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ESTERIFICATION OF OLEIC ACID

BY

NIRANJAN M. PATEL

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

AT

NEWARK COLLEGE OF ENGINEERING

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Newark, New Jersey

1964

ABSTRACT

The purpose of this paper is to determine the effects of catalyst concentrations and temperatures on the rate of reaction and energy of activation in the reaction system of oleic acid and oleyl alcohol. It is suggested by Flory^{2,3} that the p-toluenesulfonic acid catalyzed esterification reactions follow a second order mechanism. The p-toluenesulfonic acid is used in the present work.

Two different catalyst concentrations were used at two different temperatures. The uncatalyzed reaction at the same temperatures was also studied. The specific rate constants are calculated and from that, the energy of activations are calculated using the Arrhenius equation. The energy of activation of the uncatalyzed reaction is also calculated. The numerical values are given in Table VIII. The difficulty encountered in the present work is the slow rate of reaction at 50.0° C., at which a complete equilibrium was not attained, while at 90.0° C., equilibrium was attained in considerable time.

APPROVAL OF THESIS

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INTRODUCTION

The importance of esters has been increased enormously during recent years. During the past twenty years, however, a great demand has arisen for higher molecular weight esters in a variety of applications. One typical example is the use of higher molecular weight esters as plasticizers for vinyl resins. However, several attempts have been made to achieve high yields and higher molecular weight esters.

The esterification reaction of oleic acid with oleyl alcohol may produce a higher molecular weight ester can be used in the rapidly expanding chemical industry. For this reason, industrially and chemically, the chemical kinetics of oleic acid with oleyl alcohol would be an important one. The purpose of this paper is to determine the effects of concentration and temperature on the rate of esterification and energy of activation of oleic acid with oleyl alcohol. In order to get higher yield, it is necessary to examine the reaction mechanism and the energy of activation of the complex formed during the reaction under different conditions of the reaction.

Literature survey indicates that there is no work done on the esterification reaction of oleic acid with oleyl alcohol. However, Othmer and Rao¹ suggested that the

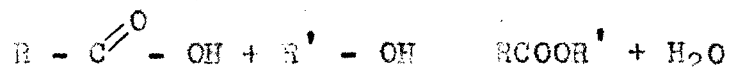
esterification of oleic acid with butanol follows a second order mechanism when sulfuric acid is used as a catalyst. Flory^{2,3} showed that the esterification reaction catalyzed by p-toluenesulfonic acid follows a second order mechanism. From this viewpoint, p-toluenesulfonic acid is selected as a catalyst for the system of oleic acid with oleyl alcohol in order to avoid complex reactions involving fractional or third order mechanism.

In the present work, two different concentrations of p-toluenesulfonic acid are taken for the catalyzed reaction at two different temperatures of 50° and 90° C. respectively. Uncatalyzed reaction is also taken into account at both of the concentrations and both of the same temperatures.

The Arrhenius equation⁴ is used to determine energy of activations using the calculated rate constants from the rate data. Owing to the fact that the rate constants are determined using the equation which is valid for the second order reversible mechanism in homogeneous reactions, and since oleyl alcohol is more or less hydrophobic compound which may repel water formed during the course of the reaction, a non-homogeneous system appears. This results in the deviations from the actual reaction mechanism. In order to avoid the deviations, vigorous agitation was applied at a constant speed.

THEORY AND MECHANISM

The basic theory of esterification is well known. An ester is usually defined as a compound formed by substituting an organic radical for an ionizable hydrogen of an acid. In the esterification of organic acids with alcohols, it has been found that the union is in between acyl-R-C(=O) and alkoxy-O-R' groups, rather than between R-C(=O)-O- and -R'. The following reaction may give the complete picture of the esterification reaction:



In the above reaction, the equilibrium constant for the reaction is:

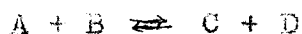
$$K_c = \frac{(\text{ester}) \times (\text{water})}{(\text{acid}) \times (\text{alcohol})} \quad (1)$$

The value of equilibrium constant changes with the increased presence of ester.

In 1850, Ludwig Wilhelmy⁵ investigated the hydrolysis of sugar by acids and he found that the velocity of inversion at any instant was proportional to the concentration of the sugar at that instant. Later in 1862, Berthelot and Pean de St Giles^{6,7} demonstrated that when equimolar quantities of ethyl alcohol and acetic acid were heated together, the esterification stopped after about two thirds of the acid had reacted. Similarly, when equimolar proportions of ethyl acetate and water were heated together, hydrolysis of

the ester stopped when approximately one third of the ester was hydrolysed. This indicates that the equilibrium is reached in both the esterification and hydrolysis phenomenon.

In 1864, Guldberg and Waage⁸ stated the law of mass action: "the rate of chemical reaction is proportional to the active masses of the reactants". The active masses were defined by the molecular concentration. Considering the reaction;



in which the reactants and the products are in equilibrium with each other, it can be stated that the molecules A and B can react giving products C and D when they collide with each other. Therefore, the velocity of the reaction must be proportional to the number of collisions and it also depends on the concentrations of A and B. The forward rate of reaction is proportional to the concentration of A and B, and the reverse rate of reaction is proportional to the concentrations of C and D as in equations;

$$r_1 = k_1 C_A C_B \quad (2)$$

$$r_2 = k_2 C_C C_D \quad (3)$$

where k_1 and k_2 are the specific rate constants and both are functions of temperature according to the Arrhenius⁸ equation which can be written as;

$$k = A e^{-E^*/RT} \quad (4)$$

$$\text{or } \ln(k) = \ln(A) - \frac{E^*}{RT} \quad (5)$$

where E is the molal energy of activation, A is the proportionality factor characteristic of the system and termed the frequency factor, and R is the gas constant. The term "energy of activation" in the Arrhenius equation is the energy possessed by those molecules which collide with each other. From the statistical mechanics, and also using the Maxwell-Boltzmann distribution law, it can be proved that the fraction of molecules energized to the activated state, where they collide and react to give products, is equal to the term $\exp. (-E/RT)$. The Arrhenius equation is also related to the theory of absolute reaction rate which is developed by Eyring¹⁰. The relationship between the Eyring equation and the Arrhenius equation can be established easily. The relationships are as;

$$E = \Delta H^* \quad \text{and} \quad (6)$$

$$\ln (A) = \ln \frac{K}{h\nu z R'} + \frac{\Delta S^*}{R} \quad (7)$$

where K is the Boltzmann constant, h is the Planck constant, ν is the fugacity coefficient of the activated complex, z is the compressibility factor, R' is the gas law constant, ΔH^* is the standard enthalpy of activation, and ΔS^* is the entropy of activation.

The forward and reverse rates of reaction are related to the equilibrium constant of the reaction. The relationship is quite simple and can be given by the equation;

$$K_c = k_1/k_2 \quad (8)$$

The equilibrium constant can also be defined in the terms of activities when the reaction proceeds in gaseous phase. However, it is unnecessary to treat of it here since the scope of this paper is restricted only to the liquid phase reaction.

For a reversible second order mechanism, the following rate equation can be integrated from the boundary conditions of conversion with time. The rate equation is;

$$\theta = \int_0^{x_A} \frac{dx_A}{V_c r} \quad (9)$$

where V_c is the volume of the batch and x_A is the conversion at any time θ . The equation (9) is integrated by many workers and given by Hougen and Watson¹¹. The integrated equation for reversible second order mechanism may be written as follows:

$$k_1 \theta = V_c X_c \frac{1}{a} \ln \left[\frac{(2cx_A + b - q)(b + q)}{(2cx_A + b - q)(b - q)} \right] \quad (10)$$

where the reaction $A + B = C + D$

$$a = K_c N_{Ao} N_{Bo} N_{Do}$$

$$b = K_c N_{Bo} - K_c N_{Ao} - N_{Co} - N_{Do}$$

$$c = K_c - 1.0$$

$$q = (-4ac + b^2)^{0.5}$$

k_1 = specific rate constant in concentration unit

K_c = Equilibrium constant

N_{Ao} , N_{Bo} , N_{Co} , and N_{Do} are the moles initially present for the components A, B, C, and D, respectively,

and x_A = moles of A converted.

The Arrhenius equation¹² (5) can be differentiated with respect to temperature to give the following equation:

$$\frac{d(\ln k)}{dT} = \frac{E}{RT^2} \quad (11)$$

when the above equation (11) is integrated between the boundary conditions of rate constants with temperatures, it yields;

$$\ln \left[\frac{k_1 - T_1}{k_1 - T_2} \right] = \frac{E (T_2 - T_1)}{R (T_1 T_2)} \quad (12)$$

The energy of activation may be determined from the experimental measurement of specific rate constants at two or more temperatures. However, it is suggested due to the fact the experimental error may cause greater deviation in the computation of the energy of activation if the experimental data are taken at only two different temperatures. Greater accuracy can be achieved if the specific rate constants are determined at large number of different temperatures.

The same values of specific rate constants can be applied in the determination of the standard enthalpy of activation and the entropy of activations, which are related to the Arrhenius equation¹².

It is understood from the above viewpoint that the energy of activation is also useful to estimate the specific rate constant which is most useful in the reactor design.

EXPERIMENTAL

A. Apparatus

A schematic diagram of the apparatus is shown in Figure 1. The apparatus used in the experiment was not of a special type, and it can be found in any well organized laboratory. The apparatus consisted of a mercury thermometer, a capacitance actuated thermoregulator, a reflux condenser with drying tube seal, an electric mantle heater with variac, an accurate electric timing clock, and a high speed electric stirrer was used in the measurement of rate data. The erlenmeyer flasks, pipettes, burettes, plunger to take a sample from the system, and gas burner as well as glassware for titration were also required. A magnetic stirrer was highly desirable for accurate titration.

B. Chemicals

Oleic Acid - Hardesty Chemical Co., equivalent
weight 282.4 gms.

Oleyl Alcohol - Du pont Chemical Co., equivalent
weight 268.4 gms.

para-Toluene Sulfonic Acid - Eastman Kodak Co.

C. Method

The esterification reaction was carried out in a three-necked flask equipped with a high speed stirrer. The thermometer, a temperature controller, and a good reflux condenser

were connected to the flask. The flask was fixed in an electric mantle heater with variac voltage controller.

The reaction temperature was maintained with the help of the variac. The flask was also connected with a good reflux condenser with drying tube seal. Equivalent molar amounts of the oleyl alcohol and oleic acid were charged to the flask in order to get the equilibrium constant at temperatures of 50° C. and 90° C.

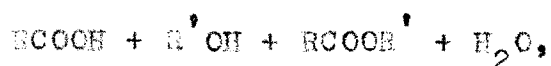
First of all, the required molar quantity of oleic acid was added to the flask by means of a funnel. One mole of oleyl alcohol was heated in a separate flask to about 5.0° C. above the required reaction temperature and then added to the flask containing one mole acid. The temperature dropped to the desired temperature when cold catalyst was added to the mixture. After the addition of catalyst, a sample was taken and titrated against known 0.1N KOH solution. The first sample should be taken after a few minutes of elapsed time for complete ionization of the complex. If this procedure is not followed, the titration analysis will be slightly lower than the actual value.

The equilibrium constant was also found by adding the p-Toluene Sulfonic Acid as a catalyst in other batches at different concentrations.

SAMPLE CALCULATIONS

The data from the experiments done in order to study the reaction mechanisms of oleic acid and oleyl alcohol were used to determine the equilibrium constant and energy of activation. The original concentrations of oleic acid and oleyl alcohol are known in these experiments. The concentrations of oleic acid and oleyl alcohol at equilibrium are determined directly or indirectly.

In the reaction:



in all the runs, one mole of oleyl alcohol and oleic acid were mixed and allowed to come to equilibrium.

The fractions of acid used in the reaction to reach the equilibrium in the system were found by the acid value method. Acid value means the number of milligrams of potassium hydroxide required to neutralize the free fatty acid in one gram of fat. The acid value was found as follows:

It was found that 2.9 cc of 0.1N KOH was required to neutralize 1.0000 gms. sample. This acid value became 16.30 KOH/gms. It is necessary to calculate the free acid as oleic acid, using the equation:

$$\text{Percentage} = \text{acid value} \times f$$

where f is taken as 0.503 and oleic acid from the table given by Mizoff¹³. Therefore, the amount of unconverted

acid is calculated using that acid value. It follows that the ester concentration must be $1-0.0805=0.9195$, where .0805 is the percentage of unconverted free acid, and the equilibrium constant is written:

$$\begin{aligned} K_c &= \frac{C_{\text{ester}} \times C_{\text{water}}}{C_{\text{acid}} \times C_{\text{alcohol}}} \\ &= \frac{0.9195 \times 0.9195}{0.0805 \times 0.0805} \\ &= 130.50 \end{aligned}$$

The rate constant k_1 was found by using equation (10) and taking the following data:

$$a = 130.50, b = -861.0, c = 129.50$$

$$k_c = 130.50, V_c = 0.650 \text{ liter}$$

$$q = 22.8, \theta = 125.0 \text{ hours}$$

Then the reaction rate is calculated using the equation (10):

$$k_1 = 3.860 \times 10^{-1} \text{ (hr.)}^{-1} \text{ (liter/gms. mole)}^{-1}$$

The energy of activation was found using equation (12):

$$\text{where } T_1 = 323^\circ\text{K}, T_2 = 363^\circ\text{K},$$

$$k_1 \text{ (at } T_1) = 9.78 \times 10^{-2} \text{ (gm. mole/hr.-liter)}$$

$$k_2 \text{ (at } T_2) = 3.86 \times 10^{-2} \text{ (gm. mole/hr.-liter)}$$

$$R = 1.987 \text{ Cal (gms. mole)} (O_K),$$

$$\text{therefore, } \ln \frac{3.86 \times 10^{-10}}{9.78 \times 10^{-2}} = \frac{R}{1.987} \frac{(363-323)}{363 \times 323}$$

$$R = 7920 \text{ Cal.}$$

Thus, the energy of activation is calculated for both the catalyzed and uncatalyzed reactions. The specific rate

constants calculated at different temperatures and different catalyst concentrations are given in Table VIII, along with the calculated energy of activations.

DISCUSSION

The reaction system is more or less difficult to handle because of the formation of water which is insoluble in oleyl alcohol yielding a heterogeneous reaction. The assumption is made that the vigorous agitation may prevent the forming of a two phase mixture. However, it is not true. The insoluble water droplets would be distributed uniformly because of the vigorous agitation. These insoluble droplets will lower the rate of reaction in the uncatalyzed reaction. Therefore, the uncatalyzed reaction may require a long reaction period.

Actually, it happened in the uncatalyzed reaction at 50.0° C. The reaction did not reach the equilibrium state, even after two months. The summary of results for the reaction at 50.0° C. is given in Table I. At the temperature of 50.0° C., the reaction is very slow, so it is difficult to estimate the equilibrium constant. Table II summarizes the experimental results of uncatalyzed reaction at 90.0° C. The reaction reached up to the equilibrium stage within 938.0 hours. The equilibrium constant is calculated from the acid number of 16.40. The numerical values of the equilibrium constant is 120.5, which is used in the computation of rate constant data. The catalyzed reaction at 90.0° C., using the catalyst concentration of 0.2%, reached up to the equilibrium state in 471.0 hours. The acid values are approximately

the same as those of the uncatalyzed reaction at 90.0° C. The catalyzed reaction gives the equilibrium value of 130.5, which was used in the computation of the specific rate constant. A summary of experimental results of 0.2% catalyst concentration, at 50.0° C. and 90.0° C., are listed in Tables III and IV, respectively.

The effect of the concentration of catalyst is effective on the rate of reaction. The experimental results of the catalyzed reaction with the catalyst concentration of 0.5%, which are given in Table VI, showed that there is a significant effect on the rate constant calculated at 90.0° C. The acid number of this reaction at 90.0° C., having a catalyst concentration of 0.5%, is 16.15, which is about the same as the uncatalyzed reaction at the same temperature. The value of the equilibrium constant is 130.5, which was used in the computations of the specific rate constant. The acid number of the acid catalyst, i.e. p-toluenesulfonic acid, was also taken into account in the calculations of catalyzed reactions by subtracting the product of a constant and the weight of the sample from the acid number of that sample. The constant used can be calculated from the following equation:

$$\text{Constant} = \frac{\text{acid no. of cat.} \times \text{wt. \%}}{\text{total charge}} \quad (13)$$

The reaction at 50.0° C. did not reach the equilibrium stage. Therefore, it is difficult to estimate the specific

rate constant at this temperature. However, equilibrium constants are calculated and are listed in Table VII along with the equilibrium constants calculated at 90.0° C. The catalyzed and uncatalyzed reactions gave approximately the same equilibrium constants. This indicates that there is not any significant effect of catalyst concentration.

The calculated rate constants are given in the Table VIII along with the energy of activations which are calculated using the Arrhenius equation; i.e. equation (12), and the reverse rates of reaction are also calculated and listed in Table VII.

Uncatalyzed and catalyzed reactions can be given as follows:



The above reactions will give the rate as:

$$\text{Uncatalyzed} \quad - \frac{dC_A}{dT} = k_1 C_A \quad (14)$$

$$\text{Catalyzed} \quad - \frac{dC_A}{dT} = k_2 C_A C_C \quad (15)$$

The next rate would be:

$$= \frac{dC_A}{dT} = k_1 C_A + k_2 C_A C_C \quad (16)$$

$$= (k_1 + k_2 C_C) C_A \quad (17)$$

where $k_{\text{obs}} = k_1 + k_2 C_C$, of which k_1 is the uncatalyzed specific rate constant and k_2 is the catalyzed rate constant.

A semi-log graph of catalyst concentrations versus the observed rate of reaction on log scale yielded straight lines at both of the temperatures. The slope of the straight line indicates the rate of the catalyzed reaction and the intercept on the Y-axis gives the rate constants of uncatalyzed reactions. The values obtained from Figure No. 2 are listed in Table VII. The values indicate that there is a sharp difference in the calculated rate constant and the rate constant evaluated from Figure No. 2 at 50.0° C. This is due to the fact that the reaction is still incomplete.

The energy of activations decreases with the increased concentrations of the catalyst. The energy of activation is given in Table VIII.

From the analysis of this reaction, it is suggested that the reaction of oleic acid with oleyl alcohol follows a second order reaction.

CONCLUSION

The esterification reaction of oleic acid and oleyl alcohol is effected by catalyst concentrations. Ostwald¹⁴ has mentioned that the catalyst present in a small quantity does not change the equilibrium constant, but it speeds up the reaction by changing the energy of activation.

The energy of activation decreased as the concentration of catalyst increased. The uncatalyzed reaction did not reach the equilibrium state. The equilibrium constant calculated at 90.0° C. was approximately the same at all the catalyst concentrations used.

The catalyst concentration of 0.2% decreased the energy of activation from 8260.0 cal/gm. mole to 8050.0 cal/gm. mole, and it decreased the reaction time 0.5% catalyst concentration decreased the energy of activation from 8260.0 cal/gm. mole to 7920.0 cal/gm. mole and decreased the reaction time to about 10% of the uncatalyzed reaction.

The rate constant was plotted against the catalyst concentration on semi-log paper, and yielded a straight line, and from the intercept and from the slope, the actual specific rate constants were calculated for both the catalyzed and uncatalyzed reactions. The catalyzed specific rate constants at 50.0° C. and 90.0° C. were 10.5 and 11.0 gm. mole per liter per hour, respectively. From the intercept of that

figure 2, the uncatalyzed specific rate constants were determined.

From these rate constants, the energy of activations can be calculated. The uncatalyzed reaction at 50.0° C. was incomplete, and did not give equilibrium constant. Therefore, the equilibrium constant was used, which was determined when the reaction was catalyzed.

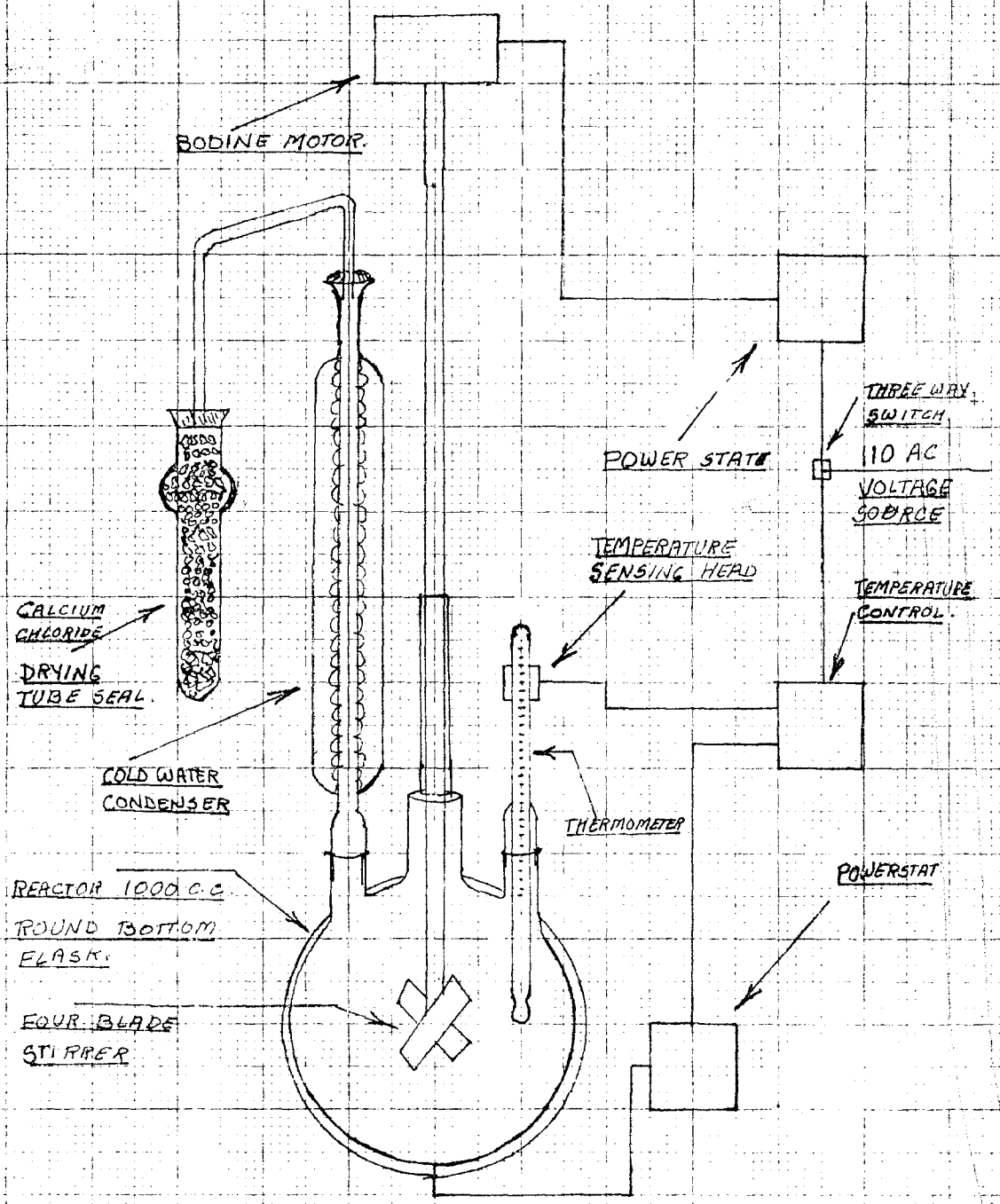
RECOMMENDATIONS

The results obtained in this present work suggest that the uncatalyzed reactions at low temperatures would be very slow. The specific rate constants can be calculated by measuring the catalyzed specific rate constant at that temperature. Further work can be done to measure the specific rate constants at various temperatures using different percentages of catalyst concentrations.

The same reaction should be carried out using solid ion exchange catalyst in order to check whether the reaction is film diffusion controlling or not.

APPENDIX

FIGURE -1



EXPERIMENTAL APPARATUS.

EUGENE DIETZGEN CO.
MADE IN U. S. A.

NO. 54370 DIETZGEN GRAPH PAPER
20 x 20 PER INCH

FIGURE - 2

RATE OF REACTION versus CATALYST CONCENTRATION

At Temperature 90°C

At Temperature 50°C

Specific Rate Constant (Gms-Mole)/(Liter x Hour)

0.50
0.40
0.30
0.20
0.10
0.09
0.08
0.07
0.06
0.05
0.000

Slope=11.0

Slope=10.5

Catalyst Concentration- Gms/C.C.

0.3350
0.085

0.001 0.002 0.003 0.004 0.005

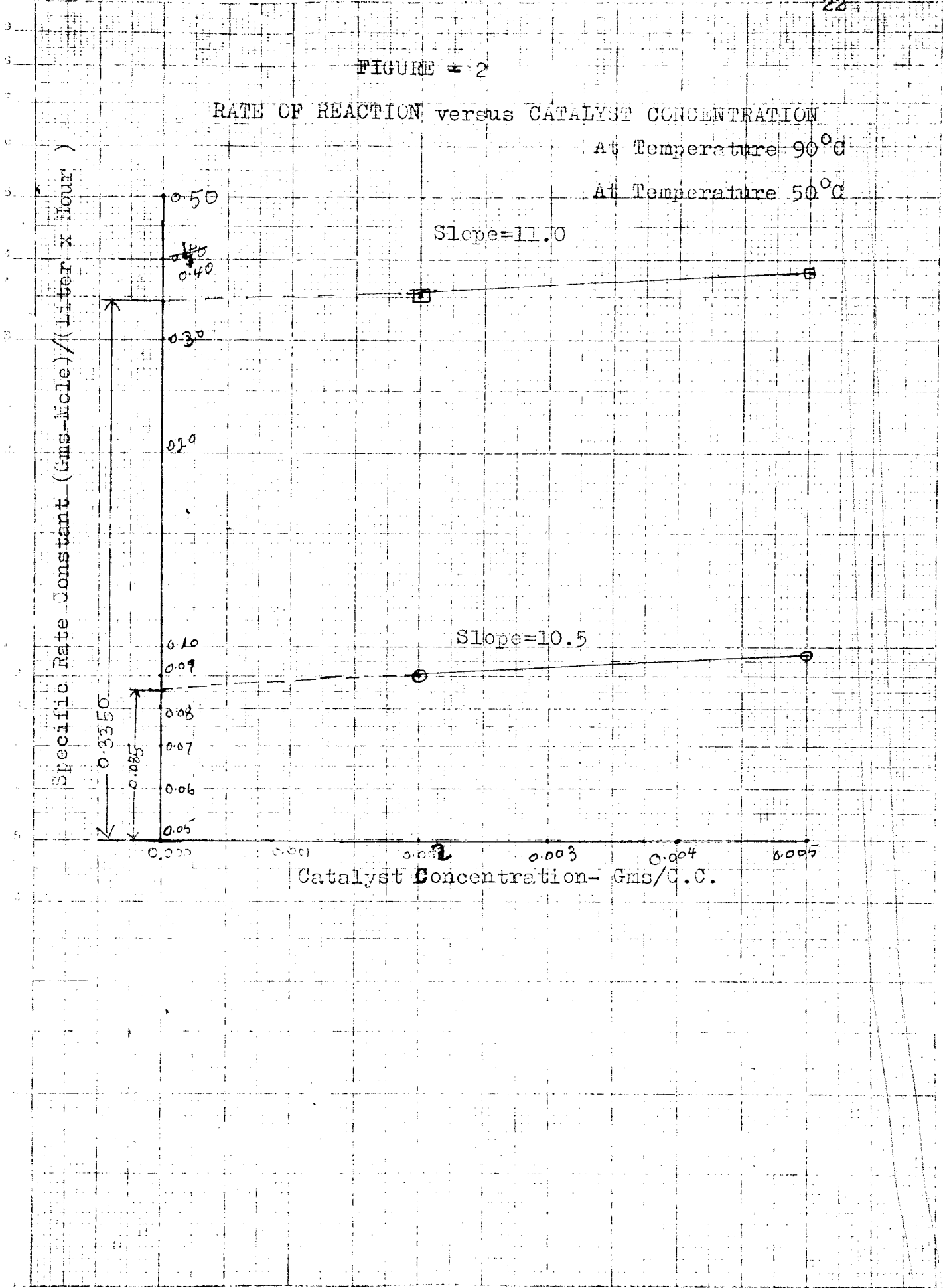


TABLE I
 SUMMARY OF DATA
 OF UNCATALYZED REACTION
 AT 50° C.

Charge: Oleic Acid - 282.4 Grams (100% pure)
 Cleyl Alcohol - 268.4 Grams (100% pure)

Sample No.	Time in Hours	Wt. of Sample in Grams	ml. KOH Required	Acid No. KOH/gms.
1	0.0	1.0000	29.40	162.00
2	1.0	1.0000	25.20	140.10
3	23.0	1.0000	25.00	139.50
4	24.0	1.0006	24.80	139.00
5	26.0	1.0000	24.40	137.00
6	30.0	1.2590	30.30	134.90
7	46.0	1.0250	23.20	133.00
8	50.0	1.0140	23.00	130.00
9	68.0	0.7461	12.30	95.00
10	88.0	0.5152	8.40	94.00
11	90.0	0.4044	6.40	91.40
12	168.0	1.0000	7.05	79.50
13	437.0	0.9216	11.80	74.50
14	476.0	1.0000	8.30	67.50
15	749.0	1.0844	11.30	64.00

TABLE I (CONTINUED)

Sample No.	Time in Hours	Wt. of Sample in Grams	ml. KOH Required	Acid No. KOH/gms.
16	752.0	1.0000	9.45	60.00
17	890.0	0.8568	8.65	58.20
18	1226.0	1.1630	11.00	55.00
19	1418.0	0.4954	11.90	45.90
20	1466.0	2.2710	17.60	45.00
21	1490.0	2.2733	10.10	44.90
22	1515.0	0.9666	6.60	40.00
23	1540.0	1.0000	8.00	45.00
24	1600.0	1.0000	8.50	48.00
25	1652.0	1.0000	8.15	46.00

Average Acid No. of 1418-1652 hours is 44.97 KOH/gms.

TABLE II
SUMMARY OF DATA
OF UNCATALYZED REACTION
AT 90° c.

Charge: Oleic Acid - 282.4 Grams (100% pure)
 Oleyl Alcohol - 268.4 Grams (100% pure)

Sample No.	Time in Hours	Wt. of Sample in Grams	ml. KOH Required	Acid No. KOH/gms.
1	0.0	1.0000	24.00	135.00
2	1.0	0.4590	9.80	119.00
3	2.0	0.4291	8.80	115.00
4	6.0	0.5731	4.80	112.00
5	27.0	0.3230	5.20	96.00
6	28.0	0.6237	9.90	89.00
7	33.0	0.6957	10.90	87.50
8	66.0	0.5291	5.50	58.20
9	70.0	0.7147	6.90	54.20
10	72.0	0.3460	4.10	53.90
11	91.0	0.9978	8.10	46.70
12	92.0	0.5694	4.50	45.50
13	103.0	1.7348	15.00	49.00
14	104.0	0.5701	5.00	49.00
15	105.0	0.3950	3.50	49.00

TABLE II (CONTINUED)

Sample No.	Time in Hours	Wt. of Sample in Grams	ml. KOH Required	Acid No. KOH/gms.
16	107.0	0.6853	4.90	49.00
17	108.0	0.4648	4.10	49.00
18	119.0	0.7787	5.90	43.90
19	121.0	0.6436	4.70	42.50
20	123.0	0.5929	4.30	41.80
21	143.0	0.9596	6.70	40.40
22	147.0	0.4849	3.20	37.80
23	167.0	0.8903	5.50	35.00
24	169.0	2.2172	13.10	34.10
25	190.0	1.0690	6.50	32.70
26	191.0	1.0880	5.90	31.20
27	192.0	0.5281	3.00	32.50
28	193.0	0.3851	3.80	33.00
29	194.0	1.0000	5.50	31.00
30	210.0	1.0000	4.65	26.20
31	451.0	0.3651	1.40	20.50
32	476.0	0.3677	1.30	20.40
33	480.0	0.3266	1.10	19.60
34	741.0	1.1170	3.20	16.50
35	864.0	1.0392	2.90	16.40
36	880.0	0.8215	2.55	17.40

TABLE II (CONTINUED)

Sample No.	Time in Hours	Wt. of Sample in Grams	ml. KOH Required	Acid No. KOH/gms.
37	890.0	0.8351	1.60	16.00
38	892.0	0.9212	2.70	16.90
39	900.0	0.9998	2.90	16.40
40	938.0	1.0000	2.90	16.40

Average Acid No. between 741-938 hours is 16.40 KOH/gms.

TABLE III
 SUMMARY OF DATA
 OF CATALYZED REACTION
 AT 50° C.

Charge: Oleic Acid - 282.4 Grams (100% pure)
 Oleyl Alcohol - 268.4 Grams (100% pure)
 para-toluene Sulfonic Acid - 1.10 Grams

Sample No.	Time in Hours	Wt. of Sample in Grams	ml. KOH Required	Acid No. KOH/gms.
1	0.0	1.0000	18.70	105.00
2	1.0	1.0000	17.60	99.00
3	1.5	1.0000	16.40	92.00
4	5.0	0.2876	4.60	90.00
5	6.0	0.5211	8.30	89.20
6	7.0	0.5984	9.40	89.00
7	8.0	0.5493	8.10	82.50
8	9.0	0.3137	4.50	82.00
9	10.0	0.1837	2.60	79.90
10	11.0	0.4676	6.70	80.50
11	12.0	0.5526	7.50	75.00
12	21.0	0.6468	8.40	73.00
13	22.0	0.6261	7.80	70.00
14	36.0	0.5825	6.70	64.50

TABLE III (CONTINUED)

Sample No.	Time in Hours	Wt. of Sample in Grams	ml. KOH Required	Acid No. KOH/gms.
15	47.0	0.4247	4.70	61.70
16	48.0	0.6907	7.40	60.00
17	49.0	0.5620	6.00	60.00
18	50.0	0.4030	11.20	60.00
19	51.0	0.5125	5.20	60.00
20	52.0	0.3693	3.90	60.00
21	53.0	0.5014	5.30	59.90
22	72.0	0.3242	3.10	53.50
23	73.0	0.5046	4.80	53.40
24	74.0	0.9851	9.30	53.00
25	75.0	0.5082	4.80	52.90
26	77.0	0.5208	4.90	52.80
27	78.0	0.4871	4.60	52.80
28	107.0	0.4572	4.10	50.50
29	108.0	0.4103	3.70	50.50
30	128.0	1.0000	8.45	47.50
31	129.0	1.0000	8.45	47.50
32	143.0	1.0000	8.45	47.50
33	144.0	1.0000	8.45	47.50

Average Acid No. between 128-148 hours is 47.50 KOH/gms.

TABLE IV
 SUMMARY OF DATA
 OF CATALYZED REACTION
 AT 90° C.

Charge: Oleic Acid - 282.4 Grams (100% pure)
 Oleyl Alcohol - 268.4 Grams (100% pure)
 para-Toluene Sulfonic Acid - 1.10 Grams

Sample No.	Time in Hours	Wt. of Sample in Grams	ml. KOH Required	Acid No. KOH/gms.
1	0.0	1.0000	17.20	96.50
2	1.0	0.4389	4.70	62.00
3	24.0	1.2589	8.90	41.20
4	25.0	1.8008	8.00	25.60
5	26.0	1.9196	8.20	25.20
6	50.0	1.8131	6.70	20.80
7	96.0	1.0900	3.40	18.00
8	97.0	0.5422	2.00	21.50
9	98.0	1.0900	3.40	20.80
10	121.0	1.4901	4.40	17.00
11	169.0	1.6569	4.60	16.00
12	170.0	1.8020	5.00	16.00
13	470.0	1.0369	3.10	16.00
14	471.0	1.3488	3.70	16.00

Average Acid No. between 169-471 hours is 16.00 KOH/gms.

TABLE V
SUMMARY OF DATA
OF CATALYZED REACTION
AT 50° C.

Charge: Oleic Acid - 282.4 Grams (100% pure)
 Oleyl Alcohol - 268.4 Grams (100% pure)
 para-Toluene Sulfonic Acid - 2.75 Grams

Sample No.	Time in Hours	Wt. of Sample in Grams	ml. KOH Required	Acid No. KOH/gms.
1	0.0	1.0000	17.20	96.50
2	0.5	1.0000	16.60	93.50
3	1.0	0.5960	9.60	91.20
4	1.5	0.5427	8.20	87.50
5	3.0	0.2834	4.20	83.00
6	4.0	0.5345	7.50	78.50
7	5.0	0.3082	4.10	74.50
8	6.0	0.5222	4.10	72.00
9	7.0	0.3675	6.70	59.50
10	23.0	0.4600	4.40	53.50
11	24.0	0.4667	4.50	53.50
12	26.0	0.5713	5.20	51.00
13	28.0	0.6596	5.40	49.50
14	29.0	0.6268	8.40	48.50
15	52.0	0.3679	3.00	45.00

TABLE V (CONTINUED)

Sample No.	Time in Hours	Wt. of Sample in Grams	ml. KOH Required	Acid No. KOH/gms.
16	53.0	0.4029	3.20	44.50
17	52.0	0.3679	3.00	45.00
18	53.0	0.4023	3.20	44.50
19	54.0	0.4400	3.50	44.00
20	55.0	0.3305	2.50	43.00
21	72.0	0.3307	2.40	39.80
22	73.0	0.4067	2.90	39.30
23	74.0	0.5258	4.10	39.30
24	78.0	0.4633	3.20	39.00
25	82.0	0.4023	2.80	39.00
26	83.0	0.4720	3.40	39.00
27	85.0	0.3737	2.60	39.00
28	119.0	1.1350	4.90	24.80
29	120.0	1.3500	5.90	25.20
30	121.0	0.6867	3.10	25.80
31	122.0	0.7210	3.70	27.80
32	143.0	1.1056	4.80	22.60
33	144.0	0.6290	3.20	20.00

Average Acid No. from 119-144 hours is 24.36 KOH/gms.

TABLE VI
SUMMARY OF DATA
OF CATALYZED REACTION
AT 90° C.

Charge: Oleic Acid - 282.4 Grams (100% pure)
 Oleyl Alcohol - 268.4 Grams (100% pure)
 para-Toluene Sulfonic Acid - 2.75 Grams

Sample No.	Time in Hours	Wt. of Sample in Grams	ml. KOH Required	Acid No. KOH/gms.
1	0.0	1.0718	16.10	86.80
2	1.0	0.6131	4.80	45.40
3	2.0	1.4326	9.60	38.60
4	5.0	0.6050	3.60	33.60
5	7.0	0.4000	2.30	32.00
6	8.0	0.5800	2.00	30.00
7	9.0	1.0000	5.00	28.50
8	10.0	1.0000	5.00	28.70
9	27.0	1.1218	3.50	18.40
10	28.0	1.0614	3.40	18.40
11	30.0	1.0000	3.50	20.00
12	52.0	1.1218	3.60	18.50
13	53.0	1.0000	4.00	22.50
14	76.0	0.6299	1.80	16.60

TABLE VI (CONTINUED)

Sample No.	Time in Hours	Wt. of Sample in Grams	ml. KOH Required	Acid No. KOH/gms.
15	77.0	0.9999	2.90	16.00
16	100.0	1.7421	4.90	16.00
17	124.0	1.0000	2.85	16.30
18	125.0	1.0000	2.80	16.00
19	128.0	1.0000	2.80	16.00

Average Acid No. between 76-128 hours is 16.15 KOH/gms.

TABLE VII
SUMMARY OF EQUILIBRIUM
AND REVERSE
RATE CONSTANTS

Temperature: 90.0° C.

Reaction	K_c	$k_2 \cdot 10^{-4}$	$k_1 \ddagger$ (fig.)
Uncatalyzed	120.50	2.58	0.335
Catalyzed (0.2%)	130.50	27.00	11.00
Catalyzed (0.5%)	130.50	28.50	11.00

Temperature: 50.0° C.

Uncatalyzed	12.60**	5.74	0.085
Catalyzed (0.2%)	9.40**	96.50	10.5
Catalyzed (0.5%)	45.00**	21.7	10.5

** Reactions at 50° C. may not be complete.

‡ k_1 is observed from the Figure 2.

TABLE VIII
 REACTION RATE CONSTANTS
 AND
 ENERGY OF ACTIVATION

$$k_1 = (\text{hr.})^{-1} (\text{liter/gms. mole})^{-1}$$

$$E^* = (\text{cal/gram-mole})$$

Temp. in °C.	Catalyst wt. in %	k_1	E^*
50	No Catalyst	7.23×10^{-3}	8260
90	No Catalyst	3.01×10^{-2}	
50	0.20	9.04×10^{-2}	8050
90	0.20	3.65×10^{-1}	
50	0.50	9.78×10^{-2}	7920
90	0.50	3.86×10^{-1}	

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