098
20	1207	20	1127
25	1272	25	1181
30	1327	30	1228
35	1367	35	1265
40	1409	41	1296
50	1459	50	1339
		Run 1	Run 2
Slope (min. ⁻¹)		0.12286	0.12105
Concentration (mole l. ⁻¹)		0.01039	0.01062
k_2 (l. mole ⁻¹ min. ⁻¹)		11.83	11.40

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