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ELECTRODIALYSIS OF TOMATO JUICE

BY

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A

THESIS

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I. INTRODUCTION

Thermal decarboxylation of carboxylic acids has been helpful in illustrating some fundamentals of reaction kinetics in solution. It has been important in formulation of the theory of unimolecular reactions. It is also used frequently in the synthetical methods of organic chemistry.

In a recent study of the anodic oxidation of malonic acid in sulfuric acid at 80°C using a platinum anode, the interpretation of some results was impossible due to the spontaneous decomposition of the malonic acid. As no information is available in the literature about decomposition rates of malonic acid in sulfuric acid at the concentrations used, it was necessary to study this aspect before continuing the anodic oxidation studies. (1)

The purpose of this investigation was to determine reaction rate, order, activation energy, pH effect, and catalytic effect of divalent metal ions on the decarboxylation at higher concentrations (0.5N to 5N) of malonic acid. Hopefully, these data could be used to extend the mechanism proposed by others in the low concentration region (2) or to suggest a mechanism to apply to these higher concentrations.

II. LITERATURE REVIEW

This literature review includes general information about the kinetics of decarboxylation reactions and reviews studies on the decarboxylation of malonic acid and the catalytic effect of divalent metal ions on decarboxylation.

Decarboxylation Reactions. The kinetics of the decomposition of carboxylic acids have been studied numerous times according to the scheme:

$$\text{R-COOH} \longrightarrow \text{R-H} + \text{CO}_2 \qquad (1)$$

It has been shown that most acids decompose unimolecularly and that several decompose in their anionic form (3), i.e.,

$$\text{R-COO}^- \longrightarrow \text{R}^- + \text{CO}_2 \qquad (2)$$

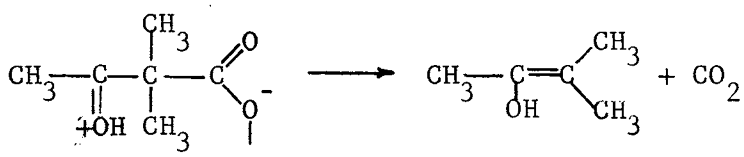
However, some acids decompose more rapidly as free acids. This behavior has been interpreted as involving unimolecular decomposition of a zwitterionic form (3):

$$\text{R-COOH} \rightleftharpoons \text{H}^+\text{R-COO}^- \longrightarrow \text{HR} + \text{CO}_2 \qquad (3)$$

It has been found that some β-ketocarboxylic acids obey a rate law of the following type:

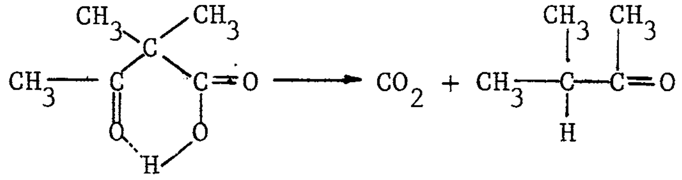
$$\text{rate} = k' \text{ (keto acid)} + k'' \text{ (keto acid anion)} \qquad (4)$$

The k' is usually much larger than k'' (4). Examples of this behavior are found for acetoacetic acid, camphor-3-carboxylic acid, and α,α-dimethylacetoacetic acid. For α,α-dimethylacetoacetic acid, the enol form is stable towards decarboxylation. The unstable keto form is thought to decompose as zwitterions (3):



(5)

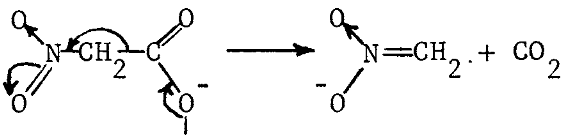
It has also been suggested that instead of the zwitterionic form, the hydrogen-bonded structure decomposes unimolecularly (3):



(6)

However, these views are identical because the nuclear configuration of the zwitterion and the hydrogen-bonded structure are the same (3).

Pedersen (5) conducted kinetic studies of the decomposition of nitroacetic acid in aqueous solutions. He showed that the monovalent nitroacetate ion decomposes unimolecularly, whereas the undissociated acid and the bivalent ion, $^{-}NO_2{:}CHCOO^{-}$, are stable. He also found that the rate of decarboxylation was equal to the rate of reaction of an intermediate with bromine, and hence proposed the following mechanism:



(7)

Wiig (6,7) and Prue (8) carried out rate measurements on the decarboxylation of acetonedicarboxylic acid. Wiig found that the rate decreased and reached a constant value with increasing hydrogen ion concentration in aqueous solutions. Since the ionization was supressed at higher hydrogen ion concentration, a constant rate was attained when the acid was in the undissociated form. Therefore, he concluded that the monovalent ion of acetonedicarboxylic acid decomposed faster than the undissociated acid. Furthermore, he assumed that two molecules of CO_2 were simultaneously lost from an acid molecule and did not consider the presence of any acetoacetic acid which would have been formed by a stepwise decomposition.

The assumption of Wiig was not supported by Prue. Since acetoacetic acid also decomposes at an appreciable rate, he proposed a new mechanism in which the decomposition consisted of two consecutive irreversible unimolecular reactions. In acetate-buffered solutions, Prue found that the second molecule of carbon dioxide was lost very slowly. The loss of the first molecule of carbon dioxide produced acetoacetic acid which was almost completely converted into the ionic form in the acetate buffer. He explained a slow loss of the second molecule of CO_2 by observing that the decomposition of the acetoacetate ion was very slow compared to that of the undissociated acid. Thus, he proposed the following kinetic scheme for the decarboxylation of acetonedicarboxylic acid in acetate-buffered solutions:

$$H_2O + {}^-COOCH_2COCH_2COO^- \xrightarrow{k_1} CH_3COCH_2COO^- + CO_2 + OH^- \qquad (8)$$

$$H_2O + CH_3COCH_2COO^- \xrightarrow{k_2} CH_3COCH_3 + CO_2 + OH^- \qquad (9)$$

A kinetic study of the decarboxylation of dihydroxymaleic acid has revealed that the univalent ion $\cdot COOHCOH{:}COHCOO^-$ decomposes and the undissociated acid is stable (3). However, a detailed mechanism for this acid has not been determined.

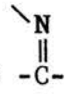
The results obtained for the above mentioned dicarboxylic acids are similar to those found for the monobasic β-keto acids.

The kinetic work of Verhoek and co-workers (9,10,11) on the decarboxylation of trichloracetic acid in several solvents has shown the reaction to be first order. The rate-determining step was proposed to be the decomposition of the trichloracetate anion forming carbon dioxide and the anion of the acid chloroform:

$$CCl_3COO^- \longrightarrow CCl_3^- + CO_2 \qquad (10)$$

This mechanism was supported by the following observations: (1) Trichloroacetic acid was completely ionized in water, (2) the activation energies for the decarboxylation of the acid and its sodium salts in water were the same, (3) the decomposition was very slow in non-ionizing solvents, and (4) in non-aqueous solvent (Ethyl alcohol), the rate was found to be proportional to the concentration of the anion produced by adding bases.

Thus, the results obtained from measurements of rates of decarboxylation indicate that some acids decompose as anions, some as zwitterions, and others from the unionized form. Some show simultaneous decomposition of more than one species. The ease of decarboxylation seems to be determined by the type of substituents present within group R of the acid R-COOH. The acids with properly situated strongly electron attracting substituents like $-NO_2$, $-CCl_3$, $-C{\equiv}N$ or $-C{=}O$ seem to decarboxylate more readily.

The following generalities were noted: (1) The acids with properly situated electrophilic groups are decarboxylated more readily in the form of their anions since they form stable carbon ions during the fission of the carbon-carbon bond. (2) β-keto acids are decarboxylated in the form of both their anions and zwitterions. (3) A number of nitrogen containing acids undergo first order decarboxylation in zwitterionic form only. This reaction takes place more readily if the  $\overset{\diagdown N}{\overset{\|}{-C-}}$ group is situated beta to the -COOH group (12).

Decarboxylation of Malonic Acid. Laskin (13) has shown that pure malonic acid undergoes decarboxylation at 138°C. He found the decomposition to be first order with a rate constant equal to 0.021 min^{-1}.

Hinshelwood (14) measured the rate of decomposition of molten malonic acid above the melting point (134°C) and of the supercooled liquid. It was found that the rate of decomposition was first order for both. The rate of decomposition of solid malonic acid was measured at different temperatures and the following expression deduced to correlate the rate constant with temperature:

$$\mathrm{Log}_{10}k = 0.04157(t-100) - 3.7778 \tag{11}$$

where,

k = rate constant, min^{-1}

t = temperature, °C

The results obtained from experiments with the supercooled liquid showed that it decomposed more rapidly than the molten solid.

Muus (15) investigated the rate of decarboxylation of dibromomalonic acid in aqueous solution at concentrations of 0.1, 0.2, and 2N and at pH's ranging from 0 to 5. The reaction in solutions of hydrochloric acid was found to be first order. However, the rate constant in buffer solutions was found to decrease slightly during the reaction. This experimental observation was not substantiated but was thought to be due to a decrease in hydrogen ion concentration owing to the disappearance of dibromomalonic acid.

It was shown that the decarboxylation in buffer solutions proceeded with a secondary salt effect but with no primary salt effect. Moreover, it was found that the ratio of the rate constant to the concentration of unionized dibromomalonic acid remained constant irrespective of the reaction medium. Therefore, it was concluded that there was no general acid or base catalysis. The rate measurements in the different reaction mediums established that the undissociated acid and $^{-}COOCBr_2COO^{-}$ ion were stable and that the rate of decarboxylation was proportional to the amount of primary ion present, i.e.,

$$COOHCBr_2COO^{-} \longrightarrow COOHCBr_2^{-} + CO_2 \qquad (12)$$

An energy of activation equal to 25 kcal/mole was found from rate measurements at 25 and 35°C in HCl solutions.

Fairclough (16) studied the kinetics of decarboxylation of the ions of three monobasic acids (trichloroacetic, tribromoacetic, and phenylpropiolic) and one dibasic acid (malonic) at different temperatures. In order to isolate the reaction of the ions of the acids from any possible reaction by the undissociated molecules, aqueous solutions of the sodium salts were used. For the monobasic acids, the reaction rate was found to be first order. A mechanism was proposed in which the rate-determining step was the rupture of a carbon-carbon bond:

$$R\text{-}COO^{-} \xrightarrow{rds} R^{-} + CO_2 \qquad (13)$$

$$R^{-} + H_2O \longrightarrow R^{-}\text{-}H + OH^{-} \qquad (14)$$

The disodium salt of malonic acid was unreactive, so sodium hydrogen malonate was used. It was found that aqueous solutions of this salt decomposed about twenty per cent as fast as solutions of malonic acid. If it were assumed that only undissociated molecules were decomposing in both cases, the difference in the rates would be much greater as the degree of hydrolysis of the hydrogen malonate was found to be very low. The same activation energy was associated with the decomposition of both species. Therefore, Fairclough predicted the possibility of both the ion and the undissociated molecule undergoing decarboxylation. Although a detailed mechanism of the decarboxylation of malonic acid was not determined, the experimental observation led to the conclusion that the mechanism of decarboxylation was not the same for monocarboxylic and dicarboxylic acids.

The rate of decarboxylation of aqueous solutions of malonic acid at temperatures of 80 and 90°C was investigated by Hall (2). He measured the rates at various concentrations (0.005 to 0.05M) of malonic acid in water. The effect of pH (0.4 to 4.89) on the decomposition was also studied. The results showed that: (1) The reaction rate was first order. (2) The values of the rate constants increased regularly with an increase in malonic acid concentration. (3) The rate constants increased with decreasing pH in the region 2.5 to 0.4, then levelled off at a pH of 0.4. Above a pH of 2.5, the rate constants decreased rapidly and approached a minimum value at a pH of about 5.0. (4) The activation energy remained essentially constant at 29 to 31 kcal with changing pH and malonic acid concentrations.

Hall stated that the concentration and pH effects were not independent, i.e., the observed concentration effect was related to the dissociation of the acid as was also the pH. He did not support the decomposition of only undissociated anion as proposed by Verhoek and co-workers for trichloroacetic acid (13,14,15). Since the rate constant levelled off at low pH's, he postulated that acid catalysis was not occurring. He further stated that the presence of only the undissociated malonic acid at low pH's and only the acid malonate at high pH's would produce the observed change in the rate constant. Thus, the decomposition of malonic acid could follow two paths:

$$\mathrm{COOHCH_2COOH} \longrightarrow \mathrm{CO_2 + CH_3COOH} \qquad (15)$$

$$\mathrm{COOHCH_2COO^-} \longrightarrow \mathrm{CO_2 + COOHCH_2^-} \qquad (16)$$

Reaction (16) is followed by another reaction in which the $\mathrm{COOHCH_2^-}$ ion reacts with solvent to form acetic acid. Therefore, the overall rate is the sum of the two rates for the unionized and singly ionized species.

$$\text{rate} = ka = k_1(a - x) + k_2x \qquad (17)$$

where,

k = observed rate constant at the stoichiometric malonic acid concentration <u>a</u>

k_1 = rate constant for reaction (15)

k_2 = rate constant for reaction (16)

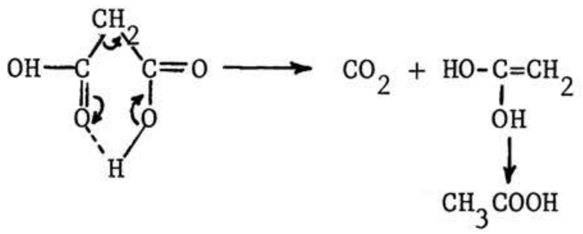
x = the concentration of acid malonate

Rearranging equation (17) gives:

$$k = k_1 + (k_2 - k_1)\, x/a \qquad (18)$$

Values of x/a were obtained from a known value of <u>a</u>, a measured value of pH, and the first dissociation constant of malonic acid. It was shown that the bivalent ion ($\mathrm{^-COOCH_2COO^-}$) did not decompose and that the second ionization constant could be safely neglected at the pH's studied. The increase in the rate constant k (see equation 18, page (9) with increasing hydrogen ion concentration was due to the increased amount of unionized malonic acid. Therefore, reaction 15 occurred predominantly. At higher pH's, the acid existed essentially in the singly ionized form and only reaction 16 took place. Thus, a decrease in the rate constant was observed at higher pH's.

Malonic acid is somewhat similar in structure to the β-keto acids. Therefore, it has been proposed that the decarboxylation of the undissociated acid should take place through hydrogen bonded or zwitterion forms yielding the enolic form of acetic acid which subsequently rearranges (3,17):



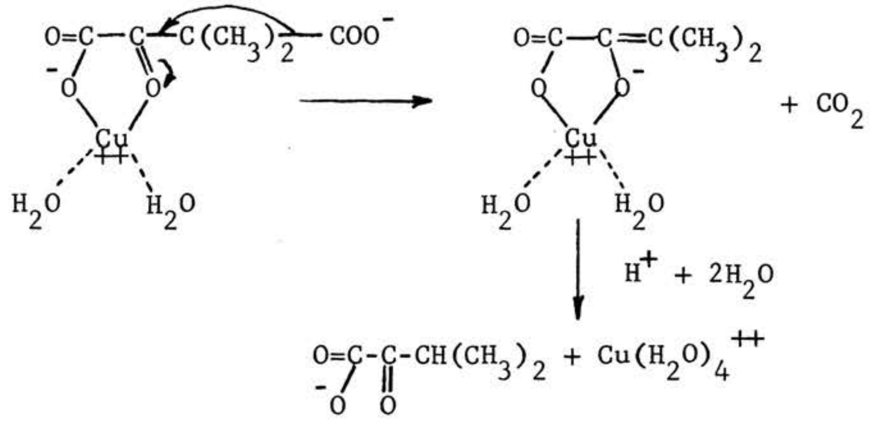
(19)

Catalytic Effect of Divalent Metal Ions on Decarboxylation.

Steinberger and Westheimer (18) have made a study of the decarboxylation of dimethyloxaloacetic acid. They found that both the monoanion A^- and dianion $A^=$ took part in the reaction and that the rate could be expressed mathematically by the equation:

$$\text{rate} = k_{A^-}(A^-) + k_{A^=}(A^=) \qquad (20)$$

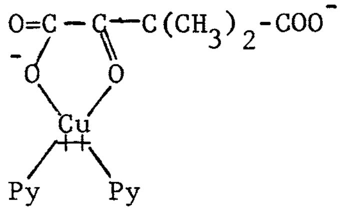
The pH-rate relationship showed that the rate increased up to pH = 3.0, decreased between pH's of 3.0 and 4.0, and then levelled off at a constant value above pH's of 4.6. It was further shown that decarboxylation was catalyzed by several metal cations (Cu^{+2}, Al^{+2}, Ni^{+2}, Mn^{+2}, Fe^{+2}, and Fe^{+3}). It was found that in the presence of low metal ion concentrations (0.0005 to 0.01M), the rate approximated a first order reaction. The effect of pH on the metal catalyzed decarboxylation revealed that a discontinuity existed at a pH of about 3.5. This was explained as a dependence of the catalyzed decarboxylation on the composition of the buffer solution. This effect was not observed with the uncatalyzed decarboxylation. The increase in the rate constant with pH indicated that the metal ions coordinated with the dianion. The following mechanism was proposed:



(21)

During the decarboxylation, an electron pair initially associated with the carboxylate ion group is transferred to another part of the molecule. A metal-ion would assist this transfer because of its positive charge. Therefore, the more readily the metal ion coordinates with the carbonyl group, the greater should be its catalytic activity. Accordingly, in buffer solutions, Cu^{+2} was found to be more effective than Al^{+3}, Ni^{+2}, and Mn^{+2}. The efficiency of copper ions as a decarboxylation catalyst was found to be different in the presence of various complexing agents.

Citrate greatly reduced the catalytic activity of Cu^{+2}. The rate was greater in the presence of pyridine than with acetate. It was suggested that those negative ions which form stable complexes with Cu^{+2} diminish its catalytic activity. A complexing agent which does not neutralize the charge on the copper ion does not destroy its catalytic activity. Thus pyridine was found to be more effective in promoting the rate since it readily formed complexes with Cu^{+2} without neutralizing the charge:



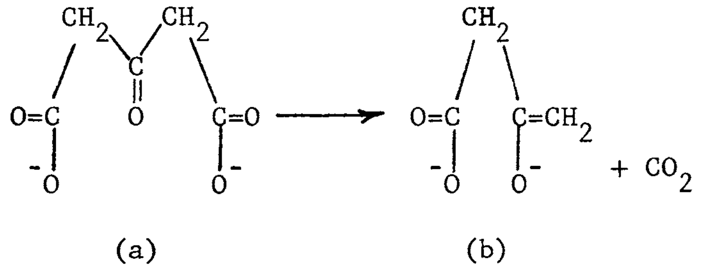
The decarboxylation of nitroacetic acid in the presence of metal ions was thought to occur through complex ions involving the metal and nitroacetate ions. These complex ions were decarboxylated less readily than noncomplexed ions. This was suggested as being due to the coordination of a metal ion with the carboxylate group making the nitroacetate ion inactive. This deactivation would be somewhat similar to that of a hydrogen ion combining with the univalent ion to give the non-reactive unionized acid. (See page 3). The association constant was found to vary for different metal ions in the order: $Al^{+3} > Cu^{+2} > Be^{+2} > Cd^{+2} > Pb^{+2} > Ni^{+2} > Zn^{+2} > Co^{+2} > Mg^{+2} > Ca^{+2}$ (19). Values of K were calculated for the equilibrium:

$$M^{+n} + X^{-} \rightleftharpoons MX^{+n-1} \qquad (22)$$

for which,

$$K = \frac{(M)(X^{+n-1})}{(M^{+n})\ (X^{-})} \qquad (23)$$

An investigation by Prue (8) pertaining to the catalyzed decarboxylation of acetonedicarboxylic acid has shown that catalysis depends on chelation between the activated complex and a metal cation. He showed that Cu^{+2} ions exerted strong catalytic effects compared to other metal ions such as Ni^{+2}, Co^{+2}, Mn^{+2}, Cd^{+2}, and Mg^{+2}. No catalytic effect was observed when Cu^{+2} ions were added to a solution containing hydrochloric acid. Prue concluded that the decarboxylation proceeded with the loss of a molecule of CO_2 from the bivalent acetonedicarboxylate ion:



(24)

Therefore, the metal ion catalysis was most effective at that pH where the dianion (b) predominated. The catalytic effect of divalent metal ions correlated very nicely with the stabilities of the complexes formed by the ions. Their order of stabilities has been shown to be: $Mn^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} > Zn^{+2}$.

III. EXPERIMENTAL

Purpose of the Investigation

The purpose of this investigation was to study the rate of decarboxylation of malonic acid at higher concentrations (0.5 to 5N) in sulfuric acid. The data obtained could be used to extend the mechanism proposed by others (2) into the high concentration region or to suggest a new mechanism that applies at these concentrations. The effect of pH was also studied in order to obtain a better understanding of the reaction mechanism.

Plan of Experimentation

The experimental plan for the study consisted of the following major parts: (1) Effect of malonic acid concentration (0.5 to 5N) on the reaction rate, (2) effect of pH on the reaction rate, (3) effect of temperature on the reaction rate, and (4) possible catalytic effect of various divalent metal ions on the reaction rate.

Materials

The materials are listed and described in Appendix A.

Experimental Set-Up

The schematic diagram of the experimental apparatus is shown is Figure 1.

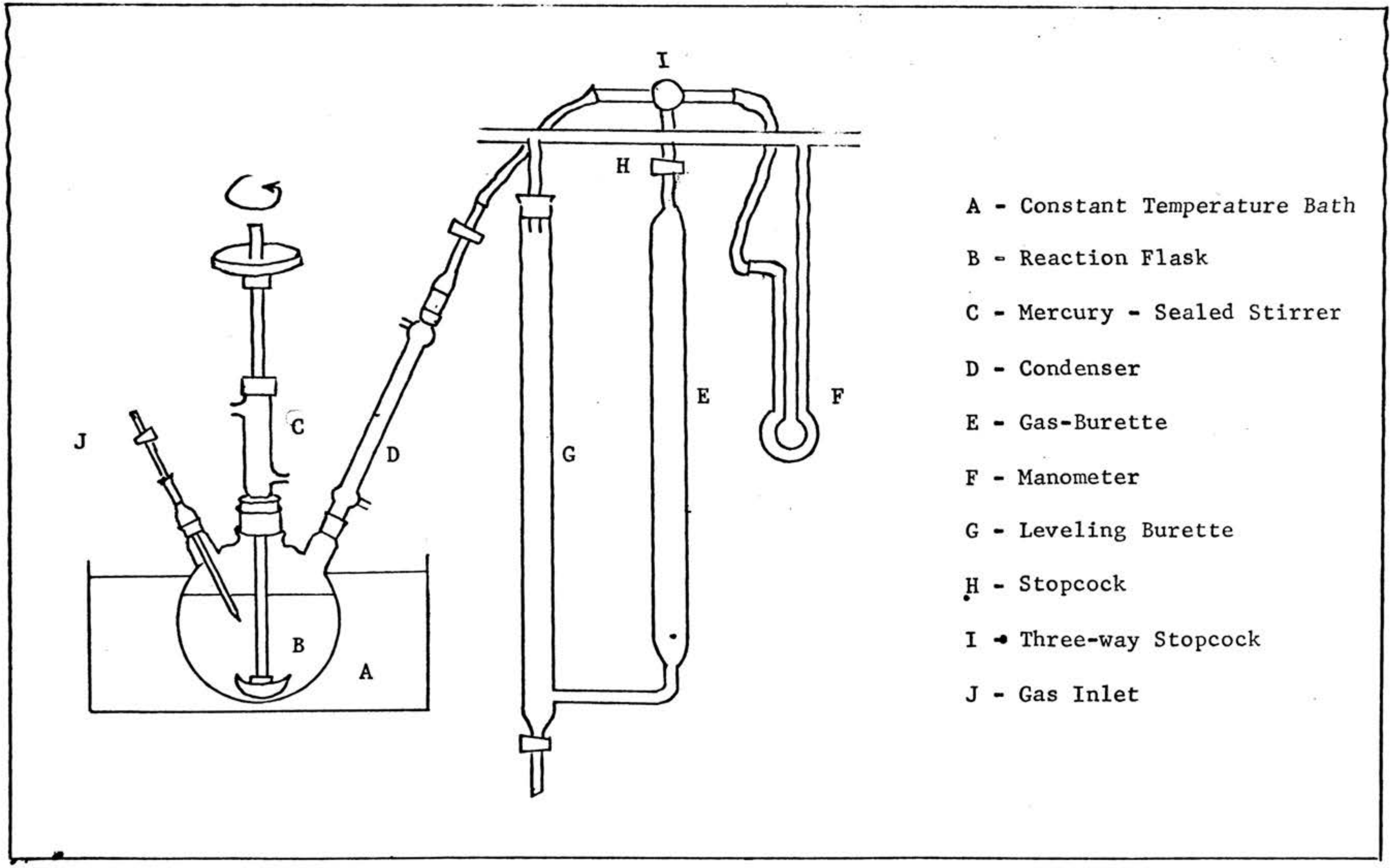


Figure 1. Diagram of apparatus for measuring decarboxylation rate of malonic acid.

Method of Procedure

The procedure followed and the method for the measurement of carbon dioxide evolution rate are described in Appendix B.

Results

The data procured for the effects of concentration, pH, temperature, and additions of divalent metal cations on the rate of decarboxylation are presented in Appendix C. Data for the concentration and pH effects are summarized in Table I.

Concentration Effect in 1 N Sulfuric Acid. The rates of decarboxylation of malonic acid were measured at a temperature of $79 \pm 0.2^{\circ}C$ and at malonic acid concentrations of 0.5, 1.0, 1.5, 2.0, and 5.0 N. A check run was made for 1.0 N malonic acid at $79^{\circ}C$. It was observed that the steady state data could be reproduced very well (within ± 5 percent). These data are presented in Tables XI through XVI.

Since only a small amount of malonic acid (less than 3 percent during a normal run) decomposed during a run, its concentration remained relatively constant. Thus the reaction rate at a particular malonic acid concentration could be calculated directly by measuring the CO_2 evolution rate. In this manner, values of k (the rate constant) for an assumed rate equation were calculated using the initial concentration of malonic acid.

Normally, the reaction solution was saturated with CO_2 before starting the measurements (see Procedure, Appendix B). However, one run was made without bubbling carbon dioxide through

TABLE I

RATE OF DECARBOXYLATION OF MALONIC ACID IN AQUEOUS SOLUTIONS AT 79°C

C_T	Average rate (ml CO_2/sec) STP		
gmol/l	pH = 0.3	1.5	2.5
0.25	0.00288	0.00290	0.00259
0.50	0.00575	0.00613	0.00517
0.75	0.00934	0.00918	0.00803
1.0	0.01240	0.01265	0.0111
2.5	0.03220	-	-

the solution. The data collected from this run are given in Table XXXIII, Appendix C. Figure 2 also shows the time behavior of this rate compared to the rate in a similar solution previously saturated with CO_2. Both methods gave essentially the same rate indicating that the decarboxylation is irreversible and that it rapidly saturates the solution with CO_2.

Rate constants, assuming the decomposition to be first order with respect to the total acid concentration, are shown in Table II. It can be seen that they increase with increasing malonic acid concentration. The increase is outside the limits of experimental error. It is probably not due to the use of concentration rather than activities as activity coefficients would be relatively constant in these solutions. It should be noted that the increase of the rate constant is regular rather than random.

The ideal gas law was assumed in order to relate the rates of carbon dioxide evolution and malonic acid decarboxylation.

pH Effect. The effect of pH on the reaction rate was studied by measuring the rates at a temperature of $79 \pm 0.2^{\circ}C$ and at pH's of 1.5 and 2.5. For each pH, malonic acid concentrations of 0.5, 1.0, 1.5, and 2.0 N were used. The solutions were prepared using calculated quantities of H_2SO_4, K_2SO_4, and malonic acid in which the sulfate composition was held constant at one normal. The pH's of the solutions were checked with a pH meter and the measured value normally agreed within ± 0.2 unit of the calculated value. The calculated values were used as the pH of the solution.
The data obtained are shown in Tables XVII through XXIV. The rate constants were evaluated using the previous assumption and

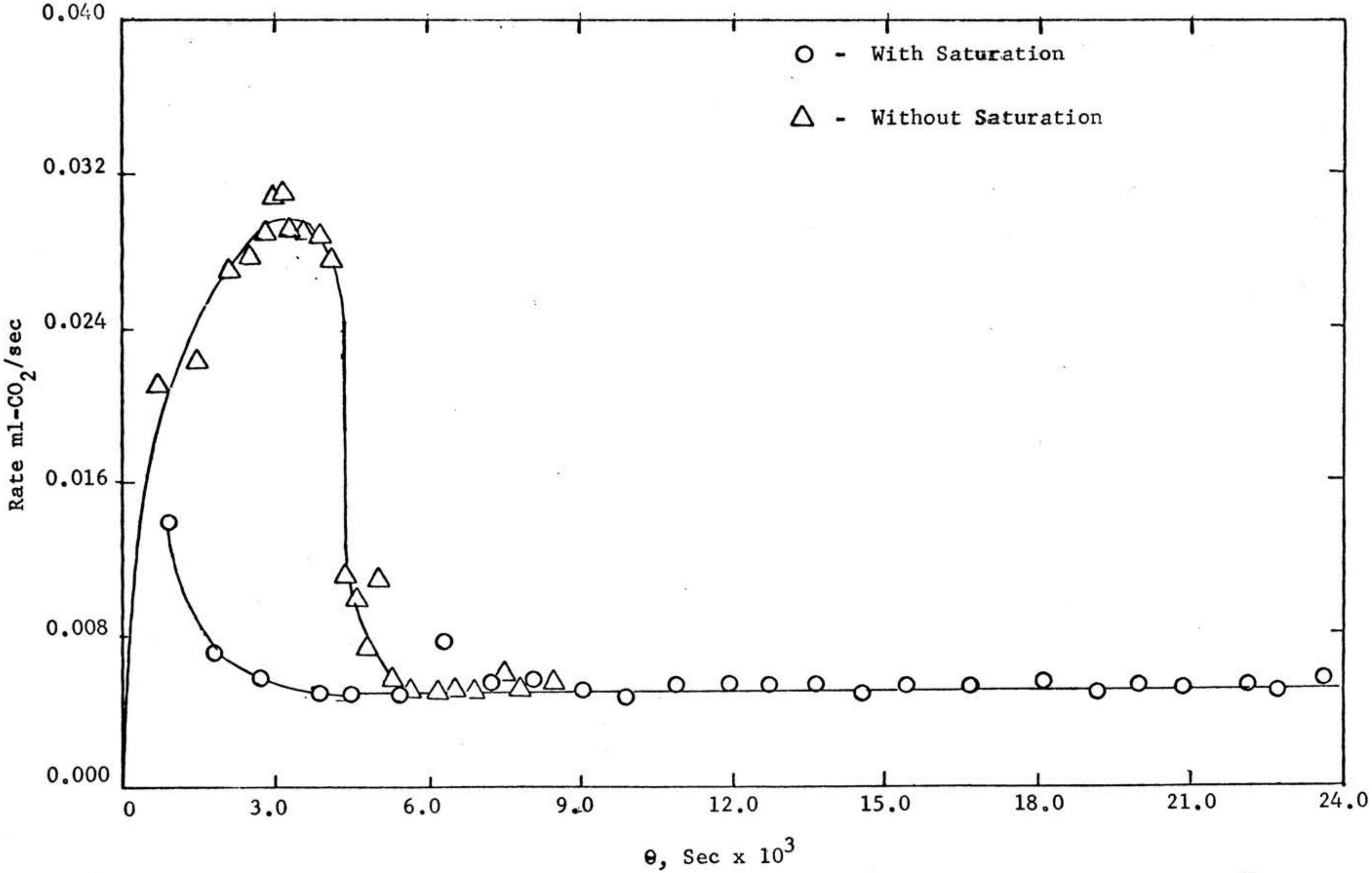


Figure 2. Rate of evolution of CO_2 with and without prior saturation with CO_2 at 79°C.

TABLE II

DECARBOXYLATION OF MALONIC ACID IN 1 N H_2SO_4 (pH = 0.3) AT 79°C

C_T gmol/l	Average rate (STP) ml CO_2/sec	k x 10^6 sec^{-1}
0.25	0.00288	1.713
0.50	0.00575	1.710
0.50 (check-run)	0.00554	1.640
0.75	0.00934	1.795
1.0	0.01240	1.852
2.5	0.03220	1.915

are shown in Tables III and IV. Again, the rate constants increase regularly with increasing malonic acid concentration for both pH's.

If the reaction is truly unimolecular, then the rate constants should not vary in the observed manner. Therefore, the following expression was used to see if a slightly different order would correlate the rate data:

$$\text{rate} = k'C^n \qquad (25)$$

Figure III is a logarithmic plot of the rates versus the total concentration of malonic acid for various pH's studied. The slopes and the intercepts were evaluated by the method of least squares. The results obtained are shown in Table V. It can be seen that the expression correlates the rate data very nicely, but that the rate constant for the solution of pH 2.5 differs significantly from those evaluated for pH's 0.3 and 1.5.

The concentrations of the undissociated malonic acid, and monovalent ion, the bivalent ion, and the hydrogen ion were calculated for the different reaction solutions and the results are given in Table VI. This table shows the amount of malonic acid ionized in solutions of pH's 0.3 and 1.5 is very small, but that a significant amount is ionized at a pH of 2.5. This suggests that the decrease of the rate constant (Table V) in the latter solution could be due to a decreased reactivity of the monovalent ion. If this were true, then the order of 1.05 and the rate constant of 1.83 would be applicable to the unionized species which were predominant at pH's of 0.3 and 1.5. Therefore,

TABLE III

DECARBOXYLATION OF MALONIC ACID IN AQUEOUS SOLUTION OF pH OF 1.5 AT 79°C

C_T g mol/l	Average rate (STP) ml CO_2/sec	k x 10^6 sec^{-1}
0.25	0.0029	1.725
0.50	0.00613	1.823
0.75	0.00918	1.820
1.00	0.02365	1.881

TABLE IV

DECARBOXYLATION OF MALONIC ACID IN AQUEOUS SOLUTION OF pH OF 2.5 AT 79°C

C_T gmol/l	Average rate (STP) ml CO_2/sec	$k \times 10^6$ sec^{-1}
0.25	0.00259	1.54
0.50	0.00517	1.54
0.75	0.00803	1.59
1.00	0.0111	1.65

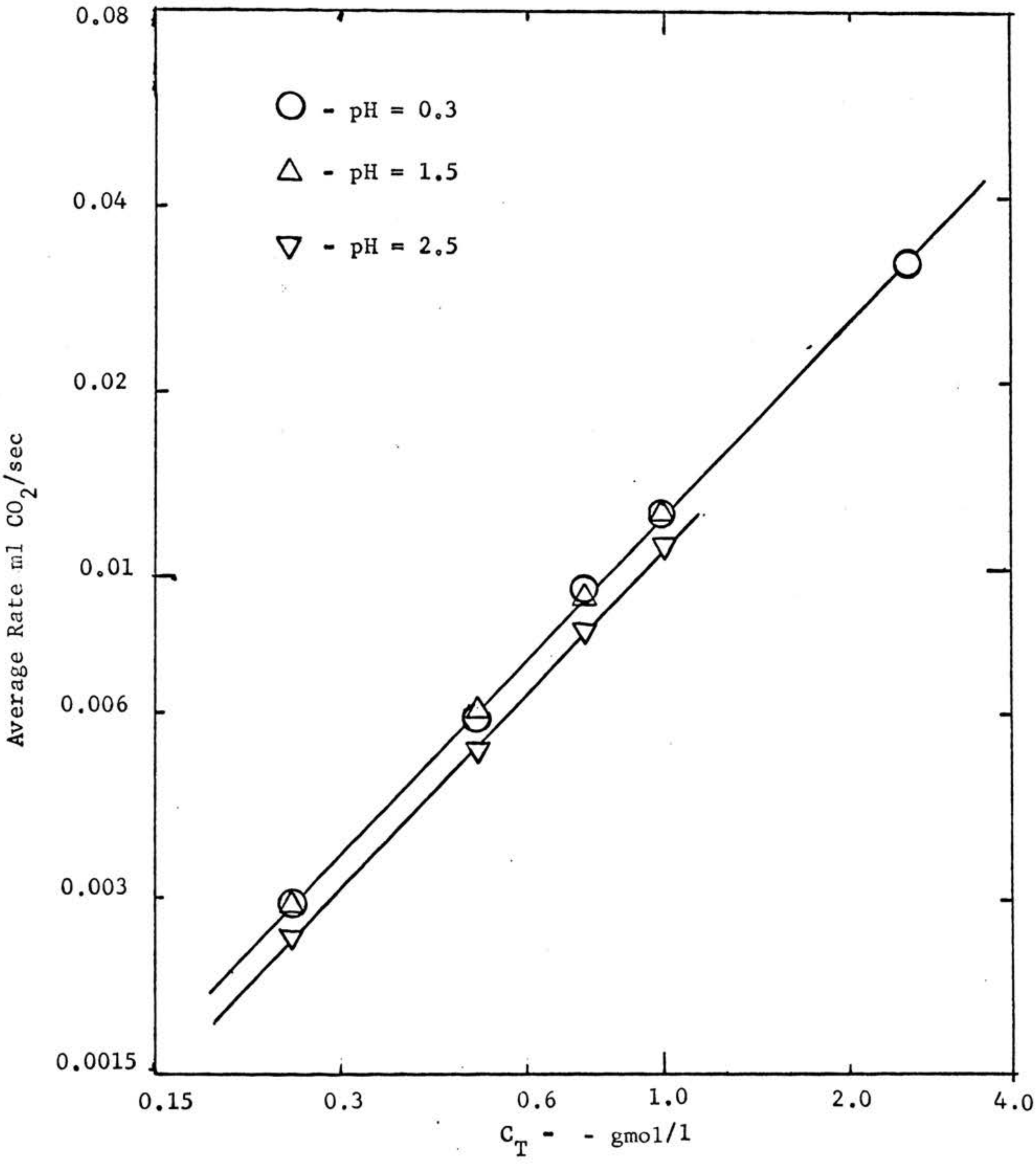


Figure 3. Rate of evolution of CO_2 from aqueous solutions of malonic acid at 79°C.

TABLE V

KINETIC PARAMETERS FOR THE DECARBOXYLATION OF MALONIC ACID AT 79°C

pH	Order	σ_b	$k \times 10^{-6}$	σ_a
0.3	1.054	±0.005	1.83	±0.02
1.5	1.058	±0.007	1.87	±0.03
2.5	1.049	±0.006	1.62	±0.02

TABLE VI

EQUILIBRIUM CONCENTRATIONS OF VARIOUS SPECIES IN MALONIC ACID, SULFURIC ACID, AND POTASSIUM SULFATE MIXTURE AT 79°C

pH	C_T gmol/1	C_{H^+}	C_{H_2M}	C_{HM^-}	$C_{M^=} \times 10^6$
0.3	0.25	0.5031	0.2493	0.000738	0
	0.50	0.5038	0.4985	0.001474	0
	0.75	0.5045	0.7478	0.002208	0
	1.00	0.5053	0.9971	0.002940	0
	2.50	0.5096	2.4927	0.007288	0
1.5	0.25	0.03157	0.2387	0.0113	0
	0.50	0.03158	0.4775	0.0225	1.0
	0.75	0.03158	0.7162	0.0338	2.0
	1.00	0.03159	0.9550	0.0450	2.0
2.5	0.25	0.003460	0.1747	0.0752	43.0
	0.50	0.003461	0.3495	0.1500	86.0
	0.75	0.003470	0.5247	0.2250	129.0
	1.00	0.003465	0.6993	0.3010	173.0

the following equation was assumed for the pH of 2.5:

$$1.487 \times 10^{-4} \text{ rate} = 1.834 \times 10^{-6} C_{H_2M}^{1.054} + k_2 C_{HM^-}^{m} \qquad (26)$$

where,

rate = CO_2 evolution, ml/sec at STP (factor 1.487×10^{-4} converts CO_2 evolution rate to malonic acid decarboxylation rate)

C_{H_2M} = concentration of the undissociated malonic acid (gmols/1)

C_{HM^-} = concentration of monovalent malonate ion (gmols/1)

m = order for malonate ion

k_2 = rate constant for malonate ion

This equation can be rearranged to the following form which was used to evaluate the rate constant and order for the monovalent malonate ion:

$$(1.487 \times 10^{-4} \text{ rate} - 1.834 \times 10^{-6} C_{H_2M}^{1.054}) = k_2 C_{HM^-}^{m} \qquad (27)$$

Figure 4 is the graphical representation of the above equation in a logarithmic (linear) form. Considering that the difference on the left side of Equation 27 was obtained from two values of approximately the same order of magnitude, the linearity of the plot is considered satisfactory. Accordingly, the rate constant $\underline{k}_2$ and order $\underline{m}$ were calculated by the method of least squares and were found to be $1.25 \pm 0.03 \times 10^{-6}$ and 1.02 ± 0.04 respectively. Thus over the region studied the decarboxylation rate (R) can be represented by the equation:

$$R = 1.83 \times 10^{-6} C_{H_2M}^{1.05} + 1.25 \times 10^{-6} C_{HM^-}^{1.02} \qquad (28)$$

During one experiment, performed at 79°C and at a pH greater than 7, only 2 ml of CO_2 was evolved after a period of ten hours. At

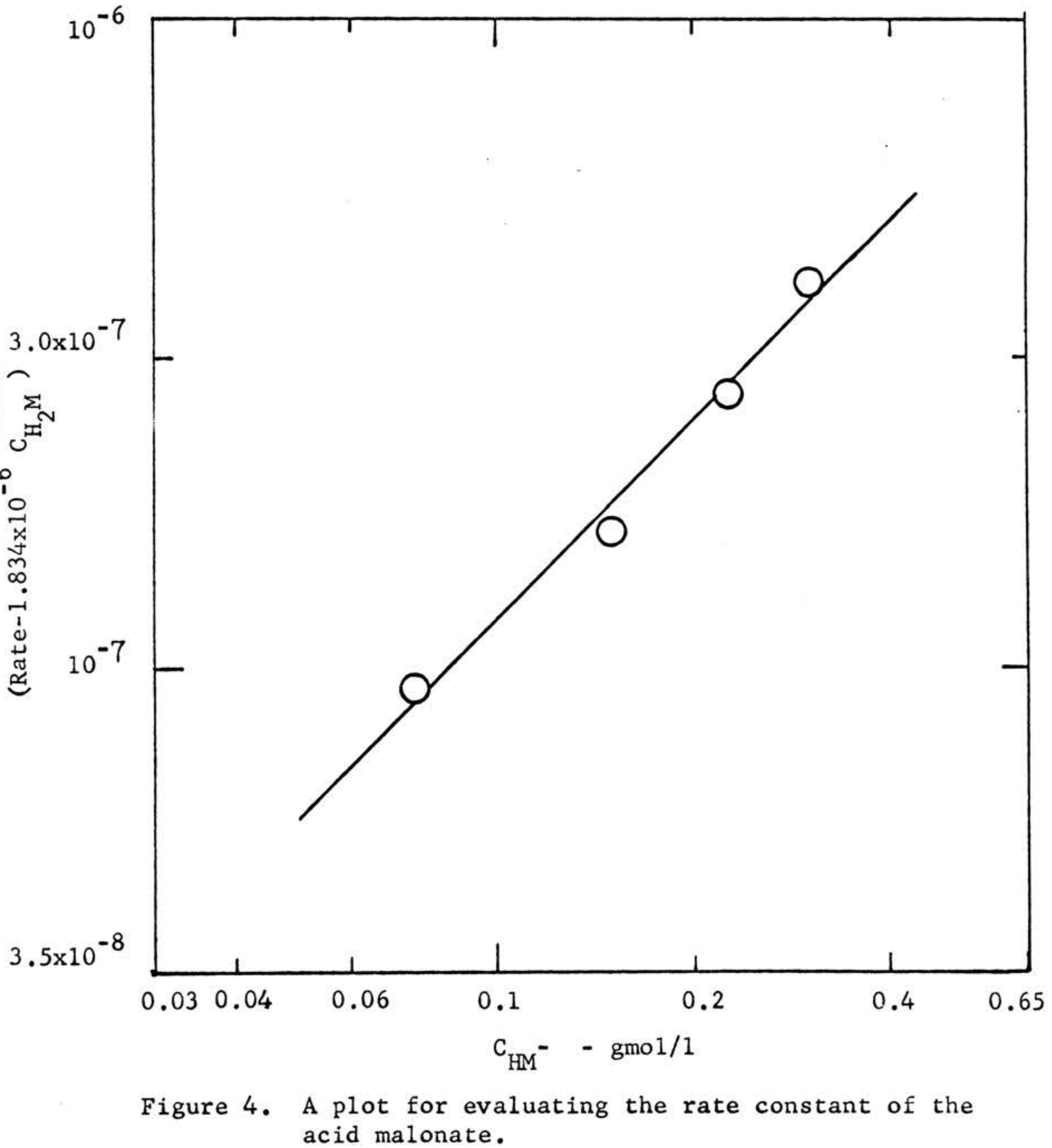


Figure 4. A plot for evaluating the rate constant of the acid malonate.

this pH, the dimalonate ion predominated. Therefore, it is believed that the dimalonate ion does not decarboxylate.

Temperature Effect. Experiments were conducted for the decarboxylation of 1.0 N malonic acid in 1.0 N H_2SO_4, at temperatures of 70, 75, 79, 85, and 90°C. The rate constants (k_{H_2M}) are shown in Table VII. They have also been plotted as a function of reciprocal absolute temperature in Figure 5. The method of least squares was used to evaluate the slope and the intercept. The calculated activation energies and frequency factors are shown in Table VIII.

The temperature effect was also studied at pH's of 1.5 and 2.5 by measuring the rates at temperatures of 70, 79, and 90°C. For each pH, one normal malonic acid was used. The data obtained from these runs are shown in Tables XII, XVIII, XXII, and XXV through XXXII. Table VII summarizes the results. The Arrhenius plots are also shown in Figure 5.

The Arrhenius activation energies and the frequency factors at the various pH's are shown in Table VIII.

Catalytic Effect of Divalent Metal Ions. Experiments were performed to determine if divalent metal ions would catalyze the decarboxylation reaction. Concentrations of 0.01 and 0.05 N nickel sulfate, cobalt acetate, calcium sulfate, and copper acetate were used. Each study was made in one normal malonic acid in 1.0 N H_2SO_4 at 79°C. The data obtained from these runs are presented in Tables XXXIV through XLIII. One more run was made using 0.1 N copper sulfate. Table IX shows a summary of the effects of the various metal ions. A slight increase can

TABLE VII

EFFECT OF TEMPERATURE ON THE DECARBOXYLATION OF 1.0 N MALONIC ACID

Temp	pH = 0.3		pH = 1.5		pH = 2.5	
^{o}C	Avg. rate ml CO_2/sec	$k^{*} \times 10^{6}$	Avg. rate ml CO_2/sec	$k^{*} \times 10^{6}$	Avg. rate ml CO_2/sec	$k^{**} \times 10^{6}$
70	0.001890	0.584	0.001791	0.554	0.001623	0.358
75	0.003566	1.110	-	-	-	-
79	0.005750	1.778	0.00613	1.895	0.005170	1.252
85	0.01262	3.901	-	-	-	-
90	0.02177	6.730	0.02149	6.659	0.001826	3.640

* Rate constant for the undissociated malonic acid.

** Rate constant for the monovalent malonate ion.

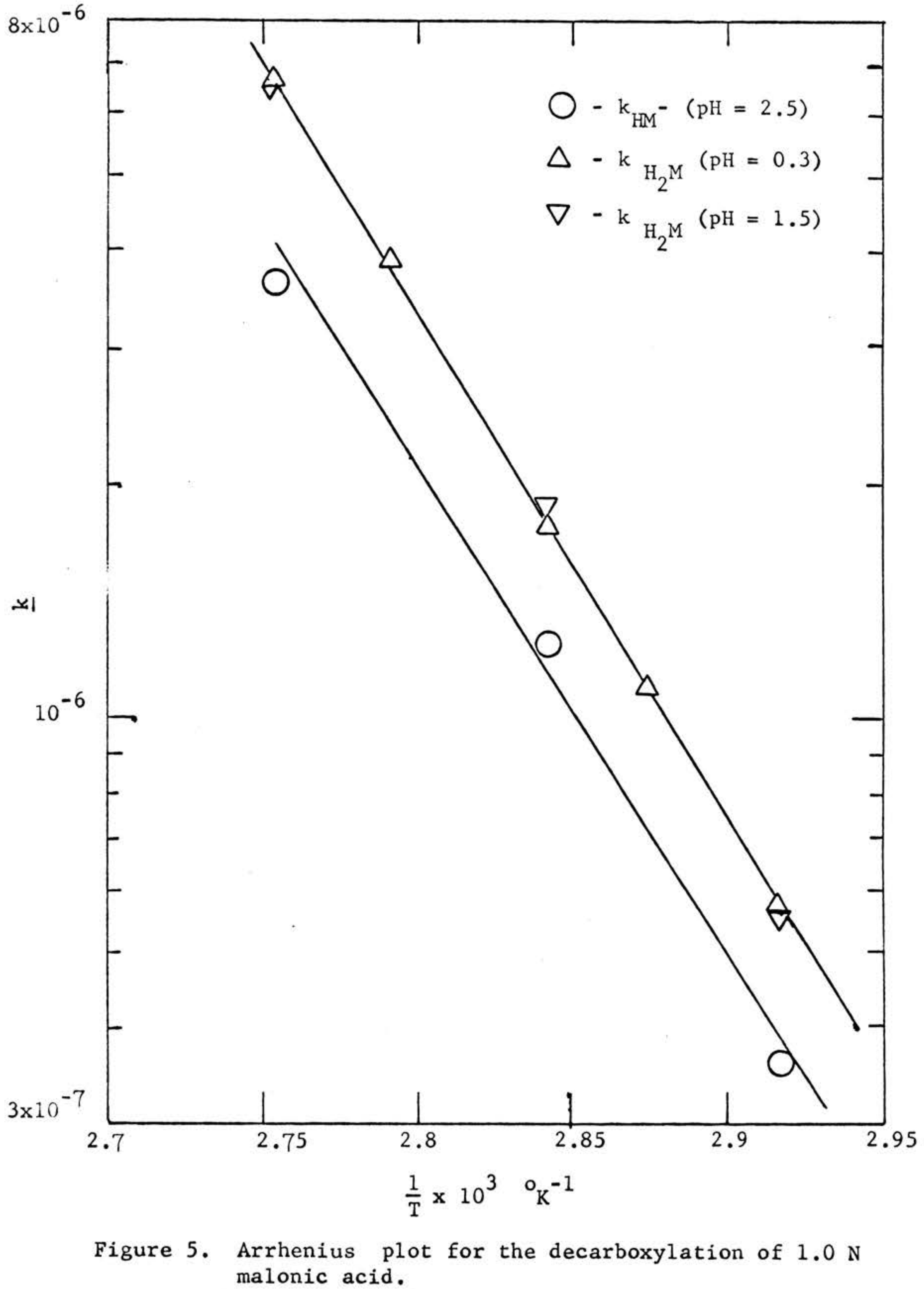


Figure 5. Arrhenius plot for the decarboxylation of 1.0 N malonic acid.

TABLE VIII

ARRHENIUS PARAMETERS FOR THE DECARBOXYLATION OF 1.0 N MALONIC ACID

pH	E	σ_E	ln A	σ_A
0.3*	30.5	±0.1	30.3	±0.2
1.5*	30.5	±1.1	30.4	±1.5
2.46**	31.4	±1.0	26.7	±0.3

* Activation energy and ln A for unionized malonic acid.

** Activation energy and ln A for monovalent malonate ion.

TABLE IX

EFFECT OF DIVALENT METAL IONS ON THE RATE OF DECARBOXYLATION OF 1.0 N MALONIC ACID IN 1.0 N H_2SO_4 AT 79°C

Salt	Conc. of Salt gmequiv/l	Avg. rate (STP) ml CO_2/sec	k x 10^6 sec^{-1}
None	-	0.00572	1.71
$NiSO_4 \cdot 6H_2O$	0.01	0.00617	1.84
	0.05	0.00625	1.86
$CO(C_2H_3O_2)_2 \cdot 4H_2O$	0.01	0.00586	1.74
	0.05	0.00633	1.88
$CaSO_4 \cdot 2H_2O$	0.01	0.00548	1.68
	0.05	0.00614	1.82
$Cu(C_2H_3O_2) \cdot H_2O$	0.01	0.00604	1.78
	0.05	0.00612	1.81
$CuSO_4$	0.10	0.00609	1.81
Platinized Pt (0.75 sq in)		0.00608	1.81

be noted in the rate in most all cases, but nothing is noted that would be called a pronounced catalytic effect.

Sample Calculations

The methods used for calculating the average rates, the rate constants, the concentrations of different species in the solutions, and the pH of the solutions are presented in Appendix C.

IV. DISCUSSION

With the assumption of a first order decarboxylation of malonic acid, the rate constants increased regularly with increasing malonic acid concentration at a constant pH (see Table II). Rate constants reported by Hall (2) at lower concentrations of malonic acid in water (0.005 to 0.05 M) also showed such an increase. He explained this as due to a decrease in pH with increasing malonic acid concentration. The various concentrations studied in this investigation were in the same pH region studied by Hall. Thus, his explanation does not seem valid. Moreover, attempts to explain this observation on the basis of salt effects also failed, as the ionic strengths of the solutions used in this study remained relatively constant. Also, the pH's of the solutions in 1.0 N H_2SO_4 were low enough so that reaction predominantly involved the neutral molecule for which the salt effect would be small. This leads to the conclusion that the decarboxylation of malonic acid is not truly unimolecular. Accordingly, an order of 1.05 was found to more accurately correlate the rate data for the neutral molecule and 1.02 for the singly ionized species.

If one were to assume a first order decomposition, the following expression can be deduced (20):

$$\text{rate} = 1.8 \times 10^{-6}\ C_{H_2M} + 1.0 \times 10^{-6}\ C_{HM^-} \qquad (29)$$

A comparison of the experimental rates with those obtained using equations 28 and 29 is presented in Table X. It can be noticed that a better agreement is obtained using equation 28. However, the constants of equation 29 have not been subjected to refinement

TABLE X

DECARBOXYLATION OF MALONIC ACID IN AQUEOUS SOLUTIONS AT 79°C

pH	C_T gmol/1	Rate x 10^7 (gmol/1-sec) Exp.	Eq. 28	Eq. 29
0.3	0.25	4.28	4.25	4.49
	0.50	8.55	8.83	8.97
	0.75	13.89	13.51	13.95
	1.00	18.43	18.32	17.95
	2.50	47.88	46.72	44.87
1.5	0.25	4.31	4.17	4.41
	0.50	9.11	8.60	8.80
	0.75	13.65	13.30	13.19
	1.00	18.81	17.90	17.59
2.5	0.25	3.85	3.80	3.39
	0.50	7.69	7.80	7.69
	0.75	11.94	11.93	11.65
	1.00	16.51	16.08	15.59

procedures. Though the rates using the first order expression are not much outside the error limit, they do not show the observed trend in the data.

The possibility of solvent activation might explain the deviation of the decarboxylation reaction from first order behavior. The influence of the solvent on a rate process in solution has been illustrated using the collision theory (21). The theory assumes an activation and deactivation of reactant molecules by collision with various other species in solution, specially solvent molecules. The general form of the equation can be developed as follows:

rate of activation = $k_1CS + k_2C^2$

rate of deactivation = $k_3aS + k_4aC$

rate of reaction = k_5a

where:

C = concentration of reactant

S = concentration of solvent

a = concentration of activated reactant

For a stationary concentration of the activated species:

rate of activation = rate of deactivation + rate of reaction

and,

$$\text{rate} = k_5a = \frac{k_5(k_1CS + k_2C^2)}{k_3S + k_4C + k_5} \qquad (30)$$

The relative magnitudes of these rate constants determine the order of the reaction and the extent of the solvent effect.

On the assumption that $k_5 > k_3S + k_4C$,

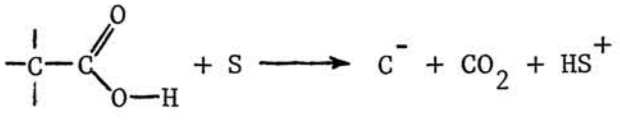
$$\text{rate} = k_1CS + k_2C^2 \qquad (31)$$

This would explain the reaction order observed in these studies if the solvent activation were predominant, i.e., $k_1CS > k_2C^2$. Since the solvent concentration is approximately constant:

$$\text{rate} = k_1CS \simeq k'C \tag{32}$$

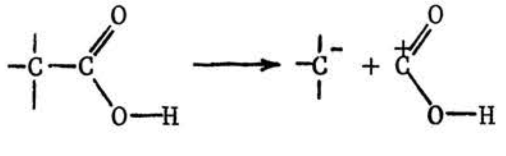
The slight variation of solvent concentration and any contribution by the term k_2C^2 would cause the order to deviate from unity. The above assumptions are somewhat substantiated by the fact that malonic acid in aqueous solutions decarboxylates faster than in the molten state (14). Also, in an experiment performed in these studies no gas was evolved when 15.6 grams of solid malonic acid was held at 79°C for 6 hours. Since the concentration of water was approximately constant in this work, the actual effect of the solvent on the decarboxylation awaits further experimentation. In this regard, it might also be added that Brown has stated in a recent paper (3), "no unambiguous evidence has been recorded to indicate the decomposition of an acid molecule by a unimolecular mechanism". As it has been hypothesized that the carboxylic group is usually in the anionic form before decarobxylation, he proposed two possibilities for the removal of a proton by a solvent molecule in a fission of the carbon-carbon bond.

1. simultaneous removal of a proton:

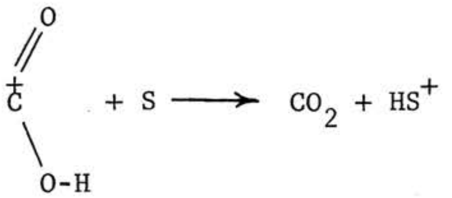


$$-\overset{|}{\underset{|}{C}}-C(=O)-O-H + S \longrightarrow C^- + CO_2 + HS^+ \tag{33}$$

2. removal of a proton after fission:



$$-\overset{|}{\underset{|}{C}}-C(=O)-O-H \longrightarrow -\overset{|}{\underset{|}{C}}^- + \overset{+}{C}(=O)-O-H \tag{34}$$



$$\mathrm{HO}-\overset{+}{\mathrm{C}}=\mathrm{O} + \mathrm{S} \longrightarrow \mathrm{CO_2} + \mathrm{HS^+} \qquad (35)$$

The measured rates in solutions of 0.3 and 1.5 pH were not appreciably different (see Table I). A slight increase in the rates at the pH of 1.5 was well within the limit of and was considered to be due to the experimental error. Thus, acid catalysis was not supported. This suggested that the appreciable decrease in the rates at a pH of 2.5 should be attributed to a decrease in concentration and/or a decrease in reactivity of some reacting species at this pH. The concentration of the malonate anion was appreciable at pH 2.5. It seemed proper therefore, to formulate the general empirical relation to represent the decarboxylation in terms of the two species, $H_4C_3O_4 (H_2M)$ and $H_3C_3O_4^-$ (HM^-). Accordingly the following equation was deduced:

$$R = 1.83 \times 10^{-6}\ C_{H_2M}^{1.05} + 1.2 \times 10^{-6}\ C_{HM^-}^{1.02} \qquad (28)$$

The magnitudes of the rate constants for the undissociated malonic acid and the acid malonate ion reported by Hall were 2.12×10^{-6} and 0.24×10^{-6} respectively. These are to be compared with 1.83×10^{-6} and 1.2×10^{-6} from this work.

The activation energies and frequency factors for the undissociated malonic acid (30.5 kcal/mole and ln A = 30.3) and the monovalent malonate anion (31.4 kcal/mole and ln A = 26.7) were evaluated from Arrhenius plots (Figure 5). Values of the activation energies reported by Hall were $E_{H_2M} = 30.8$ kcal/mole and $E_{HM^-} = 28.5$ kcal/mole.

The studies made with several salts of divalent metal ions showed a slight increase in the rates. However, the effect of these metal ions on the decarboxylation was not sufficient to interpret it as a catalytic effect.

Possible Mechanism of Decarboxylation. The thermal decomposition of malonic acid can be represented by the simple chemical reaction:

$$COOHCH_2COOH \longrightarrow CH_3COOH + CO_2 \qquad (36)$$

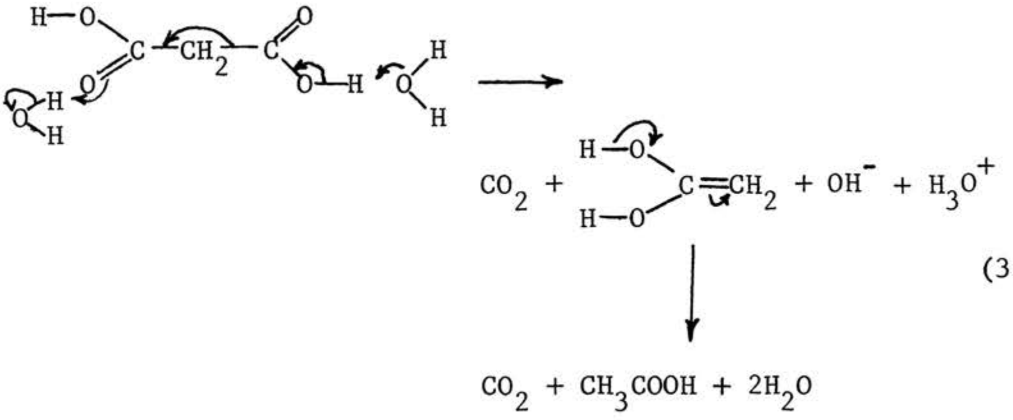
In aqueous solutions, malonic acid would dissociate as:

$$COOHCH_2COOH \rightleftharpoons COOHCH_2COO^- + H^+ \qquad (37)$$

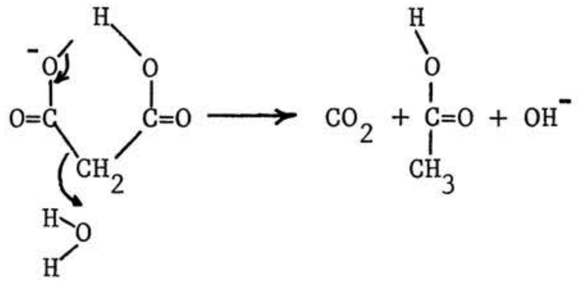
$$COOHCH_2COO^- \rightleftharpoons {}^-COOCH_2COO^- + H^+ \qquad (38)$$

These studies support the decarboxylation of two species, the undissociated malonic acid and the monovalent malonate ion, but do not support the decomposition of the divalent ion as reported by Hall and Fairclough (2,16).

Solvent activation seems favorable as postulated by Hanna (22):



(39)



(40)

Recommendations. It would be interesting to continue these studies and check the solvent activation hypothesis on the mechanism of the decarboxylation of malonic acid. This could be done by measuring the rates in glacial acetic acid and/or pure dioxane.

The kinetic studies could also be further extended to check the validity of the empirical relation derived in this investigation by measuring the rates at pH's greater than 2.5.

V. SUMMARY AND CONCLUSIONS

The kinetic studies of the decarboxylation of malonic acid were made at higher concentrations of malonic acid (0.5 to 5N) and at three pH's (0.3, 1.5, and 2.5). The experiments were conducted at a temperature of 79°C. First order rate constants were found to increase regularly with increasing malonic acid concentration. An empirical relation was found that would correlate the rates of the region studied:

$$\text{rate} = 1.83 \times 10^{-6}\, C_{H_2M}^{1.05} + 1.25 \times 10^{-6}\, C_{HM^-}^{1.02}$$

Activation energies were found allowing the rate constants to be expressed as a function of temperature:

$$k_{H_2M} = 1.42 \times 10^{13}\, e^{-30500/RT}$$

$$k_{HM^-} = 4.0 \times 10^{11}\, e^{-31400/RT}$$

Experiments with various divalent metal ions showed very little, if any, catalysis.

These studies led to the following conclusions:

1. A decarboxylation of malonic acid in aqueous solutions is not truly unimolecular.
2. The rate data can be correlated using an order slightly greater than one.
3. pH has an indirect effect on the rate only in that it affects the ionization of malonic acid.
4. The undissociated malonic acid and the monovalent malonate ion were the reactive species. The divalent ion

was decarboxylated very slowly if at all.

5. Activation energies for the decarboxylation of both the undissociated malonic acid and the monovalent malonate ion were almost the same.
6. No pronounced catalytic effect of divalent metal ions was observed.

VI. APPENDICES

APPENDIX A

MATERIALS

1. Calcium Sulfate ($CaSO_4 \cdot 2H_2O$). Analytical grade, meets ACS specifications, Fisher Scientific Company, Fair Lawn, N. J.

2. Cobalt II Acetate ($Co(C_2H_3O_2)_2 \cdot 4H_2O$). Analytical grade, meets ACS specifications. Mallinckrodt Chemical Works, St. Louis, Missouri.

3. Copper II Acetate ($Cu(C_2H_3O_2)_2 \cdot H_2O$). Analytical grade, meets ACS specifications. J. T. Baker Chemical Company, Phillipsburg, N. J.

4. Copper II Sulfate ($CuSO_4$). Analytical grade, meets ACS specification. Matheson, Coleman, and Bell, Rutherford, N. J.

5. Malonic Acid. Reagent grade, meets ACS specifications. Matheson, Coleman, and Bell, Rutherford, N. J.

6. Nickel Sulfate ($NiSO_4 \cdot 6H_2O$). Analytical grade, meets ACS specifications. J. T. Baker Chemical Company, Phillipsburg, N. J.

7. Potassium Hydroxide (KOH). Analytical grade, meets ACS specifications. Fisher Scientific Company, Fair Lawn, N. J.

8. Potassium Sulfate. Granualted, analytical grade, meets ACS specification. Mallinckrodt Chemical Works, St. Louis, Mo.

9. Sodium Carbonate (Na_2CO_3). Analytical grade, meets ACS specifications. Mallinckrodt Chemical Works, St. Louis, Mo.

10. Sodium Hydroxide (NaOH). Analytical grade, meets ACS specifications. Fisher Scientific Company, Fair Lawn, N. J.

11. Sulfuric Acid. Reagent grade, meets ACS specifications. Fisher Scientific Company, Fair Lawn, N. J.

APPENDIX B

METHOD OF PROCEDURE

A diagram of the apparatus is shown in Figure 1. A description of the experimental procedure used for this investigation is as follows:

The reaction flask B in the constant temperature bath was rinsed four to five times with distilled water. The liquid was removed by suction with a pump. Three hundred milliliters of the reaction solution, measured in a 100 ml graduated cylinder, were placed into the reaction flask. The gas burette was filled with water which had been saturated with carbon dioxide. Ground-glass fittings were lubricated to avoid leakage. All stop cocks were closed except H and I. The three-way stop cock I was open to the reaction vessel B, the gas burette E and the manometer F. The teflon-blade stirrer was started and heating commenced. When the temperature of the constant temperature bath reached $5^{\circ}C$ below the desired temperature, carbon dioxide was bubbled through the solution. In this manner, the reaction solution was saturated with carbon dixoide and air was removed from the system. As soon as the desired temperature was reached, bubbling of the gas was stopped, stop cock H was turned 90° so that the reaction flask was connected to the gas burette E. At the same time, the electric timer was started. The volume of gas evolved was measured at different time intervals by the method given below.

Measurement of the Evolved Carbon Dioxide. The method used for measuring the volume of gas in the reaction system has been described by Schubert (23). In brief, the volume of the gas in the reaction vessel B expanded due to the reaction and was passed through the water-cooled condenser D where it was collected over water previously saturated with carbondioxide. The manometer level was frequently adjusted to keep the system at atmospheric pressure. At the instant, when a reading was to be recorded, stop cock I was closed to the reaction flask by turning it 90^{o} clockwise. An amount of water was then run from the burette G so that the levels of water in the manometer F were the same. The volume of gas, temperature near the gas burette, time, and barometric pressure were recorded. Stop cock I was then turned 90^{o} anti clockwise to allow expansion of the gas for the next measurement.

APPENDIX C

DATA

TABLE XI

RATE OF DECARBOXYLATION OF 0.25 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. Press.
sec	ml	°C	°C	mm Hg
0.0	0.0			
1800.0	3.4	25.6	20.2	738.2
3600.0	9.6	25.4	20.5	737.8
5400.0	15.9	25.5	21.0	738.3
7200.0	22.4	25.6	21.0	737.9
9000.0	28.5	25.6	21.0	737.9
11000.0	35.2	25.4	20.5	739.1
12625.0	40.7	25.4	20.5	738=7
15300.0	49.6	25.2	20.2	738.2
17100.0	55.3	25.0	20.0	738.6
19000.0	61.4	25.0	20.0	739.2
20800.0	67.7	25.0	20.0	739.6
22600.0	73.4	25.0	20.0	739.6
24500.0	79.6	25.0	20.0	739.2

TABLE XII

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) AT 79°C*

Time	Vol CO_2
sec	ml
0.0	15.4
500.0	25.8
1000.0	30.8
1500.0	34.2
2000.0	37.8
2500.0	41.0
3000.0	44.4
3500.0	48.2
4000.0	51.7
4500.0	54.8
5000.0	58.0
5500.0	62.0
6050.0	65.9
6500.0	68.6
7000.0	71.4
7500.0	74.3
8000.0	78.0
8500.0	81.8
9000.0	85.2
9500.0	88.8
10000.0	92.2
10500.0	95.1
11000.0	99.4
11500.0	102.4
12000.0	105.3
12500.0	109.2
13000.0	112.1
13500.0	115.4
14000.0	118.9
14500.0	121.6
15000.0	124.6
15500.0	128.8
16000.0	132.6
16500.0	135.6
17000.0	139.0

---

* Barometric pressure = 732.8 mm Hg.
Room temperature = 25°C

TABLE XIII*

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) AT 79°C**

Time	Vol CO_2
sec	ml
0.0	8.5
900.0	23.1
1800.0	30.2
2700.0	36.4
3900.0	44.2
4500.0	47.8
5400.0	52.2
6300.0	59.9
7200.0	66.0
8100.0	72.2
9000.0	77.3
9900.0	82.2
10900.0	89.2
11800.0	95.4
12700.0	101.4
13600.0	107.3
14500.0	112.8
15400.0	118.6
16650.0	126.6
18100.0	136.7
19000.0	141.8
19900.0	147.6
20900.0	154.0
22100.0	161.8
22700.0	165.5
23600.0	171.8
24500.0	177.4

---

* Check Run

** Barometer pressure = 739.5 mm Hg
Room temperature = 27°C

TABLE XIV

RATE OF DECARBOXYLATION OF 0.75 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0	24.8		
300.0	9.4	24.6	25.0	744.0
600.0	15.4	24.8	25.0	744.0
900.0	19.2	24.8	25.5	744.0
1200.0	23.2	24.9	25.5	744.0
1500.0	26.2	24.9	25.5	744.0
1800.0	29.6	24.9	25.5	744.0
2100.0	33.0	24.9	25.5	744.0
2400.0	36.0	25.0	25.5	744.0
2700.0	39.4	25.0	25.5	744.0
3000.0	42.6	25.0	25.5	744.0
3300.0	45.8	25.0	25.5	744.0
3600.0	49.2	25.1	25.5	743.8
3900.0	52.2	25.1	25.5	743.8
4200.0	55.8	25.1	25.5	743.8
4500.0	59.0	25.0	25.5	743.9
4800.0	62.0	25.0	25.5	743.9
5100.0	65.4	25.0	25.5	744.0
5400.0	68.7	25.0	25.5	743.9

TABLE XV

RATE OF DECARBOXYLATION OF 1.0 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	10.0	26.4	26.0	737.0
900.0	21.4	26.5	26.0	737.0
1800.0	33.6	26.6	26.0	737.0
2700.0	45.0	26.6	26.0	737.0
3600.0	58.4	26.7	26.0	737.0
4500.0	72.6	26.4	26.0	736.4
5400.0	85.9	26.4	26.0	736.4
6300.0	98.8	26.5	25.9	736.3
7200.0	111.4	26.6	26.0	736.8
8100.0	124.9	26.6	26.0	736.8
9000.0	137.8	26.6	26.0	736.8
9900.0	150.9	26.4	26.0	736.8
10800.0	163.6	26.4	25.9	736.9
11700.0	176.3	26.3	25.5	737.1
13500.0	201.6	26.2	25.0	737.2
14400.0	214.6	26.1	25.0	737.4
15300.0	227.1	26.0	25.0	737.7
16200.0	240.0	26.2	25.0	737.7
17100.0	252.8	26.4	24.9	737.9
18000.0	265.5	26.3	25.0	737.6
18900.0	278.1	26.2	25.0	737.6
19800.0	291.0	26.1	25.0	737.7
20700.0	303.5	26.2	24.8	738.0
21600.0	316.1	26.2	24.8	737.8
22500.0	328.8	26.0	24.8	737.7
23400.0	341.4	26.0	24.9	737.6

TABLE XVI

RATE OF DECARBOXYLATION OF 2.5 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.8	24.1	24.0	736.2
100.0	3.8			
200.0	8.0			
300.0	11.2			
400.0	14.8			
500.0	18.0			
600.0	21.5			
700.0	25.2			
800.0	29.4	24.3		
900.0	31.8	24.3		
1000.0	36.6	24.4	24.0	736.5
1200.0	43.7	24.4	24.0	736.5
1400.0	51.2	24.4	24.0	736.4
1600.0	59.0	24.4	24.0	736.4
1800.0	66.3	24.4	24.0	736.4
2000.0	74.2	24.4	24.0	736.2
2200.0	82.2	24.6		
2400.0	89.4	24.4	24.2	736.4
2600.0	96.2			
2810.0	104.2	24.4	24.4	736.3
3000.0	111.5	24.4		
3200.0	118.8	24.4	24.1	736.4
3410.0	127.2	24.4		
3600.0	134.5	24.5	24.2	736.4
3805.0	142.4	24.4		
4000.0	149.5	24.4	24.3	736.2
4500.0	167.6	24.4	24.3	736.2
5000.0	186.6	24.4	24.4	736.4
5500.0	205.0	24.4	24.3	736.4
6000.0	219.9	24.4	24.2	736.2
6510.0	242.2	24.4	24.4	736.1
7000.0	261.1	24.4	24.3	736.0
7500.0	280.2	24.6	24.4	736.1
8000.0	298.7	24.6	24.5	736.1
8500.0	317.5	24.6	24.5	736.2
9000.0	336.4	24.6	24.5	736.2
9500.0	354.6	24.8	24.5	736.2
10000.0	373.4	24.8	24.5	736.2

TABLE XVII

RATE OF DECARBOXYLATION OF 0.25 M MALONIC ACID IN AQUEOUS SOLUTION (1.5 pH) AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0	24.0		
300.0	4.8	24.0	22.0	732.2
600.0	8.6	24.0	22.0	732.2
900.0	11.8	24.0	22.0	732.0
1200.0	13.0	24.0	22.0	732.1
1800.0	15.2	24.0	22.0	732.0
2400.0	17.4	24.0	22.0	732.0
3000.0	19.4	24.0	22.0	731.8
3300.0	20.4	24.1	22.0	731.8
3600.0	21.6	24.2	22.0	731.8
3900.0	22.6	24.2	22.0	731.8
4200.0	23.8	24.3	22.0	731.6
4800.0	25.8	24.3	22.5	731.7
5400.0	27.8	24.4	23.0	731.9
6000.0	29.8	24.4	23.0	731.7
6600.0	31.8	24.4	23.0	731.7
7200.0	33.8	24.4	23.0	731.7
7800.0	35.8	24.4	23.0	731.7

TABLE XVIII

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (1.5 pH) AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0			
300.0	6.6	24.7	25.0	734.6
600.0	10.6	24.7	25.0	734.6
900.0	13.5	24.8	25.0	734.6
1200.0	15.8	24.8	25.0	734.6
1500.0	18.1	24.9	25.0	734.6
1800.0	20.4	24.9	25.0	734.6
2100.0	22.4	25.0	25.0	734.6
2400.0	24.8	25.0	25.0	734.6
2700.0	26.8	25.1	25.0	734.6
3000.0	29.4	25.2	25.5	734.6
3300.0	31.6	25.1	26.0	734.7
3600.0	33.4	25.1	26.0	734.7
3900.0	35.6	25.1	26.0	734.6
4200.0	37.6	25.2	26.0	734.6
4500.0	40.0	25.2	26.0	734.6
4800.0	42.0	25.2	26.0	734.6
5100.0	44.0	25.2	26.0	734.6
5400.0	46.2	25.2	26.0	734.5
5700.0	48.4	25.3	26.0	734.5
6000.0	50.4	25.3	26.0	734.5
6300.0	52.4	25.2	26.0	734.6
6600.0	54.4	25.3	26.0	734.6
6900.0	56.6	25.3	26.0	734.6
7200.0	58.8	25.3	26.0	734.6

TABLE XIX

RATE OF DECARBOXYLATION OF 0.75 M MALONIC ACID IN AQUEOUS SOLUTION (1.5 pH) AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0	26.6	27.0	736.0
300.0	5.8	26.6	27.0	736.0
600.0	11.4	26.8	27.0	736.0
900.0	15.8	26.8	27.0	736.0
1200.0	19.6	26.9	27.0	735.7
1500.0	22.8	27.0	27.0	735.8
1800.0	26.0	27.0	27.0	735.7
2100.0	29.6	27.1	27.0	735.7
2400.0	32.8	27.1	27.0	735.7
2700.0	35.8	27.1	27.0	735.7
3000.0	39.4	27.2	27.0	735.9
3300.0	42.6	27.2	27.0	735.9
3600.0	45.8	27.2	27.0	735.8
3900.0	49.0	27.2	27.0	735.8
4200.0	52.4	27.2	27.0	736.0
4500.0	55.4	27.2	27.0	736.0
4800.0	58.4	27.2	27.0	736.0
5100.0	61.6	27.2	27.0	736.0
5400.0	64.6	27.2	27.0	736.0

TABLE XX

RATE OF DECARBOXYLATION OF 1.0 M MALONIC ACID IN AQUEOUS SOLUTION (1.5 pH) AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.1	23.4		
300.0	2.4	23.4	24.0	738.1
600.0	5.4	23.5	24.0	738.1
900.0	8.6	23.5	24.0	738.1
1200.0	12.0	23.6	24.0	738.0
1500.0	15.6	23.6	24.0	737.9
1800.0	19.0	23.6	24.0	737.9
2100.0	23.6	23.7	24.0	738.0
2400.0	27.4	23.7	24.0	737.9
2700.0	32.2	23.7	24.0	737.8
3000.0	36.4	23.7	24.0	737.6
3300.0	41.0	23.8	24.0	737.4
3600.0	45.2	23.8	24.0	737.5
3900.0	49.6	23.8	24.0	737.4
4200.0	54.4	24.0	24.0	737.4
4500.0	58.8	24.0	24.0	737.3
4800.0	63.1	24.0	24.0	737.3
5100.0	67.6	24.0	24.0	737.3
5400.0	72.2	24.0	24.0	737.2
5700.0	76.6	24.0	24.0	737.2
6000.0	81.0	24.1	24.0	737.3
6300.0	85.2	24.1	24.0	737.2
6600.0	89.6	24.1	24.0	737.1
6900.0	94.0	23.9	24.0	737.0
7200.0	98.4	24.0	24.0	737.0

TABLE XXI

RATE OF DECARBOXYLATION OF 0.25 M MALONIC ACID IN AQUEOUS SOLUTION (2.46 pH) AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0	23.2	24.0	743.0
600.0	3.7	23.2	24.0	743.0
900.0	4.8	23.2	24.0	743.0
1200.0	5.8	23.4	24.0	743.0
1800.0	7.4	23.4	24.0	743.0
2400.0	9.2	23.2	24.0	743.0
3000.0	10.6	23.1	24.0	743.0
3600.0	12.2	23.1	24.0	743.0
4200.0	14.0	23.1	23.0	743.0
4800.0	16.0	23.2	23.0	743.1
5400.0	17.8	23.2	23.0	743.1
6000.0	19.6	23.2	23.0	743.2
6600.0	21.3	23.1	23.0	743.1
7200.0	23.2	23.2	23.0	743.2
7800.0	25.2	23.3	23.0	743.1

TABLE XXII

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (2.46 pH) AT 79°C

Time	Vol CO_2	Temp. buret	Temp, bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0	26.4		
300.0	7.6	26.4	28.0	742.0
600.0	11.8	26.5	28.0	742.0
900.0	15.0	26.6	28.0	742.0
1200.0	16.6	26.5	28.0	742.0
1500.0	19.6	26.5	28.0	742.0
1800.0	21.4	26.5	28.0	742.0
2100.0	23.4	26.6	28.0	742.0
2400.0	25.0	26.4	28.0	742.0
2700.0	26.8	26.4	28.0	742.0
3000.0	28.7	26.4	28.0	742.0
3300.0	30.4	26.4	28.0	742.0
3600.0	32.2	26.2	28.0	742.0
3900.0	34.0	26.3	28.0	742.0
4200.0	36.0	26.4	28.0	742.0
4500.0	38.0	26.4	28.0	742.0
4800.0	39.6	26.4	28.0	742.0
5100.0	41.2	26.4	28.0	742.0
5400.0	43.0	26.4	28.0	742.0
5700.0	45.0	26.4	28.0	742.0
6000.0	46.8	26.4	28.0	742.0

TABLE XXIII

RATE OF DECARBOXYLATION OF 0.75 M MALONIC ACID IN AQUEOUS SOLUTION (2.46 pH) AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0	26.6	27.0	734.4
300.0	6.2	26.6	27.0	734.4
600.0	9.6	26.6	27.0	734.4
900.0	12.8	26.7	27.0	734.2
1200.0	16.0	26.7	27.0	734.2
1500.0	18.8	26.8	27.0	734.2
1800.0	21.8	26.8	27.0	734.2
2100.0	24.6	26.8	27.0	734.2
2400.0	27.2	26.8	27.0	734.2
2700.0	30.2	26.9	27.0	734.2
3000.0	33.4	27.0	27.0	734.2
3300.0	36.0	27.0	27.0	734.2
3600.0	39.0	27.0	27.0	734.2
3900.0	41.8	27.0	27.0	734.2
4200.0	44.6	27.0	27.0	734.2
4500.0	47.4	27.0	27.0	734.2
4800.0	50.4	27.0	27.0	734.2
5100.0	53.2	27.0	27.0	734.2
5400.0	56.0	27.0	27.0	734.2

TABLE XXIV

RATE OF DECARBOXYLATION OF 1.0 M MALONIC ACID IN AQUEOUS SOLUTION (2.46 pH) AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.1	25.4	26.0	737.2
100.0	2.4			
200.0	5.2			
300.0	7.6			
400.0	9.8			
500.0	11.5			
600.0	13.4			
700.0	15.0			
800.0	16.5			
900.0	17.8	25.4		
1000.0	19.4	25.5		
1200.0	22.0	25.5	26.0	737.2
1500.0	26.2	25.6	26.0	737.1
1800.0	29.9	25.6	26.0	737.2
2100.0	33.2	25.7	26.0	737.1
2400.0	36.8	25.8	26.0	737.2
2700.0	41.1	25.9	26.0	737.1
3000.0	44.4	25.8	26.2	737.2
3306.0	48.3	25.8	26.5	737.1
3600.0	54.8	27.0	27.0	737.1
3900.0	59.8	28.0	28.0	737.3
4200.0	64.4	28.4	28.5	737.3
4500.0	68.5	28.8	29.0	737.3
4800.0	72.2	29.0	29.5	737.4
5100.0	76.8	29.3	29.8	737.4
5400.0	81.2	29.5	30.0	737.4
5720.0	86.0	29.6	30.0	737.4
6000.0	89.6	29.8	30.0	737.4
6300.0	93.7	30.0	30.0	737.4
6600.0	97.6	30.0	30.0	737.4

TABLE XXV

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) AT 70°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.2	27.8	27.0	736.8
105.0	2.2	27.8		
200.0	4.8			
300.0	7.2			
400.0	9.6			
500.0	11.2			
600.0	13.0	27.8		
700.0	14.1	27.8		
800.0	15.2	27.9		
900.0	17.2	27.9		
1500.0	19.6	27.9	27.0	737.0
2250.0	22.0	28.0	27.0	737.1
2700.0	23.3	28.0	27.0	737.2
3300.0	24.8	28.0	27.0	737.4
3900.0	26.3	28.2	27.5	737.4
4500.0	27.6	28.2	27.5	737.4
5100.0	29.2	28.2	27.8	737.2
5700.0	30.4	28.3	27.8	737.2
6300.0	31.7	28.4	28.0	737.1
6900.0	33.1	28.4	28.0	737.1
7500.0	34.3	28.4	28.0	736.8
8100.0	35.4	28.4	28.0	737.0
8750.0	37.3	28.4	28.0	737.0
9300.0	38.3	28.4	28.0	737.0
9900.0	39.8	28.5	28.0	737.0
10500.0	41.0	28.6	28.0	737.0
11100.0	42.5	28.7	28.5	737.1
11700.0	43.5	28.8	28.8	737.2
12300.0	44.8	28.8	28.5	737.2
12900.0	46.0	28.7	28.4	737.0
13500.0	47.4	28.6	28.0	737.1
14100.0	48.8	28.6	28.0	737.2
14700.0	50.0	28.7	28.2	737.1
15300.0	51.5	28.8	28.5	737.1
15900.0	53.0	28.8	28.5	737.1

TABLE XXVI

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) AT 75°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.4	24.8	24.0	738.1
100.0	2.6			
200.0	4.2	25.2		
300.0	7.4	25.2		
400.0	9.4	25.2		
500.0	11.9	25.2		
610.0	12.8	25.2		
725.0	14.0			
800.0	14.4	25.3		
900.0	15.8	25.4	24.5	738.4
1200.0	17.4	25.4	24.5	738.4
1800.0	20.8	25.2	24.8	738.4
2400.0	23.8	25.4	24.8	738.4
3000.0	26.4	25.7	24.8	738.4
3600.0	28.6	25.8	24.9	738.4
4250.0	31.1	25.7	25.0	738.5
4800.0	33.7	26.0	25.0	738.4
5400.0	36.1	25.9	25.0	738.3
6010.0	38.7	25.9	25.0	738.4
6600.0	41.0	26.0	25.0	738.3
7200.0	43.6	26.0	25.0	738.2
7800.0	46.0	26.2	25.0	737.9
8400.0	48.4	26.1	25.0	738.1
9000.0	51.0	26.1	25.2	738.2
9600.0	53.6	26.0	25.2	738.2
10200.0	56.0	26.1	25.5	738.2
10800.0	58.4	26.2	25.5	738.1
11400.0	60.9	26.2	25.5	738.0
12000.0	63.6	26.1	25.2	738.0
12600.0	66.2	26.2	25.2	738.1
13200.0	68.6	26.2	25.3	738.4
13800.0	70.9	26.2	25.2	738.5
14400.0	73.6	26.3	25.2	738.5
15000.0	76.2	26.4	25.5	738.4
15600.0	78.8	26.4	25.5	738.4

TABLE XXVII

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) AT 85°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0	26.2	25.0	733.0
100.0	2.2			
200.0	6.4			
300.0	10.2			
400.0	13.2			
512.0	17.2			
600.0	19.2			
700.0	21.4			
800.0	23.4			
900.0	25.4	26.6		
1200.0	30.4	26.6	25.0	733.2
1500.0	35.2	26.5	25.0	733.1
1800.0	40.3	26.5	25.0	733.1
2100.0	44.9	26.4	25.0	733.0
2410.0	49.6	26.5	25.0	733.1
2700.0	53.9	26.4	25.0	733.1
3000.0	58.4	26.5	25.0	733.2
3300.0	63.0	26.6	25.0	733.2
3600.0	67.6	26.6	25.0	733.2
3900.0	71.8	26.5	25.0	733.2
4200.0	76.4	26.4	25.0	733.3
4525.0	81.1	26.4	25.0	733.3
4800.0	85.0	26.4	25.0	733.2
5100.0	89.6	26.5	25.0	733.2
5400.0	94.0	26.4	25.0	733.2
5700.0	98.6	26.4	25.0	733.2
6000.0	103.2	26.3	25.0	733.3
6300.0	107.4	26.2	24.9	733.4
7200.0	121.1	26.3	25.0	733.2
7500.0	125.7	26.2	25.0	733.2
7800.0	130.1	26.2	25.0	733.2
8100.0	134.6	26.3	25.0	733.2
8400.0	139.0	26.2	25.0	733.3
8700.0	143.6	26.2	25.0	733.2
9010.0	148.4	26.2	25.0	733.2
9300.0	152.4	26.2	25.0	733.2
9600.0	157.0	26.4	25.0	733.2

TABLE XXVIII

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) AT 90°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.3			
100.0	6.0			
200.0	10.3	25.2		
310.0	14.8			
400.0	18.0			
500.0	21.6			
600.0	24.8	25.2		
700.0	27.8			
825.0	31.4			
900.0	33.1			
1200.0	41.0	25.2		737.6
1300.0	44.1			
1400.0	46.8			
1600.0	51.8	25.4		
1800.0	57.2	25.4	24.5	737.6
2100.0	65.2	25.4	24.5	737.6
2400.0	72.8	25.5	24.5	737.4
2700.0	80.0	25.4	24.6	737.5
3000.0	87.9	25.4	24.7	737.6
3300.0	95.7	25.4	24.8	737.3
3700.0	105.5	25.6	24.8	737.4
3900.0	110.3	25.5		
4200.0	118.3	25.5	25.0	737.2
4500.0	126.1	25.5	25.0	737.4
4800.0	132.9	25.8	25.0	737.2
5100.0	140.8	25.8	25.0	737.2
5400.0	147.7	25.8	25.0	737.2
5700.0	155.7	25.8	25.0	737.2
6000.0	163.5	25.6	25.0	737.3
6300.0	170.9	25.7	25.0	737.2
6600.0	178.3	25.8	25.0	737.2
6900.0	185.9	25.8	25.0	737.2
7200.0	193.3	25.9	25.0	737.2
7500.0	200.7	25.7	25.0	737.2
7800.0	207.8	25.8	25.0	737.6
8100.0	215.2	25.8	25.0	737.9
8400.0	222.8	25.8	25.0	738.0
8710.0	230.5	26.0	25.0	738.1

TABLE XXIX

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (1.5 pH) AT 70°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0			
600.0	5.8	24.8	24.5	734.6
900.0	7.0	24.8		
1200.0	7.8	24.8	24.0	734.4
1800.0	8.8	24.8	24.0	734.5
2400.0	10.0	24.8	24.0	734.4
3000.0	11.3	24.7	24.0	734.4
3600.0	12.4	24.6	24.0	734.4
4200.0	13.8	24.6	24.0	734.2
5000.0	15.6	24.6	24.0	734.2
5400.0	16.4	24.6	24.0	734.2
6000.0	17.6	24.6	24.0	734.2
6600.0	18.9	24.5	24.0	734.0
7200.0	20.2	24.4	23.5	733.6
7800.0	21.6	24.4	23.5	733.6
8400.0	22.8	24.4	23.5	733.6
9000.0	24.0	24.4	23.5	733.7
9600.0	25.2	24.4	23.5	733.7

TABLE XXX

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID

IN AQUEOUS SOLUTION (1.5 pH) AT 90^{o}C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	^{o}C	^{o}C	mm Hg
0.0	0.0	23.8		
300.0	10.0	24.0	22.0	737.3
600.0	18.8	23.4	22.0	737.3
900.0	26.8	23.4	22.0	737.3
1200.0	34.8	23.4	23.5	737.4
1500.0	42.4	23.4	23.5	737.4
1800.0	49.6	23.4	23.5	737.3
2100.0	57.0	23.6	23.5	737.4
2400.0	64.6	23.5	24.0	737.4
2700.0	72.0	23.6	24.0	737.4
3000.0	79.6	23.8	24.0	737.4
3300.0	86.2	23.5	24.0	737.4
3600.0	94.2	23.8	24.0	737.4
3900.0	101.6	23.8	24.0	737.4
4200.0	108.8	23.8	24.0	737.4
4500.0	116.2	23.8	24.0	737.4
4800.0	123.4	23.8	24.0	737.3
5100.0	130.8	24.0	24.0	737.3
5400.0	137.9	24.0	24.0	737.2
5700.0	145.0	24.0	24.0	737.2
6000.0	152.2	24.0	24.0	737.2

TABLE XXXI

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (2.46 pH) AT 70°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0	23.8	25.0	744.1
600.0	6.2	23.8	25.0	744.2
900.0	7.2	23.8	25.0	744.2
1200.0	8.6	23.8	25.0	744.0
1800.0	9.8	23.9	25.0	743.8
2400.0	10.8	24.0	25.0	743.6
3300.0	13.0	24.0	25.0	743.4
3600.0	13.6	24.0	25.0	743.4
4200.0	14.8	24.1	25.0	743.0
4800.0	15.8	24.1	25.0	743.0
5400.0	16.8	24.0	25.0	743.0
6000.0	17.8	24.0	25.0	743.0
6600.0	19.0	24.0	25.0	742.8
7200.0	20.0	24.0	25.0	742.8
7800.0	21.2	24.2	25.0	742.6
8400.0	22.2	24.2	25.0	742.0

TABLE XXXII

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (2.46 pH) AT 90°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0			
900.0	25.0	25.0	24.0	738.0
1200.0	33.8	25.2	24.0	738.0
1500.0	40.4	25.2	24.0	737.8
1800.0	48.4	25.3	24.5	737.6
2100.0	54.8	25.4	24.5	737.6
2400.0	61.4	25.4	24.5	737.7
2700.0	68.4	25.5	24.5	737.7
3000.0	74.8	25.5	24.5	737.6
3300.0	81.2	25.6	24.5	737.6
3600.0	87.4	25.8	25.0	737.6
3900.0	93.8	25.8	25.0	737.6
4200.0	100.2	25.8	24.5	737.6
4500.0	106.6	25.8	24.5	737.6
4800.0	112.8	25.6	24.5	737.4
5100.0	119.2	25.4	24.5	737.4
5400.0	125.4	25.2	24.5	737.4
5700.0	131.8	25.4	24.5	737.4
6000.0	138.4	25.4	24.5	737.4

TABLE XXXIII

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION ($1 \text{ N } H_2SO_4$) WITHOUT PRIOR SATURATION WITH CO_2 AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0			
400.0	8.6	24.0		
1000.0	23.2	24.0	24.0	738.0
2150.0	56.5	24.0	25.0	738.1
2500.0	66.8	24.0	25.0	738.0
2800.0	76.1	23.8		
3000.0	82.5	23.8		
3100.0	86.1	23.8		
3320.0	93.5	23.8		
3600.0	103.0	23.8	25.0	737.9
3900.0	113.1	23.8		
4165.0	121.5	23.8		
4300.0	127.0	23.8		
4400.0	128.3	23.8		
4600.0	130.6	23.8	25.0	737.7
4800.0	132.3	23.8		
5000.0	135.4	23.0		
5065.0	135.8	23.0	28.0	737.4
5365.0	137.8	23.0	27.5	737.0
5665.0	139.6	23.0	27.5	737.2
5965.0	141.4	23.0	27.0	737.0
6265.0	143.2	23.0	27.0	736.9
6565.0	245.0	22.9	27.0	736.9
6865.0	146.7	22.8	27.5	736.8
7165.0	148.6	22.8	27.5	736.7
7465.0	150.6	22.8	27.0	736.7
7765.0	152.4	22.8	27.3	736.7
8065.0	153.2	22.9	27.3	736.7
8365.0	155.2	22.9	27.3	736.7
8665.0	157.2	22.9	27.0	736.7
8965.0	159.0	22.9	27.0	736.6
9265.0	160.8	22.8	27.0	736.5
9565.0	162.7	22.8	27.0	736.5
9865.0	164.5	22.8	27.0	736.6
10165.0	166.2	22.7	27.0	736.4

TABLE XXXIV

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) WITH ADDITION OF 0.01 N NICKEL SULFATE AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0	23.3		
300.0	3.8	23.5	22.0	738.0
600.0	7.0	23.4	22.0	738.0
900.0	9.3	23.4	22.0	738.0
1200.0	11.6	23.4	22.0	737.9
1800.0	15.0	23.4	22.0	737.9
2100.0	17.0	23.4	22.0	737.9
2400.0	19.2	23.4	22.0	737.9
2700.0	21.3	23.4	22.0	737.9
3000.0	23.4	23.4	22.0	737.9
3300.0	25.6	23.4	22.0	737.9
3600.0	27.8	23.4	22.0	737.9
3900.0	29.8	23.5	22.0	737.9
4200.0	32.2	23.5	22.0	737.9
4500.0	34.4	23.6	22.0	737.9
4800.0	36.6	23.5	22.0	737.9
5100.0	38.6	23.5	22.0	737.9
5700.0	43.0	23.5	22.0	737.6
6000.0	45.0	23.5	22.0	737.6
6300.0	47.0	23.5	22.0	737.2
6600.0	49.4	23.5	22.0	737.3
6900.0	51.4	23.5	22.0	737.2
7200.0	53.4	23.5	22.0	737.3
7500.0	55.8	23.5	22.0	737.3

TABLE XXXV

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) WITH ADDITION OF 0.05 N NICKEL SULFATE AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0			
300.0	5.2	22.0	21.5	734.0
600.0	8.8	22.1	22.0	734.1
900.0	11.4	22.1	22.0	734.1
1200.0	14.0	22.2	22.0	734.1
1800.0	18.2	22.2	22.0	734.0
2100.0	20.4	22.3	22.0	734.0
2400.0	22.6	22.4	22.0	734.0
2700.0	24.8	22.3	22.0	734.0
3000.0	27.0	22.4	22.0	734.0
3300.0	29.0	22.4	22.0	734.0
3600.0	31.2	22.4	22.0	734.0
3900.0	34.4	22.4	22.0	734.0
4200.0	35.6	22.4	22.0	734.0
4500.0	37.8	22.4	22.0	734.0
4800.0	40.2	22.4	22.0	734.0
5100.0	42.6	22.4	22.0	734.0
5400.0	44.6	22.4	22.0	733.8
6000.0	48.6	22.4	22.0	733.8
6300.0	50.6	22.6	22.0	733.8
6600.0	53.0	22.6	22.0	733.8
6900.0	55.0	22.6	22.0	733.8
7200.0	57.0	22.6	22.0	733.8

TABLE XXXVI

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) WITH ADDITION OF 0.01 N COBALT ACETATE AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0	26.5		
300.0	6.0	26.5	26.0	736.8
600.0	9.8	26.6	26.0	736.8
900.0	12.2	26.2	26.0	736.8
1200.0	14.4	23.6	26.0	736.8
1500.0	17.0	23.2	26.0	736.8
1800.0	19.0	23.0	26.0	736.8
2100.0	21.0	22.8	25.5	736.5
2400.0	22.8	22.8	25.5	736.5
2700.0	25.0	22.5	25.5	736.5
3000.0	27.0	22.5	25.0	736.2
3300.0	28.8	22.4	25.0	736.2
3600.0	30.8	22.3	25.0	736.2
3900.0	32.8	22.3	25.0	736.1
4200.0	34.8	22.3	25.0	736.0
4500.0	36.8	22.3	24.5	736.0
4800.0	38.8	22.3	24.5	736.0
5100.0	41.0	22.0	25.0	736.0
5400.0	43.0	22.0	25.0	736.0
5700.0	45.0	22.0	25.0	736.0
6000.0	47.2	22.0	25.0	736.0
6300.0	49.2	22.0	25.0	736.0
6600.0	51.2	22.0	25.0	735.7
6900.0	53.4	22.0	25.0	735.7
7200.0	56.4	22.0	25.0	735.7

TABLE XXXVII

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) WITH ADDITION OF 0.05 N COBALT ACETATE AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0	23.0	24.5	733.6
105.0	2.7	23.2		
200.0	4.6	23.2		
300.0	7.0	23.4		
400.0	9.2	23.2		
605.0	12.2	23.2		
720.0	13.7			
800.0	14.4	23.3		
900.0	15.6	23.3		
1200.0	18.2	23.4	24.5	733.6
1500.0	21.0	23.4	24.5	733.6
1800.0	23.4	23.4	24.5	733.6
2100.0	25.8	23.4	24.5	733.6
2400.0	27.8	23.4	24.5	733.6
2700.0	30.4	23.4	24.5	733.6
3000.0	32.6	23.4	24.5	733.6
3300.0	34.6	23.6	24.5	733.6
3600.0	36.8	23.6	24.5	733.6
3900.0	39.0	23.6	24.5	733.6
4200.0	41.0	23.6	24.5	733.6
4500.0	43.4	23.6	24.5	733.6
4800.0	45.6	23.8	24.5	733.6
5100.0	47.8	23.7	24.5	733.6
5400.0	49.8	23.8	25.0	733.6
5700.0	52.0	23.8	25.0	733.6
6000.0	54.6	23.9	25.0	733.6
6300.0	56.4	23.8	25.0	733.6
6600.0	58.5	23.8	25.0	733.4
6900.0	60.6	23.8	24.5	733.5
7200.0	63.0	23.8	25.0	733.4

TABLE XXXVIII

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) WITH ADDITION OF 0.01 N CALCIUM SULFATE AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.2	25.0	27.0	739.4
300.0	5.7	25.1	27.0	739.4
600.0	9.2	25.1	27.0	739.4
900.0	11.8	25.1	27.0	739.4
1250.0	14.3	25.1	27.0	739.3
1500.0	16.2	25.1	27.0	739.3
1800.0	18.4	25.1	27.0	739.4
2150.0	20.7	25.0	27.0	739.3
2400.0	22.0	25.1	27.0	739.4
3000.0	26.2	25.2	27.0	739.2
3600.0	30.2	25.3	27.0	739.3
3900.0	31.4	25.2	27.5	739.3
4200.0	33.4	25.2	27.0	739.3
4500.0	35.0	25.2	27.5	739.3
5100.0	38.0	25.2	27.5	739.2
5400.0	39.6	25.2	27.5	739.2
5700.0	41.4	25.2	27.5	739.2
6000.0	43.4	25.2	27.0	739.2
6300.0	45.4	25.2	27.0	739.2
6600.0	47.4	25.2	27.0	739.3
6900.0	49.3	25.2	27.0	739.3
7200.0	51.2	25.2	27.0	739.2

TABLE XXXIX

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) WITH ADDITION OF 0.05 N CALCIUM SULFATE AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0	22.0		
300.0	5.2	22.0	24.0	732.2
600.0	9.3	22.0	24.0	732.2
900.0	12.1	22.2	24.0	732.2
1200.0	14.7	22.2	24.0	732.1
1500.0	17.2	22.2	24.0	732.0
1800.0	19.2	22.5	24.0	732.1
2100.0	21.2	22.4	24.0	732.1
2400.0	23.2	22.5	24.0	732.1
2700.0	25.4	22.5	24.0	732.1
3000.0	27.4	22.5	24.0	732.1
3300.0	29.6	22.4	24.0	732.1
3600.0	32.0	22.4	24.0	732.1
3900.0	34.0	22.4	24.0	732.1
4200.0	36.2	22.4	24.0	732.1
4500.0	38.2	22.5	24.0	732.0
4800.0	40.4	22.6	24.0	732.0
5400.0	44.8	22.2	24.0	732.0
5700.0	47.2	22.4	24.0	732.0
6000.0	49.2	22.2	24.0	732.0
6300.0	51.3	22.2	24.0	732.1
6600.0	53.4	22.4	24.0	732.1
6900.0	55.6	22.4	24.0	732.1

TABLE XL

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) WITH ADDITION OF 0.01 N COPPER ACETATE AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0	26.4		
100.0	2.6	26.4		
200.0	4.8	26.5		
400.0	8.4	26.5		
500.0	10.0	26.5		
600.0	11.4	26.5		
700.0	12.5	26.5		
800.0	13.4	26.5		
900.0	14.3	26.5		
1000.0	15.3	26.5		736.0
1200.0	16.9	26.6	27.0	
1500.0	18.5			735.8
1800.0	20.6	25.2	27.0	735.8
2100.0	22.8	25.2	27.0	735.8
3000.0	29.4	25.3	27.0	735.8
3300.0	31.6	25.4	27.0	735.7
3600.0	33.8	25.4	27.0	735.6
3900.0	35.4	25.4	27.0	735.6
4200.0	37.8	25.3	27.0	735.6
4505.0	40.0	25.3	27.0	735.6
4800.0	42.4	25.3	27.0	735.6
5100.0	44.6	25.3	27.0	735.6
5400.0	46.8	25.3	27.0	735.4
5700.0	48.0	25.2	27.0	735.4
6000.0	50.3	25.2	27.0	735.4
6300.0	52.2	25.2	27.0	735.2
6600.0	54.6	25.2	27.0	735.2
6900.0	57.2	25.2	27.0	735.2

TABLE XLI

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) WITH ADDITION OF 0.05 N COPPER ACETATE AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0			
200.0	4.8	23.8	19.0	735.6
400.0	8.9	23.6	19.0	735.6
600.0	12.0	23.6	19.0	735.4
800.0	14.4	23.6	19.0	735.4
900.0	15.4	23.6	19.0	
1200.0	18.3	23.6	19.0	735.4
1500.0	20.6	23.6	19.0	735.4
1800.0	23.2	23.6	19.0	735.4
2100.0	25.3	23.6	19.0	735.4
2400.0	27.4	23.6	19.0	735.3
2700.0	29.8	23.6	19.0	735.3
3000.0	32.0	23.7	19.0	735.3
3350.0	34.4	23.7	19.0	735.3
3600.0	36.4	23.7	19.0	735.3
3900.0	38.5	23.7	19.0	735.2
4200.0	40.3	23.7	19.0	735.2
4500.0	42.6	23.7	19.0	735.2
4800.0	45.0	23.7	19.0	735.2
5100.0	47.2	23.7	19.0	735.2
5400.0	49.4	23.7	19.0	735.2
5700.0	51.6	23.7	19.0	735.2
6000.0	53.6	23.8	19.0	735.2
6300.0	55.6	23.8	19.0	735.2
6600.0	58.0	24.2	20.0	735.2
6900.0	59.8	23.8	21.2	735.2
7200.0	61.6	24.0	21.0	735.0

TABLE XLII

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) WITH ADDITION OF 0.1 N COPPER SULFATE AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0			
200.0	4.0	19.9	19.0	734.4
400.0	7.6	20.0		
600.0	9.8	20.0		
800.0	11.9	20.2	19.0	734.3
900.0	12.6	20.2		
1200.0	15.2	20.4	19.0	734.3
1500.0	18.0	21.4	19.0	734.3
1800.0	20.0	21.5	19.5	734.3
2100.0	21.4	21.4	21.0	734.4
2400.0	23.4	21.4	21.0	734.4
2700.0	25.6	21.6	21.0	734.3
3000.0	27.8	21.6	21.0	734.3
3300.0	29.8	21.6	20.5	734.3
3600.0	31.9	21.5	20.5	734.3
3900.0	33.6	21.5	20.5	734.3
4500.0	38.0	21.6	20.5	734.3
4800.0	40.0	21.5	20.5	734.3
5100.0	42.2	21.6	20.5	734.2
5400.0	44.2	21.6	20.5	734.3

TABLE XLIII

RATE OF DECARBOXYLATION OF 0.50 M MALONIC ACID IN AQUEOUS SOLUTION (1.0 N H_2SO_4) USING PLATINIZED Pt GAUZE (0.75 sq in) AT 79°C

Time	Vol CO_2	Temp. buret	Temp. bar.	Bar. press.
sec	ml	°C	°C	mm Hg
0.0	0.0	24.6	26.0	734.3
100.0	3.0	24.6		
200.0	4.8	24.6		
300.0	6.9	24.6		
400.0	8.5	24.6		
500.0	9.9	24.6		
600.0	11.0	24.6		
700.0	12.0	24.6		
800.0	12.7	24.6		
900.0	13.6	24.8		
1200.0	16.2	24.8	26.0	734.1
1500.0	18.5	24.8	26.0	734.1
1800.0	21.0	24.8	26.0	734.0
2100.0	23.4	25.0	26.0	734.1
2400.0	25.6	25.0	26.0	734.2
2700.0	27.8	25.0	26.0	734.2
3000.0	29.8	25.1	26.5	734.3
3300.0	31.6	25.2	26.5	734.3
3600.0	33.6	25.2	26.5	734.2
3900.0	35.8	25.2	26.5	734.2
4200.0	38.0	25.2	26.5	734.2
4500.0	40.3	25.2	26.5	734.2
4800.0	42.5	25.2	26.5	734.3
5100.0	44.6	25.2	26.5	734.3
5400.0	46.6	25.2	26.5	734.3
5700.0	49.0	25.3	26.0	734.4
6320.0	53.2	25.4	26.5	734.4
6600.0	55.2	25.4	26.5	734.4
6900.0	57.3	25.3	26.5	734.6
7500.0	61.5	25.4	26.5	734.5

APPENDIX D

SAMPLE CALCULATIONS

1. Sample Calculation of the Decarboxylation Rate. The method used for calculating the average rates of the decarboxylation of malonic acid at various concentrations and temperatures was the same. The data from Table XXVII have been used to illustrate the calculation.

$$-\frac{dC_T}{d\theta} = kC_{H_2M}$$

$$-\frac{\Delta C_T}{\Delta\theta} = kC_T$$

$$-\frac{\Delta C_T}{\Delta\theta} = -\frac{1}{V_o}\ \frac{\Delta N_{H_2M}}{\Delta\theta} = \frac{1}{V_o}\ \frac{\Delta N_{CO_2}}{\Delta\theta}$$

Using the ideal gas law

$$PV = N_{CO_2}RT$$

$$P\Delta V = \Delta N_{CO_2}RT$$

Dividing both sides by $\Delta\theta$

$$P\,\frac{\Delta V}{\Delta\theta} = \frac{\Delta N_{CO_2}}{\Delta\theta}\,RT$$

or

$$\frac{P}{RT}\ \frac{\Delta V}{\Delta\theta} = \frac{\Delta N_{CO_2}}{\Delta\theta}$$

Therefore,

$$-\frac{\Delta C_T}{\Delta\theta} = \frac{1}{V_o}\ \frac{P}{RT}\ \frac{\Delta V}{\Delta\theta}$$

$$-\frac{\Delta C_T}{\Delta\theta} = \left(\frac{1}{\text{liter}}\right)_{\text{solu.}}\left(\frac{\text{atm}}{{}^{\circ}\text{K}}\right)\left(\frac{\text{gmol}}{\text{ml}}\right)_{CO_2}\left(\frac{{}^{\circ}\text{K}}{\text{atm}}\right)\left(\frac{\text{ml}}{\text{sec}}\right)_{CO_2}\left(\frac{\text{gmol } H_2M}{\text{gmol } CO_2}\right)$$

$$-\frac{\Delta C_T}{\Delta\theta} = \frac{\text{gmol}}{\text{liter-sec}}$$

$V_o = 0.3$ liter

$P = 1.0$ atm

$R = 82.058 \ \frac{\text{atm-ml}}{\text{gmol } {}^{\circ}\text{K}}$

$T = 273^{\circ}\text{K}$

Therefore, the conversion factor is

$$\frac{1}{V_o} \ \frac{P}{RT} = 1.487 \times 10^{-4}$$

The computer program was written to evaluate $(\Delta V/\Delta\theta)$ STP as a function of time for each run and is shown on page 84. The average values of the temperatures of the gas burette and barometric pressures were considered for evaluating the average rates. From Table XXVII

Average gas burette temperature = 26.4°C

Average barometer temperature = 25°C

Average pressure = 733.2 mm Hg

Vapor pressure of water (at 26.4°C) = 25.812 mm Hg

Correction = 2.983 mm Hg

Corrected pressure = 704.405 mm Hg

2. <u>Sample Calculations for Preparing Malonic Acid Solutions of a Desired pH</u>. Solutions of constant pH's (1.5 and 2.46) were prepared using different concentrations of malonic acid (0.25, 0.50, 0.75, and 1.0 M). The SO_4 concentration was held constant

Program No. 1

PROGRAM FOR EVALUATING DECARBOXYLATION RATES

```
C     CNX026 GUJARATHI R.N.
C     KINETIC STUDIES ON DECARBOXYLATION OF MALONIC ACID
      DIMENSION T(100),V(100)
      PRINT 50
      READ 200,P1,T1,P2,T2,L
      READ 300,(T(J),J=1,L),(V(J),J=1,L)
      DO 15 J=2,L
      VT2=(P2*V(J)*T1)/(P1*T2)
      VT1=(P2*V(J-1)*T1)/(P1*T2)
      DELV=VT2-VT1
      DELT=T(J)-T(J-1)
      P=DELV/DELT
      PUNCH 400,T(J),V(J),VT2,DELT,DELV,P
   15 PRINT 400,T(J),V(J),VT2,DELT,DELV,P
   50 FORMAT(3X8HTIME-SEC,4X6HVOL-ML,5X5HV-STP,5X4HDELT,6X4HDELV,6X9HDEL
     1V/DELT)
  200 FORMAT(4F10.3,I10)
  400 FORMAT(2F10.1,F10.3,F10.1,F10.3,F14.8)
  300 FORMAT(7F10.2)
      CALL EXIT
      END
```

OUTPUT OF PROGRAM NO. 1

```
TIME-SEC    VOL-ML    V-STP      DELT     DELV      DELV/DELT

  100.0      2.2       1.859    100.0     1.859    .01859269
  200.0      6.4       5.408    100.0     3.549    .03549514
  300.0     10.2       8.620    100.0     3.211    .03211465
  400.0     13.2      11.155    100.0     2.535    .02535368
  512.0     17.2      14.536    112.0     3.380    .03018294
  600.0     19.2      16.226     88.0     1.690    .01920732
  700.0     21.4      18.085    100.0     1.859    .01859270
  800.0     23.4      19.775    100.0     1.690    .01690245
  900.0     25.4      21.466    100.0     1.690    .01690245
 1200.0     30.4      25.691    300.0     4.225    .01408537
 1500.0     35.2      29.748    300.0     4.056    .01352196
 1800.0     40.3      34.058    300.0     4.310    .01436708
 2100.0     44.9      37.946    300.0     3.887    .01295854
 2410.0     49.6      41.918    310.0     3.972    .01281315
 2700.0     53.9      45.552    290.0     3.634    .01253112
 3000.0     58.4      49.355    300.0     3.803    .01267683
 3300.0     63.0      53.242    300.0     3.887    .01295854
 3600.0     67.6      57.130    300.0     3.887    .01295855
 3900.0     71.8      60.679    300.0     3.549    .01183172
 4200.0     76.4      64.567    300.0     3.887    .01295853
 4525.0     81.1      68.539    325.0     3.972    .01222177
 4800.0     85.0      71.835    275.0     3.295    .01198538
 5100.0     89.6      75.722    300.0     3.887    .01295853
 5400.0     94.0      79.441    300.0     3.718    .01239514
 5700.0     98.6      83.329    300.0     3.887    .01295853
 6000.0    103.2      87.216    300.0     3.887    .01295854
 6300.0    107.4      90.766    300.0     3.549    .01183172
 7200.0    121.1     102.344    900.0    11.578    .01286464
 7500.0    125.7     106.231    300.0     3.887    .01295856
 7800.0    130.1     109.950    300.0     3.718    .01239513
 8100.0    134.6     113.753    300.0     3.803    .01267683
 8400.0    139.0     117.472    300.0     3.718    .01239513
 8700.0    143.6     121.359    300.0     3.887    .01295850
 9010.0    148.4     125.416    310.0     4.056    .01308580
 9300.0    152.4     128.796    290.0     3.380    .01165686
 9600.0    157.0     132.684    300.0     3.887    .01295853
```

at 0.50 M in each solution using H_2SO_4 and K_2SO_4. The first ionization of sulfuric acid was assumed to be complete. The second ionization constant of malonic acid was so small that it was not used in developing the following equations.

$$HSO_4^- \rightleftharpoons H^+ + SO_4^= \qquad (41)$$

$$H_2M \rightleftharpoons H^+ + HM^- \qquad (42)$$

$$K_1 = \frac{(H^+)(SO_4^=)}{(HSO_4^-)} \qquad (43)$$

$$K_2 = \frac{(H^+)(HM^-)}{(H_2M)} \qquad (44)$$

$SO_4^=$ Balance:

$$HSO_4^- + SO_4^= = 0.5 \qquad (45)$$

Charge Balance:

$$H^+ + 2\ K^+ = HM^- + HSO_4^- + 2\ SO_4^= \qquad (46)$$

From Equation 45:

$$SO_4^= = 0.5 - HSO_4^- \qquad (47)$$

Using Equations 43 and 47:

$$HSO_4^- = \frac{0.5\ H^+}{K_1 + H^+} \qquad (48)$$

X_o = Initial concentration of H_2M gmol/1

Y_o = Initial concentration of H_2SO gmol/1

Therefore,

$$K^+ = 0.5 - Y_o \qquad (49)$$

$$H_2M = X_o - HM^- \qquad (50)$$

From Equations 44 and 50:

$$HM^- = \frac{K_2\ X_o}{K_2 + H^+} \qquad (51)$$

From Equations 46, 47, and 49:

$$2\ Y_o = H^+ + HSO_4^- - HM^- \tag{52}$$

Substituting in Equation 52 for HSO_4 and HM^- from equations 48 and 51:

$$2\ Y_o = H^+ + \frac{0.5\ H^+}{K_1 + H^+} - \frac{K_2\ X_o}{K_2 + H^+} \tag{53}$$

For pH = 1.5 and Y_o = 1 M = 1 gmol/1:

$$H^+ = 10^{-1.5} = 0.0316\ \text{gmol/1}$$

$$K_1 = 0.00236\ \text{at}\ 80^\circ C\quad (24)$$

$$K_2 = 0.00149\ \text{at}\ 25^\circ C\quad (25)$$

Using Equation 53:

$$2\ Y_o = 0.0316 + \frac{0.5\quad 0.0316}{0.00236 + 0.0316} - \frac{0.00149\quad 1}{0.00149 + 0.0316}$$

$$2\ Y_o = 0.0316 + 0.462 - 0.04502$$

$$2\ Y_o = 0.4518$$

$$Y_o = 0.2259\ \text{gmol/1}$$

$$\text{gmols of}\ K_2SO_4 = 0.5 - 0.2259$$

$$= 0.2741$$

For preparation of 1 liter of solution of pH 1.5 and Y_o = 1 M

Malonic Acid = 52.0 gm

H_2SO_4 (10.2 N) = 45.0 ml

K_2SO_4 = 47.762 gm

3. Sample Calculations of the Concentration of Different Species at Equilibrium.

$$HSO_4^- \rightleftharpoons H^+ + SO_4^=$$

$$H_2M \rightleftharpoons H^+ + HM^-$$

$$HM^- \rightleftharpoons H^+ + M^=$$

$$K_1 = \frac{(H^+)(SO_4^=)}{(HSO_4^-)}$$

$$K_2 = \frac{(H^+)(HM^-)}{(H_2M)}$$

$$K_3 = \frac{(H^+)(M^=)}{(HM^-)}$$

P = gmol/l of K_2SO_4 added

$U = H^+$ at equilibrium

$X = H_2M$ at equilibrium

$Y = HSO_4^-$ at equilibrium

$Z = HM^-$ at equilibrium

Charge Balance:

$$H^+ + 2\ K^+ = HM^- + HSO_4^- + 2\ M^= + 2\ SO_4^=$$

$$U + 2P = Z + Y + 2(X_o - X - Z) + 2(Y_o - Y + P)$$

$$U = 2X_o + 2Y_o - 2X - Y - Z \tag{54}$$

$$K_1 = \frac{(2X_o + 2Y_o - 2X - Y - Z)(P + Y_o - Y)}{Y} \tag{55}$$

$$K_2 = \frac{(2X_o + 2Y_o - 2X - Y - Z)(Z)}{X} \tag{56}$$

$$K_3 = \frac{(2X_o + 2Y_o - 2X - Y - Z)(X_o - X - Z)}{Z} \tag{57}$$

Equations 55 - 57 were solved by the Newton-Raphson method. The value of U could be calculated by using equation 54. A computer program (Fortran II) was written for the Newton-Raphson Method and is shown on page 91.

Newton-Raphson Method:

$$F = \frac{(2X_o + 2Y_o - 2X - Z - Y)(P + Y_o - Y)}{Y} - K_1$$

$$G = \frac{(2X_o + 2Y_o - 2X - Z - Y)(Z)}{X} - K_2$$

$$H = \frac{(2X_o + 2Y_o - 2X - Z - Y)(X_o - X - Z)}{Z} - K_3$$

$$F_x = \frac{\partial F}{\partial X} = \frac{2(Y - P - Y_o)}{Y}$$

$$F_y = \frac{\partial F}{\partial Y} = \frac{(2X + Z - 2X_o - 2Y_o)(P + Y_o)}{Y^2} + 1$$

$$F_z = \frac{\partial F}{\partial Z} = \frac{(Y - P - Y_o)}{Y}$$

$$G_x = \frac{\partial G}{\partial X} = \frac{(Z + Y - 2X_o - 2Y_o)(Z)}{X^2}$$

$$G_y = \frac{\partial G}{\partial Y} = -\frac{Z}{X}$$

$$G_z = \frac{\partial G}{\partial Z} = \frac{(2X_o + 2Y_o - 2X - Y)}{X} - 2ZX$$

$$H_x = \frac{\partial H}{\partial X} = \frac{(Z + Y - 2X_o - 2Y_o)}{Z} + \frac{2(Z + 2X - X_o)}{Z}$$

$$H_y = \frac{\partial H}{\partial Y} = \frac{(X + Z - X_o)}{Z}$$

$$H_z = \frac{\partial H}{\partial Z} = \frac{(Y + 2X - 2X_o - 2Y_o)(X_o - X)}{Z^2} + 1$$

$$D_j = \begin{vmatrix} F_x & F_y & F_z \\ G_x & G_y & G_z \\ H_x & H_y & H_z \end{vmatrix} \qquad \Delta X = \frac{\begin{vmatrix} -F & F_y & F_z \\ -G & G_y & G_z \\ -H & H_y & H_z \end{vmatrix}}{D_j}$$

$$\Delta Y = \frac{\begin{vmatrix} F_x & -F & F_z \\ G_x & -G & G_z \\ H_x & -H & H_z \end{vmatrix}}{D_j} \qquad \Delta Z = \frac{\begin{vmatrix} F_x & F_y & -F \\ G_x & G_y & -G \\ H_x & H_y & -H \end{vmatrix}}{D_j}$$

$$X_{i+1} = X_i + \Delta X$$

$$Y_{i+1} = Y_i + \Delta Y$$

$$Z_{i+1} = Z_i + \Delta Z$$

Program No. 2

PROGRAM FOR EVALUATING EQUILIBRIUM CONCENTRATIONS AT 79°C

```
      DIMENSION X0(20),Y0(20),P(20)
      N=11
      READ 100,(X0(I),Y0(I),P(I),I=1,N)
      PRINT 400
      DO 11 J=1,N
      IF(J-5)45,46,47
   45 X=0.1
      Y=0.1
      Z=0.1
      GO TO 7
   46 X=2.
      Y=0.001
      Z=0.01
      GO TO 7
   47 X=0.1
      Y=0.2
      Z=0.1
    7 PK1=0.00236
      PK2=0.00149
      PK3=2.E-06
      C=2.*X0(J)+2.*Y0(J)-2.*X-Z-Y
      F=(C*(P(J)+Y0(J)-Y))/Y-PK1
      G=(C*Z)/X-PK2
      H=(C*(X0(J)-X-Z))/Z-PK3
      FX=(2.*(Y-P(J)-Y0(J)))/Y
      FY=((2.*X+Z-2.*X0(J)-2.*Y0(J))*(P(J)+Y0(J)))/Y**2+1.
      FZ=(Y-P(J)-Y0(J))/Y
      GX=((Z+Y-2.*X0(J)-2.*Y0(J))*Z)/X**2
      GY=-Z/X
      GZ=(2.*X0(J)+2.*Y0(J)-2.*X-Y)/(X)-2.*Z*X
```

Program 2 (cont)

```
    HX=(Z+Y-2.*X0(J)-2.*Y0(J))/Z+(2.*(Z+2.*X-X0(J)))/Z
    HY=(X+Z-X0(J))/Z
    HZ=((Y+2.*X-2.*X0(J)-2.*Y0(J))*(X0(J)-X))/Z**2+1.
    DJ=FX*(GY*HZ-GZ*HY)-FY*(GX*HZ-GZ*HX)+FZ*(GX*HY-GY*HX)
    D1 =-F*(GY*HZ-GZ*HY)-FY*(-G*HZ+GZ*H)+FZ*(-G*HY+GY*H)
    D2 =FX*(-G*HZ+GZ*H)+F*(GX*HZ-GZ*HX)+FZ*(-GX*H+G*HX)
    D3 =FX*(-GY*H+G*HY)-FY*(-GX*H+G*HX)-F*(GX*HY-GY*HX)
    DELX=D1/DJ
    DELY=D2/DJ
    DELZ=D3/DJ
    IF(ABSF(DELX)-5.E-07)1,1,2
  1 IF(ABSF(DELY)-5.E-07)3,3,2
  3 IF(ABSF(DELZ)-5.E-07)4,4,2
  2 X=X+DELX
    Y=Y+DELY
    Z=Z+DELZ
    GO TO 7
  4 X=X+DELX
    Y=Y+DELY
    Z=Z+DELZ
    U=2.*X0(J)+2.*Y0(J)-2.*X-Y-Z
    SM=X0(J)-X-Z
    PH = -LOGF(U)/2.303
    PRINT 300,X0(J),Y0(J),U,PH,X,Z,SM
 11 CONTINUE
100 FORMAT(3E18.8)
300 FORMAT(7F10.6)
400 FORMAT(3X65HMLNACID    H2S04      H+        PH       H2M        HM
   1-        M=)
    CALL EXIT
    END
```

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IX. VITA

The author of this thesis, Ramesh N. Gujarathi, son of Natwarlal and Pushpauati Gujarathi, was born on February 3, 1941 in Dharangaon, India. He received his elementary and secondary high school education in Dharangaon, India and graduated from high school in May, 1958.

He received his college education in Amalner and Bombay and his Bachelor of Science in Chemistry from the University of Bombay, Bombay, India in June, 1962.

In September 1962, he came to this country and was enrolled at the University of Missouri at Rolla, In May 1964, he received the Bachelor of Science in Chemical Engineering.

In September 1964, he continued his studies at UMR as a candidate for the Master of Science degree in Chemical Engineering. Since then he has been assisting the freshman chemistry laboratories. He received a student assistantship from the Department of Chemistry in the spring of 1965.