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Wallace Wyman Stuart
University of Massachusetts Amherst

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A STUDY OF THE EFFECT OF NEUTRAL SALTS UPON THE DISSOCIATION OF BENZOIC ACID BY MEANS OF THE CATALYTIC DECOMPOSITION OF ETHYL DIAZOACETATE

STUART - 1935

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Wallace W. Stuart

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CONTENTS

Introduction

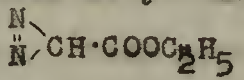
The accurate measurement of hydrogen ion concentation has long been an important phase of Chemistry; and one upon which much work has been done. In the case of strong acids(acids which are, at moderate concentration, 100% dissociated) the determination is relatively simple, since it is assumed that total acidity is a direct measure of hydrogen ion concentration, and since the effects of neutral salts are manifested in a relatively simple manner. However, in the case of weak, partially ionized acids the problem becomes more complicated.

There are three general methods by means of which hydrogen ion concentration of a solution may be measured, viz., potentiometrically, by means of the hydrogen electrode or some other electrode, as the quinhydrone electrode, referred to the hydrogen electrode as standard, colorimetrically by means of indicators and catalytically by means of suitable reactions catalyzed by the oxonium ion(H_3O^+).

It is purposed in this work to study the ionization of benzoic acid in solutions of varying ionic strength, measuring the concentration of H_3O^+ catalytically by means of the decomposition of ethyl diazoacetate, and to ascertain what relationship, if any, exists between the ionization constant of the acid and the total ionic strength of the solvent medium.

REVIEW AND DISCUSSION OF LITERATURE

I. Ethyl Diazoacetate

Curtius(1)reported the synthesis and general organic properties of a compound which he called ethyl diazoacetate, and to which he ascribed the formula  $\overset{N}{\underset{N}{\|}}\rangle CH\cdot COOC_2H_5$. In discussing the properties of the compound in this and in a subsequent paper(2,3), Curtius called attention to the fact that the diazo esters react with water with the evolution of nitrogen gas and the formation of the corresponding hydroxy acid in accordance with the equation:

$$N_2CH.COOC_2H_5 + H_2O = HOCH_2COOC_2H_5 + N_2$$

Almost simultaneously Traube(4) published an account of his work with diazo compounds, his investigations being similar to ~~that~~ those of Curtius.

Following the lead indicated by Curtius, subseqent workers have made use of the acid catalyzed decomposition of the ester in water solution as a means by which to measure hydrogen ion concentration, investigations being made largely from a kinetic rather than an organic standpoint.

In a comprehensive series of experiments, Fraenkel(6,5), by measuring the volume of nitrogen evolved, established beyond question that the reaction follows the unimolecular law and that the rate of reaction is strictly proportional to the hydrogen ion concentration. As a result of his experiments covering a wide range of concentration and using ten differant acids as catalysts, he showed the close parallel between the acid catalyzed inversion of sucrose and the decomposition of ethyl diazoacetate, pointing out the much greater sensitivity of the diazo reaction compared to the more common sugar inversion. Hydrogen ion concentrations as low as .0002 M..were measured. Fraenkel also reported that, when catalyzed with the halogen acids or sulfuric acid, a side reaction occurs, using up the catalyst; and as a consequence the reaction may cease altogether before the diazo ester is entirely decomposed. The reaction constant,K, when divided by the hydrogen ion concentration gave a value,K_H, which he called the catalytic constant and which was found to be independant of the kind of acid used. The value of the diazo reaction in the measurement of hydrogen ion concentration lies in the fact that K_H may be determined using a strong acid in which the hydrogen ion concentration is known to be equivalent to the total concentration of acid, and then, by means of the relationship

$$[H^+] = \frac{K}{K_H}$$

where K is the reaction constant, experimentally determined, the hydrogen ion concentration of the solution of a weak acid may be calculated. Actually the problem is not as simple as this, since in all except very dilute solutions, the ionic strength of the medium may introduce "salt errors". This phase will be discussed at greater length in suceeding sections.

Bredig and Ripley (7) confirmed the work of Fraenkel, observing a side reaction in the case of nitric as well as hydrochloric and sulfuric acids. A the result of a more detailed study of the nature of the side reaction, these investigators concluded that the side reaction might be represented by the equation:

$$N_2CHCOOC_2H_5 + H^+ + NO_3^- = CH_2(O\cdot NO_2)COOC_2H_5 + N_2$$

when nitric acid is the catalyst.

Because of its extreme sensitivity to hydrogen ion catalysis, Spitalsky (8) employed the diazo reaction in his study of the hydrolysis of potassium dichromate. In this work hydrogen ion concentrations as low as .000098 moles per liter were measured. Cumming (9) employed it for the same reason in his study of amphoteric electrolytes.

As a result ~~of his~~ own investigations and a study of the work of Bredig and Ripley, Otto Munn (10) postulated the following mechanism for the decomposition of ethyl diazoacetate in water:

$$\begin{tikzcd}
C_2H_5OOC\cdot CH\overset{N}{\underset{N}{\|}} + H^+ + OH^- \arrow[r, leftrightharpoons] & C_2H_5OOC\cdot CH_2N\equiv N^+ + OH^- \arrow[d, shift left] \\
 & C_2H_5OOC\cdot CH_2N=NOH \arrow[u, shift left] \arrow[d] \\
 & C_2H_5OOC\cdot CH_2OH + N_2
\end{tikzcd}$$

the first two reactions being rapid and reversible, while the final irreversible reaction being slow determines the velocity of the decomposition. He also proposed a similar mechanism for the side reaction observed by Fraenkel and Bredig and Ripley.

In studying the reaction kinetics of strong acids and the nature of the hydrogen halides, Hantzsbh (11), and Hantzsch and Weisberger (12) made use of the diazo reaction. They observed the similarity between the diazo reaction and the sucrose inversion reaction.

The effect of temperature upon the decomposition of ethyl diazoacetate was reported by St~~r~~audinger and Hirzel (13) as a part of their general study of diazo compounds.

More recently, the diazo reaction has been utilized by Brönsted and his coworkers in their study of the kinetic salt effect. An extended review and discussion of their work will be given as a part of the following section on the kinetic salt effect.

II. The Kinetic Salt Effect

Since 1887, when Arrhenius(14,15,16)in his classical study of the inversion process, showed that kinetic experiments may be profoundly effected by the presence of neutral salts, the effect of salts upon reaction velocity has intrigued the chemist. Following Arrhenius' announcement many tentative explanations(17,18,19 of the so-called neutral salt effect have been advanced, only to crumble under more rigorous examination and experimentation. As exemplifying this type of explanation may be mentioned the "hydration theory" of Caldwell (19), who attempted to explain the increasing effect of neutral salts upon the inversion of sucrose by the increase in concentration of the reactants because the formation of hydrates decreased the amount of free water in the solution.

However, little real progress was made toward a satisfactory explanation of the problem until the important Debye-Hückel (22) paper was published in 1923 and the results of J.N.Brönsteds kinetic studies were presented in a series of papers which together comprise the so-called Brönsted Theory of kinetic salt effects.

To account for observed deviations from the classical Mass Action Law, and also as a result of thermodynamic reasoning G.N.Lewis $\overset{21}{(20)}$ in 1901 introduced the activity concept, according to which the activity, a, of an ion is related to the concentration c, by the expression

$$a = fc \qquad :1:$$

where f is the activity coefficient of the ion. In a brilliant mathematical paper published by Debye and Hückel(22) in 1923, the activity coefficient was shown to depend upon the nature of the solvent, the number of unit charges on the ion and the concentration of electrolyte in the solution. Specifically,

$$-\log f = Az^2\sqrt{u} + Bu \qquad :2:$$

where $\underline{z}$ is the number of unit charges on the ion, $\underline{B}$ is an empirical constant, $\underline{u}$ is the ionic strength of thessolution, defined as the equivalent concentration of the ions times the average valence

$$u = c\,\frac{Z_1 + Z_2}{2}$$

A is constant for a given temperature and solvent, and has the following value:

$$A = \frac{N^2 e^3 \sqrt{2\pi}}{2.303(10RDT)^{3/2}}$$

where N is Avogadro's number, e is the absolute charge on the electron, D is the dialectric constant of the solvent, R is the gas constant and T is the absolute temperature. When the solvent is water, and the temperature is 25°C., the value of A (23,24) is taken as 0.5, and for a univalent ion, equation :2: may be rewritten

$$-\log f = 0.5\sqrt{u} + Bu \qquad :3:$$

Bronsted(25, 26), in accounting for the effect of neutral salts upon the kinetic process, postulates an intermediate "critical complex", the velocity of the reaction depending upon the concentration of this complex. Let A and B be two reacting molecules and X be the intermediate complex; then

$$A + B \rightleftharpoons X \rightarrow C + D \qquad :4:$$

and the velocity of the changing of A and B into C and D will depend upon the concentration of X which, in turn, is in equilibrium with A and B. In other words

$$V \propto C_x \qquad :5:$$

where V is the velocity and C_x is the concentration of X. The thermodynamic mass action expression for the reaction of A and B to give X may be stated thus:

$$K_m = \frac{a_x}{a_A a_B} = \frac{C_x f_x}{C_A f_A C_B f_B} \qquad :6:$$

where the a's, C's and f's have the usual meanings.

From :6: we have

$$C_x = K_m \frac{C_A f_A C_B f_B}{f_x} \qquad :7:$$

and sustituting the value of C_x so obtained in :5:, we get

$$V \propto C_A C_B \frac{f_A f_B}{f_x} K_m \qquad :8:$$

or

$$V = K C_A C_B \frac{f_A f_B}{f_x} \qquad :9:$$

It becomes immediately apparent from an inspection of :9:, which is the general equation derived by Bronsted to express the velocity of a reaction, that the velocity of a reaction may, in general, be altered in two ways.

That the addition of a neutral salt exercises a profound effect upon the activity coefficient of an ion has already been shown. Thus, by directly changing the value of the expression $\frac{f_A f_B}{fx}$ in equation :9: by the addition of a neutral salt, the velocity of the reaction will be altered. The changing of the velocity of a reaction by changing the activity coefficients of the reactants in the primary reaction is termed by Bronsted the "Primary Salt Effect". Further examination of this phenomenom shows the following rules to be, in general, true:

1. No primary salt effect should be expected in the case of the reaction of an ion with ancuncharged molecule, for, if in equation :4: B is a charged ion, while A is a neatral molecule, then it follows that the charge on B and that on X must be the same, and consequently f_B and f_X should be the same.

It should be noted, however, that this conclusion requires the assumption that the linear term <u>Bμ</u> in equation :3: may be disregarded - an assumption certainly ~~is~~ not justified except in dilute solution, and which is even then open to criticism.

2. The primary salt effect may be positive or negative depending on whether the reaction occurs between ions of like or unlike signs.

The other general way in which the velocity of a reaction may be altered is by changing the concentration of the reactants(C_A or C_B in :9:). When both reactants are furnished by non-electrolytes(unionized) or by strong electrolytes (100% ionized), it is obvious that the addition of neutral salts can have no effect upon the <u>concentration</u> of the reactants, and the only possible salt effect will be of a primary nature. Consider, however, the case in which one of the reactants in the primary reaction is furnished by the dissociation of a weak electrolyte, as for example the weak acid <u>HA</u>. In addition to the primary reaction, there willalso occur a secondary, ionization reaction which may represented as follows

$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \qquad :10:$$

Thus salts, by shifting the equilibrium in this secondary reaction, may alter the concentration of one or both reactants in the primary reaction. This type of salt effect is termed by Bronsted the "Secondary Salt Effect"

I In testing the validity of the general Brönsted theory, and especially the theory of the secondary salt effect, Brönsted and ~~Streeter~~ Teeter (27) made use of the diazo reaction. According to them, the decomposition of ethyl diazoacetate in water, when catalyzed by acid, may be looked upon as a reaction between the uncharged ester molecule and the hydrogen ion to give the intermediate, "critical complex". If A is the diazo molecule,

$$A + H^+ \longrightarrow AH^+$$

from which we may write, in accordance with the Brönsted theory

$$V = KC_A C_{H^+} \frac{f_A f_{H^+}}{f_{AH^+}} \qquad :11:$$

According to these authors, since in *dilute* solutions the activity coefficient of an ion may be assumed to depend only upon the charge upon the ion and the ionic strength, and in no wise upon the specific nature of the ion, and furthermore, since the activity coefficient of an uncharged molecule may, in dilute solution, be looked upon as *one*, it follows that f_{H^+} and f_{AH^+} will be equal, and that f_A will become one in dilute solutions. Reasoning in this way, they rewrote equation :11: in this way:

$$V = K\,C_A C_{H^+} \qquad :12:$$

and from which they concluded that no primary salt effect should be expected in this reaction. They did not test this conclusion.

They next considered the reaction from the standpoint of possible secondary salt effect, as follows. When the reaction is catalyzed by a strong acid, there obviously is no possibility of a secondary salt effect. Consider the case when a weak acid is used. As has already been observed, the addition of a neutral salt may shift the equilibrium in the secondary or ionization reaction in such a manner as to cause an increase in the concentration of hydrogen ions. From this it would be expected that the value of the classical ionization constant

$$K_c = \frac{C_H C_A}{C_{HA}} \qquad :13:$$

for the weak acid, HA, should change upon the addition of a neutral salt. The thermodynamic ionization constant

$$K_a = \frac{C_{H^+} C_{A^-}}{C_{HA}} \cdot \frac{f_{H^+} f_{A^-}}{f_{HA}} \qquad :14:$$

should, however, be a true constant and unchanged by the addition of neutral salts. By assuming f_{H^+} and f_{A^+} to be equal, and making the further assumption that for the uncharged molecule, HA, the activity coefficient in dilute solution is one, equation :14: becomes

$$K_a = \frac{C_{H^+} C_{A^-}}{C_{HA}} \cdot f_1^2 \qquad :15:$$

where f_1 is the activity coefficient of any univalent ion. Reasoning in this manner, Bronsted and Teeter concluded that, when measured by the decomposition of ethyl diazoacetate, the concentration of hydrogen ions furnished by the dissociation of a weak acid should increase steadily upon the addition of a neutral salt, and in consequence the classical ionization constant, K_c, should also increase, but by precisely that amount whereby K_c when multiplied by the square of the activity coefficient should give a true constant, K. These authors studied the decomposition of ethyl diazoacetate by acetic acid in solutions of varying ionic strength of KNO_3 (up to .05 M.) . As shown by Table 1 which contains a summary of their data, they found that, as required by theory, the value of K_c does increase with increased salt concentration. They apparently made no attempt to apply their theory quantitatively; that is, to multiply K_c by f_1^2 and see whether K so obtained would be constant througout the salt range studied. The present author has done this to their data, the results being shown in column 3 of Table 1. The values of the activity coefficients were calculated from the Debye-Hückel limiting law.

Table 1

Conc. of KNO_3	K_cx 10^5	$K_c f_1^2$ x 10^5
0	1.85	1.85
.005	1.94	1.64
.01	2.07	1.64
.02	2.15	1.55
.05	2.30	1.37

The values of $K_c f_1^2$ so obtained are in no sense constant. For this apparent divergence between the experimental and theoretical results, there are several possible explanations.

In the first place, Brönsted and Teeter assumed the total absence of any primary salt effect, i.e. they assumed the activity coefficients of the hydrogen ion and the critical complex to be identical and the activity coefficient of the uncharged diazo molecule to be one. This assumtion necessitates the disregarding of the linear term *Bu* in the general Debye-Hückel equation(equation :3:). In other words, it is necessary to assume that the so-called limiting law is a reasonable approximation of the general Debye-Hückel equation under the conditions of the experiment. Since all concentrations were less than 0.1 M., this assumption was not unreasonable. On the other hand, it is entirely conceivable that the value of *B* may depend upon the specific nature of the ion, and furthermore that it may not be negligible even at concentrations less than 0.1 M., in which case a primary salt effect might be expected to occur. Actually, Brönsted and Duus(28), publishing at a later date, reported a strong primary salt effect in the case of the diazo reaction.

In the second place, Brönsted and Teeter had the same difficulty with a side reaction between the nitrate ion from the salt, the hydrogen ion from the acid and the ethyl diazoacetate as was reported by earlier investigators. This has already beem discussed. Brönsted and Teeter stated that in their calculations only the first portion of the curve was used, presumably before the side reaction manifested itself very strongly. However, since early in the reaction nitrogen will be evolved both as a result of the normal reaction and the side reaction, it is entirely possible that even the first readings may be erroneous. Also, if the reaction constant is calculated in such a manner as to require a final or "a" reading, the value of this reading may be rendered uncertain as a result of the side reaction.

In the third place, the error introduced by assuming the validity of the limiting law in evaluating the quantity $K_c f_1^2$ may not be negligible.

In a more ~~thorough~~ extensive peice of work, Bronsted and King(29), studying the hydroxyl ion catalysis of the decomposition of nitrso-triacetone-amine, first evaluated the primary salt effect in the reaction by using the strong base, NaOH, as catalyst. By correcting the total salt effect observed when the catalyst was a weak base for the primary salt effect, they were then able to separate the two effects. However, they also were only interested in showing that the reaction did substantiate the theory in a rough, qualitative manner; they made no attempt to treat their results in a precise, mathematical way.

From this it appeared that a thorough and significant study of the effect of added neutral salts upon the ionization of a weak acid by means of the diazo reaction would necessitate, first, the measurement of the primary salt effect, using a strong acid as catalyst, secondly, measurement of combined primary and secondary salt effects, using a weak acid as catalyst and in the third place, such a choice of acids and salts as would, if possible, preclude the occurence of a side reaction.

III. The Calculation of Reaction Rate Constants

In a study of this nature, considerable importande attaches itself to the method used in the calculation of the reaction rate. Until recently the usual expression from which the reaction constant, k, of a first order reaction was calculated was

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \qquad :16:$$

in which t is the time, a is the initial concentration and x is the amount changed at time t.

As early as 1911 Rosanoff, Clark and Sibley(30)observed that a small error in ascertaining the value of a may cause a decided error in the value of k as calculated above. The usual method of determining a was to let the final reading, after complete reaction, represent the initial concentration of the reactant. These authors recommended a method of extrapolation in the determination of a. Table 2, taken from their work, is presented to show the decided influence of a upon a rate constant calculated as above.

Apropos, the work of Brönsted and Teeter, published in 1924, was doubtless calculated by a formula similar to :16: When it is recalled that Fraenkel found incomplete evolution of nitrogen to be characteristic of the side reaction, and that a in the above equation is based upon the total amount of nitrogen evolved, another possible explanation of the failure of the data of Bronsted and Teeter to follow the theoretical laws becomes apparent.

Roseveare(31) has made an exhaustive study of the calculation of rate constants, in which he observes that an equation of the type given above(equation :16:) gives unjustifiable weight to the value of a unless it is known with much greater precision than the values of x. Because of the nature of the diazo reaction, the a value is probably the least reliable.

He also shows that where the value of k is determined from an arithmetic average of several values obtained by the

Table 2

(From Rosanoff, Clark and Sibley(30)

T (min.)	a	k^1	$k^{\frac{1}{2}}$
0	65.09°	----	------
7	65.18(?)	.0000302	------
10	65.14(?)	258	-------
24	64.96	195	.0000275
38	64.88	151	280
55	64.80	119	269
72	64.71	106	269
98	64.58	95	266
296	63.38	79	297
400	62.89	73	283
430	62.81	70	270
1500	57.20	67	281
	-20.28		

Data from rate of inversion of cane sugar.

k^1 calculated from <u>a</u> obtained in usual way. <u>a</u> = 65.36°

$k^{\frac{1}{2}}$ " " " " by Rosanoff, Clark and Sibley

by extrapolation. <u>a</u> = 65.09°

so-called"interval formula"

$$k = \frac{2.303}{T_n - T_{n-1}} \log\frac{(a-x_{n-1})}{(a-x_n)} \qquad :17:$$

the final value will be determined by the average of only the first and last values, all intervening values cancelling out.

Guggenheim(32) has devised a method of calculating rate constants for first order reactions which eliminates entirely the "*a*" value. If a series of readings(for example, changes in nitrogen pressure) are taken without regard as to interval, these readings to be designated the *v* readings, and if a second series of readings, *v'*, are taken in such a manner that there is always a constant time interval, *p*, between the *v* readings and the corresponding *v*& readings, then, according to Guggenheim, the straight line obtained by plotting log(v&-v) against the time *T* will have a slope -k log e, *k* being the reaction constant.

Since this method of calculation requires no final or end reading (*a* value), which may be decidedly inexact in this particular reaction, it is especially suited to the reaction being studied, and,except where noted for some particular reason, it is the method of calculation used throughout this study.

PRELIMINARY EXPERIMENTATION

I. The Apparatus

The designing and construction of the apparatus to be used was an essential part of this work. Briefly, the mechanical aspect of the problem was to devise an apparatus which would immediately record extremely small changes of pressure and which would give reproducible results. The problem was further complicated by the tendency for nitrogen to form supersaturated solutions, increasing the solubility of the gas several thousand times with the consequent introduction of major errors. To prevent supersaturation of nitrogen in the reaction mixture it ## was required that the reaction mixture be thoroughly agitated throughout the entire course of a "run". With these requirements in mind, several differant types of apparatus and many modifications of these types were tried before a satisfactory form was evolved.

The first type tried was that described by Harned(18) and used by him in investigating the rate of decomposition of H_2O_2 by the measurement of volume of oxygen evolved. This apparatus was later modified by Launer(33) who adapted it to use it in studying rate of reaction of pemanganate and oxalate by measuring the pressure of the CO_2 evolved . The Launer apparatus , as well as several minor modifications of the same, proved unsatisfactory for this work - and so it will not be further dicussed here except to point out some outstanding objections to it.

Bothe Harned and Launer used the commom mercury seal stirrer to agitate the reaction mixture. Since all pressure measurements are predicated upon constant volume, the change in volume due to increased pressure forcing the mercury back into the outer cup of the stirrer introduced a constant source of error. In one og the modifications of this apparatus tried, the stirrer was replaced by a shaking device to insure agitation. The pressure was measured by means of an open end water manometer. This arrangement is susceptible to changes in atmospheric pressure, for which a correction must be made. In many cases the correction factor amounted to one third of the total reading. Reaction constants obtained by the use of this apparatus were not satisfactory for a precise examination of the effect of salts. The apparatus was finally discarded.

An apparatus resembling that used by Brönsted and King(29) in their study of the decomposition of nitroso-triacetone-amine was more satisfactory. Several changes were found to be desirable. A short peice of thick-walled capillary rubber tubing was sustituted for the fine glass spring described by these authors to connect the reaction flask, which must be shaken vigorously, and the manometer, which is stationary. This arrangement was more convenient, facilitating cleaning and filling the the reaction flask; it was found by experimentation to have no discernible effect on the reaction constant. A minor change in the design of the manometer allowed the elimination of one stopcock, while the reaction flask was redesigned, being made with two bulbs instead of one ~~bulb~~. This type of reaction flask was very satisfactory in that the upper bulb prevented the splashing of the reaction mixture up into the side arm where it would act as a liquid valve. The apparatus of Bronsted and King as modified for the purpose of this experiment is shown diagramatically in Fig.1. The reaction mixture was introduced into flask F, which was then sealed by means of a parafin soaked cork stopper and molten paraffin. With stopcock E open the entire system was partially evacuated through T. E was then closed and the evacuation continued until the mercury column rose to the bottom of scale C. An old Beckmann thermometer scale was found to be especially suitable for the measurement of small pressure changes. The reaction flask was then rapidly shaken by means of an electric motor. The form of apparatus just described was used in that part of the experimental work dealing with the effect of potassium nitrate on the dissociation of benzoic acid and the primary salt effect of potassium perchlorate. It will susequently be referred to as apparatus A.

It was found, however, that the evacuation of the reaction flask was not necessary. Preliminary runs showed very definitely that the value of the reaction constant was not effected by the evacuation of the reaction flask. With this established, it was possible to further simplify the apparatus by the elimination of the remaining two stopcocks, which at high vacuums showed some tendency to leak. The simplified apparatus also had other advantages. The mercury in the manometer column, as well as the capillary tube, showed less tendency to become fouled, since they were completely sealed from outside contamination. The sealing of the reaction flask was rendered easier and more certain than when it was evacuated. The simplified apparatus, shown in fig. 2b, was used throughout the remainder of the research, and proved to be more satisfactory than that shown in fig.1. The lower bulb (A in fig.2b) was about half filled with redistilled mercury and a high vacuum pump applied to the upper end of the manometer column. When the pressure had been reduced to less than 5 mm., the tube, E, was sealed off just above the upper bulb, B. The manometer was connected to the reaction flask by means of thick walled rubber tubing in the same manner as apparatus A and the whole apparatus immersed in the thermosthat bath as shown in the figure.

As has been already pointed out, the reaction mixture must be thoroughly agitated to prevent supersaturation. For this purpose, the reaction flask was fastened to a rack, and this frame shaken by means of the arrangemennt shown in fig.2a. Several investigators (34,35) have studied the effect of rate of shaking upon the evolution of gasses from supersaturated solutions, and have shown that there is a certain optimum rate rate of shaking which depends upon the size and shape of the flask containing the reaction mixture. Faster or slower rates of shaking decrease the evolution of nitrogen by increasing supersaturation. From this it is apparent that while it is best to have the shaking machine run at the optimum rate, it is imperative that it run at a constant rate. In the first experiments a small 1/50 H.P. electric motor was used. It was soon found, however, that the load was too heavy for this size

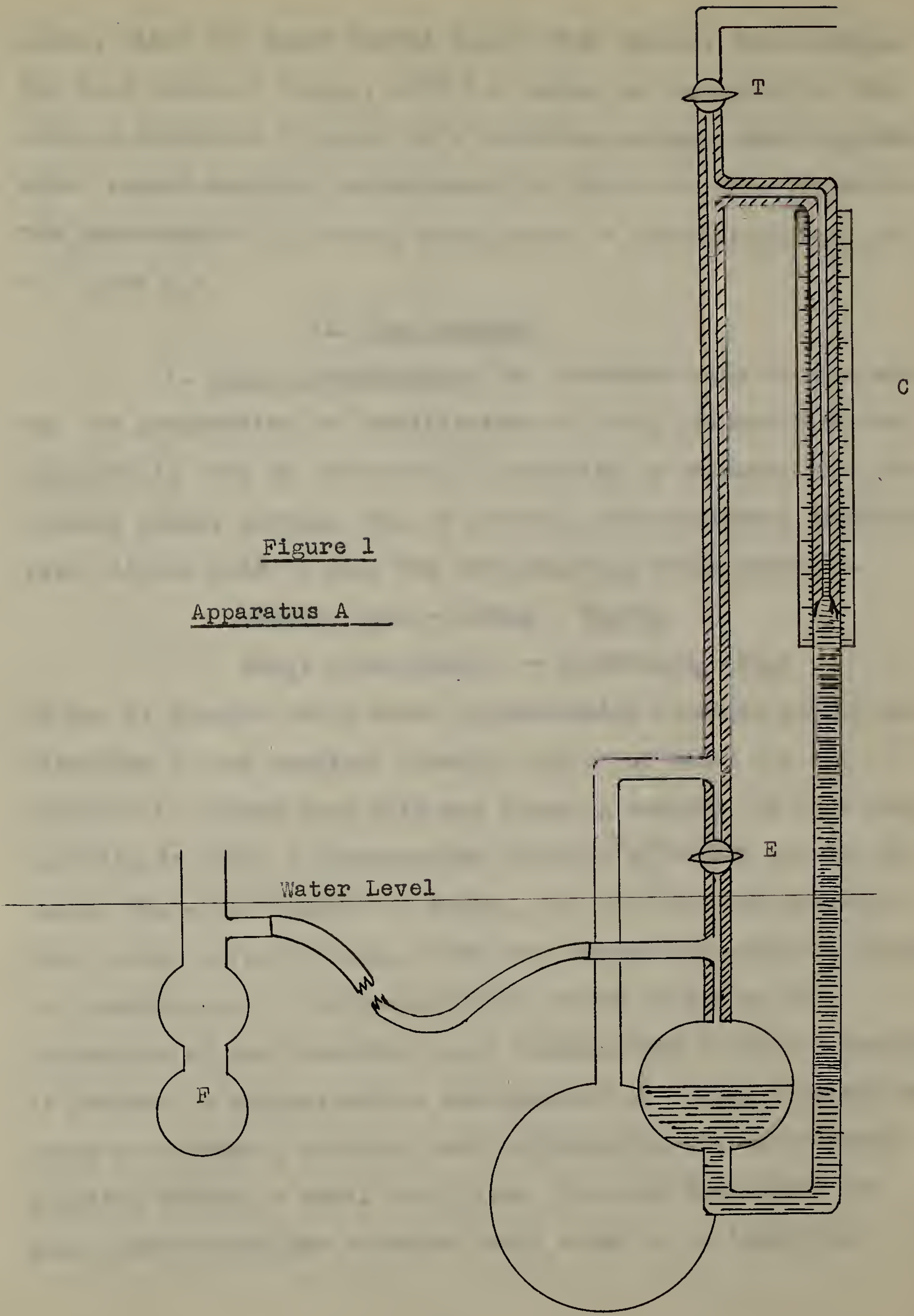


Figure 1

Apparatus A

motor, since the speed varied widely with current fluctuations. For this reason a larger, 1/12 H.P. motor was connected to the shaking apparatus by means of a reduction pulley, an arrangement which proved entirely satisfactory and which was used throughout the experiment. The shaking arrangement is shown diagrammatically in figure 2 a.

II. The Reagents

1. Ethyl Diazoacetate. The procedure used in this work for the preparation and purification of ethyl diazoacetate was essentially that of Curtius(2,3) modified by Hantzsch(11). The primary amine, glycine, may be reacted, under suitable conditions, with nitrous acid to give the corresponding diazo compound.

$$2NaNO_2 + H_2SO_4 \rightarrow 2HNO_2 + Na_2SO_4$$

$$HNO_2 + H_2NCH_2COOC_2H_5 \rightarrow N_2CHCOOC_2H_5 + 2H_2O$$

50 gm. of glycine ethyl ester hydrochloride (Eastman Kodak) are dissolved in the smallest possible amount of water and the solution is placed in a salt-ice freezing mixture. To this cold solution is added a concentrated solution of 25 g. of sodium nitrite in water. The whole mixture is cooled, and then treated dropwise with dilute sulfuric acid. After each successive addition of acid the resulting milky white turbidity, which is due to the separation of the insoluble ethyl diazoacetate in minute droplets, is removed by shaking with a small amount of ether, in which the ester is extremely soluble, and then decanting the ether-ester solution through a small dry filter. The acid treatments and ether extractions are repeated until there is no longer any

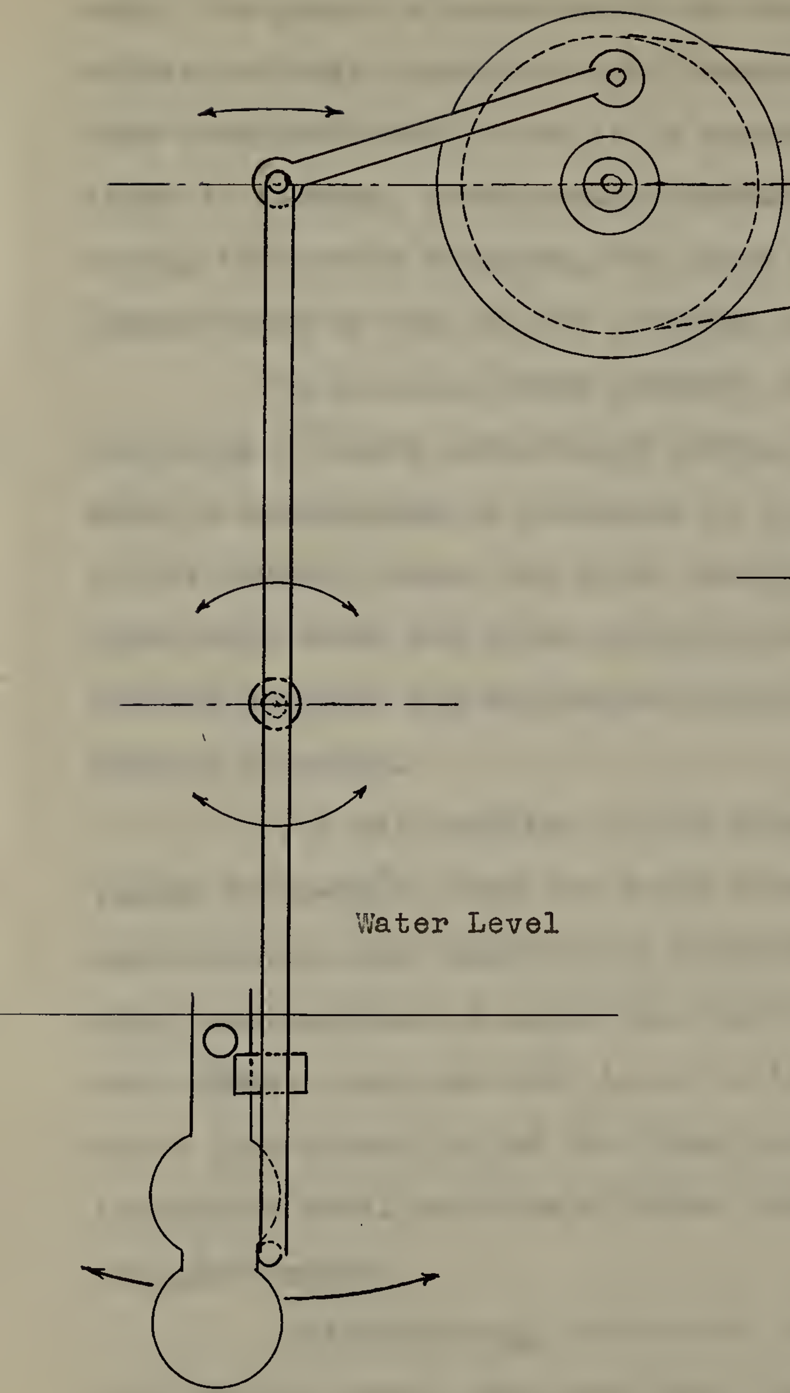


Figure 2 a

The Shaking Apparatus

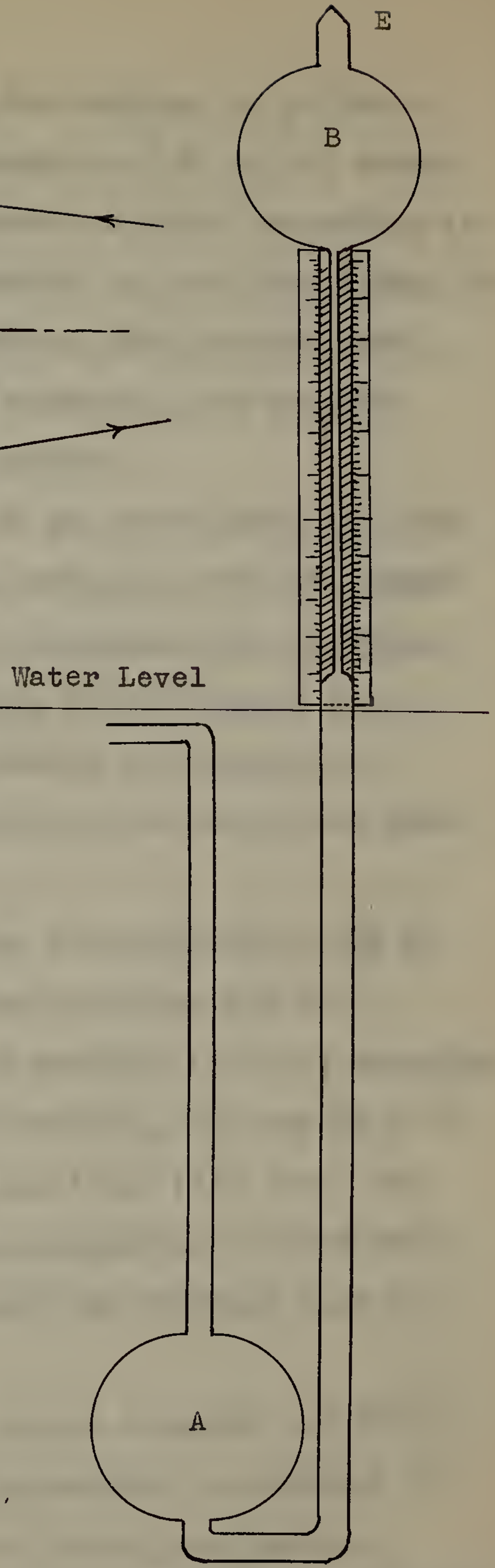


Figure 2 b

Apparatus B

separation of ethyl diazoacetate upon the addition of sulfuric acid. The yield is increased by the addition of 15 gm. of sodium nitrite at this point. The acid treatment and ether extraction is then continued until there is no separation of the diazo ester, but there is instead, considerable formation of free nitrous acid. During the entire reaction, the flask containing the reaction mixture must be kept in the freezing mixture.

The combined ether extracts of the crude ester are then washed with a dilute solution of sodium carbonate until all excess acid is neutralized as indicated by a persistent red coloration of the aqueous phase. The ether solution is then washed three times with water and dried by brief shaking with anhydrous calcium chloride and subsequent standing for 24 hours over fresh calcium chloride.

The main portion of the ether is distilled off ## in vacuum at 30-35°C. from the dried ether solution, and the concentrated ether solution is further purified by being saturated with pure anhydrous ammonia gas. Upon standing for from 24 to 48 hours ### a dark red oily layer of impurities will form. The clear golden solution of the ester is decanted and washed with successive small portions of water until the washings show no trace~~s~~ of ammonia.

After drying, first over calcium chloride and then over calcium oxide, the pure ethyl diazoacetate is obtained by direct vacuum distillation over calcium oxide, the portion boiling at 49.5-50.5°C.(16mm.) being collected in a flask immersed in a freezing mixture.

Since granular calcium chloride shows a strong tendency to adsorb ethyl diazoacetate, the adsorbed material resisting even repeated washing with ether, all calcium chloride used for drying the ester solutions should first be fused.

The pure ethyl diazoacetate solution may be kept for several months unchanged in a refrigerator.

Since the preparation was to be used for kinetic experiments, the emphasis was placed upon a pure product rather than a high yield. For this reason, whenever it was a question of increasing the yield at the expense of the purity of the product, the yield was always sacrificed. The theoretical yield based upon mass relationships is 83.8% of the weight of ethyl ester of glycine hydrochloride taken. Because of the nature of the reaction this yield may not be obtained. Fraenkel(35) and Vanino(36) reported yields of 25 gm. of pure ester from 50 gm. of hydrochloride, corresponding to a yield of 60% of the theoretical. The following data are a summary of the yields obtained in three distinct syntheses of the compound:

Wt. of glycine ethyl ester hydrochloride - -	150 gm.
Theoretical yield of ethyl diazoacetate - -	126 gm.
Actual " " " " - -	76.6 "
Yield (% of theoretical) - - - - - -	60.8%

The degree of purity of the preparation was checked in several ways.

1. The purified ester was unchanged upon several months

standing.

2. There was practically no evolution of nitrogen when the ester was dissolved in pure (conductivity) water. This test indicates the absence of those impurities which would interfere with the use of the preparation for kinetic experiments.

3. There was no appreciable change in the conductivity of a very dilute acid solution upon dissolving ethyl diazoacetate in it. Since the conductivity of a solution is very sensitive to the addition of electrolytes, this test showed the preparations to be relatively free of electrolytes which probably are the only impurities with serious deleterious effect.

4. As a more complete check on the purity of the preparations, a weighed amount of the ester was dissolved in water and quantitatively decomposed by acid. The liberated nitrogen was volumetrically determined, and from a comparison of the percent nitrogen found to the theoretical, a measure of the purity was obtained. The results are given in the following table.

Sample	Vol. N_2	Wt. N_2	wt. sample	%N_2	Theor. %
1	31.49cc.	.0393 gm.	0.1608 gm.	24.46	24.60
2	30.04"	.0376 "	0.1534 "	24.50	24.60

Fraenkel(5) reported percentage of nitrogen for several preparations of ethyl diazoacetate as follows: 24.19, 24.45, 24.25, 24.23 and 24.54.

2. Benzoic Acid Solution. Bakers C.P. Benzoic Acid (sublimed) was resublimed and the properly weighed amount dissolved in carbon dioxide free water and the solution made up to one liter in a calibrated flask. This was not further standardized.

3. Standard Perchloric Acid. Approximately 0.1 N. solution of Bakers C.P. Analyzed(meets A.C.S. Standards) Perchloric Acid(60%) was made up, using conductivity water. This was standardized against pure sodium carbonate, prepared by heating the monohydrate for 36 hours in an oven at 110°C. Dilutions were made from this solution using calibrated volumetric glassware.

4. Standard Salt Solutions were made up by dissolving the proper weight of the salt(Bakers C.P."Analyzed") which had been previously dried to constant weight in an electric oven. Conductivity water(specific conductance less than 3.0×10^{-6}) was used in making all solutions and dilutions.

It was found that the dissolving of basic material from the glass in the case of soft glass bottles was not without appreciable effect on the solutions stored in them, the solutions growing steadily more basic as they were kept. For this reason it was found necessary to use only glass stoppered Pyrex bottles for the storage of reagents.

III. The Experimental Procedure

Although each change in the conditions of the experiment necessitated certain changes in the procedure, the general method of carrying out a "run" may be outlined.

Approximately 25 cc. of pure (conductivity) water, or salt solution of the required concentration, were placed in a small glass stoppered bottle, and in this about nine drops of ethyl diazoacetate were dissolved. It was more convenient to measure the diazo ester by drops rather than weight, since the exact amount of ester used was not important. Exactly 25 cc. of the ester solution were transferred by means of a calibrated pipette to a clean dry receptacle. At all times care was taken to prevent the solutions from dissolving carbon dioxide from the air, since the reaction was sensitive enough to be effected by the carbonic acid formed. Pipettes were protected by a carbon dioxide absorbing tube containing soda-lime.

Exactly the required amount of standard acid solution was added to the accurately measured ester(or ester-salt) solution from a calibrated pipette. The final concentrations of acid and salt were determined from this. This reaction mixture, after thorough stirring, was placed in the reaction flask, and the flask was sealed by means of molten paraffin, as already described. After agitating for about five minutes to insure equilibrium between the dissolved and gaseous nitrogen, the initial reading was made. Readings were then made at five minute intervals for a period of 135 minutes (in some cases the reaction was terminated in 90 minutes).

In most cases the reaction flask was then unsealed, thoroughly washed and dried; in a few cases the reaction wa s allowed to go to completion in order to obtain an end("a") value.

Timing was done by means of a Meylan stopwatch, Laboratory number 11, which had recently (1934) been checked against a seconds pendulum. The height of the mercury column on the scale was read by means of a small telescope. Changes in the temperature of the thermosthat bath were indicated by a Beckmann thermometer which had been "set" by means of a Bureau of Standards calibrated mercury thermometer. The maximum temperature variation was .01°C. on either side of the mean.

The general method of calculation has already been discussed. More specifically, if the first half of the readings are designated the v readings, the last half the v', there results a series of v readings and a corresponding series of v', each of which is separated from the corresponding v reading by a constant time interval, p. By subtracting each v reading from the corresponding v' reading, a series of values, $(v'-v)$, are obtained. The slope of the straight line obtained by plotting $\log(v'-v)$ against the time, when multiplied by log e gives $-k$ where k is the reaction constant. The procedure has been to divide the series of $\log(v'-v)$ values into two equal groups, indicated for purposes of tabulating by a double space in the data ~~####~~, and then to take the arithmetic average of the $\log(v'-v)$ values and the time values for each group. These averages are given on the extreme right of each data sheet. From these values two simultaneous equations are set up, and the slope determined as shown at the bottom of each data sheet.

For each run, the values of log(v'-v) were plotted as abscissae against time as ordinates using a large scale graph. This gave a convenient method of testing the apparatus and to a certain extent the validity of the data, since the result should be a straight line. For obvious reasons it is not possible to include these graphs in this thesis. In a few cases where readings were, from the graph, obviously in error, they were eliminated.

Experimental Data

Presentation, Calculations and Discussion.

For convenience the experimental data are divided into several Parts. A short introduction consisting of a statement of the work attempted and the general conditions under which the work is carried out will be given before each Part. An extended discussion of the results of each Part along with calculations made from the data and results of these calculations will be attempted at the end of each Part.

A few words of explanation concerning the tabulation of data are necessary at this time. The time t is given in minutes; v and v', being simply scale readings, have no units. The double spaceing in the middle of the data sheet divides the $\log(v'-v)$ values into two groups, and for each group the average time and average $\log(v'-v)$ values are given on the extreme right. Readings in parentheses were taken, but were omitted in the calculation because, either as a result of the side reaction already mentioned or because a large scale graph indicated that they were in error.

Part I

The Rate of Decomposition of Ethyl Diazoacetate Catalyzed by Benzoic Acid and in the presence of Potassium Nitrate

In studying the effect of added salt on the reaction rate, the first salt to be tried was potassium nitrate. As already discussed in the review of the literature Brönsted and Teeter (27.) studied the effect of the addition of potassium nitrate on the decomposition of ethyl diazoacetate, when catalyzd by acetic acid. While their results showed qualitative agreement with the theory, a quantitative application of the theory was not so successful. Several possible explanations for this discrepancy were given. More specifically, it was decided to avoid as much as possible the effects of the side reaction which they mentioned by calculating the results from the Guggenheim formula, thus eliminating a very doubtful end reading.

S#####/###/###e Table 3, in which the value of *k* is calculated from the formula, $k = \frac{2.303}{t} \log \frac{a}{a-x}$, gives a series of values for k over a time of 60 minutes. It is immediately apparent that the value of *k* is not constant, but steadily decreases with time, a decrease directly attributable to the side reaction already discussed. The value of *k* calculated from the same data by the Guggenheim method is given in Table 4. This value is seen to be considerably different from that of Table 3.

Since the effect of the side reaction increases in magnitude as the reaction progresses, only the first readings should be used in determining the reaction constant. In most cases the first eight readings were divided into two parts, giving the *v* and *v'* readings. As a result, four values for (v'-v) were obtained, and from these the constant determined in the manner already outlined. While only eight readings were used in the calculation, the remaining readings are given in the data sheets, such readings being inclosed in parentheses.

~~The data contained in this Part are very unsatisfactory; because of the side reaction it is possible to widely vary the value of the constant by simply changing the number of readings used in the calculation. Check results were difficult to obtain, especially in the presence of high salt concentrations. While these data indicate a decided positive salt effect, it was imposible to treat the results quantitatively.~~

Table 3

The Effect of the Side Reaction in Changing the Rate with Time- Decompostion of Ethyl Diazoacetate by Benzoic Acid In the Presence of Potassium Nitrate

Conc. of KNO_3	Conc. Benzoic Acid
0.0833 M.	0.003333 M.

Time	Reading	(a-x)	log(a-x)	k
0	0	5.090	.70672	
5	428	4.662	.66857	.00763
10	782	4.308	.6342	.00724
15	1081	4.009	.6030	.00691
20	1338	3.752	.5743	.00662
25	1583	3.507	.5440	.00647
30	1798	3.292	.5175	.00650
35	1980	3.110	.4928	.00611
40	2144	2.946	.4692	.00593
45	2289	2.801	.4473	.00576
50	2421	2.669	.4263	.00560
55	2549	2.541	.4050	.00548
60	2671	2.410	.3836	.00538

a = 5090

Table 4

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in Presence of .0833 M. KNO_3

Concentration of KNO_3	Conc. of Benzoic Acid
0.0833 M.	0.003333

Time	v	v'	(v'-v)	log(v'-v)	
0	0	13.38	13.38	1.1265	Aver. time 2.5 " log(v'-v) 1.0945
5	428	15.83	11.56	1.0626	
10	782	17.98	10.16	1.0069	Aver. time 12.5 " log(v'-v) 0.9803
15	1081	19.80	8.99	.9537	
20	(13.38)				
25	(15.83)				
30	(17.98)				
35	(19.80)				
40	(21.44)				
45	(22.89)				
50	(24 .21)				
55	(25.49)				
60	(26.71)				

$$\begin{array}{l} 1.0945 = 2.5m - b \\ \underline{0.9803 = 12.5m - b} \end{array}$$

$$.1142 = 10\ m$$

$$m = .01142$$

$$k = .02630$$

Table 5

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of .0833 M. KNO_3

Conc. of KNO_3	Conc. of Benzoic Acid
0.0833	0.003333

Time	v	v'	(v'-v)	log(v'-v)	
0	0	12.35	12.35	1.0917	Aver. time 2.5 " log(v'-v) 1.0619
5	3.81	14.58	10.77	1.0322	
10	7.10	16.59	9.49	.9773	Aver. time 12.5 " log(v'-v) 0.9541
15	9.85	18.38	8.53	.9309	
20	(12.35)				
25	(14.58)				
30	(16.59)				
35	(18.38)				
40	(19.87)				
45	(21.37)				
50	(22.70)				
55	(23.88)				
60	(24.12)				

$$1.0619 = 2.5\,m - b$$

$$\underline{.9541 = 12.5\,m - b}$$

$$.1078 = 10.0\,m$$

$$m = 0.01078$$

$$k = 0.02483$$

Table 6

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of .0417 M. KNO_3

Conc. of KNO_3 0.0417 M.

Conc. of Benzoic Acid 0.003333

Time	v	v'	(v'-v)	log(v'-v)	
0	9.13	21.50	12.37	1.0924	Aver. time 2.5 " log(v'-v) 1.0649
5	12.90	23.80	10.90	1.0374	
10	16.14	25.90	9.76	.9894	Aver. time 12.5 " log(v'-v) .9681
15	19.00	27.85	8.85	.9469	
20	(21.50)				
25	((23.80)				
30	(25.90)				
35	(27.85)				
40	(29.57)				
[illegible]	[illegible]				
[illegible]	[illegible]				
[illegible]	[illegible]				

$$1.0649 = 2.5\ m - b$$

$$.9681 = 12.5\ m - b$$

$$.0967 = 10.0\ m$$

$$m = 0.00967$$

$$k = 0.02227$$

[illegible]

Table 7

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of .0417 M. KNO_3

Conc. of KNO_3
0.0417 M.

Conc. of Benzoic Acid
0.003533 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	0	12.32	12.32	1.0806	Aver. time 2.5 " log(v'-v) 1.0590
5	3.70	14.60	10.90	1.0374	
10	6.95	16.70	9.75	.9890	Aver. time 12.5 " log(v'-v) 0.9672
15	9.78	18.60	8.82	.9455	
20	(12.32)				
25	(14.60)				
30	(16.70)				
35	(18.60)				
40	(20.20)				
45	(21.69)				
50	(23.20)				
55	(24.75)				

$$1.0590 = 2.5\ m - b$$
$$.9672 = 12.5\ m - b$$
$$.0918 = 10.0\ m -$$
$$m = 0.00918$$
$$k = 0.02114$$

Table 8

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of .0208 M. KNO_3

Conc. of KNO_3
0.0208 M.

Conc. of Benzoic Acid
0.003333 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	0	13.85	13.85	1.1415	Aver. time 2.5 " log(v'-v) 1.1180
5	4.05	16.48	12.43	1.0946	
10	7.69	18.87	11.18	1.0484	Aver. time 12.5 " log(v'-v) 1.0289
15	10.88	21.00	10.22	1.0095	
20	(13.85)				
25	(16.48)				
30	(18.87)				
35	(21.00)				
40	(23.03)				
45	(25.10)				
50	(26.50)				
55	(28.00)				
60	(29.45)				

$$\begin{array}{rcl} 1.1180 & = & 2.5\,m - b \\ 1.0289 & = & 12.5\,m - b \\ \hline .0891 & = & 10.0\,m \end{array}$$

$m = 0.00891$

$k = 0.02052$

Table 9

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of .0208 M. KNO_3

Conc. of KNO_3 0.0208 M.

Conc. of Benzoic Acid 0.003333 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	0	15.37	15.37	1.1867	Aver. time 2.5 " log(v'-v) 1.1642
5	4.52	18.38	13.86	1.1418	
10	8.51	20.95	12.44	1.0948	Aver. time 12.5 " log(v'-v) 1.0736
15	12.10	23.38	11.28	1.0523	
20	(15.37)				
25	(18.38)				
30	(20.95)				
35	(23.38)				
40	(25.70)				
45	(27.64)				
50	(29.31)				
55	(30.99)				
60	(32.68)				

$$1.1642 = 2.5\,m + b$$
$$1.0736 = 12.5\,m + b$$

$$0.0906 = 10.0\,m$$
$$m = 0.00906$$
$$k = 0.02087$$

Table 10

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of .0104 M. KNO_3

Conc. of KNO_3
0.0104 M.

Conc. of Benzoic Acid
0.003333 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	0	13.68	13.68	1.1361	Aver. time 2.5 " log(v'-v) 1.1165
5	3.93	16.43	12.50	1.0969	
10	7.53	18.83	11.34	1.0546	Aver. time 12.5 " log(v'-v) 1.0339
15	10.74	21.05	10.31	1.0133	
20	(13.68)				
25	(16.43)				
30	(18.83)				
35	(21.05)				
40	(23.10)				
45	(25.45)				
50	(26.64)				
55	(28.22)				
60	(29.73)				
65	(31.04)				

$$1.1165 = 2.5\,m + b$$
$$1.0339 = 12.5\,m + b$$

$$0.0826 = 10.0\,m$$
$$m = 0.00826$$
$$k = 0.01942$$

Table 11

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of .0104 N. KNO_3

Conc. of KNO_3
0.0104 N.

Conc. of Benzoic Acid
0.003333M.

Time	v	v'	(v'-v)	log(v'-v)	
0	0	16.70	16.70	1.2227	Aver. time 2.5 " log(v'-v) 1.2028
5	4.71	19.95	15.24	1.1830	
10	9.10	22.90	13.80	1.1399	Aver. time 12.5 " log(v'-v) 1.1213
15	13.18	25.85	12.67	1.1028	
20	(16.70)				
25	(19.95)				
30	(22.90)				
35	(25.85)				
40	(28.05)				
45	(30.25)				
50	(32.45)				
55	(34.35)				
60	(36.15)				

$1.2028 = 2.5m - b$

$1.1213 = 12.5m - b$

$0.0815 = 10.0m -$

$m = 0.00815$

$k = 0.01877$

Table 12

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of .0062 M. KNO_3

Conc. of KNO_3 0.0052 M.	Conc. of Benzoic Acid 0.003333

Time	v	v'	(v'-v)	log(v'-v)	
0	0	13.89	13.89	1.1421	Aver. time 2.5 " log(v'-v) 1.1231
5	3.98	16.69	12.71	1.1042	
10	7.53	19.22	11.69	1.0678	Aver. time 12.5 " log(v'-v) 1.0449
15	10.88	21.40	10.52	1.0220	
20	(13.89)				
25	(16.69)				
30	(19.22)				
35	(21.40)				
40	(23.30)				
45	(25.70)				
50	(27.05)				

$$1.1231 = 2.5\,m + b$$
$$1.0449 = 12.5\,m + b$$
$$0.0782 = 10.0\,m$$
$$m = 0.00782$$
$$k = 0.01801$$

Table 13

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the presence of .0052 M. KNO_3

Conc. of KNO_3
0.0052 M.

Conc. of Benzoic Acid
0.002533

Time	v	v'	(v'-v)	log(v'-v)	
0	0	12.00	12.00	1.0792	Aver. time 2.5 " log(v'-v) 1.0612
5	3.43	14.47	11.04	1.0430	
10	6.39	16.61	10.22	1.0094	Aver. time 12.5 " log(v'-v) 0.9915
15	9.38	18.79	9.41	.9740	
20	(12.00)				
25	(14.47)				
30	(16.61)				
35	(18.79)				
40	(20.53)				
45	(22.27)				
50	(24.22)				
55	(25.77)				
60	(26.81)				

$$1.0612 = 2.5\,m + b$$

$$.9915 = 12.5\,m + b$$

$$.0697 = 10.0\,m$$

$$m = 0.00697$$

$$k = 0.01605^{*}$$

*This value not very reliable.

Table 14

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Absence of Added KNO_3

Conc. of KNO_3
0.000

Conc. of Benzoic Acid
0.003333 M.

Time	v	v' 6	(v'-v)	log(v'-v)	
0	.80	12.98	12.18	1.08565	
5	3.03	14.14	11.11	1.0457	Average time 7.5 " log(v'-v) 1.0279
10	5.11	15.30	10.19	1.0082	
15	6.94	16.32	9.38	.9722	
20	8.68	17.25	8.57	.9330	
25	10.19	18.13	7.94	.8998	Average time 27.5 " log(v'-v) 0.8801
30	11.60	18.90	7.30	.8633	
35	12.98	19.65	6.67	.8241	

$$1.0279 = 7.5\ m - b$$

$$.8801 = 27.5\ m - b$$

$$.1478 = -20.0\ m$$

$$-m = 0.00739$$

$$k = 0.01702$$

Table 15

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Absence of Added KNO_3

Conc. of KNO_3	Conc. of Benzoic Acid
0.00	0.003333 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	5.02	19.78	14.76	1.1691	Average time 7.5
5	7.50	21.00	13.50	1.1303	" log(v'-v)
10	9.89	22.12	12.23	1.0874	1.1091
15	11.92	23.13	11.21	1.0496	
20	13.75	24.08	10.33	1.0141	Average time 27.5
25	15.40	24.96	9.56	.9805	" " log(v'-v)
30	16.99	25.78	8.79	.9440	0.9608
35	18.44	26.47	8.03	.9047	

$$1.1091 = 7.5\ m - b$$

$$0.9608 = 27.5\ m - b$$

$$0.1483 = -20.0\ m$$

$$-m = 0.00741$$

$$k = 0.01706$$

Table 16

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Absence of Added KNO_3

Conc. of KNO_3	Conc. of Benzoic Acid
0.00	0.003333M.

Time	v	v'	(v'-v)	log(v'-v)	
0	1.68	17.28	15.60	1.1931	Average time 7.5
5	4.28	18.57	14.29	1.1550	" log(v'-v)
10	6.64	19.75	13.11	1.1176	1.1370
15	8.77	20.86	12.09	1.0824	
20	10.82	21.87	11.05	1.0434	Average time 27.5
25	12.60	22.78	10.18	1.0077	" log(v'-v)
30	14.30	23.62	9.32	.9694	0.9882
35	15.85	24.41	8.56	.9323	

1.1370 = 7.5 m - b

0.9882 = 27.5 m 6 b

0.1488 = 620.0 m

-m = 0.00744

k = 0.01713

Examination of the date reported in this Part shows that the use of potassium nitrate is unsatisfactory for the study of salt effects in this particular reaction. At all salt concentrations duplicate determinations were carried out under identical conditions; however, the reaction constants obtained for duplicate "runs" checked each other only within wide limits. It was found that by changing the number of readings uded in its calculation the value of the reaction constant could be changed almost at will. This was especially true at high salt concentrations and must be attributed to the side reaction already discussed. In order to make the data at various salt concentrations comparable, it was arbitrarily decided to use the same number of readings in the calculation of the constant for the differant salt concentrations. Since this gives only four points from which to determine the value of *k*, it is a very unsatisfactory arrangement. However, to use more readings would have magnified the effect of the side reaction. It should also be noted that because of the nature of the measurements to be made the reaction must be allowed to run for at least five minutes before any readings are taken. This time lapse is necessary to allow the saturation of the reaction mixture with nitrogen and cannot be eliminated. Hence, it is impossible to obtain readings for the first part of the reaction.

The average values of *k* when plotted as ordinates against the concentration of potassium nitrate in the reaction mixture do not yield a smooth curve. This is shown in Fig. 3

and constitutes further evidence that the data obtained using potassium nitrate is not reliable. The graph does show, however, that there is a positive salt effect, and that the salt effect is probably not linear. These results are in agreement with the Brönsted theory and with the results obtained by Brönsted and Teeter (27) and already discussed.

It must be concluded that the elimination of the final reading("a" value) from the calculation of the reaction constant does not reduce the effect of the side reaction to negligible proportions, even though the value of the constant be based on only the initial part of the reaction. Since the object of this research was the quantitative study of the salt effect, it was apparent that some other salts would have to be found which would not give a significant side reaction with the ester molecule.

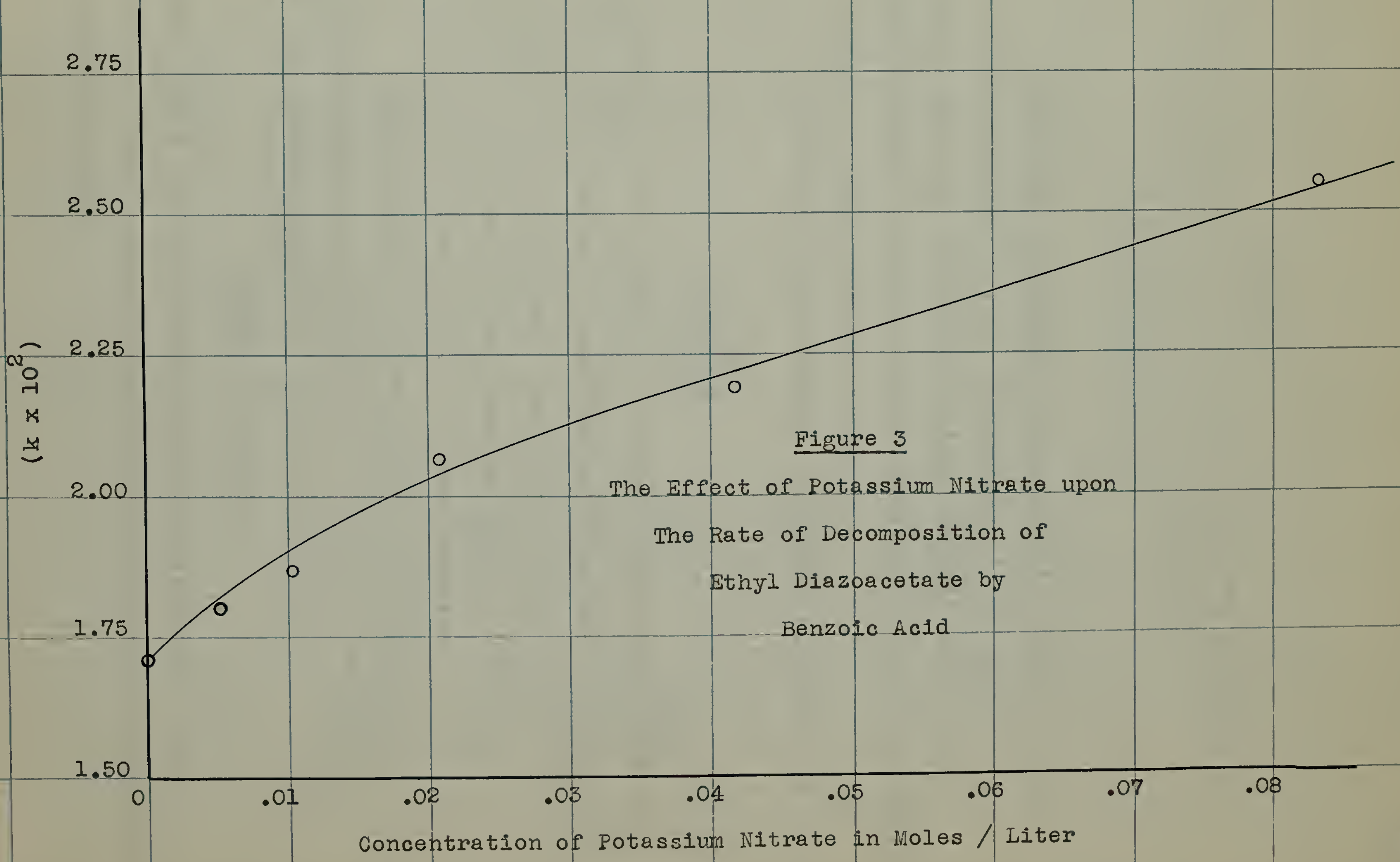


Figure 3

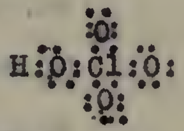
The Effect of Potassium Nitrate upon The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid

Part II

The Rate of Decomposition of Ethyl Diazoacetate Catalyzed By Perchloric Acid and in the Presence of Potassium Perchlorate

The number of neutral salts from which one may choose is rather limited. With the elimination of all salts of the halogen acids, of nitric acid and of sulfuric acid, all of which are known to give a side reaction with ethyl diazoacetate, the choice is still further restricted.

Examination of the electron formula of perchloric acid



$$\begin{array}{c} \ddot{\underset{\cdot\cdot}{:O:}} \\ H:\ddot{\underset{\cdot\cdot}{O}}:\ddot{\underset{\cdot\cdot}{Cl}}:\ddot{\underset{\cdot\cdot}{O}}: \\ \ddot{\underset{\cdot\cdot}{:O:}} \end{array}$$

suggested that the perchlorate radical should show slight tendency to react with the ethyl diazoacetate molecule, since electronically the radical is "saturated". From this it appeared that perchloric acid and the perchlorates might be well suited to the study of salt effects in the diazo reaction.

Experimentation indicated that this reasoning was correct. Table 17-a, in which the value of k is calculated at five minute intervals by means of the formula

$$k \quad \frac{2.303}{t} \log \frac{a}{a-x}$$

shows that k does not change significantly with the time. This table may be compared with Table 3, which gives similar data for nitrates.

Table 17-a

Showing the Absence of Side Reactions in the Decomposition of Ethyl Diazoacetate When Catalyzed by Perchloric Acid

Conc. of Perchloric Acid
0.000442 M

Time	Reading	(a-x)	log(a-x)	k/2.303
0	0	27.00	1.4314	
5	2.35	24.65	1.3918	.00790*
10	4.30	22.70	1.3560	.00753
15	6.11	20.89	1.3199	.00743
20	7.79	19.21	1.2835	.00739
25	9.38	17.62	1.2460	.00741
30	10.84	16.16	1.2084	.00743
35	12.22	14.78	1.1697	.00747
40	13.43	13.57	1.1326	.00747
45	14.58	12.42	1.0941	.00749
50	15.57	11.43	1.0580	.00747
55	16.49	10.51	1.0216	.00745
60	17.33	9.67	.9854	.00743
65	18.11	8.89	.9489	.00742
70	18.80	8.20	.9138	.00739

a = 27.00

* Probably in error.

The experiments reported in Part II were designed to allow measurement of the primary salt effect, if any exists, in the diazo reaction. For this reason, the concentration of perchloric acid is not changed throughout this Part. The concentration of added potassium perchlorate is varied from zero in Table 17 to .0714 M. in Table 33. Hence, changes in the value of k will be directly due to the added salt. The concentration of both acid and salt is given at the top of each table, and, in all cases, refers to final concentration.

Table 17

The Rate of Decomposition of Ethyl Diazoacetate by Perchloric Acid in the Absence of Added Salts

Conc. of Added Salt	Conc. of Perchloric Acid
0.00	0.001474 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	26.70	38.50	11.80	1.0719	
5	27.77	39.19	11.42	1.0577	
10	28.77	39.82	11.05	1.0434	Average time 15
15	29.67	40.48	10.81	1.0340	[illegible] log(v'-v) 1.0327
20	30.58	41.07	10.49	1.0208	
25	31.48	41.65	10.17	1.0073	
30	32.39	42.26	9.87	.9943	
35	33.22	42.80	9.58	.9814	
40	34.00	43.38	9.38	.9722	
45	34.83	43.91	9.08	.9581	Average time 50
50	35.60	44.43	8.83	.9460	" log(v'-v) 0.9460
55	36.38	44.94	8.56	.9325	
60	37.09	45.45	8.36	.9222	
65	37.80	45.92	8.12	.9096	

$$
\begin{array}{rcl}
1.0327 & = & 15\,m + b \\
.9460 & = & 50\,m + b \\
\hline
.0867 & = & -35\,m \\
-m & = & .002479 \\
k & = & .005709
\end{array}
$$

Table 18

The Rate of Decomposition of Ethyl Diazoacetate by Perchloric Acid in the Absence of Added Salts

Conc. of Added Salt
0.00

Conc. of Perchloric Acid
0.0001474 M.

Time	v	v'	(v8-v)	log(v'-V)
0	24.00	35.90	11.90	1.0755
5	25.00	36.60	11.60	1.0647
10	26.00	37.24	11.24	1.0508
15	26.97	37.88	10.91	1.0391
20	27.87	38.53	10.66	1.0278
25	28.79	39.16	10.37	1.0159
30	29.67	39.70	10.03	1.0013
35	30.52	40.29	9.77	.9899
40	31.36	40.87	9.51	.9782
45	32.19	41.46	9.27	.9671
50	32.97	41.95	8.98	.9533
55	33.75	42.46	8.76	.9400
60	34.48	42.97	8.49	.9284
65	35.20	43.45	8.25	.9164

Average time 15
" log(v'-v)
1.0391

Average time 50
" log(v'-v)
0.9533

1.0391 = 15 m - b
.9533 = 50 m - b

.0858 = 635 m
-m = 0.002450
k = 0.005642

Table 19

The Rate of Decomposition of Ethyl Diazoacetate by Perchloric Acid in the Absence of Added Salts

Conc. of Added Salts
0.00

Conc. of Perchloric Acid
0.001474 M.

Time	v	v'	(v'-v)	log(v'-v)
0	19.00	29.90	10.90	1.0374
5	19.96	30.54	10.58	1.0245
10	20.88	31.18	10.30	1.0128
15	21.76	31.77	10.01	1.0004
20	22.60	32.35	9.75	.9890
25	23.48	32.95	9.47	.9763
30	24.27	33.46	9.19	.9633
35	25.02	34.00	8.98	.9533
40	25.91	34.53	8.62	.9355
45	26.56	35.02	8.46	.9274
50	27.28	35.50	8.22	.9149
55	27.90	35.99	8.09	.9079*
60	28.59	36.48	7.89	.8971*
65	29.25	36.89	7.64	.8831*

Average time 10
" log(v'-v)
1.0128

Average time 37.5
" log(v'-v)
0.9451

* In error (from graph)

$$1.0128 = 10.0\,m + b$$

$$0.9451 = 37.5\,m + b$$

$$.0677 = -27.5\,m$$

$$-m = 0.002463$$

$$k = 0.005667$$

Table 20

The Rate of Decomposition of Ethyl Diazoacetate by Perchloric Acid in the Absence of Added Salts

Conc. of Added Salt	Conc. of Perchloric Acid
0.00	0.001474 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	40.50	50.80	10.30	1.0128	Average time 7.5
5	41.38	51.39	10.01	1.0004	" log(v'-v) 0.9948
10	42.20	51.95	9.75	.9890	
15	43.07	52.55	9.48	.9768	
20	43.87	53.08	9.21	.9643	Average time 25.0
25	44.64	53.56	8.92	.9504	" log(v'-v) 0.9510
30	45.40	54.08	8.68	.9385	

$$0.9948 = 7.5\ m + b$$

$$0.9510 = 25.0\ m + b$$

$$.0438 = -17.5\ m$$

$$-m = 0.002498$$

$$k = 0.005753$$

Table 21

The Rate of Decomposition of Ethyl Diazoacetate by Perchloric Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.00447 M.

Conc. of Perchloric Acid
0.001474 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	8.16	19.89	11.73	1.0693	
5	9.21	20.60	11.39	1.0565	
10	10.17	21.30	11.13	1.04650	
15	11.13	21.89	10.76	1.0318	Average time 15 " log(v'-v) 1.0335
20	12.00	22.47	10.47	1.0199	
25	12.90	23.18	10.28	1.0120	
30	13.77	23173	9.96	.9983	
35	14.67	24.28	9.61	.9827	
4 0	15.50	24.83	9.33	.9699	
45	16.25	25.37	9.12	.9600	
50	17.08	25.88	8.80	.9445	Average time 50 " log(v'-v) 0.9455
55	17.82	26.35	8.53	.9309	
60	18.50	26.84	8.34	.9212	
65	19.20	27.32	8.12	.9097	

$$1.0335 = 15\,m - b$$

$$\underline{.9455 = 50\,m - b}$$

$$.0880 = -35\,m$$

$$-m = 0.002513$$

$$k = 0.005787$$

Table 22

The Rate of Decomposition of Ethyl Diazoacetate by Perchloric Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.00447 M.

Conc. of Perchloric Acid
0.0001474 M.

Time	v	v'	(v'-v)	log(v'-v)
0	3.28	15.03	11.75	1.0700
5	4.17	15.69	11.52	1.0614
10	5.23	16.38	11.15	1.0473
15	6.19	17.00	10.81	1.0338
20	7.15	17.60	10.45	1.0191
25	8.00	18.25	10.25	1.0107
30	8.87	18.78	9.91	.9961
35	9.75	19.27	9.52	.9786
40	10.50	19.88	9.38	.9722
45	11.35	20.42	9.07	.9576
50	12.18	21.00	8.82	.9455
55	12.90	21.50	8.60	.9345
60	13.65	21.98	8.33	.9206
65	14.38	22.44	8.06	.9063

Average time 15
" log(v'-v)
1.0341

Average time 50
" log(v'-v)
0.9451

$$1.0341 = 15\,m - b$$

$$.9451 = 50\,m - b$$

$$.0890 = -35\,m$$

$$-m = 0.002515$$

$$k = 0.005792$$

Table 23

The Rate of Decomposition of Ethyl Diazoacetate by Perchloric Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.00447
6

Conc. of Perchloric Acid
0.0001474

Time	v	v'	(v'-v)	log(v'-v)	
0	7.39	18.85	11.46	1.0592	
5	8.39	19.56	11.17	1.0480	
10	9.38	20.25	10.87	1.0362	
15	10.35	20.93	10.58	1.0245	Average time 15
20	11.25	21.46	10.21	1.0090	" log(v'-v) 1.0219
25	12.10	22.02	9.92	.9965	
30	13.04	22.58	9.54	.9795	
35	13.77	23.09	9.32	.9694	
40	14.59	23.70	9.11	.9595	
45	15.35	24.24	8.89	.9489	
50	16.13	24.72	8.59	.9340	Average time 50
55	16.87	25.19	8.32	.9201	" log(v'-v) 0.9334
60	17.58	25.70	8.12	.9096	
65	18.32	26.12	7.80	.8921	

$$1.0219 = 15\,m + b$$

$$.9334 = 50\,m + b$$

$$.0885 = -35\,m$$

$$-m = 0.002528$$

$$k = 0.005822$$

Table 24

The Rate of Decomposition of Ethyl Diazoacetate by Perchloric Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.00895 M.

Conc. of Perchloric Acid
0.0001474 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	8.43	22.77	14.34	1.1565	
5	9.60	23.59	13.99	1.1458	
10	10.82	24.36	13.54	1.1316	
15	11.91	25.13	13.22	1.1212	Average time 15
20	13.10	25.95	12.85	1.1089	" log(v'-v) 1.1210
25	14.15	26.67	12.52	1.0976	
30	15.20	27.32	12.12	1.0836	
35	16.24	28.05	11.81	1.0722	
40	17.26	28.73	11.47	1.0596	
45	18.28	29.40	11.12	1.0461	
50	19.23	29.98	10.75	1.0314	Average time 50
55	20.18	30.58	10.40	1.0170	" log(v'-v) 1.0319
60	21.05	31.20	10.15	1.0065	
65	21.93	31.72	9.79	.9908	

$$1.1210 = 15\ m + b$$
$$1.0319 = 50\ m + b$$
$$\overline{0.0891 = -35\ m}$$
$$-m = 0.002546$$
$$k = 0.005861$$

Table 25

The Rate of Decomposition of Ethyl Diazoacetate by Perchloric Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.00895 M.

Conc. of Perchloric Acid
0.0001474 M.

Time	v	v'	(v'-v)	log(v'-v)
0	8.77	23.42	14.65	1.1658
5	9.97	24.10	14.13	1.1501
10	11.15	25.01	13.86	1.1418
15	12.34	25.75	13.41	1.1274
20	13.38	26.41	13.03	1.1149
25	14.43	27.00	12.57	1.0993
30	15.44	27.75	12.31	1.0903
35	16.61	28.58	11.97	1.0781
40	17.45	28.93	11.48	1.0599
45	18.38	29.61	11.23	1.0504
50	19.28	30.19	10.91	1.0378
55	20.13	30.73	10.60	1.0253
60	21.01	31.28	10.27	1.0116
65	21.83	31.83	10.00	1.0000
70	22.64	32.30	9.66	.9850

Average time 15
" log(v'-v)
1.1271

Average time 52.5
" log(v'-v)
1.0308

$$
\begin{array}{rcl}
1.1271 & = & 15.0\ m\ +\ b \\
1.0308 & = & 52.5\ m\ +\ b \\
\hline
0.0963 & = & -37.5\ m \\
-m & = & 0.002569 \\
k & = & 0.005916
\end{array}
$$

Table 26

The Rate of Decomposition of Ethyl Diazoacetate by Perchloric Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.0179 M.

Conc. of Perchloric Acid
0.0001474 M.

Time	v	v'	(v'-v)	log(v'-v)
0	6.69	20.73	14.04	1.1474
5	7.95	21.54	13.59	1.1332
10	9.10	22.30	13.20	1.1206
15	10.26	22.99	12.73	1.1048
20	11.39	23.74	12.35	1.0917
25	12.42	24.45	12.03	1.0803
30	13.49	25.11	11.62	1.0652
35	14.50	25.80	11.30	1.0531
40	15.47	26.45	10.98	1.0406
45	16.40	27.07	10.67	1.0282
50	17.32	27.68	10.34	1.0145
55	18.20	28.25	10.05	1.0022
60	18.99	28.80	9.81	.9917*
65	19.87	29.36	9.49	..9773*

Average time 12.5
" log(v'-v)
1.1130

Average time 42.5
" log(v'-v)
1.0340

* in error(from graph)

$$1.1130 = 12.5\,m + b$$
$$1.0340 = 42.5\,m + b$$
$$.0790 = -30.0\,m$$
$$-m = 0.002634$$
$$k = 0.006066$$

Table 27

The Rate of Decomposition of Ethyl Diazoacetate by Perchloric Acid in the Presence of $KClO_4$

Conc. of $KClO_4$ 0.0179 M.

Conc. of Perchloric Acid 0.0001474 M.

Time	v	v'	(v'-v)	log(v'-v)
0	2.35	16.99	14.64	1.1655
5	3.62	17.82	14.20	1.1523
10	4.74	18.67	13.93	1.1439
15	5.90	19.37	13.47	1.1294
20	7.12	20.14	13.02	1.1146
25	8.17	20.89	12.72	1.1045
30	9.20	21.60	12.40	1.0934
35	10.25	22.28	12.03	1.0803
40	11.30	22.90	11.60	1.0645
45	12.32	23.58	11.26	1.0515
50	13.37	24.20	10.83	1.0346
55	14.28	24.88	10.60	1.0253
60	15.26	25.48	10.22	1.0094
65	16.11	26.05	9.94	.9974

Average time 15
" log(v'-v) 1.1291

Average time 50
" log(v'-v) 1.0376

$$1.1291 = 15\ m - b$$
$$1.0376 = 50\ m - b$$
$$.0915 = -35\ m$$
$$-m = 0.002612$$
$$k = 0.006015$$

Table 28

The Rate of Decomposition of Ethyl Diazoacetate by Perchloric Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.0179 M.

Conc. of Perchloric Acid
0.0001474 M.

Time	v	v'	(v'-v)	log(v'-v)
0	9.90	24.94	15.07	1.1781
5	11.17	25.82	14.65	1.1658
10	12.43	26.65	14.22	1.1529
15	13.68	27.45	13.77	1.1389
20	14.90	28.20	13.30	1.1238
25	15.99	28.96	12.97	1.1129
30	17.10	29.70	12.60	1.1004
35	18.22	30.42	12.20	1.0864
40	19.19	31.11	11.92	1.0763
45	20.20	31.78	11.58	1.0637
50	21.30	32.40	11.10	1.0453
55	22.23	33.03	10.80	1.0334
60	23.17	33.67	10.50	1.0212
65	24.04	34.22	10.13	1.0056*

Average time 12.5
" log(v'-v)
1.1454

Average time 45.0
"
" log(v'-v)
1.0609

* in error (from graph)

$$\begin{array}{rl} 1.1454 = & 12.5\ m - b \\ 1.0609 = & 45.0\ m - b \\ \hline .0845 = & -32.5\ m \end{array}$$

$$-m = 0.002599$$

$$k = 0.005985$$

Table 29

The Rate of Decomposition of Ethyl Diazoacetate by Perchloric Acid in the Presence of $KClO_4$

Conc. of $KClO_4$ 0.0357 M.

Conc. of Perchloric Acid 0.0001474 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	7.05	18.89	11.84	1.0733	
5	8.05	19.55	11.50	1.0607	
10.	9.05	20.23	11.18	1.0484	
15	10.00	20.89	10.89	1.0370	Average time 15
20	10.95-	21.50	10.55	1.0232	" log(v'-v) 1.0347
25	11.87	22.05	10.18	1.0077	
30	12.78	22.60	9.82	.9921	
35	13.62	23.17	9.55	.9800	
40	14.48	23.71	9.23	.9652	
45	15.26	24.29	9.03	.9557	
50	16.03	24.75	8.72	.9405	Average time 50
55	16.80	25.18	8.38	.9232	" log(v'-v) 0.9393
60	17.52	25.68	8.16	.9117	
65	18.22	26.14	7.92	.8987	

$$1.0347 = 15\ m - b$$

$$.9393 = 50\ m - b$$

$$.0954 = -35\ m$$

$$-m = 0.002724$$

$$k = 0.006273$$

Table 30

The Rate of Decomposition of Ethyl Diazoacetate by Perchloric Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.0537 M.

Conc. of Perchloric Acid
0.0001474 M.

Time	v	v'	(v'-v)	log(v'-v)
0	10.35	25.51	15.16	1.1807
5	11.72	26.35	14.63	1.1652
10	12.99	27.13	14.14	1.1505
15	14.22	27.95	13.73	1.1377
20	15.40	28.71	13.31	1.1242
25	16.53	29.48	12.95	1.1123
30	17.65	30.21	12.56	1.0990
35	18.73	30.89	12.16	1.0849
40	19.84	31.59	11.75	1.0700
45	20.87	32.22	11.35	1.0550
50	21.85	32.85	11.00	1.0414
55	22.78	33.52	10.74	1.0310
60	23.74	34.09	10.35	1.0149
65	24.64	34.64	10.00	1.0000

Average time 15
" log(v'-v)
1.1385

Average time 50
" log(v'-v)
1.0425

$$\begin{array}{rcl} 1.1385 & = & 15\,m + b \\ 1.0425 & = & 50\,m + b \\ \hline .0960 & = & -35\,m \\ -m & = & 0.002744 \\ k & = & 0.006319 \end{array}$$

Table 31

The Rate of Decomposition of Ethyl Diazoacetate by Perchloric Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.0357 M.

Conc. of Perchloric Acid
0.0001474 M.

Time	v	v'	(v'-v)	log(v'-v)
0	15.04	30.60	15.54	1.1914
5	16.49	31.53	15.04	1.1773
10	17.90	32.47	14.57	1.1635
15	19.22	33.37	14.16	1.1511
20	20.58	34.19	13.61	1.1339
25	21.82	35.05	13.23	1.1216
30	23.01	35.86	12.85	1.1089
35	24.24	36.68	12.44	1.0948
40	25.38	37.42	12.04	1.0806
45	26.49	38.18	11.69	1.0678
50	27.58	38.90	11.32	1.0538
55	28.63	39.60	10.97	1.0402
60	29.62	40.28	10.66	1.0278

Average time 12.5
" log(v'-v)
1.1564

Average time 45.0
" log(v'-v)
1.0677

$$1.1564 = 12.5\ m - b$$

$$1.0677 = 45.0\ m - b$$

$$.0887 = -32.5\ m$$

$$-m = 0.002730$$

$$k = 0.006287$$

Table 32

The Rate of Decomposition of Ethyl Diazoacetate by Perchloric Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.0714 M.

Conc. of Perchloric Acid
0.0001474 M.

Time	v	v'	(v'-v)	log(v'-v)
0	10.20	28.89	18.69	1.2716
5	11.80	29.87	18.07	1.2570
10	13.50	30.83	17.33	1.2388
15	15.08	31.79	16.71	1.2230
20	16.60	32.71	16.11	1.2071
25	18.07	33.54	15.47	1.1895
30	19.49	34.45	14.96	1.1749
35	20.80	35.30	14.50	1.1614
40	22.06	36.12	14.06	1.1480
45	23.27	36.82	13.55	1.1319
50	24.45	37.50	13.05	1.1156
55	25.62	38.20	12.58	1.0997
60	26.70	38.98	12.28	1.0892
65	27.83	39.62	11.77	1.0718

Average time 15
" log(v'-v)
1.2231

Average time 50
" log(v'-v)
1.1167

$$1.2231 = 15\,m - b$$
$$1.1167 = 50\,m - b$$
$$.1064 = -35\,m$$
$$-m = 0.003040$$
$$k = 0.007001$$

Table 33

The Rate of Decomposition of Ethyl Diazoacetate by Perchloric Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.0714 M.

Conc. of Perchloric Acid
0.0001474 M.

Time	v	v'	(v'-v)	log(v'-v)
0	4.92	19.04	14.12	1.1498
5	6.08	19.80	13.72	1.1373
10	7.28	20.54	13.26	1.1225
15	8.47	21.25	12.78	1.1065
20	9.60	21.93	12.33	1.0910
25	10.69	22.60	11.91	1.0759
30	11.77	23.30	11.53	1.0618

Average time 15
" log(v'-v)
1.1064

Time	v	v'	(v'-v)	log(v'-v)
35	12.76	23.90	11.14	1.0469
40	13.78	24.54	10.76	1.0318
45	14.69	25.15	10.46	1.0195
50	15.64	25.70	10.06	1.0026
55	16.55	26.14	9.59	.9818
60	17.40	26.72	9.32	.9694
65	18.22	27.25	9.03	.9557

Average time 50
" log(v'-v)
1.0011

$$1.1064 = 15\ m + b$$

$$1.0011 = 50\ m + b$$

$$.1053 = -35\ m$$

$$-m = 0.003009$$

$$k = 0.006929$$

The data embodied in Tables 17 through 33 show that the effect of a neutral salt upon the velocity of decomposition of diazoacetate should not be neglected, even though a strong acid is used as catalyst. Plotting the reaction constants as ordinates against the concentration of potassium perchlorate as abscissae(Fig. 4) indicates that a simple linear relationship exists between these two variables. This confirms the work of Brösted and Duus (28) who reported a strong linear salt effect for this reaction.

At zero salt concentration(the concentration of the $HClO_4$ is .000147 M., and hence the salt effect of the acid may be disregarded), the value of the reaction constant, k_0, was found to be 5.705×10^{-3}. Several investigators have shown that the so-called catalytic constant, $k_{H_3O^+}$, obtained by dividing the reaction constant,k, by the concentration of ~~##~~ H_3O^+, is a constant independent of the source and concentration of the hydrogen ions.

$$k_{H_3O^+} = \frac{k_0}{H_3O^+} = \frac{5.705 \times 10^{-3}}{1.47 \times 10^{-4}} = 38.88 \qquad :1:$$

This value may be compared to those of Fraenkel(5), who obtained 38.6 using nitric acid and 38.9 using picric acid.

As has been observed, there exists a simple linear relationship between the reaction constant, k, and the molar salt concentration, C. In accordance with the general linear equation, this relationship may be stated mathematically

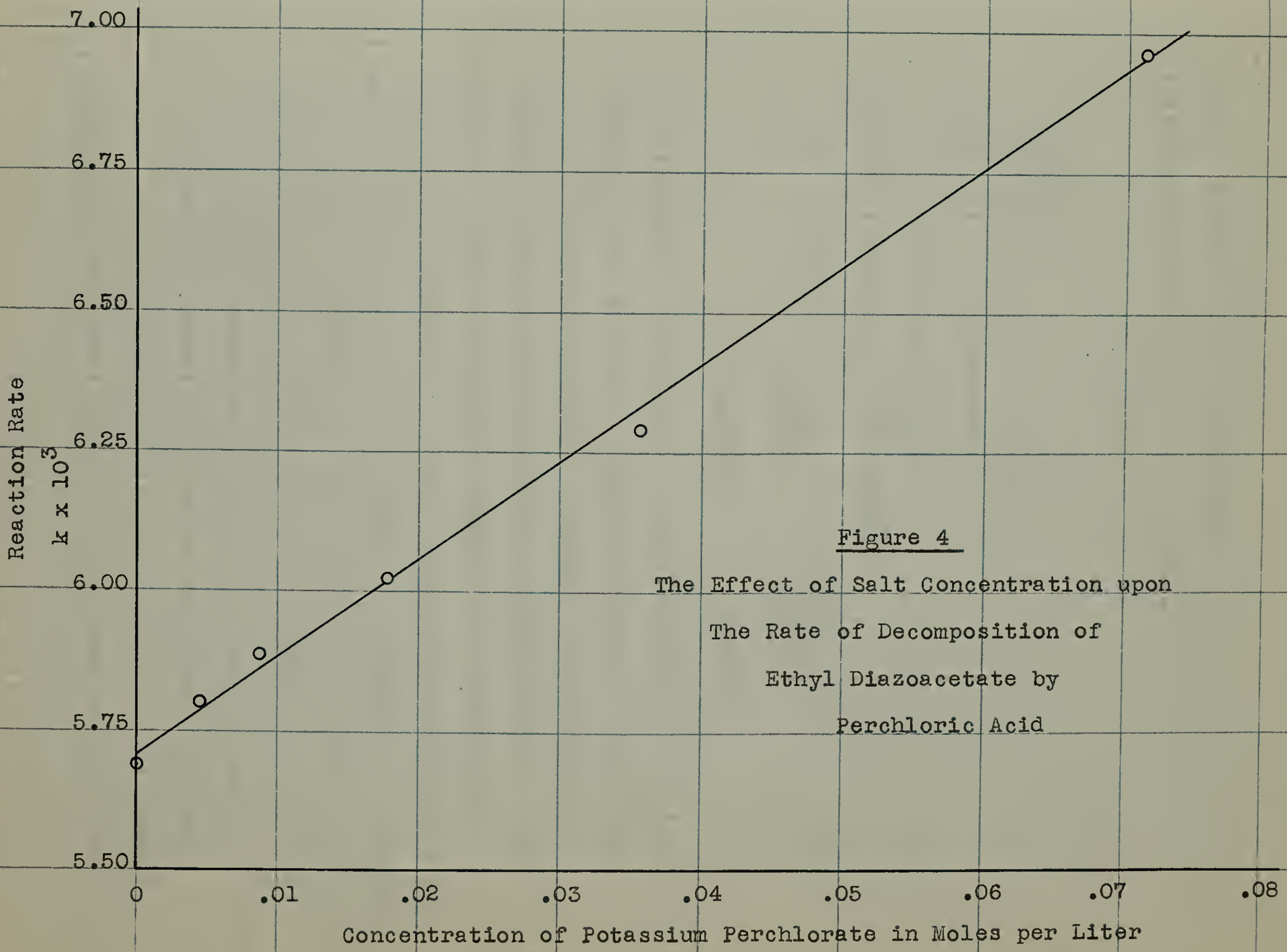


Figure 4

The Effect of Salt Concentration upon The Rate of Decomposition of Ethyl Diazoacetate by Perchloric Acid in this manner.

$$k = k_0 + mC \qquad ;2:$$

where m is the slope of the line in fig.4, and is numerically 0.0177. Hence, the above equation becomes

$$k = k_0 + 0.0177\ C \qquad :3:$$

and from which

$$k_0 = k - 0.0177\ C \qquad :4:$$

But from :1: it is seen that

$$(H_3O^+) = \frac{k_0}{38.88} \qquad :5:$$

Combining ;4: and :5:, one obtains

$$(H_3O^+) = \frac{k}{38.88} - \frac{0.0177}{38.88}\ C \qquad :6:$$

$$= 0.02572\ k - .00046\ C \qquad :7:$$

The first term in equation :7: is independent of the acid used and of the salt. The second term may be looked upon as the correction factor for the primary salt effect,* and hence the coefficient might vary somewhat because of the specific nature of the ions. However, exen though m was evaluated in equation :3: using potassium perchlorate as the salt, the extension of the validity of equation :7: to include all salts of the univalent type involves no serious assumptions, since differences in the value of the coefficient of C due to the specific nature of the salt would be very small, and for low values of C should introduce no significant error.

It is not concievable that the linear salt effect discussed in this Part should be due to any further ionization of the perchloric acid, which is already completely ionized. Hence, the effect must be attributed to some other cause, as, possibly, the changing of the activity coefficient of the ethyl diazoacetate, or, since the effect is linear, more probably a "salting out" phenomenon. In any case, correction must be made for this linear effect in studying the secondary salt effect manifested when the reaction is catalyzed by a weak acid. For this reason, in studying secondary salt effects equation :7: will be used to calculate the hydrogen ion concentration from the reaction constant and the salt concentration.

Part III

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of Potassium Perchlorate- The Effect of Potassium Perchlorate upon The Dissociation of Benzoic Acid

The data presented in Part II showed that no significant side reaction occurs between the ethyl diazoacetate molecule and perchlorates. Hence, it seemed desirable to repeat the work reported in PartI using potassium perchlorate in place of potassium nitrate in an attempt to obtain data from which the effect of added salts upon the dissociation of benzoic acid could be quantitatively studied.

As a result of experience obtained, some minor changes were made. The concentration of benzoic acid added was reduced, thus slowing down the reaction. This made it possible to base the calculation of the reaction constant upon more readings with a consequent improvement in the constant. Apparatus"A" (see discussion of apparatus) was used in the two preceding sections. Apparatus "B" was used in this section and in the following sections of this work. Constants obtained with this apparatus were more satisfactory than those obtained with the previous apparatus.

The concentration of benzoic acid was held constant throughout this Part, while the concentration of potassium perchlorate was varied from zero to .0833 M. The data are given in Tables 34 through 51.

Table 34

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Absence of Added Salts

Conc. of Added Salt
0.0000

Conc. of Benzoic Acid
0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)
0	28.85	46.95	18.10	1.2577
5	30.53	47.80	17.27	1.2373
10	32.15	48.70	16.55	1.2188
15	33.73	49.50	15.77	1.1978
20	35.22	50.30	15.08	1.1784
25	36.65	51.08	14.43	1.1593
30	37.98	51.80	13.82	1.1405
35	39.29	52.49	13.20	1.1206
40	40.50	53.15	12.65	1.1021
45	41.70	53.75	12.05	1.0810

Average time 10
" log(v'-v)
1.2180

Average time 35
" log(v'-v)
1.1207

$$1.2180 = 10\ m + b$$

$$1.1207 = 35\ m + b$$

$$.0973 = -25\ m$$

$$-m = 0.003892$$

$$k = 0.008963$$

Table 35

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Absence of Added Salts

Conc. of Added Salts
0.00

Conc. of Benzoic Acid
0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	15.30	40.49	25.19	1.4012	
5	17.79	41.77	23.98	1.3798	
10	20.00	42.93	22.93	1.3604	
15	22.18	44.09	21.91	1.3406	Average time 15
20	24.20	45.18	20.98	1.3218	" log(v'-v) 1.3415
25	26.12	46.21	20.09	1.3030	
30	28.00	47.21	19.21	1.2836	
35	29.81	48.19	18.38	1.2643	
40	31.58	4 9.10	17.52	1.2435	
45	33.20	50.00	16.80	1.2253	
50	34.80	50.85	16.05	1.2055	Average time 50
55	36.31	51.65	15.34	1.1858	" log(v'-v) 1.2051
60	37.77	52.40	14.63	1.1652	
65	39.17	53.17	14.00	1.1461	

$$1.3415 = 15\,m - b$$

$$1.2051 = 50\,m - b$$

$$.1364 = -35\,m$$

$$-m = 0.003896$$

$$k = 0.008972$$

Table 36

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.0052 M.

Conc. of Benzoic Acid
0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)
0	28.20	41.62	13.42	1.1277
5	29.45	42.30	12.85	1.1089
10	30.70	42.89	12.19	1.0860
15	31.87	43.49	11.62	1.0652
20	33.00	44.07	11.07	1.0441
25	34.06	44.63	10.57	1.0241
30	35.04	45.17	10.13	1.0056
35	36.00	45.66	9.66	.9850
40	36.93	46.17	9.24	..9657
45	37.81	46.60	8.79	.9440
50	38.66	47.01	8.34	.9212
55	39.48	47.44	7.96	.9009
60	40.20	47.81	7.61	.8814
65	40.94	48.21	7.27	.8615

Average time 15
" log(v'-v)
1.0660

Average time 50
" log(v'-v)
0.9228

$$\begin{aligned} 1.0660 &= 15\ m - b \\ .9228 &= 50\ m - b \\ \hline .1432 &= -35\ m \\ -m &= 0.004090 \\ k &= 0.009419 \end{aligned}$$

Table 37

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.0052 M.

Conc. of Benzoic Acid
0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	16.20	35.78	19.58	1.2918	
5	18.10	36.78	18.68	1.2714	
10	19.88	37.69	17.81	1.2506	
15	21.59	38.55	16.96	1.2294	Average time 15
20	23.19	39.38	16.19	1.2092	" log(v'-v) 1.2303
25	24.78	40.19	15.41	1.1878	
30	26.11	40.96	14.85	1.1717	
35	27.57	41.67	14.10	1.1492	
40	28.89	42.39	13.50	1.1303	
45	30.19	43.08	12.89	1.1102	
50	31.41	43.60	12.19	1.0860	Average time 50
55	32.57	44.19	11.62	1.0652	" log(v'-v) 1.0879
60	33.69	44.77	11.08	1.0449	
65	34.59	45.29	10.70	1.0294	

$$\begin{array}{l} 1.2303 = 15\,m + b \\ \underline{1.0879 = 50\,m + b} \\ .1424 = -35\,m \\ -m = 0.004070 \\ k = 0.009373 \end{array}$$

Table 38

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of $KClO_4$

Conc. of $KClO_4$ 0.0104 M.	Conc. of Benzoic Acid 0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	15.44	33.08	17.64	1.2465	
5	17.24	33.98	16.74	1.2238	
10	18.89	34.78	15.89	1.2011	
15	20.46	35.57	15.11	1.1793	Average time 15
20	21.89	36.29	14.40	1.1584	" log(v'-v) 1.1805
25	23.28	36.98	13.70	1.1367	
30	24.57	37.68	13.11	1.1176	
35	25.87	38.32	12.45	1.0942	
40	26.99	38.90	11.91	1.0759	
45	28.20	39.48	11.28	1.0523	
50	29.20	40.04	10.84	1.0350	Average time 50
55	30.28	40.53	10.25	1.0107	" log(v'-v) 1.0327
60	31.22	41.05	9.83	.9925	
65	32.19	41.49	9.30	.9685	

$$\begin{array}{rcl} 1.1805 & = & 15\,m + b \\ 1.0327 & = & 50\,m + b \\ \hline .1478 & = & -35\,m \\ -m & = & 0.004221 \\ k & = & 0.009721 \end{array}$$

Table 39

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of $KClO_4$

Conc. of $KClO_4$ 0.0104 M.

Conc. of Benzoic Acid 0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	13.38	31.48	18.10	1.2577	
5	15.19	32.39	17.20	1.2355	
10	16.95	33.22	16.27	1.2114	Average time 15
15	18.50	34.00	15.50	1.1903	" log(v'-v) 1.1918
20	20.00	34.80	14.80	1.1703	
25	21.40	35.55	14.15	1.1501	
30	22.87	36.28	13.41	1.1274	
35	24.03	36.83	12.80	1.1072	
40	25.34	37.51	12.17	1.0853	
45	26.47	38.09	11.62	1.0652	Average time 50
50	27.64	38.69	11.05	1.0434	" log(v'-v) 1.0441
55	28.68	39.21	10.53	1.0224	
60	29.69	39.76	10.07	1.0030	
65	30.60	40.20	9.60	.9823	

$$1.1918 = 15\,m - b$$

$$1.0441 = 50\,m - b$$

$$.1477 = -35\,m$$

$$-m = 0.004220$$

$$k = 0.009718$$

Table 40

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of $KC10_4$

Conc. of $KC10_4$
0.0208 M.

Conc. of Benzoic Acid
0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)
0	27.10	39.17	12.07	1.0817
5	28.27	39.73	11.46	1.0592
10	29.35	40.29	10.94	1.0390
15	30.40	40.82	10.42	1.0179
20	31.45	41.30	9.85	.9934
25	32.38	41.80	9.42	.9740
30	33.36	42.22	8.86	.9474
35	34.17	42.67	8.50	.9294
40	35.00	43.07	8.07	.9069
45	35.77	43.45	7.68	.8854
50	36.53	43.86	7.33	.8651
55	37.23	44.17	6.94	.8414
60	37.90	44.57	6.67	.8241
65	38.55	44.87	6.32	.8007

Average time 15
" log(v'-v)
1.0161

Average time 50
" log(v'-v)
0.8647

$$\begin{array}{rcl} 1.0161 & = & 15\,m + b \\ .8647 & = & 50\,m + b \\ \hline .1514 & = & -35\,m \end{array}$$

$-m = 0.004325$

$k = 0.009960$

Table 41

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.0208 M.

Conc. of Benzoic Acid
0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)
0	26.01	38.89	12.88	1.1099
5	27.26	39.49	12.23	1.0874
10	28.48	40.10	11.62	1.0652
15	29.59	40.68	11.09	1.0449
20	30.67	41.21	10.54	1.0228
25	31.60	41.73	10.13	1.0056
30	32.60	42.23	9.63	.9836
35	33.54	42.68	9.14	.9609
40	34.44	43.12	8.68	.9385
45	35.27	43.51	8.24	.9159
50	36.07	43.90	7.83	.8938
55	36.80	44.27	7.47	..8733
60	37.53	44.62	7.09	.8506
65	38.22	44.97	6.75	.8295

Average time 15
" log(v'-v)
1.0456

Average time 50
" log(v'-v)
0.8946

$$1.0456 = 15\ m + b$$

$$\frac{.8946 = 50\ m + b}{.1510 = -35\ m}$$

$$-m = 0.004315$$

$$k = 0.009937$$

Table 42

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.0208 M.

Conc. of Benzoic Acid
0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)
0	27.06	38.62	11.56	1.0630
5	28.14	39.08	10.94	1.0390
10	29.18	39.60	10.42	1.0179
15	30.20	40.10	9.90	.9956
20	31.16	40.58	9.42	.9740
25	32.08	41.00	8.92	.9504
30	32.91	41.45	8.54	.9315
35	33.78	41.90	8.12	.9096
40	34.58	42.28	7.70	.8865
45	35.31	42.62	7.31	.8639
50	36.00	42.99	6.99	.8445
55	36.71	43.34	6.63	.8215
60	37.32	43.66	6.34	.8021
65	37.96	43.94	5.98	.7767

Average time 15
" log(v'-v)
0.9959

Average time 50
" log(v'-v)
0.8435

0.9959 = 15 m - b
0.8435 = 50 m - b

.1524 = -35 m
2m = 0.004354
k = 0.01003

Table 43

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.0208 M.

Conc. of Benzoic Acid
0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	26.70	39.18	12.48	1.0962	
5	27.95	39.83	11.88	1.0748	
10	29.10	40.38	11.28	1.0523	
15	30.19	40.97	10.78	1.0326	Average time 15
20	31.20	41.48	10.28	1.0120	" log(v'-v) 1.0319
25	32.20	41.98	9.68	.9859	
30	33.14	42.46	9.32	.9694	
35	34.08	42.86	8.78	.9435	
40	34.97	43.29	8.32	.9201	
45	35.74	43.67	7.93	.8993	
50	36.53	44.05	7.52	.8762	Average time 50
55	37.27	44.47	7.20	.8573	" log(v'-v) 0.8788
60	37.92	44.80	6.88	.8376	
65	38.59	45.16	6.57	.8176	

$$1.0319 = 15\,m - b$$

$$0.8788 = 50\,m - b$$

$$.1531 = -35\,m$$

$$-m = 0.004374$$

$$k = 0.01007$$

Table 44

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.0208 M.

Conc. of Benzoic Acid
0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)
0	14.39	32.14	17.75	1.2492
5	16.19	33.00	16.81	1.2256
10	17.87	33.78	15.90	1.2014
15	19.43	34.56	15.13	1.1798
20	20.89	35.29	14.40	1.1584
25	22.18	36.00	13.82	1.1405
30	23.60	36.66	13.06	1.1159
35	24.86	37.28	12.42	1.0941
40	26.03	37.88	11.85	1.0750
45	27.16	38.46	11.30	1.0531
50	28.28	38.99	10.71	1.0298
55	29.32	39.56	10.24	1.0103
60	30.30	40.02	9.72	.9877
65	31.20	40.50	9.30	.9685

Average time 15
" log(v'-v)
1.1815

Average time 50
" log(v'-v)
1.0309

$$\begin{array}{rcl} 1.1815 & = & 15\ m - b \\ 1.0309 & = & 50\ m - b \\ \hline .1506 & = & -35\ m \end{array}$$

$$-m = 0.004304$$

$$k = 0.009912$$

Table 45

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.0417 M.

Conc. of Benzoic Acid
0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	15.02	33.11	18.09	1.2574	
5	16.98	34.00	17.02	1.2310	
10	18.65	34.80	16.15	1.2082	Average time 15
15	20.24	35.59	15.35	1.1861	" log(v'-v) 1.1864
20	21.75	36.36	14.61	1.1646	
25	23.17	37.00	13.83	1.1408	
30	24.48	37.57	13.09	1.1169	
35	25.79	38.19	12.40	1.0934	
40	26.99	38.79	11.80	1.0719	
45	28.16	39.36	11.20	1.0492	Average time 50
50	29.23	39.96	10.73	1.0306	" log(v'-v) 1.0282
55	30.28	40.47	10.19	1.0082	
60	31.28	40.89	9.61	.9827	
65	32.23	41.38	9.15	.9614	

$$1.1864 = 15\ m + b$$

$$1.0282 = 50\ m + b$$

$$.1582 = -35\ m$$

$$-m = 0.004521$$

$$k = 0.01041$$

Table 46

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.0417 M.

Conc. of Benzoic Acid
0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)
0	26.30	38.10	11.80	1.0719
5	27.47	38.67	11.20	1.0492
10	28.56	39.21	10.65	1.0273
15	29.60	39.70	10.10	1.0043
20	30.62	40.18	9.56	.9805
25	31.54	40.60	9.06	.9571
30	32.43	41.06	8.63	.9360
35	33.29	41.47	8.18	.9127
40	34.08	41.85	7.77	.8904
45	34.82	42.20	7.38	.8681
50	35.56	42.58	7.02	.8463
55	36.27	42.88	6.61	.8202
60	36.89	43.18	6.29	.7986
65	37.51	43.50	5.99	.7774

Average time 15
Σ log(v'-v)
1.0038

Average time 50
" log(v'-v)
0.8448

$$\begin{aligned} 1.0038 &= 15\,m + b \\ .8448 &= 50\,m + b \\ \hline .1590 &= -35\,m \\ -m &= 0.004541 \\ k &= 0.01046 \end{aligned}$$

Table 47

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.0417 M.

Conc. of Benzoic Acid
0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)
0	33.42	43.12	9.70	.9868
5	34.42	43.58	9.16	.9619
10	35.31	43.97	8.66	.9375
15	36.16	44.41	8.25	.9164
20	36.98	44.77	7.79	.8915
25	37.77	45.14	7.37	.8675
30	38.46	45.50	7.04	.8476
35	39.17	45.84	6.67	.8241
40	39.82	46.17	6.35	.8028
45	40.42	46.43	6.01	.7789
50	41.02	46.71	5.69	.7551
55	41.59	46.98	5.39	.7316
60	42.10	47.28	5.18	.7143
65	42.60	47.52	4.92	.6920

Average time 15
" log(v'-v)
0.9156

Average time 50
" log(v'-v)
0.7570

$$\begin{aligned} 0.9156 &= 15\,m - b \\ 0.7570 &= 50\,m - b \\ \hline .1586 &= -35\,m \\ -m &= 0.004532 \\ k &= 0.01044 \end{aligned}$$

Table 48

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of $KClO_4$

Conc. of $KClO_4$ 0.0417 M.	Conc. of Benzoic Acid 0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	22.10	35.75	13.65	1.1351	
5	23.46	36.38	12.92	1.1113	
10	24.80	37.01	12.21	1.0867	
15	25.99	37.60	11.61	1.0648	Average time 15 " log(v'-v) 1.0659
20	27.10	38.19	11.09	1.0449	
25	28.17	38.59	10.42	1.0179	
30	29.19	39.20	10.01	1.0004	
35	30.18	39.69	9.51	.9782	
40	31.05	40.15	9.10	.9590	
45	31.89	40.49	8.60	.9345	
50	32.75	40.92	8.15	.9112	Average time 50 " log(v'-v) 0.9126
55	33.50	41.29	7.79	.8915	
60	34.30	41.69	7.39	.8686	
65	35.07	42.07	7.00	.8451	

$$1.0659 = 15\ m - b$$

$$\underline{0.9126 = 50\ m - b}$$

$$.1533 = -35\ m$$

$$-m = 0.004380$$

$$k = 0.01009$$

Table 49

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.0417 M

Conc. of Benzoic Acid
0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)
0	15.58	30.50	14.92	1.1738
5	17.10	31.27	14.17	1.1514
10	18.60	31.85	13.25	1.1222
15	19.92	32.48	12.56	1.0990
20	21.17	33.15	11.98	1.0785
25	22.50	33.70	11.20	1.0492
30	23.49	34.22	10.73	1.0306
35	24.49	34.75	10.26	1.0111
40	25.50	35.24	9.74	.9886
45	26.47	35.70	9.23	.9652
50	27.38	36.10	8.88	.9484
55	28.21	36.50	8.29	.9185
60	29.06	36.90	7.84	.8943
65	29.80	37.27	7.47	.8733

Average time 15
" log(v'-v)
1.1007

Average time 50
" log(v'-v)
0.9428

$$1.1007 = 15\ m + b$$
$$.9428 = 50\ m + b$$
$$.1579 = -35\ m$$
$$-m = 0.004511$$
$$k = 0.01039$$

Table 50

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of $KClO_4$

Conc. of $KClO_4$
0.0833 M.

Conc. of Benzoic Acid
0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	18.88	39.70	20.82	1.3185	
5	20.96	40.68	19.72	1.2949	
10	22.90	41.59	18.69	1.2716	
15	24.78	42.48	17.70	1.2480	Average time 15
20	26.48	43.30	16.82	1.2258	" log(v'-v) 1.2491
25	28.10	44.10	16.00	1.2041	
30	29.70	44.85	15.15	1.1804	
35	31.20	45.55	14.35	1.1568	
40	32.58	46.20	13.62	1.1342	
45	33.99	46.80	12.81	1.1075	
50	35.25	47.45	12.20	1.0864	Average time 50
55	36.45	48.00	11.55	1.0626	" log(v'-v) 1.0864
60	37.58	48.55	10.97	1.0402	
65	38.69	49.09	10.40	1.0170	

$$1.2491 = 15\,m + b$$

$$1.0864 = 50\,m + b$$

$$.1627 = -35\,m$$

$$-m = 0.004645$$

$$k = 0.01070$$

Table 51

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of $KClO_4$

Conc. of $KClO_4$ 0.0833 M.	Conc. of Benzoic Acid 0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	30.30	43.89	13.59	1.1332	
5	31.77	44.56	12.79	1.1069	
10	33.10	45.14	12.04	1.0806	
15	34.23	45.68	11.45	1.0588	Average time 15 " log(v'-v) 1.0590
20	35.39	46.22	10.83	1.0346	
25	36.46	46.70	10.24	1.0103	
30	37.46	47.20	9.74	.9887	
35	38.42	47.67	9.25	.9661	
40	39.36	48.11	8.75	.9420	
45	40.25	48.55	8.30	.9191	
50	41.02	48.95	7.93	.8993	Average time 50 " log(v'-v) 0.8967
55	41.81	49.28	7.47	.8733	
60	42.55	49.62	7.07	.8494	
65	43.21	49.94	6.73	.8280	

$$1.0590 = 15\,m + b$$
$$0.8967 = 50\,m + b$$
$$\overline{}$$
$$.1623 = -35\,m$$
$$-m = 0.004636$$
$$k = 0.01068$$

In an extension of the discussion of the secondary salt effect already given, consider an aqueous solution of the weak acid, HB. From the modern conception of acids and bases, the following equilibrium may be considered to obtain:

$$HB + H_2O \rightleftharpoons H_3O^+ + B^-$$

The classical mass action expression for this equilibrium is written

$$K_c = \frac{c_{H_3O^+} \, c_{B^-}}{c_{HB} \cdot c_{H_2O}} \qquad :1:$$

where the symbols have their usual meanings. The quantity K_c is not, however, a true constant, but varies with the ionic strength of the solution. Expression :1: may be rewritten to conform with the activity theory by substituting for ionic concentrations, the respective activities of the ions. Thus,

$$K_a = \frac{a_{H_3O^+} \cdot a_{B^-}}{a_{HB} \cdot a_{H_2O}} \qquad :2:$$

where K_a is a true constant independent of the ionic strength. Since the a's in equation :2: are related to the c's in equation :1: by the fundamental law of the activity theory, $a = c\,f$, equation :2: may be rewritten:

$$K_a = \frac{a_{H_3O^+} \; a_{B^-}}{a_{HB} \cdot a_{H_2O}} = \frac{c_{H_3O^+} \cdot c_{B^-}}{c_{HB} \cdot c_{H_2O}} \cdot \frac{f_{H_3O^+} \, f_{B^-}}{f_{HB} \cdot f_{H_2O}} = K_c \, \frac{f_{H_3O^+} \, f_{B^-}}{f_{HB} \cdot f_{H_2O}} \quad :3$$

Applying the Debye-Hückel expression for the change of the activity coefficient with ionic strength, and which for a univalent ion in aqueous solution is

$$-\log f = .5\sqrt{u} + B'u \qquad :4:$$

$$-\log f^2 = \sqrt{u} + B\,u \qquad :5:$$

to equation :3:, one obtains

$$\log K_a = \log K_c - \sqrt{u} - B\,u \qquad :6:$$

and

$$\log K_c = \log K_a + \sqrt{u} + B\,u \qquad :7:$$

With this discussion in mind, consider the data given in Tables 34 through 51. In column two of Summary Table A, the average values of the reaction constants at the various salt concentrations are given. These values, when plotted graphically against the corresponding salt concentrations, give the curve shown in Fig.5, which indicates a positive exponential salt effect.

By means of the equation derived in Part II, according to which

$$(H_3O^+) = 0.02572\ k - 0.00046\ C\ ,$$

it is possible to calculate the hydrogen ion concentration from the experimentally determined reaction constant and the salt concentration. By the use of this equation, correction is made for the linear salt effect. Since one benzoate ion must be formed for each hydrogen ion, it follows that the concentration of benzoate ions in the solution must be the same as the concentration of hydrogen ions. Also, since the total concentration of benzoic acid is known, it is a simple matter to determine the concentration of unionized benzoic acid. By substituting these data, which are presented in Summary Table A, in equation :1:, a series of values of $\underline{K_c}$ at various salt concentrations are obtained. By glancing at the column headed $\underline{K_c}$ in Summary Table A or inspection of the graphical presentation of ~~####~~ these data in Fig. 6, it is immediately apparent that K_c is not a true

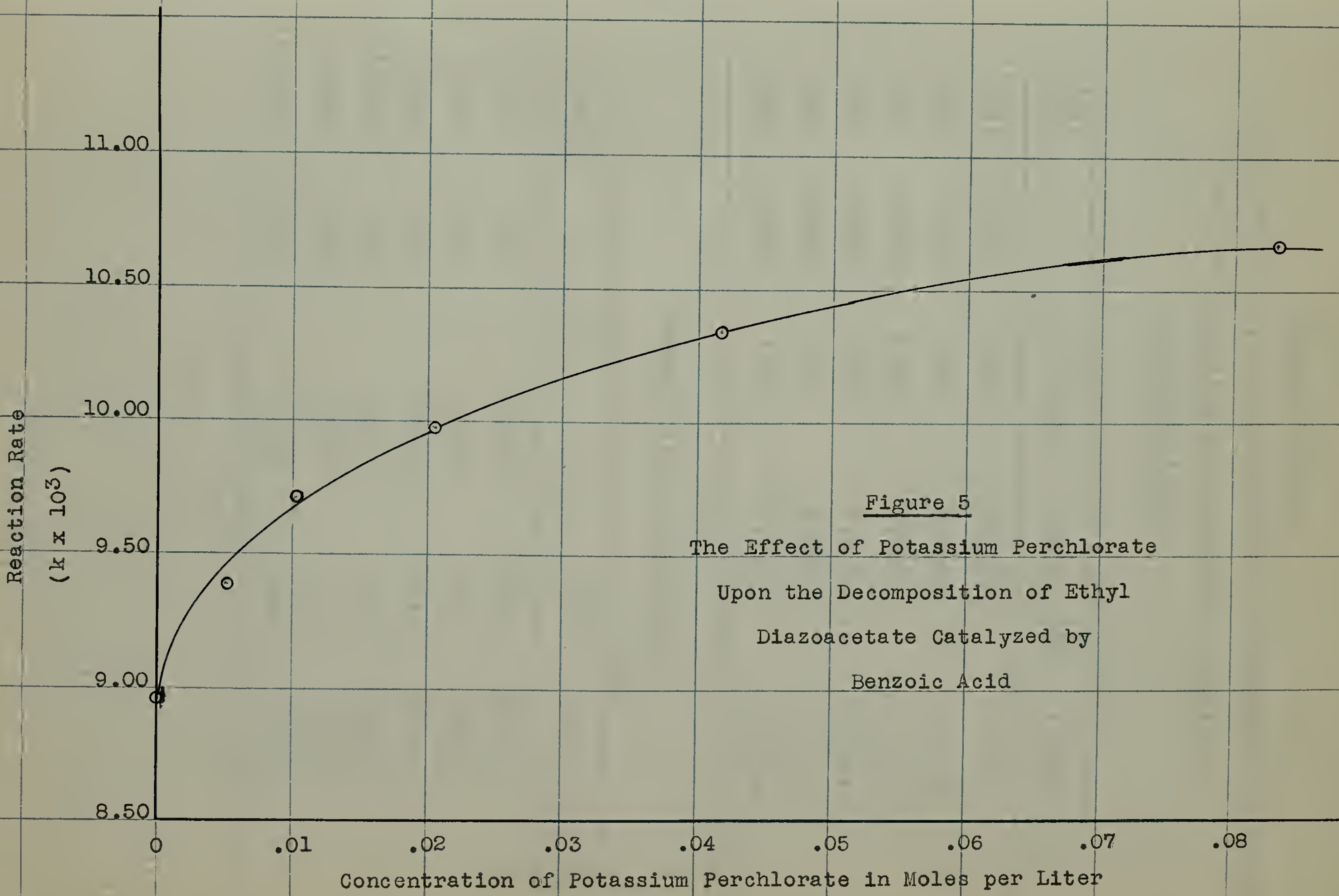


Figure 5

The Effect of Potassium Perchlorate Upon the Decomposition of Ethyl Diazoacetate Catalyzed by Benzoic Acid

Summary Table A

The Effect of Varying Concentrations of Potassium Perchlorate Upon the Ionization of a 0.001040 M. Solution Of Benzoic Acid

Salt Conc.	k	$H_3O^+ \times 10^4$	$\log(H_3O^+)^2_x$	$\log(HB)$ Union.
.0833	.01068	2.368	$\bar{8}.7488$	$\bar{4}.9047$
.0417	.01035	2.477	$\bar{8}.7879$	$\bar{4}.8987$
.0208	.009981	2.480	$\bar{8}.7889$	$\bar{4}.8987$
.0104	.009718	2.461	$\bar{8}.7822$	$\bar{4}.8998$
.0052	.009396	2.403	$\bar{8}.7615$	$\bar{4}.9031$
.0002	.008968	2.317	$\bar{8}.7300$	$\bar{4}.9074$

Summary Table A (Continued)

$\log K_c$	$K_c \times 10^5$	u	$\sqrt{u}$	$(\log K_c - u)$
$\bar{5}.8440$	6.98	.0836	.2890	$\bar{5}.5550$
$\bar{5}.8891$	7.75	.0420	.2047	$\bar{5}.6844$
$\bar{5}.8902$	7.76	.0211	.1449	$\bar{5}.7453$
$\bar{5}.8824$	7.63	.0107	.1029	$\bar{5}.7795$
$\bar{5}.8584$	7.22	.0054	.0735	$\bar{5}.7849$
$\bar{5}.8226$	6.65	.0002	.0153	$\bar{5}.8073$

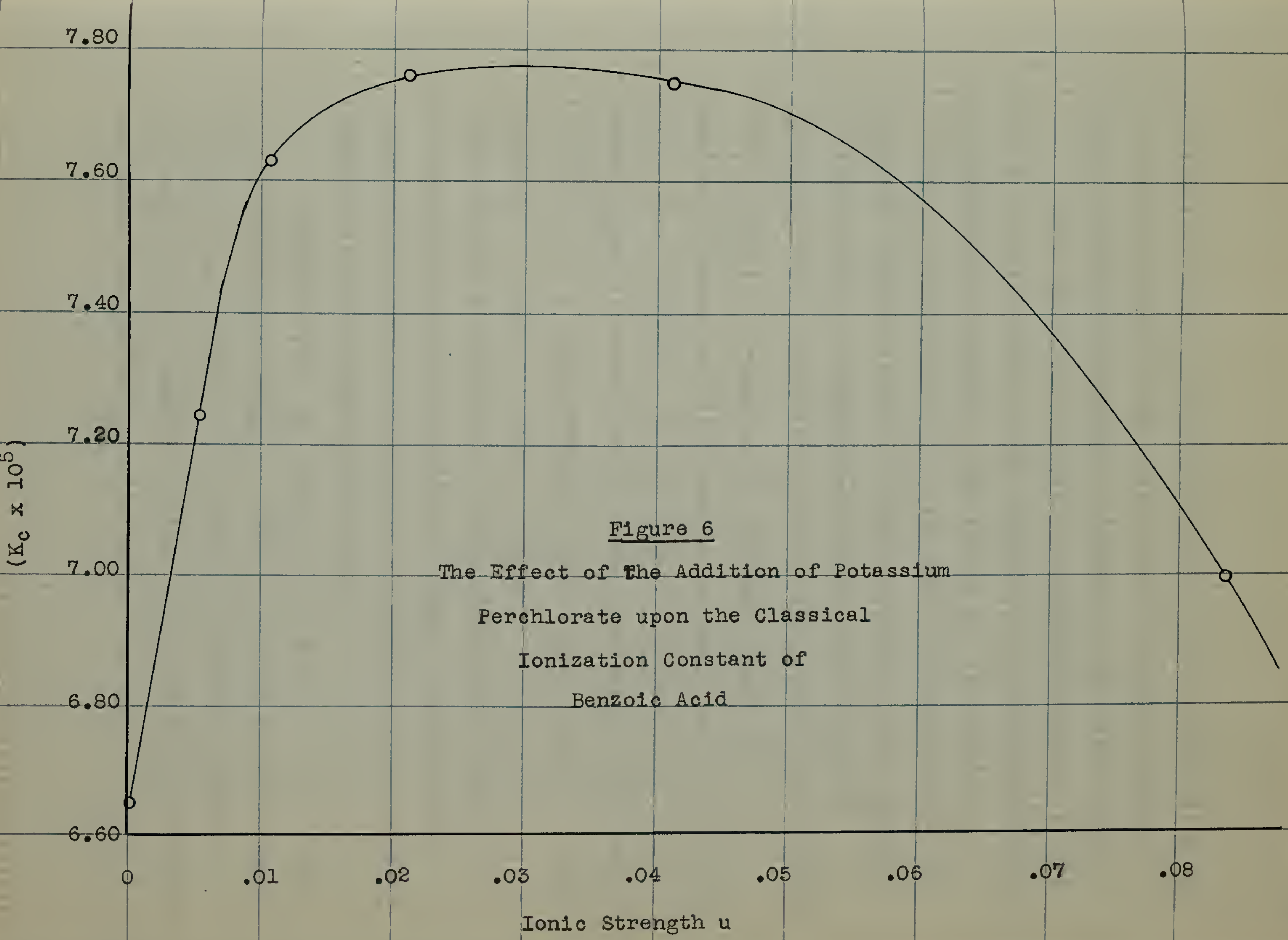


Figure 6

The Effect of The Addition of Potassium Perchlorate upon the Classical Ionization Constant of Benzoic Acid constant, but rather increases with the salt concentration up to a certain maximum value, after which a further increase in salt concentration causes a decrease in the value of K_c.

From these experimentally determined values of K_c and from the ionic stength of the solution, it now becomes possible to evaluate the constants , log K_a and B , in equation :7:. It should be observed at this time that the concentration of potassium perchlorate and the ionic strength are not *exactly* the same* since the ionization of the benzoic acid will contribute some ions to the solution. These two quantities have been assumed to be equal in the foregoing work. This was permissable since the difference is too small to be reflected in the term, 0.00046 C, in the equation derived in Part II. However, the difference, though small, can not be neglected in equation :7:* which contains a square root term of u . The total ionic strengths of the solutions at various salt concentrations are given in a column under that heading in the summary table* and are slightly larger than the salt concentrations. For the purpose of evaluation of the constants, equation :7: may be rearranged to give

$$(\log K_c - \sqrt{u}\,) = \log K_a + B\,u \qquad :8:$$

Now, if the quantity $(\log K_c - \sqrt{u})$ be treated as one variable while u is the second, then equation :8: may be looked upon as a simple linear equation in which log K_a is the intercept at zero ionic strength and B is the slppe. The values of $(\log K_c - \sqrt{u})$

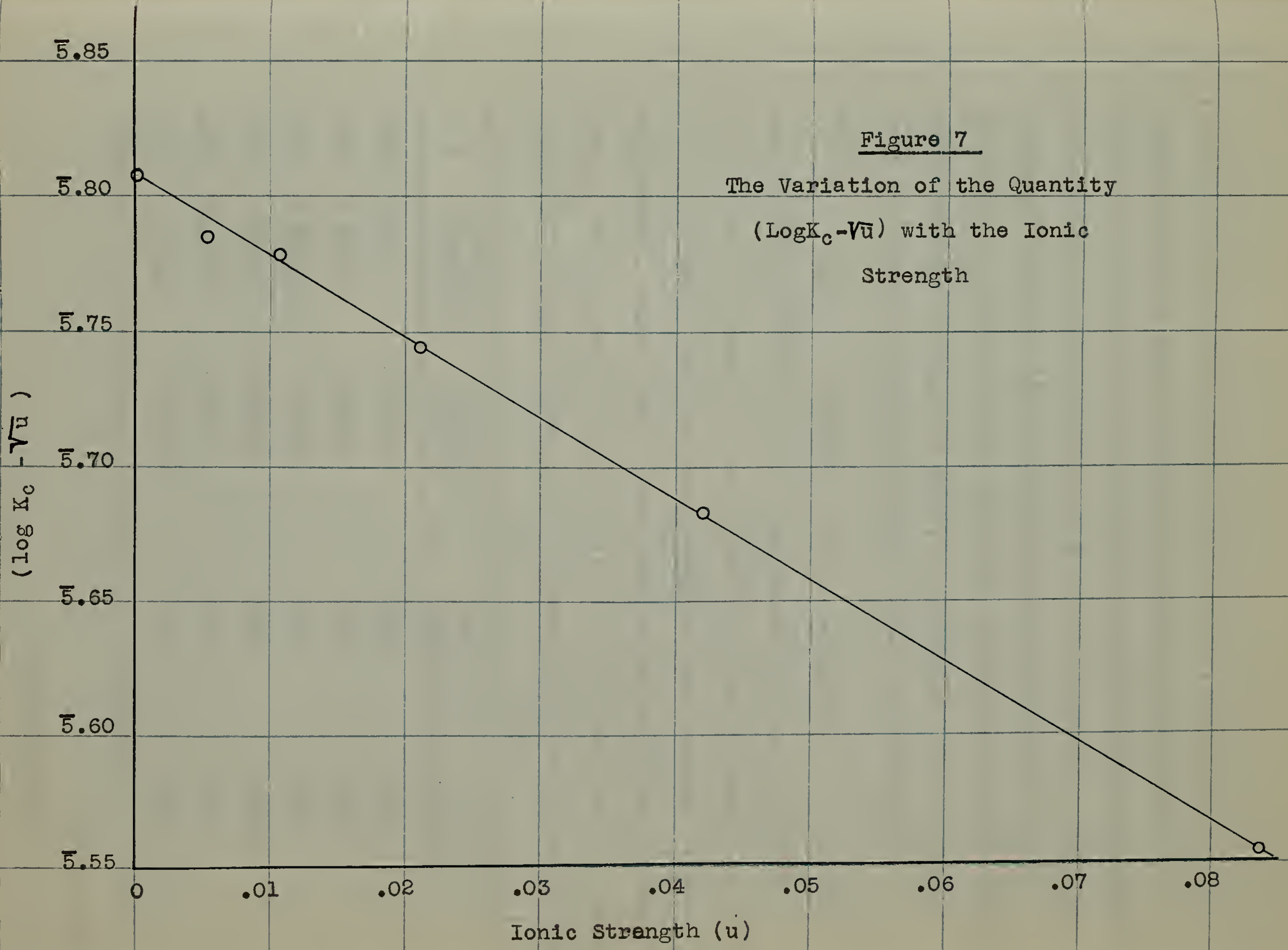


Figure 7

The Variation of the Quantity ($\log K_c - \sqrt{u}$) with the Ionic Strength and the corresponding values of u are given in columns under those headings in Summary Table A. These two variables are plotted in fig. 7* from which it is seen that a linear relation does exist and that the value of B must be negative. From the values of (log Kc - $\sqrt{u}$) and the corresponding values of u, the value of B was found to be -3.03. By extrapolation to zero ionic strength, log K_a was found to be $\bar{5}.8080$. Substituting these values of the constants log K_a and u in equation :7: gives

$$\log K_c = \overset{6}{\bar{5}}.8080_a + \sqrt{u} - 3.03\,u \qquad :9:$$

That this equation accurately represents the data reported in this part is shown by the following table* in which the values of K_c calculated from the above equation are compared to the experimental values. Since these same experimental values were used in the deriving of equation :9: , this table serves merely to show how closely equation :9: represents the experimental data.

u	log K_c (calc'd)	log K_c (exp't)	$K_c \times 10^5$ (calc'd)	$K_c \times 10^5$ (exp't)
.0836	$\bar{5}.8437$	$\bar{5}.8440$	6.98	6.98
.0420	5.8845	$\bar{5}.8891$	7.66	7.75
.0211	$\bar{5}.8890$	$\bar{5}.8901$	7.75	7.76
.0107	$\bar{5}.8785$	$\bar{5}.8824$	7.56	7.62
.0054	$\bar{5}.8652$	$\bar{5}.8582$	7.33	7.22
.0002	$\bar{5}.8226$	$\bar{5}.8226$	6.65	6.65

The value of log K_a used in equation :9: was $\bar{5}.8080$, from which the value of K_a is seen to be 6.43×10^{-5}. As has been discussed, this value is the thermodynamic ionization constant for benzoic acid, and a true "constant" without regard to ionic strength. This fundamental constant for benzoic acid has been determined by many different methods and is frequently reported in the literature. The following values are taken from the literature. In some cases K_c is given in place of K_a, in which cases the value of K_c given is for extreme dilution. The numbers in parentheses after the name of the investigator refer to the bibliography.

$K_c \times 10^5$	= 6.0	Ostwald, 1889 (37)
"	= 6.9	Euler, 1896 (38)
"	= 6.75-6.81	Schaller, 1898 (39)
"	= 6.07	Dhar and Datta, 1913 (40)
$K_a \times 10^5$	= 6.27	Dippy and Williams, 1934 (41)
"	= 6.7	Kolthoff and Bosch, 1932 (42)
"	= 6.46	Ives, Linstead and Riley, 1933 (43)
"	= 6.527	Ives, 1933 (44)
"	= 6.295	Saxton and Meier, 1918 (45)
"	= 6.373	Vogel and Jeffery, 1934 (46)

As has already been observed, equation :9: gives the secondary salt effect for the decomposition of ethyl diazacetate by benzoic acid when potassium perchlorate is the salt. In other words, it gives the effect of the added potassium perchlorate in increasing the dissociation of benzoic acid. By means of this equation, it is possible to calculate the value of K_c from a knowledge of the ionic strength of the solution, and from K_c so obtained and the total concentration of benzoic acid, the hydrogen ion concentration ~~in~~ at any ###(within the limits studied) salt concentration may be calculated from equation :1:. This method of calculating the hydrogen ion concentration of a benzoic acid solution is much more accurate than the customary procedure of calculating from the usual "ionization constant", which has been shown to vary widely with the ionic strength. Even in the absence of added salts, the salt effect of the ionized benzoic acid is sufficient to cause considerable error except at low #### concentrations.

K_a in equation :9: is independent of the specific salt present; however, the value of B might possibly depend upon the specific salt present. That is, the value of B for potassium chloride might differ from that for potassium perchlorate. Before the validity of equation :9: can be extended to include salts other than potassium perchlorate, it is necessary to settle this point. Parts IV and V take up this question.

As a partial answer to this question, the work of Grove ('47) may be mentioned. Studying the dissociation of monochloro-acetic acid by the catalytic hydrolysis of certain acetals as measured by a dilatometer, this worker found the change in K_c with concentration to be given by

$$\log K_c = (7.150 - 10) + \sqrt{u} - 3.2\,u$$

Since this worker used a different acid, a different "salt" (the "salt" in this case being the ionized monochloro-acetic acid) and measured the velocity of the reaction by a different method, it is extremely interesting to observe that his value of B (i.e. 3.2) compares very well with the value obtained in this work. The value of K_a (~~##~~ which is characteristic of the acid alone) obtained by Grove for monochloro-acetic acid is, as is to be expected, different from that obtained in this work for benzoic acid. The work of Grove would tend to support the view that the value of B is independent (or nearly so) of the specific "salt or salts" present, and hence tends to justify the extension of equation :9;

$$\log K_c = \bar{5}.8080 + \sqrt{u} - 3.03\ u$$

Part IV

The Effect of Potassium Iodate upon the Rate of Decomposition of Ethyl Diazoacetate when Catalyzed by Benzoic Acid

At the close of the preceding Part the question of the general validity of equation :9: , derived for potassium perchlorate, was discussed. As was pointed out at that time, it seemed desirable to repeat the work of Part III using a different salt, however the question of what salt to use, which would give no side reaction was difficult. Since perchlorates gave no significant side reaction, it seemed at least possible that iodates might also be suitable. For this reason, it was decided to try potassium iodate. It was soon found that the velocity of the reaction was less in a higher salt concentration. Investigation of the literature showed that the value of the ionization constant for iodic acid is 7.17×10^{-2} (48). It is probable that there would be slight hydrolysis of the potassium iodate~~,~~ with the formation of a slightly basic solution. This would account for the decrease in the velocity of the reaction as the concentration of potassium iodate was increased. Since this work was concerned with the neutral salt effect, there seemed to be no object in carrying the work with this salt further. The data taken are presented in the following tables.

Table 52

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of KIO_3

Conc. of KIO_3 0.0417 M.

Conc. of Benzoic Acid 0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	22.35	32.52	10.17	1.0073	
5	23.32	33.00	9.68	.9859	
10	24.23	33.46	9.23	.9652	
15	25.16	33.90	8.74	.9415	Average time 15 " log(v'-v) 0.9412
20	26.09	34.35	8.26	.9170	
25	26.85	34.77	7.92	.8982	
30	27.60	35.17	7.56	.8785	
35	28.30	35.52	7.22	.8585	
40	29.00	35.90	6.90	.8388	
45	29.67	36.24	6.57	.8176	
50	30.28	36.54	6.26	.7966	Average time 50 " log(v'-v) 0.7971
55	30.88	36.85	5.97	.7760	
60	31.44	37.17	5.73	.7581	
65	31.98	37.40	5.42	.7340	

$$0.9412 = 15\ m + b$$

$$\underline{0.7971 = 50\ m + b}$$

$$.1441 = -35\ m$$

$$-m = 0.00411$$

$$k = 0.00948$$

Table 53

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of KIO_3

Conc. of KIO_3
0.0417 M.

Conc. of Benzoic Acid
0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)
0	6.25	21.16	14.91	1.1735
5	7.67	21.86	14.19	1.1520
10	9.07	22.51	13.44	1.1284
15	10.45	23.20	12.75	1.1055
20	11.67	23.80	12.13	1.0839
25	12.82	24.37	11.55	1.0626
30	13.95	24.98	11.03	1.0426
35	14.96	25.50	10.54	1.0228
40	15.99	26.03	10.04	1.0017
45	16.98	26.50	9.52	.9786
50	17.90	26.95	9.05	.9566
55	18.78	27.38	8.60	.9345
60	19.57	27.83	8.26	.9170
65	20.38	28.22	7.84	.8943

Average time 15
" log(v'-v)
1.1072

Average time 50
" log(v'-v)
0.9579

$$1.1072 = 15\ m + b$$

$$.9579 = 50\ m + b$$

$$.1493 = -35\ m$$

$$-m = 0.00426$$

$$k = 0.00982$$

Table 54

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of KIO_3

Cons. of KIO_3
0.0833 N.

Conc. of Benzoic Acid
0.001040 N.

Time	v	v'	(v'-v)	log(v'-v)	
0	8.08	21.60	13.52	1.1310	
5	9.45	22.39	12.94	1.1119	
10	10.68	22.90	12.22	1.0871	
15	11.79	23.54	11.75	1.0700	Average time 15
20	12.90	24.09	11.19	1.0488	" log(v'-v) 1.0695
25	13.99	24.67	10.68	1.0286	
30	15.00	25.22	10.22	1.0094	
35	15.98	25.70	9.72	.9877	
40	16.93	26.20	9.27	.9671	
45	17.82	26.65	8.83	.9460	
50	18.69	27.06	8.37	.9227	Average time 50
55	19.44	27.50	8.06	.9063	" log(v'-v) 0.9263
60	20.20	27.90	7.70	.8865	
65	20.95	28.33	7.38	.8681	

$$
\begin{array}{rl}
1.0695 = & 15\ m - b \\
.9263 = & 50\ m - b \\
\hline
.1432 = & -35\ m \\
-m = & 0.00409 \\
k = & 0.00942
\end{array}
$$

Table 55

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Presence of KIO_3

Conc. of KIO_3 0.0832 M.

Conc. of Benzoic Acid 0.001040 M.

Time	v	v'	(v'-v)	log(v'-v)
0	23.08	32.47	9.39	.9727
5	24.07	32.98	8.91	.9499
10	24.89	33.38	8.49	.9289
15	25.70	33.82	8.12	.9096
20	26.44	34.22	7.78	.8910
25	27.16	34.64	7.48	.8739
30	27.84	34.98	7.14	.8537
35	28.53	35.37	6.84	.8350
40	29.16	35.70	6.54	.8156
45	29.77	36.02	6.25	.7959
50	30.39	36.34	5.95	.7745
55	30.95	36.66	5.71	.7566
60	31.47	36.91	5.44	.7356
65	31.97	37.16	5.19	.7143

Average time 15
" log(v'-v) 0.9114 M.

Average time 50
" log(v'-v) 0.7754

$$0.9114 = 15\,m + b$$
$$\underline{.7754 = 50\,m + b} \;-$$
$$.1360 = -35\,m$$
$$-m = 0.00389$$
$$k = 0.00896$$

Part V

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Absence of Added Salts - The Dissociation of Benzoic Acid in the Absence of Added Salts

Previous work with benzoic acid seemed to show that the benzoate ion gives no side reaction. However, benzoate salts are not suitable for the study of neutral salt effects, since they are considerably hydrolyzed in aqueous solution. As was pointed out in Part III , in considering the ionic strength of a solution, one must take into account not only the concentration of the salt, but also the ions formed by the dissociation of the acid itself. From this it appears that there should be a slight "salt effect" even in the absence of salts in the usual sense, because of the ionization of the acid. Perhaps a better term than *salt effect* would be *ionic effect*. The work of Grove(47) in studying the "salt effect" of the ionized acid upon the dissociation of monochloro-acetic acid has already been mentioned. For these reasons, it seemed of interest to attempt the verification of equation :9;,Part III, by a study of the "salt effect" in solutions of benzoic acid in the absence of *added* salts.

With this in mind, the rate of decomposition of ethyl diazoacetate by benzoic acid at varying concentrations of acid was studied. The data is contained in the following tables in this Part and in Part I, Tables 14, 15 and 16 and PartIII, Tables 34 and 35.

Table 56

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Absence of Added Salts

Conc. of Benzoic Acid
0.001111 M.

Time	v	v'	(v'-v)	log(v'-v)
0	28.81	43.99	15.18	1.1813
5	30.22	44.76	14.54	1.1626
10	31.60	45.46	13.86	1.1417
15	32.93	46.18	13.25	1.1222
20	34.18	46.80	12.62	1.1011
25	35.38	47.45	12.07	1.0817
30	36.55	48.02	11.47	1.0596
35	37.67	48.60	10.93	1.0386
40	38.69	49.08	10.39	1.0166
45	39.65	49.59	9.94	.9974
50	40.57	50.11	9.54	.9795
55	41.50	50.60	9.10	.9590
60	42.40	51.08	8.68	.9385
65	43.20	51.51	8.31	.9196

Average time 15
" log(v'-v)
1.1214

Average time 50
" log(v'-v)
0.9785

$$1.1214 = 15\ m - b$$

$$0.9785 = 50\ m - b$$

$$.1429 = -35\ m$$

$$-m = 0.004085$$

$$k = 0.009408$$

Table 57

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Absence of Added Salts

Conc. of Benzoic Acid
0.001111 M.

Time	v	v'	(v'-v)	log(v'-v)
0	15.29	36.66	21.37	1.3298
5	17.37	37.75	20.38	1.3092
10	19.30	38.78	19.48	1.2896
15	21.11	39.70	18.59	1.2693
20	22.88	40.68	17.80	1.2504
25	24.54	41.52	16.98	1.2299
30	26.17	42.37	16.20	1.2095
35	27.69	43.16	15.47	1.1895
40	29.13	43.90	14.77	1.1694
45	30.50	44.63	14.13	1.1501
50	31.88	45.30	13.42	1.1277
55	33.10	45.99	12.89	1.1102
60	34.38	46.60	12.22	1.0871
65	35.52	47.22	11.70	1.0682

Average time 15
" log(v'-v)
1.2697

Average time 50
" log(v'-v)
1.1289

$$1.2697 = 15\,m - b$$
$$1.1289 = 50\,m - b$$
$$.1408 = -35\,m$$
$$-m = 0.004022$$
$$k = 0.009263$$

Table 58

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Absence of Added Salts

Conc. of Benzoic Acid
0.001111 M.

Time	v	v'	(v'-v)	log(v'-v)
0	23.23	34.79	11.56	1.0630
5	24.31	35.33	11.02	1.0422
10	25.35	35.90	10.55	1.0232
15	26.32	36.38	10.06	1.0026
20	27.38	36.92	9.54	.9795
25	28.28	37.40	9.12	.9600
30	29.10	37.85	8.75	.9420
35	29.95	38.26	8.31	.9196
40	30.71	38.67	7.96	.9009
45	31.47	39.06	7.59	.8802
50	32.21	39.45	7.24	.8597
55	32.90	39.80	6.90	.8388
60	33.52	40.12	6.60	.8195
65	34.16	40.45	6.29	.7986

Average time 15
" log(v'-v)
1.0018

Average time 50
" log(v'-v)
0.8596

$$1.0018 = 15\ m - b$$

$$.8596 = 50\ m - b$$

$$.1422 = -35\ m$$

$$-m = 0.004061$$

$$k = 0.009352$$

Table 59

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Absence of Added Salts

Conc. of Benzoic Acid
0.001905 M.

Time	v	v'	(v'-v)	log(v'-v)
0	27.89	43.69	15.80	1.1987
5	29.52	44.40	14.88	1.1726
10	31.07	45.03	13.96	1.1449
15	32.52	45.66	13.14	1.1186
20	33.87	46.25	12.38	1.0927
25	35.17	46.76	11.59	1.0641
30	36.40	47.21	10.81	1.0338
35	37.52	47.70	10.18	1.0077
40	38.56	48.18	9.66	.9850
45	39.58	48.61	9.03	.9557
50	40.51	48.98	8.47	.9279
55	41.42	49.35	7.93	.8993
6 0	42.23	49.67	7.44	.8716
65	42.97	49.96	6.99	.8445

Average time 15
" log(v'-v)
1.1179

Average time 50
" log(v'-v)
0.9274

1.1179 = 15 m - b
.9274 = 50 m - b

.1905 = -35 m
-m = 0.005444
k = 0.01254

Table 69

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Absence of Added Salts

Conc. of Benzoic Acid
0.001905 N.

Time	v	v'	(v'-v)	log(v'-v)	
0	12.78	31.09	18.31	1.2630	
5	14.77	31.89	17.12	1.2336	
10	16.59	32.62	16.03	1.2049	
15	18.27	33.30	15.03	1.1770	Average time 15
20	19.88	33.99	14.11	1.1495	" log(v'-v) 1.1780
25	21.28	34.57	13.29	1.1235	
30	22.70	35.15	12.45	1.0952	
35	23.95	35.69	11.74	1.0697	
40	25.20	36.19	10.99	1.0410	
45	26.33	36.65	10.32	1.0137	
50	27.39	37.09	9.70	.9868	Average time 50
55	28.39	37.50	9.11	.9595	" log(v'-v) 0.9871
60	29.34	37.89	8.55	.9322	
65	30.22	38.29	8.07	.9069	

$$1.1780 = 15\,m + b$$

$$0.9871 = 50\,m + b$$

$$.1909 = -35\,m$$

$$-m = 0.005455$$

$$k = 0.01256$$

Table 61

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Absence of Added Salts

Conc. of Benzoic Acid
0.001905 M

Time	v	v'	(v'-v)	log(v'-v)	
0	27.30	40.43	13.13	1.1183	
5	28.77	41.06	12.29	1.0895	
10	30.04	41.58	11.54	1.0622	
15	31.21	42.07	10.86	1.0358	Average time 12.5
20	32.36	42.48	10.12	1.0052	" log(v'-v) 1.0483
25	33.40	42.92-	9.52	.9786	
30	34.37	43.33	8.96	.9523	
35	35.31	43.69	8.38	.9232	
40	36.20	44.08	7.88	.8965	
45	37.05	44.47	7.42	.8704	Average time 42.5
50	37.81	44.77	6.96	.8426	" log(v'-v) 0.8836
55	38.50	45.05	6.55	..8162	
60	39.26	45.32	6.06	.7825*	
65	39.85	45.56	5.71	.7566*	

* in error (from graph)

$$1.0483 = 12.5\ m - b$$

$$0.8836 = 42.5\ m - b$$

$$.1647 = -30.0\ m$$

$$-m = 0.005491$$

$$k = 0.01264$$

Table 62

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Absence of Added Salts

Conc. of Benzoic Acid
0.001005 M.

Time	v	v'	(v'-v)	log(v'-v)
0	27.87	43.25	15.38	1.1869
5	29.90	44.28	14.38	1.1578
10	31.76	45.28	13.52	1.1310
15.	33.53	46.20	12.67	1.1028
20	35.19	47.16	11.97	1.0781
25	36.74	47.99	11.25	1.0511
30	38.20	48.72	10.52	1.0220
35	39.60	49.47	9.87	.9943
40	40.87	50.16	9.29	.9680
45	42.09	50.78	8.67	.9380

Average time 10
" log(v'-v)
1.1313

Average time 35
" log(v'-v)
0.9947

$$1.1313 = 10\ m - b$$
$$.9947 = 35\ m - b$$
$$.1366 = -25\ m$$
$$-m = 0.005462$$
$$k = 0.01259$$

Table 63

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Absence of Added Salts

Conc. of Benzoic Acid
0.001905 M.

Time	v	v'	(v'-v)	log(v'-v)
0	14.35	36.19	21.84	1.3392
5	17.29	37.68	20.39	1.3094
10	19.97	39.10	19.13	1.2817
15	22.43	40.48	18.05	1.2565
20	24.75	41.76	17.01	1.2307
25	26.99	42.91	15.92	1.2019
30	29.05	44.00	14.95	1.1746
35	31.00	45.00	14.00	1.1461
40	32.85	45.99	13.14	1.1186
45	34.56	46.90	12.34	1.0913

Average time 10
" log(v'-v)
1.2835

Average time 35
" log(v'-v)
1.1465

$$1.2835 = 10\,m - b$$
$$1.1465 = 35\,m - b$$
$$\overline{.1370 = -25\,m}$$
$$-m = 0.005480$$
$$k = 0.01262$$

Table 64

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Absence of Added Salts

Conc. of Benzoic Acid
0.003333 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	27.16	41.29	14.13	1.1501	
5	28.86	41.77	12.91	1.1109	
10	30.37	42.19	11.82	1.0726	
15	31.72	42.68	10.96	1.0398	Average time 15
20	32.98	42.97	9.99	.9996	" log(v'-v) 1.0373
25	34.18	43.36	9.18	.9628	
30	35.28	43.70	8.42	.9253	
35	36.28	44.00	7.72	.8876	
40	37.20	44.28	7.08	.8500	
45	38.02	44.50	6.48	.8116	
50	38.78	44.74	5.96	.7752	Average time 50
55	39.48	44.96	5.48	.7388	" log(v'-v) 0.7756
60	40.10	45.17	5.07	.7050	
65	40.72	45.30	4.58	.6609	

$$1.0373 = 15\ m - b$$

$$.7756 = 50\ m - b$$

$$.2617 = -35\ m$$

$$-m = 0.007478$$

$$k = 0.01722$$

Table 65

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Absence of Added Salts

Conc. of Benzoic Acid
0.003333 M.

Time	v	v'	(v'-v)	log(v'-v)
0	11.60	31.70	20.10	1.3032
5	13.99	32.41	18.42	1.2653
10	16.21	33.08	16.87	1.2271
15	18.25	33.70	15.45	1.1889
20	20.00	34.21	14.21	1.1526
25	21.77	34.76	12.99	1.1136
30	23.23	35.19	11.96	1.1077
35	24.66	35.66	11.00	1.0414
40	25.95	36,07	10.07	1.0030
45	27.09	36;38	9.29	.9680
50	28.20	36.68	8.48	.9284
55	29.18	37.05	7.87	.8960
60	30.09	37.30	7.21	.8579
65	30.91	37.67	6.76	.8299

Average time 15
" log(v'-v)
1.1898

Average time 50
" log(v'-v)
0.9321

1.1898 = 15 m + b

0.9321 = 50 m + b

.2577 = -35 m

-m = 0.007362

k = 0.01695

Table 66

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Absence of Added Salts

Conc. of Benzoic Acid
0.005714 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	16.49	38.09	21.60	1.3344	
5	19.90	39.23	19.33	1.2862	
10	22.96	40.20	17.24	1.2365	Average time 10
15	25.69	41.08	15.39	1.1872	" log(v'-v) 1.2362
20	28.18	41.87	13.69	1.1364	
25	30.38	42.55	12.17	1.0853	
30	32.27	43.10	10.83	1.0346	
35	33.98	43.67	9.69	.9863	Average time 35
40	35.57	44.10	8.53	.9309	" log(v'-v) 0.9844
45	36.89	44.56	7.67	.8848	

$$1.2362 = 10\,m - b$$

$$0.9844 = 35\,m - b$$

$$.2518 = -25\,m$$

$$-m = 0.01007$$

$$k = 0.02319$$

Table 57

The Rate of Decomposition of Ethyl Diazoacetate by Benzoic Acid in the Absence of Added Salts

Conc. of Benzoic Acid
0.005714 M.

Time	v	v'	(v'-v)	log(v'-v)	
0	29.60	45.80	16.20	1.2095	
5	32.15	46.63	14.48	1.1608	
10	34.48	47.34	12.86	1.1092	Average time 10
15	36.50	48.03	11.53	1.0618	" log(v'-v) 1.1107
20	38.32	48.60	10.28	1.0120	
25	39.98	49.08	9.10	.9590	
30	41.45	49.49	8.04	.9053	
35	42.72	49.90	7.18	.8561	Average time 35
40	43.86	50.29	6.43	.8082	" log(v'-v) 0.8572
45	44.90	50.62	5.72	.7574	

$$1.1107 = 10\ m + b$$

$$.8572 = 35\ m + b$$

$$.2535 = -25\ m$$

$$-m = 0.01014$$

$$k = 0.02335$$

The change in the average values of the reaction constant with the acid concentration is shown graphically in fig. 8. From the average values of the reaction constants and following the same procedure as was outlined in Part III, it is possible to calculate the hydrogen ion concentrations at the various acid concentrations and, from these values, the classical dissociation "constant" for the corresponding acid concentrations. The results of these calculations are given in Summary Table B. From the hydrogen ion concentrations calculated in the above manner, the ionic strengths(u) of the solutions are obtained.

By means of equation :9:, Part III, which states

$$\log K_c = \bar{5}.8080 + \sqrt{u} - 3.03\,u$$

a series of calculated values for K_c may be obtained for the various ionic strengths. Such a series is given in Summary Table B under the column headed $K_c \times 10^5$(calc'd). By comparing the calculated values with the experimental values for the same concentrations(also given in Table B), it is seen that the agreement is excellent. This gives a measure of the general validity of equation :9:.

It is also possible to check the general form of equation :9: in another way. Using the experimental values of K_c and the known values of u , a series of values of K_a at the different concentrations may be obtained. If the equation be valid, K_a should be a constant independent of u, and furthermore it should check the value of K_a obtained in Part III, namely $\bar{5}$.

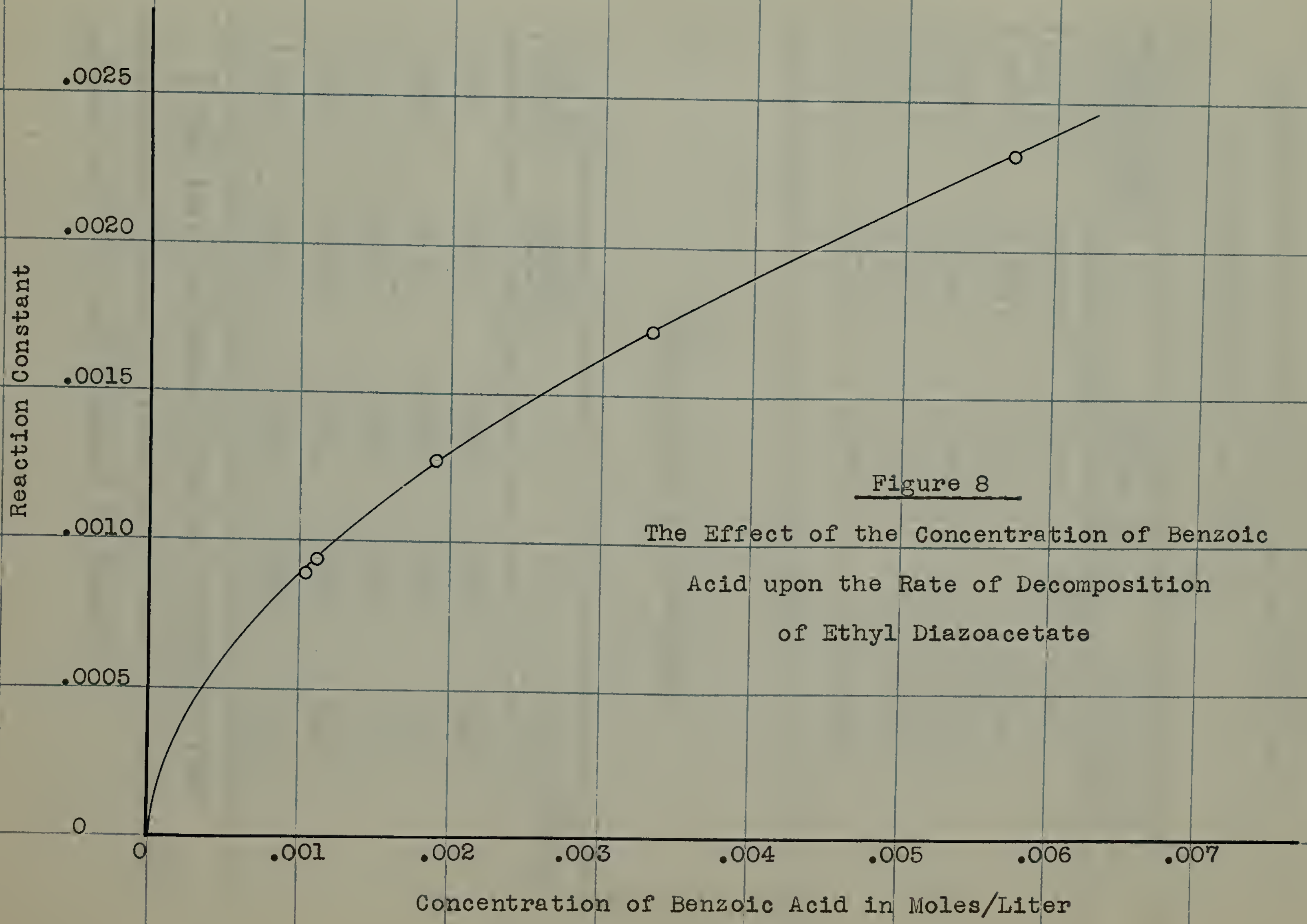


Figure 8

The Effect of the Concentration of Benzoic Acid upon the Rate of Decomposition of Ethyl Diazoacetate

Summary Table B

The Ionization Constants of Benzoic Acid in Diferrent Concentrations as Determined Experimentally and As Calculated from Equation :9:

Benzoic Acid Moles/liter	k	$(H_3O^+) \times 10^4$	log K_c(exp't)
0.001040	.008963	2.317	$\bar{5}$.8226
0.001111	.009341	2.414	$\bar{5}$.8259
0.001905	.01259	3.250	$\bar{5}$.8259
0.003333	.01709	4.409	$\bar{5}$.8273
0.005714	.02319	5.992	$\bar{5}$.8463

Summary Table B (Continued)

$K_c \times 10^5$ (exp't)	$K_c \times 10^5$ (calc'd)	u	$\sqrt{u}$	$K_a \times 10^5$ *
6.65	6.66	.00023	.0151	6.43
6.70	6.66	.00024	.0156	6.48
6.70	6.68	.00032	.0179	6.43
6.72	6.73	.00044	.0210	6.42
7.02	6.77	.00060	.0246	6.66

* This series of values of Ka are calculated from experimental values of K_c obtained in this Part and is to be compared to 6.43×10^{-5} obtained in Part III

6.43×10^{-5}. The values of K_a calculated from the data in this Part are given under a column so designated in the summary table. It is apparent that except for the last value in the column, the value of K_a is constant and agrees very closely with that obtained in Part III using potassium perchlorate as the salt. As the concentration of benzoic acid is increased above a certain point, the data tends to become more qestionable, since the reaction proceeds too rapidly to permit precise measurement of the rate constants. At concentrations of benzoic acid above 0.005714 M., it was deemed impracticable to obtain rate constants with the equipment used. The value obtained at 0.005714 M. is questionable; and this probably explains why the value of K_a calculated from it fails to agree with the other values obtained.

While equation :9: is excellently checked by the data given in this Part, it is easy to overstate the importance of this. It must be observed that the salt concentration was necessarily very low in this Part, and for this reason the correction due to the linear term in equation :9: was extremely small. This much, however, may be safely said: The work of this Part, as far as it goes, completely verifies equation:9:, which probably is valid for all aqueous solutions of benzoic acid in the absence of other salts, since the solubility of benzoic acid is so low as to prevent a small error in the linear term(the only term questionable) in equation:9: from having much influence on the calculated value of K_c.

Summary

(1)AAn apparatus has been designed for the determination of reaction rates by the measurement of the pressure of an evolved gas.

(2). This apparatus has been applied to a study of the effect of neutral salts in various concentrations on the rate of decomposition of ethyl diazoacetate, catalyzed by perchloric and benzoic acids; ~~and~~ from this study the effect of neutral salts on the ionization of ### benzoic acid has been deduced.

(3). The velocity of decomposition of ethyl diazoacetate catalyzed by benzoic acid has been studied in the presence of several different concentrations of potassium nitrate, and the salt effect was found to be positive and exponential. This is in accord with theory. An interfering side reaction prevented quantitative treatment of results.

(4). The velocity of the same reaction catalyzed by perchloric acid and in the presence of varying concentrations of potassium perchlorate has been studied; the salt effect in this case was positive and linear over the range of concentrations studied. From this work, the following equation ~~was derived~~, relating hydrogen ion conc. to salt concentration and reaction constant, was derived:

$$(H_3O^+) = 0.02572\ k - 0.00046\ c$$

where the last term is a correction for the linear salt effect. This equation is valid only for the diazo reaction.

(5). The effect of concentration of potassium perchlorate on the velocity of the reaction catalyzed by benzoic acid has been studied; the salt effect was found to be positive and exponential.

(6). The hydrogen ion concentration has been catalytically determined for solutions of benzoic acid in the presence of varying concentrations of potassium perchlorate.

(7). The classical ionization constant of benzoic acid has been calculated from these data and found to vary with the salt concentration.

(8). The thermodynamic ionization constant has been likewise calculated and found to be independent of the salt concentration and to have the value 6.43 x 10^{-5}.

(9). The classical ionization constant of benzoic acid has been found to be related to the ionic strength (u) of the solution by the expression

$$\log K_c = \bar{5}.8080 + \sqrt{u} - 3.03\ u$$

(10). This equation has been verified for aqueous solutions of benzoic acid at concentrations from 0.001 to .006 M. in the absence of added salts.

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Approved by:

Paul Serex

C. R. Fellers

G. W. Alderman

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