1965

Kinetics of base-catalysed reactions

Kunjvihari Ramanlal Mehta

Department:

KINETICS OF BASE-CATALYSED REACTIONS

BY

KUNJVIHARI RAMANLAL MEHTA

A

THESIS

submitted to the faculty of

THE UNIVERSITY OF MISSOURI AT ROLLA

in partial fulfillment of the requirements for the

Degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

Rolla, Missouri

1965

Approved by

D S Wolfman (advisor) Samir S. Hanna

R H Lund Bill Wallek

TABLE OF CONTENTS

		Page
	TITLE PAGE	i
	TABLE OF CONTENTS	ii
	LIST OF FIGURES	iv
	LIST OF TABLES	v
	GLOSSARY OF TERMS	vi
I.	INTRODUCTION	1
II.	LITERATURE REVIEW	3
III.	EXPERIMENTAL	17
	A. Purpose of Investigation	17
	B. Plan of Experimentation	17
	C. Experimental Set-Up	17
	D. Analytical Techniques	18
	1. Gas Chromatography	20
	2. Operating Conditions	21
	3. Sampling	21
	E. Preparation of Calibration Curve	21
	F. Experimentation	23
	G. Data and Results	23
IV.	TREATMENT OF EXPERIMENTAL DATA	32
V.	DISCUSSION	37
	A. Discussion of Data and Results	37

B. Discussion of the Standard Curve 38

C. Limitations 38

D. Recommendations 39

VI. CONCLUSIONS 47

VII. SUMMARY 48

VIII. APPENDICES 49

Appendix A, List of Computer Programs 50

1. A Program for the Calculations of Adduct Concentrations 50

2. A Program for the Calculation of Rate and Logarithm of Rate 51

3. A Program for the Calculation of Rate and Equilibrium Constants 54

Appendix B, List of Equipment and Materials 56

IX. BIBLIOGRAPHY 58

X. ACKNOWLEDGEMENTS 60

XI. VITA 61

LIST OF FIGURES

Figure		Page
1.	Experimental Set-Up.	19
2.	Standard Curve of Area-Ratio as a Function of Mole-Ratio.	22
3.	Concentration of Adduct as a Function of Time (Run 1).	40
4.	Concentration of Adduct as a Function of Time (Run 2).	41
5.	Concentration of Adduct as a Function of Time (Run 3).	42
6.	Concentration of Adduct as a Function of Time (Run 4).	43
7.	Concentration of Adduct as a Function of Time (Run 5).	44
8.	Concentration of Adduct as a Function of Time (Run 6).	45
9.	Concentration of Adduct as a Function of Time (Run 7).	46

LIST OF TABLES

Table		Page
I.	Experimental Data for Run 1	24
II.	Experimental Data for Run 2	25
III.	Experimental Data for Run 3	26
IV.	Experimental Data for Run 4	27
V.	Experimental Data for Run 5	28
VI.	Experimental Data for Run 6	29
VII.	Experimental Data for Run 7	30
VIII.	Table of Results	31

GLOSSARY OF TERMS

Area-Ratio: Ratio of one area to another.

AdH: Adduct

BH: Base

MH: Malonate ester

K_m: Dissociation constant for malonic ester.

K_b: Dissociation constant for base (t-BuOK).

K_a: Dissociation constant for adduct.

I. INTRODUCTION

The mechanisms of base-catalysed reactions have received little attention due to their complexity. Studies which have been made, by and large, were limited to product, by-product and intermediate analyses. Kinetic studies have in general been avoided because of the number of competing side reactions and frequent necessity of using heterogeneous media. This has resulted in a number of mechanisms being accepted on the basis of very flimsy or non-existent evidence. In the few cases where thorough studies have been carried out, highly complex mechanisms have usually been proposed to account for the kinetic and isotopic data obtained (10). One of the most common and least thoroughly studies class of reactions in this general area is the 'Michael Reaction'. To date, only three kinetic studies of these reactions have been published in any abstracted publication and the studies performed have been on atypical systems (5). In the late 1940's studies were begun by Shafer, Loeb and Johnson (23) on the related reaction, i.e. the abnormal Michael reaction. Later studies by Korst (12) and by Wulfman (29) indicated the need for thorough kinetic treatment of both the normal and abnormal Michael reactions before any definitive mechanisms could be proposed for these reactions. The work presented here was undertaken to furnish kinetic data for the normal Michael reaction. It is a direct

extrapolation and continuation of the work of Wulfman (29) and uses and expands upon the techniques developed by him.

Wulfman (29) observed a mixed kinetic path for the normal Michael reaction. In his original studies he observed initial pseudo first order and then pseudo zero order kinetics. These observations were taken to imply a change from homogeneous to heterogeneous media as the reaction proceeds coupled with fortuitous relationships between the various terms required to describe the reaction kinetics. The first problem has been avoided in the studies described here by using more dilute solutions. In addition, an improved mathematical treatment is being used which takes into account the acidity of the products and solvent as well as that of the starting material. This technique has necessitated the writing of computer programs to process the analytical data obtained.

II. LITERATURE REVIEW

The term Michael Reaction or Addition is the name commonly assigned to the base-catalysed addition of an activated olefin, the acceptor, to furnish a product which is known as a Michael adduct. It can best be described as the addition of an activated methylene compound (donor) to a double bond conjugated to a strong electron attracting substituent (acceptor). Such substituents include cyano, nitro, sulphonyl and all types of carbonyl functions. A typical example and the one studied by the author is shown in Equation (1), Chart 1, on Page 4.

In a general form, the Michael reaction may be written as:

$$C=C-X \quad + \quad Y-CH-Z \longrightarrow Y-\underset{\displaystyle C-C-X}{\overset{\displaystyle H}{\overset{|}{C}}}-Z \qquad (4)$$

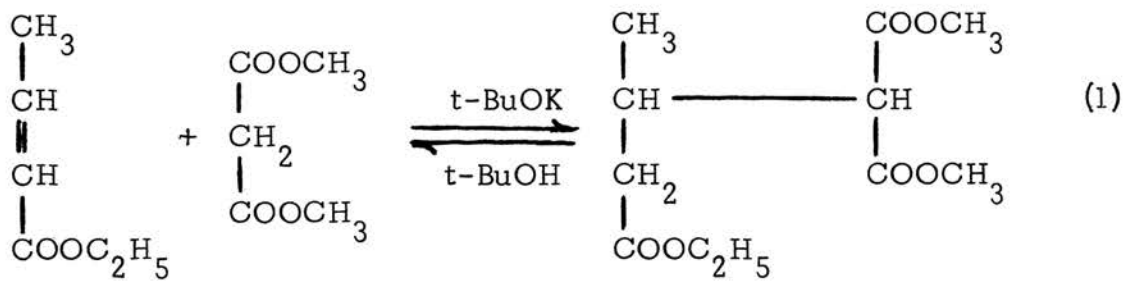
where, Y and Z may be COOR, COR, $CONH_2$, NO_2, SO_2R, CN or CHO. Y and X may be the same as or different than Z.

The product (III) in Chart 1, Page 4 is known as the normal Michael product. In addition to this, the Michael reactions may yield an abnormal product (V) and retrogression products (VI, VII) which result from the reverse Michael process on the abnormal product as shown in Equation (3), Chart 1.

In the normal product, the fragments of the addendum appear to add to the α,β-unsaturated system as H^+ and unrearranged carbanion

Chart 1

The Michael Reactions

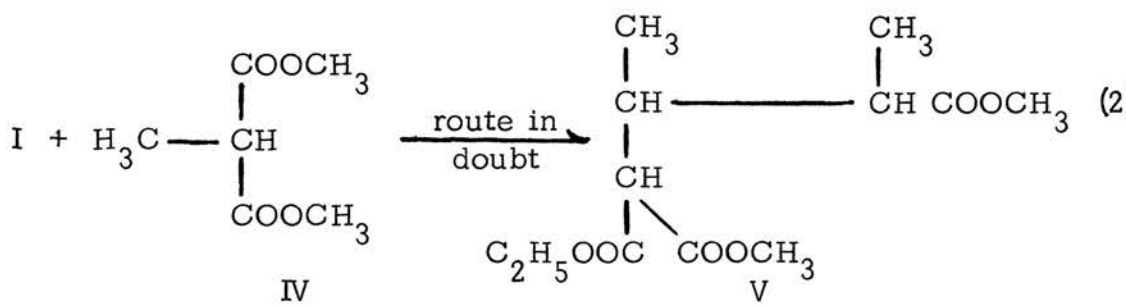


(1)

I
Ethyl
Crotonate

II
Dimethyl
Malonate

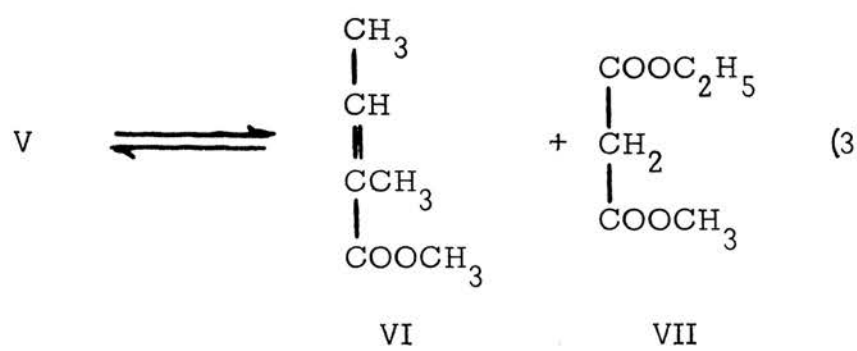
III
1,1-Dicarbomethoxy-3-Carboethoxy-2-Methyl Propane



(2)

IV

V



(3)

VI

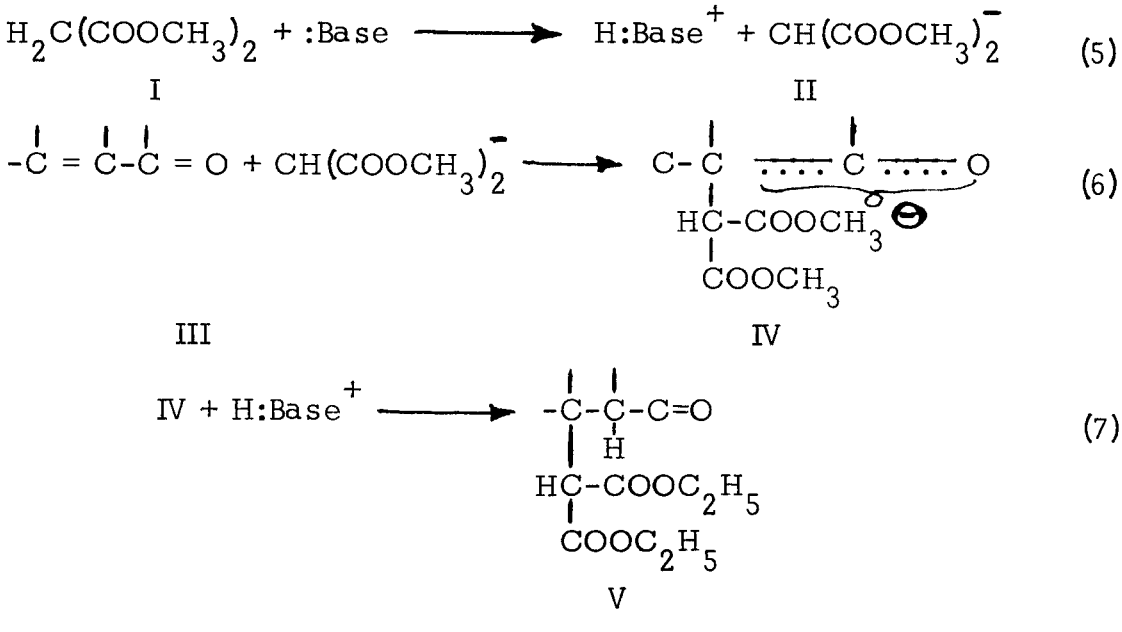
VII

(for example, $^{\ominus}$: $CH(COOCH_3)_2$). In the abnormal product, neither the carbon skeleton of the addendum nor the acceptor molecule remains intact(1). Retrogression products are sometimes called reversal or rearrangement-retrogression products and they may or may not be the same as initial reactants.

The normal Michael addition (1) reaction appears to be an example of addition to a double bond initiated by the attack of a carbanion in a manner suggestive of a vinylogous aldol reaction. It is believed to proceed by the mechanism shown in Chart 2. At present, there is some debate as to what is the mechanism of the abnormal Michael reaction.

Chart 2

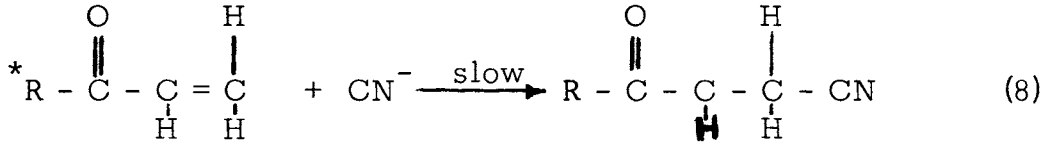
Presently Accepted Mechanism
of Normal Michael Reaction



The function of the base appears to be the abstraction of a proton from malonic ester (I) to generate a carbanion (II) which then attacks the β-carbon of the conjugated system. This is followed by addition of a proton from the solvent to the product anion (IV) to yield the product (V). The mechanism has been given some support through kinetic studies carried out on the addition of barbituric acid to β-nitrostyrene (10), the addition of ethyl acetoacetate, malonic ester, acetyl acetone, methanol and ethanolamine to acrylonitrile (16), and the addition of hydrogen cyanide to α, β-unsaturated ketones (9). Ingold (19) suggests the above mechanism (Chart 2) by analogy to mechanism proposed by Jones (9) for the addition of hydrogen cyanide to α, β-unsaturated ketones (Chart 3).

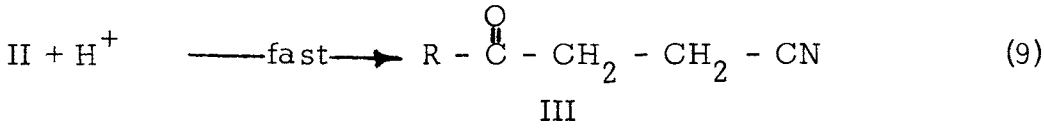
Chart 3

Jones' Mechanism



(8)

I II



(9)

III

The cyanide ion (Chart 3) adds across the double bond of (I) to yield the product anion (II) which then accepts a proton from the

---

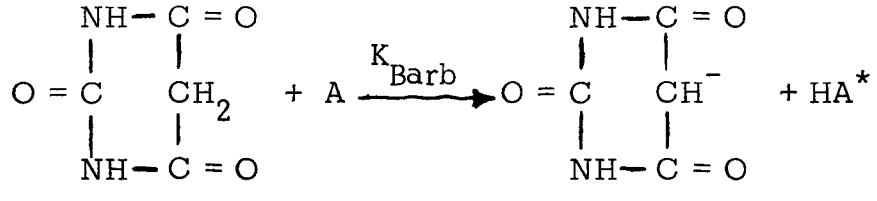
*R is an alkyl group.

solvent to yield the product (III). The slow step is the addition of cyanide to the double bond and the rate is proportional to the concentrations of cyanide ion and unsaturated ketone.

Kamlet and Glover (10) studied the addition of barbituric acid to β-nitrostyrene in slightly acidic media. The rate followed a second-order rate law. The rate showed dependence upon the concentrations of β-nitrostyrene and the barbituric acid. They studied the effects of solvent, dielectric constant, pH and substituents. They noted that the reaction is atypical in the sense that the reaction takes place in neutral or slightly acidic media and does not undergo the abnormal reaction. It was postulated that the Jones-Ingold mechanism applied. A sufficiently high quantity of the anion of the active methylene compound was present without using alkaline catalysts as a result of the comparatively high dissociation constant of barbituric acid. The mechanism proposed by Kamlet and Glover (10) is shown in Chart 4.

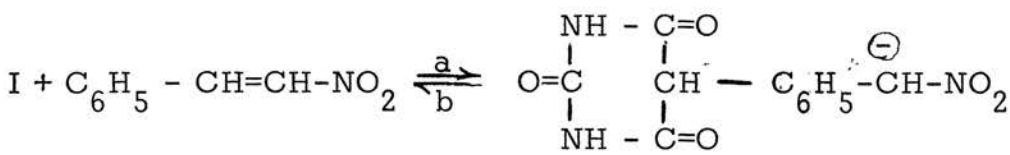
Chart 4

Kamlet and Glover Mechanism



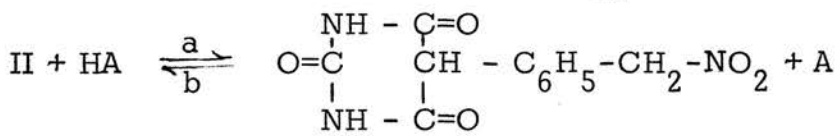
(10)

I



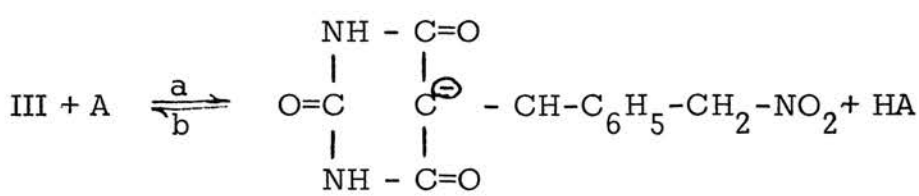
(11)

II



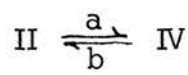
(12)

III



(13)

IV



(14)

According to the above mechanism (Chart 4), the barbiturate anion concentration is governed by the concentration of barbituric acid and by the ionization constant of barbituric acid. The anion reacted with the β-nitrostyrene to furnish (II). A subsequent rapid protonation step furnishes the un-ionized substituted barbituric acid (III) which then undergoes a rapid internal proton transfer to furnish the more stable adduct anion (IV).

---

*HA repesents oxonium ion, water or other proton donor, while A represents the corresponding conjugate base. The forward and reverse reactions are represented by symbols a and b, respectively.

Cyanoethylation reactions are special cases of the normal Michael reactions in which acrylonitrile is the acceptor molecule. The kinetics of the cyanoethylations of ethanolamine, acetylacetone and methanol have been studied by Ogata, Okano, Furuya and Tabushi (16). Their investigation of potassium hydroxide-catalysed cyanoethylations of ethanolamine and acetylacetone in aqueous media, by the estimation of remaining acrylonitrile by the n-dodecyl mercaptan method, suggested that the rates are proportional to the concentrations of corresponding reagents i.e. ($H_2NCH_2CH_2OH$) and (CH_2=CHCN) or ($CH_3COC^{\ominus}HCO\ CH_3$)($CH_2$=CHCN). The rate of reaction of acrylonitrile with sodium methoxide in methanol has also been measured. The reaction was first order with respect to the concentrations of acrylonitrile and the initial concentrations of methoxide ion. The rate expression agreed with that of the electronic theory which predicts that the reaction would involve a nucleophillic attack on the β-carbon atom of acrylonitrile (31).

Abnormal products have been reported for Michael additions carried out with unsubstituted malonic esters in only three instances.(29). Korst (12) has shown that the reaction of t-butyl crotonate with malonic ester yields a product which behaves as a mixture of normal and abnormal products. Abnormal products have also been obtained by reacting cyanoacetic ester and malonic ester with 3-methyl cyclohexanone.(22).

There are two mechanisms reported, which fit the observed data, for the abnormal Michael reactions. However, neither has any kinetic justification. Michael and Ross (14) haveproposed that the methyl group of dimethyl methyl malonate migrates directly to the α-carbon of the crotonic ester (Chart 5); however, Holden and Lapworth (6) criticized the Michael and Ross mechanism and suggested that the normal adduct (I) may result from a Dickmann type condensation followed by decomposition of cyclobutanone (III) as shown in Chart 6.

Chart 5

Michael and Ross Mechanism

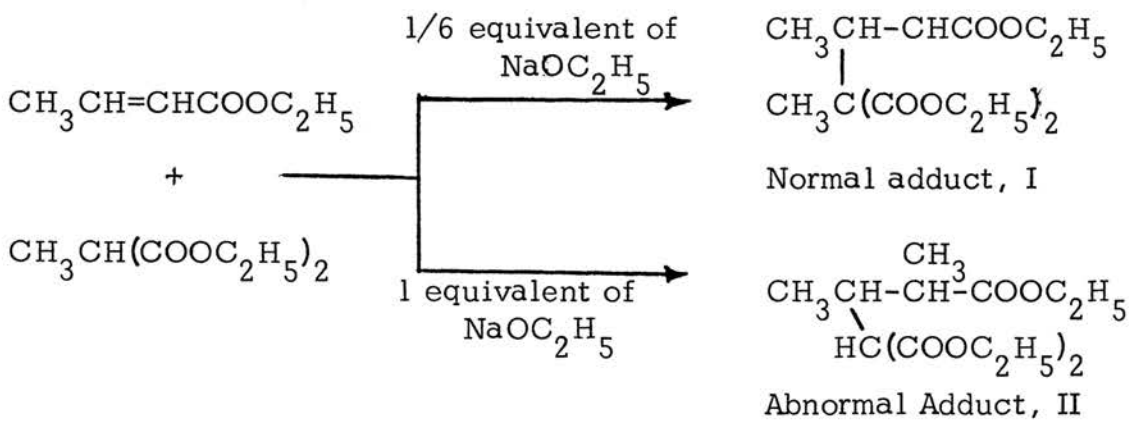
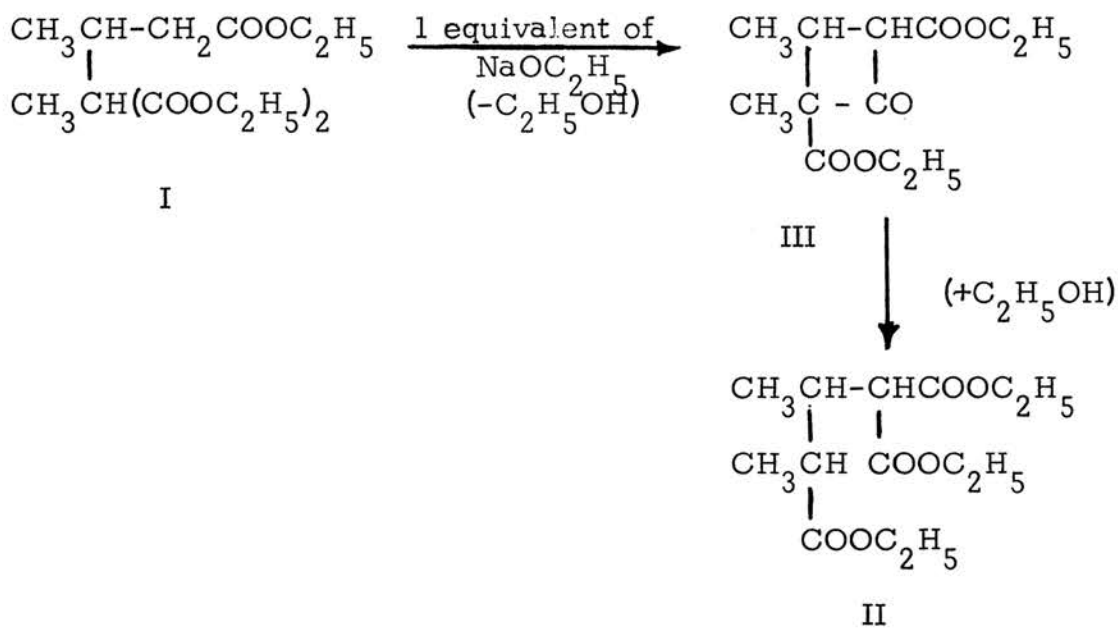


Chart 6

Holden and Lapworth Mechanism



I

II

Gardner and Rydon(4) examined both the above mechanisms and suggested that the course of addition reaction is affected markedly not only by the amount of condensing agent but also by the structures of the reactants.

Tsurata, Yasuhara and Farukawa (28) studied the competitive rates of the alkoxide catalysed formation of the normal and abnormal products of the reaction between diethyl ethyl malonate and diethyl fumarate as a function of catalyst concentration, reaction time and temperature. The total yield of products was determined by distillation and the relative amounts of the normal and abnormal products were

determined from the linear plot of the density against the percentages of the normal products. It was found that the total yield was not sensitive to the concentration, reaction time or temperature but the formation of the abnormal products was favored at higher catalyst concentrations, longer reaction times and higher temperatures.

Tsurata, Yasuhara and Farukawa (28) proposed that an adduct anion (VII) was formed first and then the normal adduct (IV) itself as shown in Equation (9).

$$C_2H_5OOCCH{=}CHCOOC_2H_5 + [C_2H_5C(COOC_2H_5)_2]^- \rightleftharpoons \left[\begin{array}{c} C_2H_5OOCCH\text{-}CHCOOC_2H_5 \\ | \\ C_2H_5C(COOC_2H_5)_2 \end{array}\right]^- \quad (9)$$

VI VII

They suggested two courses for the stabilization of the adduct anion (VII):

1. Interaction with free ethylmalonic ester to form the normal adduct (IV) together with the malonic ester anion (VI).

$$VII + C_2H_5CH(COOC_2H_5)_2 \xrightarrow{V_1} IV + VI \quad (10)$$

The rate of formation of the normal adduct was expressed as:

$$V_1 = k_1 \text{ (adduct anion (VII)) (free ethyl malonic ester)} \qquad (11)$$

2. An isomerization to the abnormal type according to which the rate would be proportional to the concentration of adduct anion (VII) only.

Isotopic studies (21, 24, 25, 27) have shown that the abnormal Michael reaction involves a formal carbalkoxyl migration and, therefore, invalidated the Michael and Ross mechanism. These studies, however, neither confirm nor disprove the Holden and Lapworth mechanism.

Shimamura, Inamoto and Suehiro (25) studied the addition of diethyl methyl malonate to ethyl crotonate using C^{14} labeled carbonyl, in ether solution with sodium ethoxide as the catalyst. Acid catalysed hydrolysis and decarboxylation of the mixed adducts followed by isotopic analysis of the liberated CO_2 showed conclusively that the reaction involved a carbonyl migration.

Samuel and Ginsburg (21) carried out essentially the same study and obtained the same results using O^{18} labeled diethyl methyl malonate.

Swan (27) and Shimamura and Inamoto (24) studied the addition of diethyl malonate to C^{14} labeled ethyl crotonate in the presence of

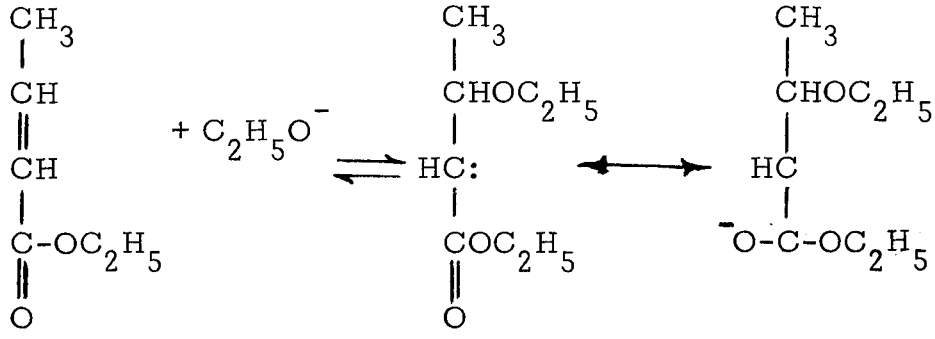
one equivalent of sodium ethoxide in ether solution. These conditions are standard for the abnormal additions and were used in previous articles. They observed no abnormal product formation and concluded that abnormal Michael reactions are not undergone by unsubstituted malonic esters.

Shafer (22) proposed an alternative mechanism to explain carbalkoxyl migration which involves a Claisen attack of the malonate moeity by an anion derived from the acceptor. The resulting intermediate undergoes a concerted cleavage and internal displacement reaction to yield the abnormal product. This mechanism (Chart 7) is consistent with the work of Tsurata, Yasuhara and Farukawa (28) but is no more supported by this work than the Holden and Lapworth and the Michael and Ross mechanisms are disproved.

The mechanism of the decomposition of a Michael product to starting materials should be the reverse of that of the addition process (17). Studies by Patai, Weinstein and Rappoport (17) on the system, the Michael adduct of 4-nitrochalcone and malononitrile in methanol, are consistent with the Jones-Ingold mechanism.

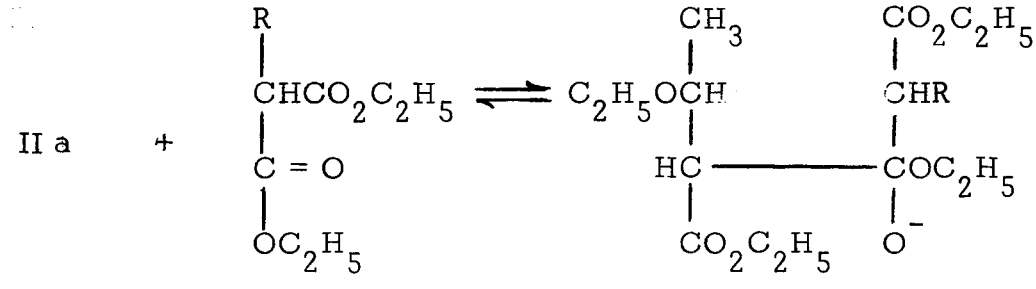
Chart 7

Shafer Mechanism

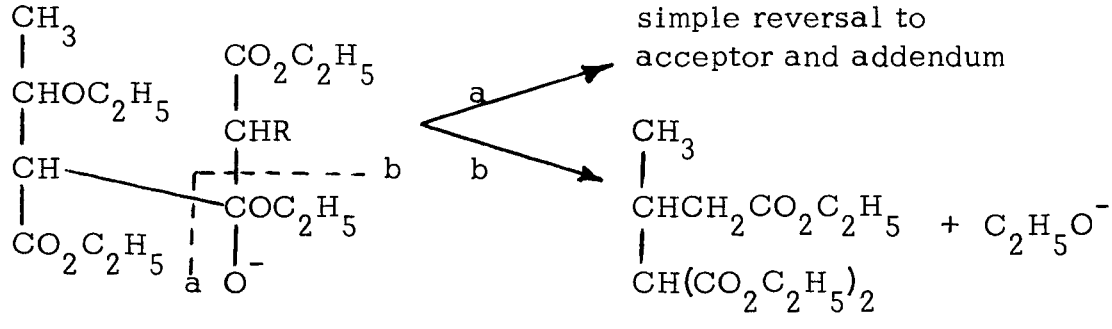


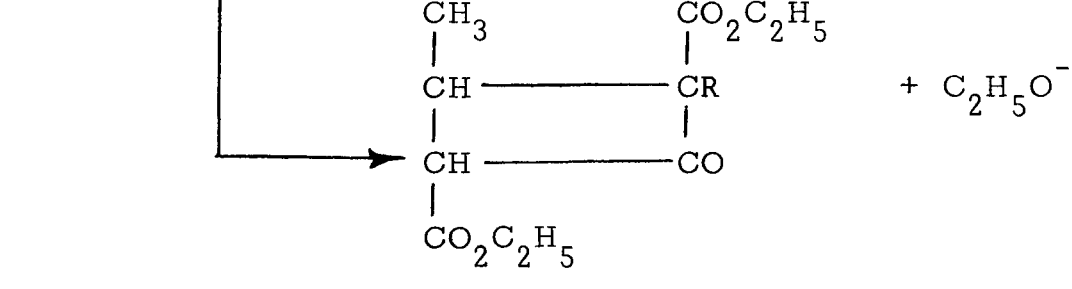
(12)

I II a II b



III IV a





R is an alkyl group.

A Michael reaction between ethyl crotonate (I) and diethyl methyl malonate (II) in the presence of one equivalent of NaOEt in ether produces 2,3-dimethyl propane-1,1,3-tricarboxylate. Degradation of the product from this reaction with I-carbonyl-C^{14} demonstrates that an EtOCO group migrates in the intermediate carbanion from the added methyl malonate to the α-carbon atom of I. This migration does not take place in the reaction between I and diethyl malonate. In the Michael reaction between ethyl tiglate -(carbonyl-C^{14}) and II, the migration of the EtOCO group takes place to the extent of 5 percent in ether and 3 percent in alcohol (26).

EXPERIMENTAL

A. Purpose of Investigation. The work of Wulfman (29) on the mechanism of the Michael reactions suggests that the normal Michael reaction is second order kinetically, with the rate being proportional to the concentration of the acceptor and the active form of the addendum. A detailed reaction mechanism of normal Michael reaction was not proposed due to insufficient data which resulted from analytical difficulties. This investigation involves the study of the kinetics of normal Michael reaction from the stand point of base strength, solvent concentration and acidity of the reactants, solvent and products.

B. Plan of Experimentation. In this investigation, the effect of the change in base strength and acidity of the reactants on the rate of reaction was studied. A Gas Chromotograph (GC) was used for the purpose of analysing the reaction mixtures. Concentrations were determined using phenyl cyclohexane as an internal standard.

The reaction of ethyl crotonate and dimethyl malonate with potassium tertiary butoxide as base in tertiary butyl alcohol was studied.

C. Experimental Set-Up. Reactions were carried out in a 3-necked, 500 ml. round bottomed flask equipped with two stoppers

and a Friederic's condenser equipped with a soda-lime drying tube. The flask was heated with a heating mantle which was always set at the same voltage for each run to insure that heating be as constant as possible. Samples were removed through one of the necks of the flask with the aid of a two cc. hypodermic syringe. A schematic diagram of the experimental arrangements appears in Figure 1, page 19.

D. Analytical Techniques. One of the major problems in the kinetic study is the analysis of the reaction mixture. The common way of analysis is by determining the rate of disappearance of reactants with time or alternatively, when this is not possible or is inconvenient one may analyse the rate of appearance of products with time. Ideally, one would like to analyse for the change in concentrations of all components with respect to time and be able to account for side reactions.

In the present work, the technique used for studying the system, ethyl crotonate, dimethyl malonate, t- potassium butoxide, t-butyl alcohol, 1,1-dicarbomethoxy-3-carboethoxy-2-methyl propane (product) and side products, was the quantitative estimation of the components using Gas-Liquid Partion Chromatography. This technique permitted the determination of changes in concentration of adduct with respect to time with an accuracy of better than two percent. The possibility of titrating the unreacted crotonate with

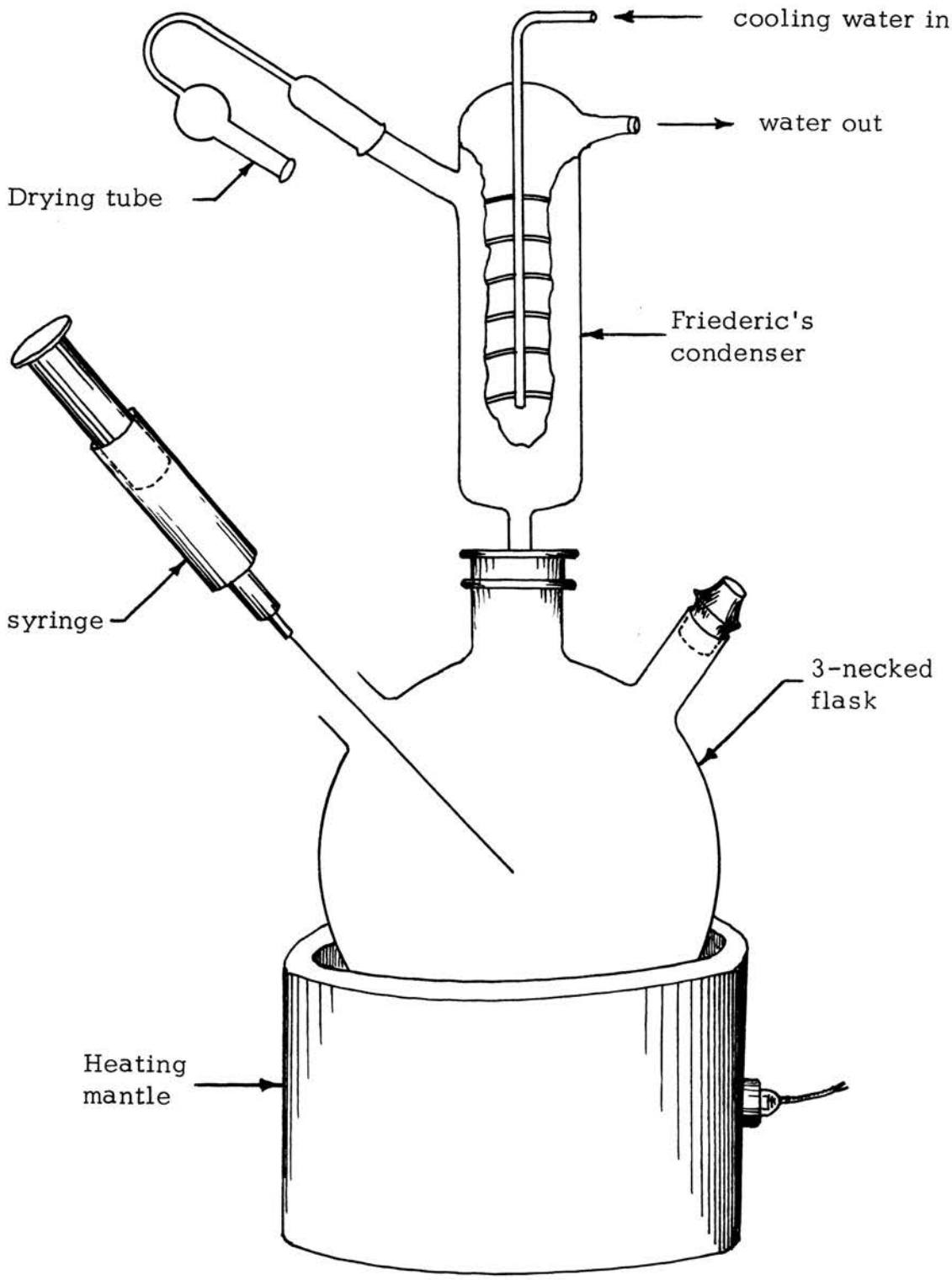


Figure 1. Experimental Set-Up

iodine monochloride had been studied previously, however, this technique is of insufficient sensitivity to rival the use of gas chromatography (29).

1. Gas Chromatography (GC). In recent years an increasing number of publications have appeared which have reported the use of GC as an analytical tool. The technique was developed by James and Martin (8) for the analysis of fatty acids and has found widespread use in the petroleum and fats and oil industries as well as a general research tool by most organic chemists. Several general references (2, 3, 8, 11, 13, 15, 18, 19, 20) on gas chromatography are given on page 58.

The technique is essentially an elution technique in which the sample to be analysed is placed on a column consisting of a liquid phase deposited on an inert solid support. The components are differentially partitioned between the liquid phase and the carrier gas, in this case, helium, and as a result the mixture is separated as it percolates through the column.

The column used in this investigation was a six foot, 10 percent silicone rubber, (Se 30) on 30-60 mesh firebrick, (Model 72OU column, furnished by F & M Scientific Corporation, Avondole, Pennsylvania).

2. Operating Conditions. Operating conditions were chosen to give the best resolution of peaks and still maintain moderate retention times. The gas chromatograph used in this investigation was operated under the following conditions.

Detector Temperature: 350 degrees Centigrade.

Injection Port Temperature: 300 degrees Centigrade.

Oven Temperature: 165-170 degrees Centigrade.

Current: 150 milliamperes DC.

Helium Flow Rate: 86-90 cc. per minute.

3. Sampling. One to two microliters of the sample to be analysed was introduced into the column using a ten microliter hypodermic syringe.

E. Preparation of Calibration Curve. For the purpose of calibration of the equipment, an internal standard, phenyl cyclohexane was used. Several samples were made from known amounts of standard and adduct. These samples were analysed by gas chromatography and the area under the adduct peaks and standard peaks were measured. A plot of area ratio of adduct to standard against mole ratio of adduct to standard was prepared as in Figure 2 , page 22. This technique is discussed in Keulemans' (11) book on gas chromatography.

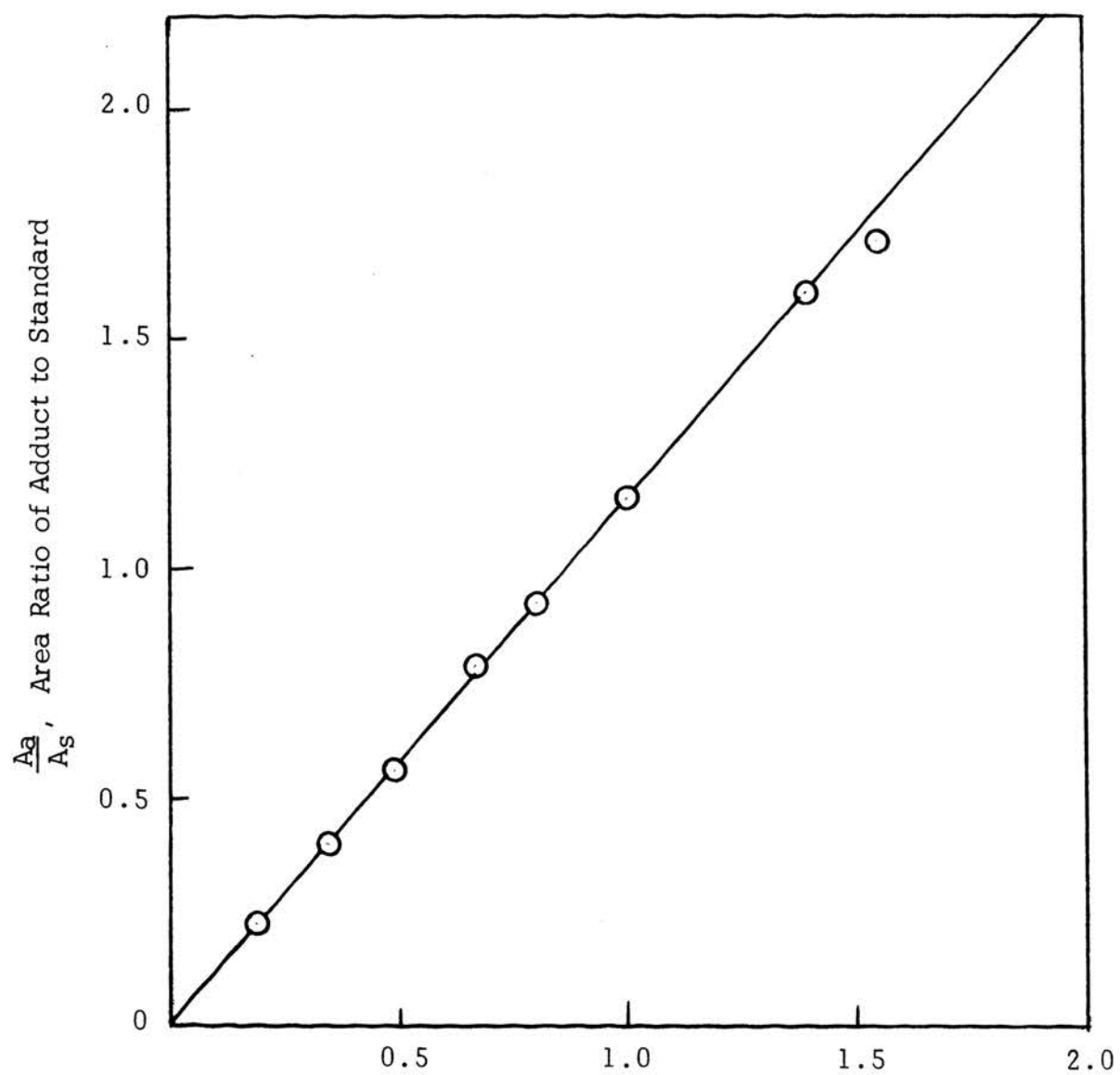


Figure 2. Standard Curve of Area-Ratio as a Function of Mole-Ratio.

F. Experimentation. The mixture of ethyl crotonate and dimethyl malonate was allowed to react under the influence of potassium t-butoxide in t-butyl alcohol, at reflux (83° C.) for a period of time sufficient to allow the reaction to go to at least 60 percent completion. The reflux time varied when initial concentrations of crotonate, malonate and base were changed.

Initially, at small intervals of time, and later at hourly or longer intervals of time, samples were taken out of the reaction mixture using a two cc. hypodermic syringe. The samples were treated with several drops of 0.1000 N HCl to inhibit further reaction and a small amount of anhydrous potassium carbonate was added to dry the samples and remove any excess acid. The samples were centrifuged, the liquid was removed by decantation, numbered and saved for later analysis by gas chromatography.

G. Data and Results. Experimental data for various runs made are listed in Tables I to VII. Run 1 and 6 and 4 and 7 were identical. Results of experiments are summed up in Table VIII. A general program for sample calculations of the concentrations of adduct is shown on Page 50, Appendix A.

TABLE I

Experimental Data for Run 1

Weight of Ethyl Crotonate = 22.7985 gm. (0.2 mole)
Weight of Dimethyl malonate = 26.4060 gm. (0.2 mole)
Weight of Phenyl cyclohexane = 20.0007 gm.
Amount of 0.106 N t-BuOK = 10.0 ml

Sample No.	Time Minutes	Area of Adduct / Area of Standard	Adduct-Conc. Moles/liter
1	10	0.0470	0.0203
2	30	0.1890	0.0816
3	40	0.2320	0.1001
4	50	0.2460	0.1062
5	60	0.2710	0.1170
6	75	0.2880	0.1243
7	90	0.2960	0.1278
8	105	0.3040	0.1312
9	120	0.3450	0.1489
10	140	0.3490	0.1506
11	160	0.3560	0.1536
12	180	0.3890	0.1679
13	210	0.3980	0.1718
14	240	0.4090	0.1765
15	270	0.4210	0.1817
16	300	0.4370	0.1886
17	345	0.4740	0.2046
18	390	0.5050	0.2180
19	435	0.5230	0.2257
20	480	0.5110	0.2464
21	540	0.6050	0.2611
22	600	0.6350	0.2741
23	660	0.6660	0.2874
24	720	0.6940	0.2995
25	780	0.7100	0.3064
26	840	0.7300	0.3151
27	900	0.7650	0.3302

TABLE II

Experimental Data for Run 2

Weight of Ethyl crotonate = 22.8018 gm (0.2 mole)
Weight of Dimethyl Malonate = 26.4019 gm (0.2 mole)
Weight of Phenyl Cyclohexane = 24.0009 gm
Amount of 0.106 N t-BuOK = 20.0 ml

Sample No.	Time Minutes	Area of Adduct / Area of Standard	Adduct-Conc. Moles/liter
1	10	0.0671	0.0348
2	30	0.2440	0.1264
3	40	0.3770	0.1953
4	50	0.4400	0.2279
5	60	0.4830	0.2502
6	75	0.5030	0.2605
7	90	0.5300	0.2745
8	105	0.5510	0.2854
9	120	0.5700	0.2952
10	140	0.6400	0.3315
11	180	0.6750	0.3496
12	210	0.7040	0.3646
13	240	0.7350	0.3807
14	270	0.7550	0.3910
15	300	0.7890	0.4086
16	345	0,8390	0.4345
17	390	0.9000	0.4661
18	435	0.9650	0.4998
19	480	1.0310	0.5340
20	540	1.0800	0.5593
21	600	1.1150	0.5775
22	660	1.1500	0.5956
23	720	1.1980	0.6205
24	780	1.2520	0.6484
25	840	1.2880	0.6671

TABLE III

Experimental Data for Run 3

Weight of Ethyl crotonate = 45.5976 gm (0.4 mole)
Weight of Dimethyl Malonate = 26.4016 gm (0.2 mole)
Weight of Phenyl Cyclohexane = 24.0005 gm
Amount of 0.106 N t-BuOK = 10.0 ml

Sample No.	Time Minutes	Area of Adduct / Area of Standard	Adduct-Conc. Moles/liter
1	10	0.0503	0.0261
2	20	0.1730	0.0896
3	30	0.2340	0.1212
4	40	0.2720	0.1409
5	60	0.3380	0.1751
6	75	0.3600	0.1864
7	90	0.3770	0.1952
8	105	0.3900	0.2020
9	120	0.4060	0.2103
10	160	0.4700	0.2434
11	180	0.5080	0.2631
12	210	0.5210	0.2698
13	240	0.5570	0.2885
14	270	0.5860	0.3035
15	300	0.6140	0.3180
16	345	0.6500	0.3366
17	390	0.7170	0.3713
18	435	0.7360	0.3812
19	480	0.8010	0.4148
20	540	0.8500	0.4402
21	600	0.9060	0.4692
22	660	0.9310	0.4822
23	720	0.9550	0.4946

TABLE IV

Experimental Data for Run 4

Weight of Ethyl Crotonate = 22.7930 gm (0.2 mole)
Weight of Dimethyl Malonate = 52.7951 gm (0.4 mole)
Weight of Phenyl Cyclohexane = 24.0000 gm
Amount of 0.106 N t-BuOK = 10.0 ml

Sample No.	Time Minutes	Area of Adduct / Area of Standard	Adduct-Conc. Moles/liter
1	10	0.0685	0.0355
2	20	0.1460	0.0756
3	30	0.2240	0.1160
4	40	0.2566	0.1329
5	50	0.2900	0.1502
6	60	0.3300	0.1709
7	75	0.3740	0.1937
8	90	0.3860	0.1999
9	120	0.3960	0.2051
10	140	0.4050	0.2097
11	160	0.4450	0.2305
12	180	0.4900	0.2538
13	210	0.5580	0.2890
14	240	0.5840	0.3024
15	270	0.6200	0.3211
16	300	0.6460	0.3346
17	345	0.6670	0.3454
18	390	0.7090	0.3672
19	485	0.8400	0.4350
20	540	0.8510	0.4407
21	600	0.9580	0.4961
22	660	0.9860	0.5106
23	720	1.0200	0.5282

TABLE V

Experimental Data for Run 5

Weight of Ethyl Crotonate = 22.8060 gm (0.2 mole)
Weight of Dimethyl Malonate = 26.4095 gm (0.2 mole)
Weight of Phenyl Cyclohexane = 12.0034 gm
Amount of 0.106 N t-BuOK = 5.0 ml

Sample No.	Time Minutes	Area of Adduct / Area of Standard	Adduct-Conc. Moles/liter
1	12	0.0513	0.0133
2	17	0.0671	0.0174
3	22	0.0983	0.0255
4	27	0.1725	0.0447
5	32	0.2280	0.0591
6	37	0.2620	0.0679
7	42	0.3770	0.0977
8	47	0.3950	0.1023
9	52	0.4500	0.1166
10	57	0.4790	0.1241
11	62	0.4880	0.1264
12	75	0.5640	0.1461
13	90	0.6400	0.1658
14	105	0.6690	0.1733
15	120	0.6870	0.1779
16	150	0.7750	0.2007
17	210	0.8950	0.2318
18	270	1.0600	0.2746
19	331	1.1400	0.2953
20	390	1.2440	0.3222
21	450	1.2620	0.3269
22	510	1.3860	0.3590
23	570	1.7100	0.4429
24	693	1.8500	0.4792
25	750	2.0100	0.5206

TABLE VI

Experimental Data for Run 6

Weight of Ethyl Crotonate = 22.7995 gm (0.2 mole)
Weight of Dimethyl Malonate = 26.5404 gm (0.2 mole)
Weight of Phenylcyclohexane = 16.0404 gm
Amount of 0.106 N t-BuOK = 10.0 ml

Sample No.	Time, Minutes	Area of Adduct / Area of Standard	Adduct-Conc. Moles/liter
1	5	0.0810	0.0280
2	20	0.1250	0.0433
3	27	0.2380	0.0824
4	35	0.4250	0.1471
5	40	0.4860	0.1682
6	45	0.5110	0.1769
7	50	0.5480	0.1897
8	55	0.5890	0.2039
9	60	0.6100	0.2111
10	65	0.6470	0.2239
11	75	0.6750	0.2336
12	85	0.7000	0.2423
13	95	0.7150	0.2475
14	110	0.7500	0.2596
15	125	0.7740	0.2679
16	157	0.8000	0.2769
17	185	0.9500	0.3288
18	245	0.8240	0.2852
19	305	1.0000	0.3461
20	365	1.2270	0.4247
21	428	1.2800	0.4430
22	487	1.3600	0.4707
23	557	1.4400	0.4984
24	618	1.5000	0.5192
25	670	1.5500	0.5365
26	725	1.7150	0.5936

TABLE VII

Experimental Data for Run 7

Weight of Ethyl Crotonate = 22.8002 gm (0.2 mole)
Weight of Dimethyl Malonate = 52.9018 gm (0.4 mole)
Weight of Phenyl Cyclohexane = 16.0089 gm
Amount of 0.106 N t-BuOK = 10.0 ml

Sample No.	Time, Minutes	Area of Adduct / Area of Standard	Adduct-Conc. Moles/liter
1	10	0.1420	0.0490
2	20	0.2860	0.0988
3	31	0.5150	0.1779
4	40	0.6020	0.2080
5	50	0.6620	0.2287
6	60	0.6500	0.2245
7	70	0.6850	0.2366
8	85	0.7240	0.2501
9	100	0.7640	0.2639
10	120	0.7800	0.2695
11	140	0.8720	0.3012
12	160	0.9000	0.3109
13	182	0.8880	0.3068
14	270	0.8160	0.2819
15	300	0.9670	0.3341
16	331	0.9520	0.3289
17	360	1.0700	0.3696
18	430	1.1180	0.3862
19	482	1.2400	0.4284
20	527	1.2820	0.4429
21	614	1.3900	0.4802
22	665	1.6460	0.5686
23	850	1.7500	0.6045

TABLE VIII

TABLE OF RESULTS

Run No.	Crotonate Moles	Malonate Moles	Base ml.	$k_{forward}$	$k_{reverse}$	$^{*}K_e$
1	0.2	0.2	10.0	0.6690	42.36	1.26
2	0.2	0.2	20.0	0.7675	1.75	35.05
3	0.4	0.2	10.0	0.4728	26.97	1.40
4	0.2	0.4	10.0	0.6974	22.49	2.48
5	0.2	0.2	5.0	2.0002	51.20	3.13
6	0.2	0.2	10.0	1.1193	7.92	12.05
7	0.2	0.4	10.0	1.2690	64.25	1.58

$^{*}K_e$ stands for equilibrium constant.

IV. TREATMENT OF EXPERIMENTAL DATA

The following assumptions were made.

1. The rate of appearance of products is proportional to the concentration of crotonate ester and malonate anion and the reverse rate, that is, the rate of appearance of reactants is proportional to the concentration of the adduct anion formed.

$$\frac{d\,[AdH]}{dt}^{*} = k_1\,[Crot]\,[M^-] - k_2\,[Ad^-]$$

where, k_1 and k_2 are forward and reverse rate constants, respectively, and Ad^- and M^- are adduct anion and malonate ester anion, respectively.

2. $[MH]_o = b - [AdH]$

where, $b = [MH]_o$ = initial concentration of dimethyl malonate.

This assumption is true if the concentration of base added is small compared to concentration of unreacted dimethyl malonate, i.e., when $[MH] >> [M^-]$ since the dissociation constant for malonic ester is approximately 1.6×10^{-18} (29).

3. $[BH] >> [B^-]$

where, B^- is the base anion.

The dissociation constant for t-butyl alcohol is approximately 1.0×10^{-19} (29). Since t-butyl alcohol is not consumed in the reaction its concentration remains constant throughout.

---

* [ ] represents the molar concentrations.

The following relationships were used to develop expressions to calculate the rate constants.

I. The reaction was studied under the conditions that only the normal adduct was formed, therefore

$$\text{rate} = V = \frac{d[\text{Crot}]}{dt} = \frac{d[\text{AdH}]^*}{dt}$$

II. $[M^-] + [Ad^-] + [B^-] = [K^+]$ = concentration of potassium ion = constant, C.

III. $[\text{Crot}] = a - [\text{AdH}]$

where, a = Crot = initial concentration of ethyl crotonate

IV. $[M^-] = \frac{Km\,[MH]}{[H^+]}$

V. $[Ad^-] = \frac{Ka\,[AdH]}{[H^+]}$

VI. $[B^-] = \frac{K_b\,[BH]}{[H^+]}$

VII. $[H^+] = \frac{Km\,[MH]}{[M^-]} = \frac{Ka\,[AdH]}{[Ad^-]} = \frac{K_b\,[BH]}{[B^-]}$

Assuming that, the expression for the over-all rate is,

$$V^{**} = k_1\,[M^-]\,[\text{Crot}] - k_2\,[Ad^-]$$

$$= k_1 \frac{Km\,[MH]}{H^+}\,[\text{Crot}] - k_2 \frac{Ka\,[AdH]}{[H^+]}$$

$$= \frac{k_1 Km\,(b-[\text{AdH}])(a-[\text{AdH}]) - k_2\,Ka\,[\text{AdH}]}{[H^+]}$$

---

*AdH is the adduct formed.

**k_1 is the forward rate constant and k_2 is the reverse rate constant.

From the established relationships II, V, VI and VII,

$$[H^+] = \frac{K_m [MH] + K_a [AdH] + K_b [BH]}{C}$$

$$= \frac{\phi}{c}$$

where, $\phi^* = K_m [MH] + K_a [AdH] + K_b [BH]$

substituting x for $[AdH]$, and rearranging, the expression for overall rate becomes,

$$V = k_1 K_m C \frac{(a - x)(b - x)}{\phi} - k_2 K_a C \frac{X}{\phi}$$

substituting, $a_1 = k_1 K_m C$

$$a_2 = k_2 K_a C$$

the rate expression becomes,

$$V = a_1 \frac{(a - x)(b - x)}{\phi} - a_2 \frac{X}{\phi} \qquad (13)$$

The parameters a, b and ϕ are known in the above expression. The experimental data to be described by the above relation are V as a function x. The data may be presented as V_i and x_i where i varies from one to N, where N is the total number of data points. The values of a_1 and a_2 may be determined by a least-squares fit of the data to the above postulated model.

Let Y_i = observed rate of reaction = $V_i = (\Delta X/\Delta t)_i$

$\hat{Y}_i$ = rate of reaction calculated from Equation (13)

---

*ϕ is a variable term

By the least-squares treatment, the following expression is to be minimized with respect to the two unknown parameters a_1 and a_2:

$$\Delta = \sum_{i=1}^{N} (Y_i - \hat{Y}_i)^2$$

$$= \sum_{i=1}^{N} \left[Y_i - \left\{ \frac{a_1 (a - x_i)(b - x_i)}{\phi_i} - \frac{a_2 x_i}{\phi_i} \right\} \right]^2 \qquad (14)$$

Minimizing Δ with respect to a_1 and a_2:

$$\frac{\partial \Delta}{\partial a_1} = 0 = \sum_{i=1}^{N} (2) \left[Y_i - \left\{ a_1 \frac{(a - x_i)(b - x_i)}{\phi_i} - a_2 \frac{x_i}{\phi_i} \right\} \right] \left(- \frac{(a-x_i)(b-x_i)}{\phi_i} \right) \qquad (15\,a)$$

$$\frac{\partial \Delta}{\partial a_2} = 0 = \sum_{i=1}^{N} (2) \left[Y_i - \left\{ a_1 \frac{(a-x_i)(b-x_i)}{\phi_i} + a_2 \frac{x_i}{\phi_i} \right\} \right] \left(\frac{x_i}{\phi_i} \right) \qquad (15\,b)$$

From Equations (15 a) and (15 b):

$$0 = \sum_{i=1}^{N} Y_i \left[\frac{(a-x_i)(b-x_i)}{\phi_i} \right] - a_1 \sum_{i=1}^{N} \frac{(a-x_i)^2 (b-x_i)^2}{\phi_i^2} + a_2 \sum_{i=1}^{N} \frac{x_i (a-x_i)(b-x_i)}{\phi_i^2} \qquad (16\,a)$$

$$0 = \sum_{i=1}^{N} \frac{Y_i x_i}{\phi_i} - a_1 \sum_{i=1}^{N} \frac{(a-x_i)(b-x_i)x_i}{\phi_i^2} + a_2 \sum_{i=1}^{N} \left(\frac{x_i}{\phi_i} \right)^2 \qquad (16\,b)$$

by substituting,

$$c_1 = \sum_{i=1}^{N} Y_i \left[\frac{(a-x_i)(b-x_i)}{\phi_i} \right] \quad ; \quad c_2 = \sum_{i=1}^{N} \frac{(a-x_i)^2 (b-x_i)^2}{\phi_i^2}$$

$$c_3 = \sum_{i=1}^{N} \frac{x_i (a-x_i)(b-x_i)}{\phi_i^2} \quad ; \quad c_4 = \sum_{i=1}^{N} \frac{Y_i x_i}{\phi_i} \quad ; \quad c_5 = \sum_{i=1}^{N} \left(\frac{x_i}{\phi_i} \right)^2$$

The Equations (16 a) and (16)b) become,

$$0 = -C_1 + a_1 C_2 - a_2 C_3 \qquad (17)$$

$$0 = C_4 - a_1 C_3 + a_2 C_5 \qquad (18)$$

from Equation (17),

$$a_2 = \frac{a_1 C_2 - C_1}{C_3}$$

substituting for a_2 in Equation (18) and solving for a_1, we get,

$$a_1 = \frac{C_3 C_4 - C_1 C_5}{C_3 C_3 - C_2 C_5}$$

by dividing a_1 by $K_m C$ and a_2 by KaC we get the values of k_1 and k_2, the forward and reverse rate constant, respectively.

At equilibrium, the forward rate and reverse rates are equal, hence,

$$k_1 K_m C \frac{(a - x_e)^* (b - x_e)}{\Phi_e} = k_2 K_a C \frac{x_e}{\Phi_e}$$

or

$$K_e = \text{K-EQUILIBRIUM} = \frac{x_e}{(a - x_e)(b - x_e)} = \frac{k_1 K_m}{k_2 Ka}$$

---

*subscript 'e' denotes equilibrium values.

V. DISCUSSION

A. Discussion of Data and Results. In the course of this investigation, seven runs were made with different concentrations of reactants or different amounts of base. The data of Runs 1 to 7 are listed in Tables I to VII. Runs 1 and 6, and 4 and 7 were identical.

The adduct concentrations were evaluated using computer program (Appendix A, Page 50). The plots of adduct concentrations as a function of time (Figures 3 to 9) and the calculations for rate (Appendix A, Page 51) indicate that the reaction studied behaves mainly as a pseudo zero order reaction after two hours of reaction time. The behavior of the reaction within the first two hours of reaction time was extremely complex.

The data were treated by the least-square method, using the special program (≠≠XEQSHCHPLS) stored in the computer center of UMR, to evaluate a relation between adduct concentration and time. Except the data of Run 5, all the data were evaluated by the least-squares method within five percent error at 95 percent confidence level. Run 5 had 18 percent error for the curved portion (Figure 7) up to 110 minutes and seven percent error for the straight-line portion.

Due to some difficulties in measuring the area under the standard and adduct peaks from the gas chromatography measurements, the

data were not good enough to give us reproducible values for the equilibrium constant. The values of the equilibrium constant (Table VIII) lie between 1.2 and 3.1 which is not in agreement with the observations that the reaction was 70 percent complete at equilibrium. In particular, Run 2 has a large equilibrium constant. The author believes, however, (without substantiating evidence) that the values of the forward rate constants (which are of the order 10^{-1}) are good; however, the reverse rate constants are too large by a factor of five or more.

B. Discussion of the Standard Curve. The standard plot of mole ratio of adduct to standard versus area ratio of adduct to standard (Figure 2) included abnormal and retrogression products along with normal products of the reaction. Since the reaction here was studied for the normal products mainly, the concentrations of products evaluated using the standard plot involves a 30 percent error. This might account for some of the discrepancies in the values of equilibrium constants obtained. However, this could also result from a small error in the reported (29) values of the ionization constants for malonic esters and mono-substituted malonic esters.

C. Limitations. The reaction studied was limited to only one concentration of potassium t-butoxide viz. 0.004 moles/liter.

D. Recommendations. The author would like to make the following recommendations.

1. A new standard curve of mole ratio of adduct to standard versus the area ratio of adduct to standard should be made considering the normal adduct only.

2. The reaction should be studied for 10-12 hours with increasing intervals of time.

3. Reaction samples should be analysed as quickly as possible. If stored, they should be stored in a freezer.

4. The rate of reverse reaction of the normal Michael adduct should be studied.

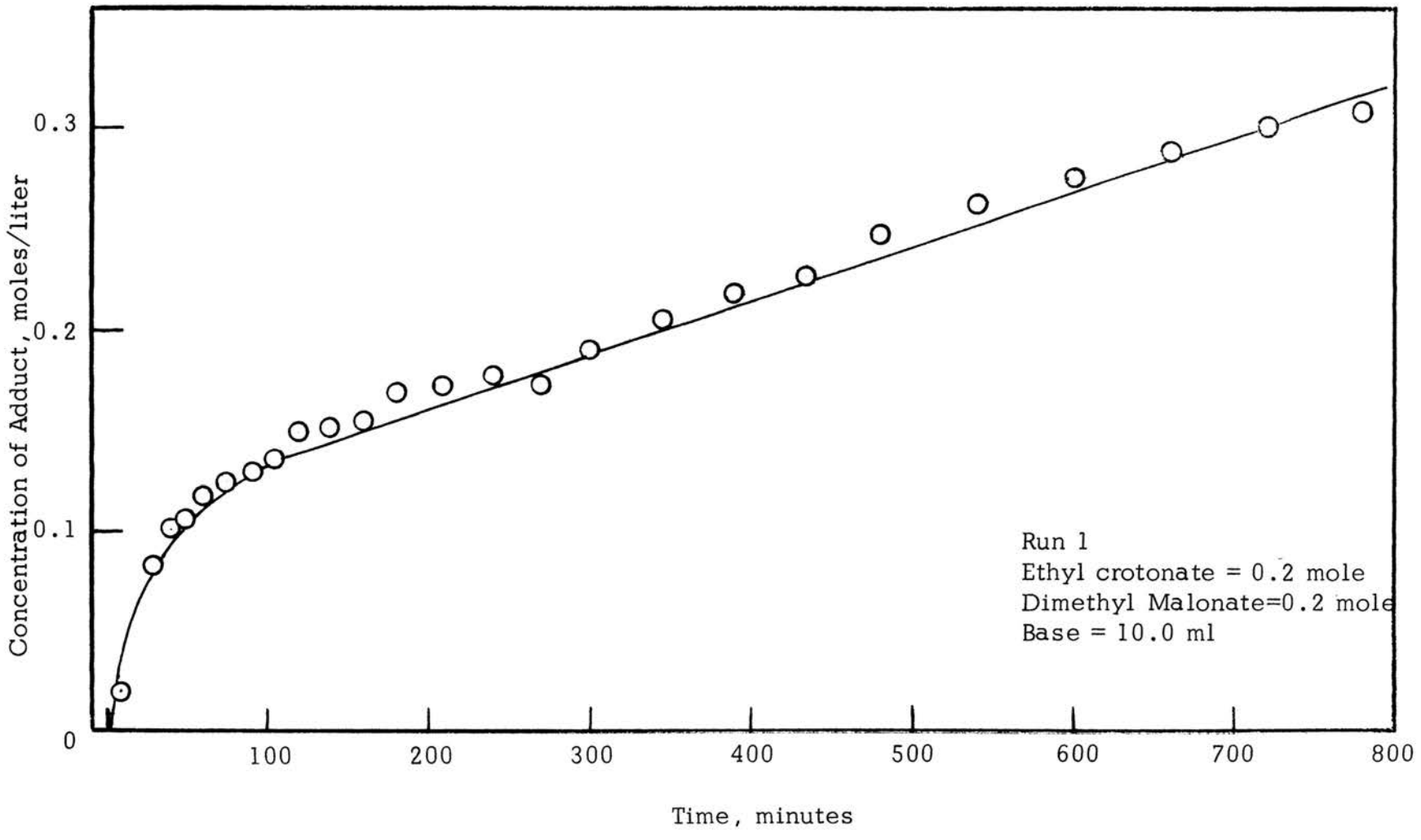


Figure 3. Concentration of Adduct as a Function of Time

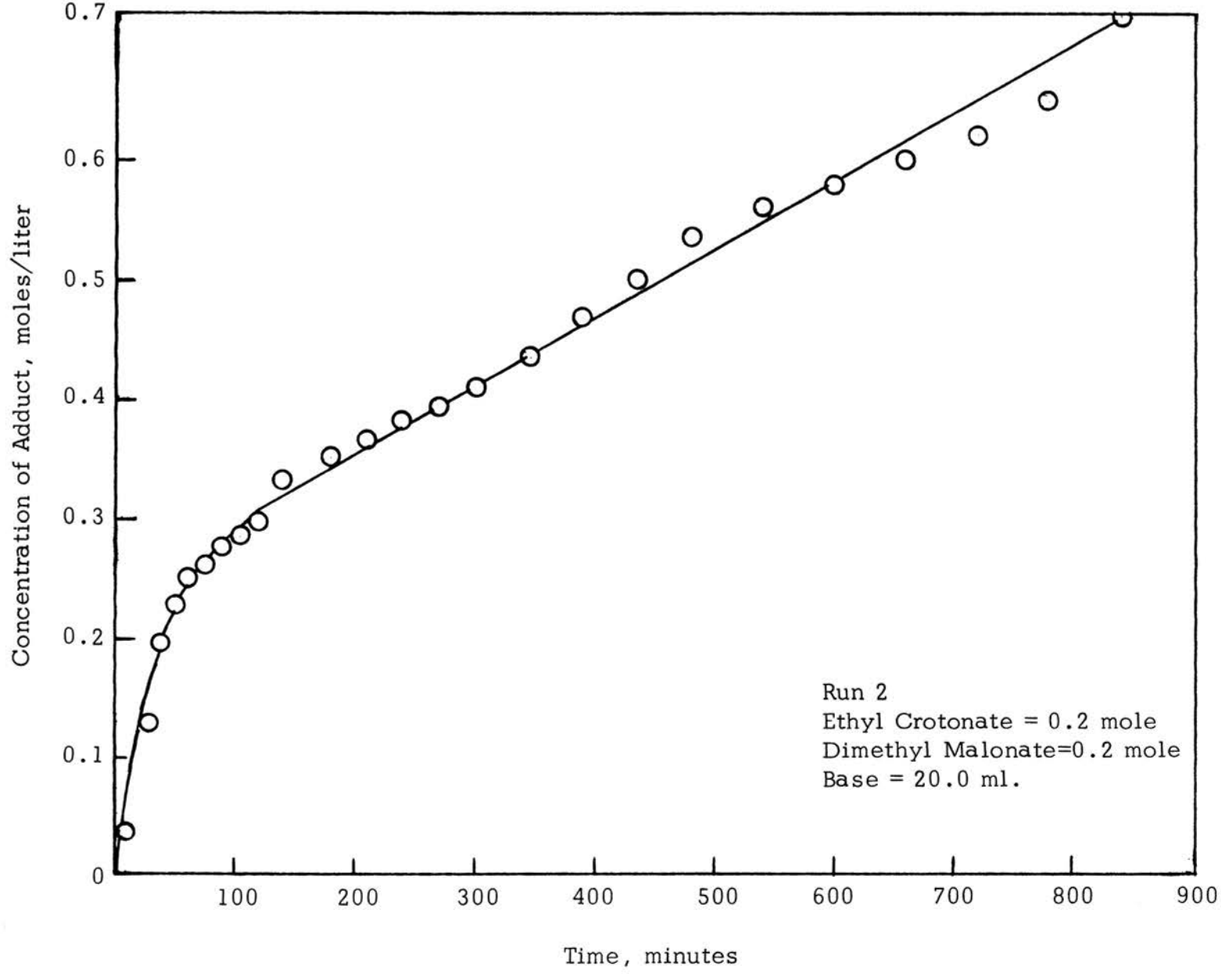


Figure 4. Concentration of Adduct as a Function of Time

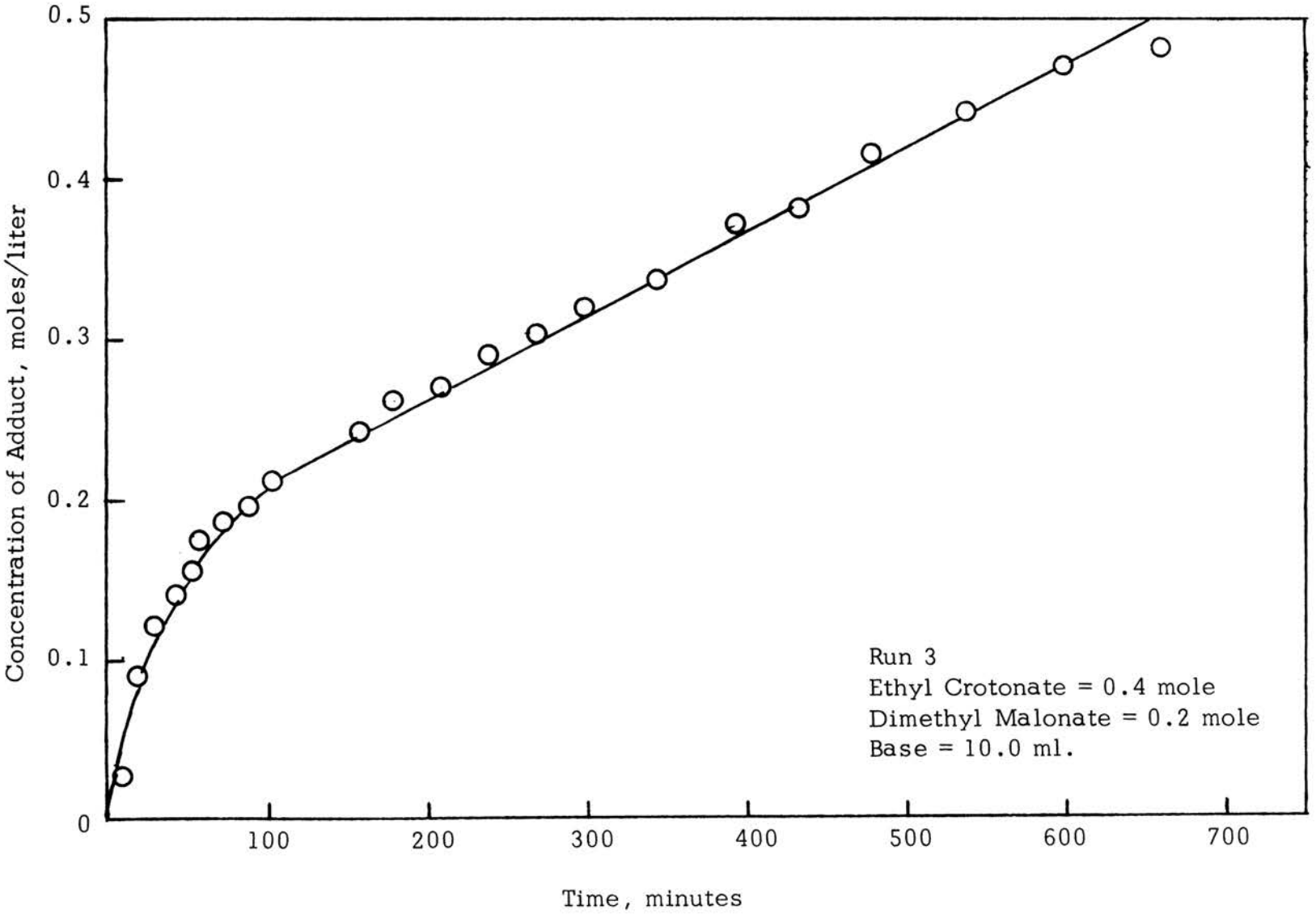


Figure 5. Concentration of Adduct as a Function of Time

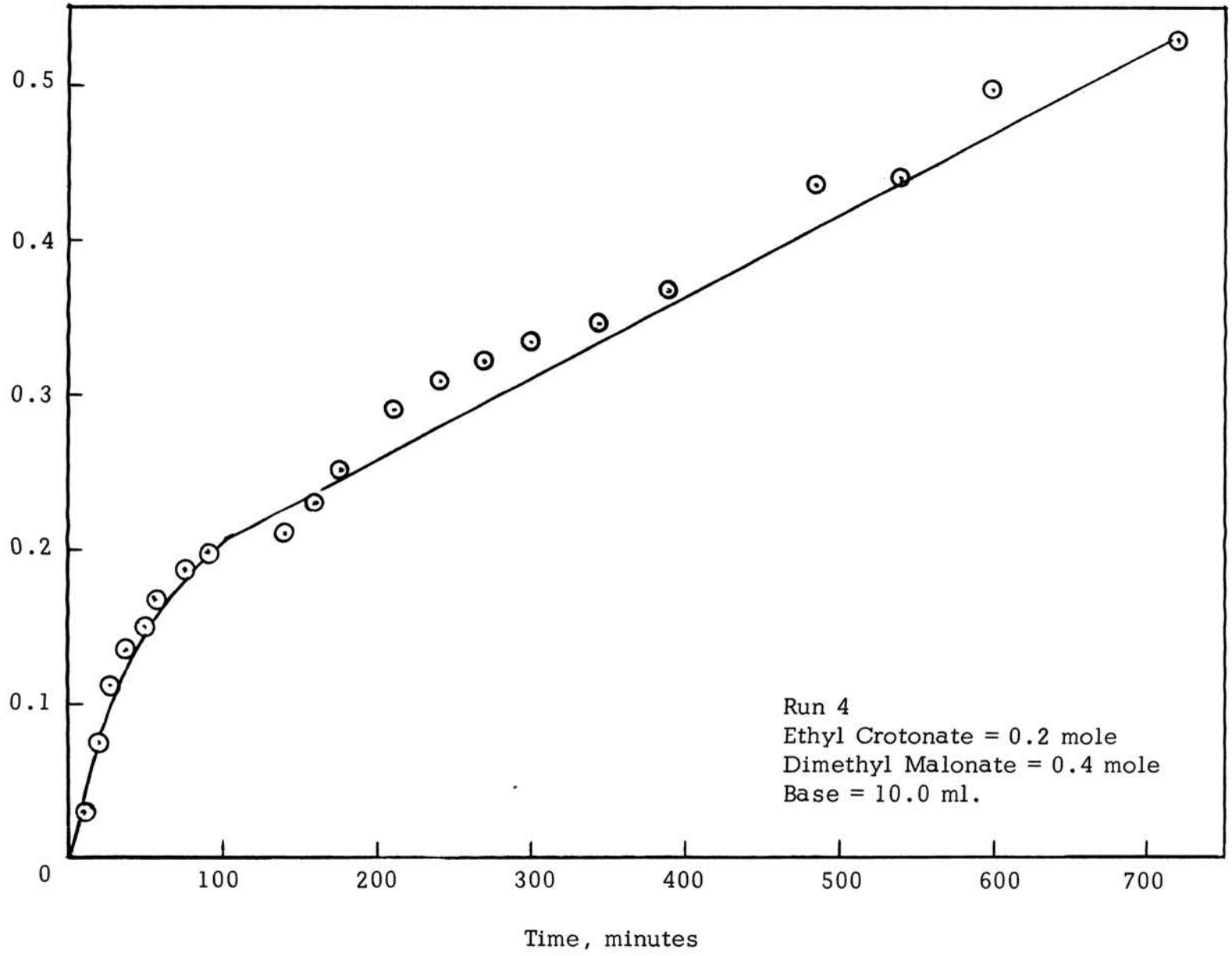


Figure 6. Concentration of Adduct as a Function of Time

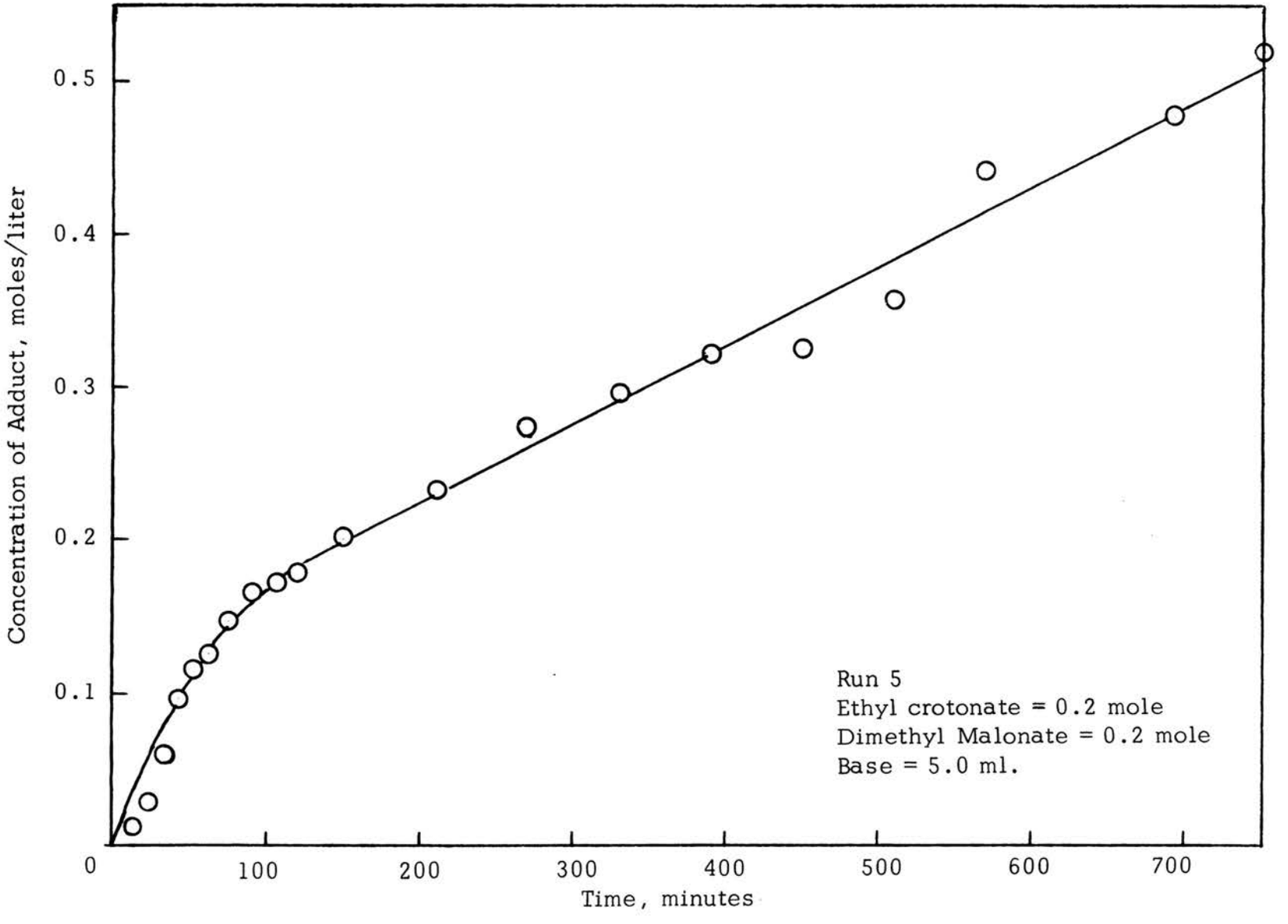


Figure 7. Concentration of Adduct as a Function of Time

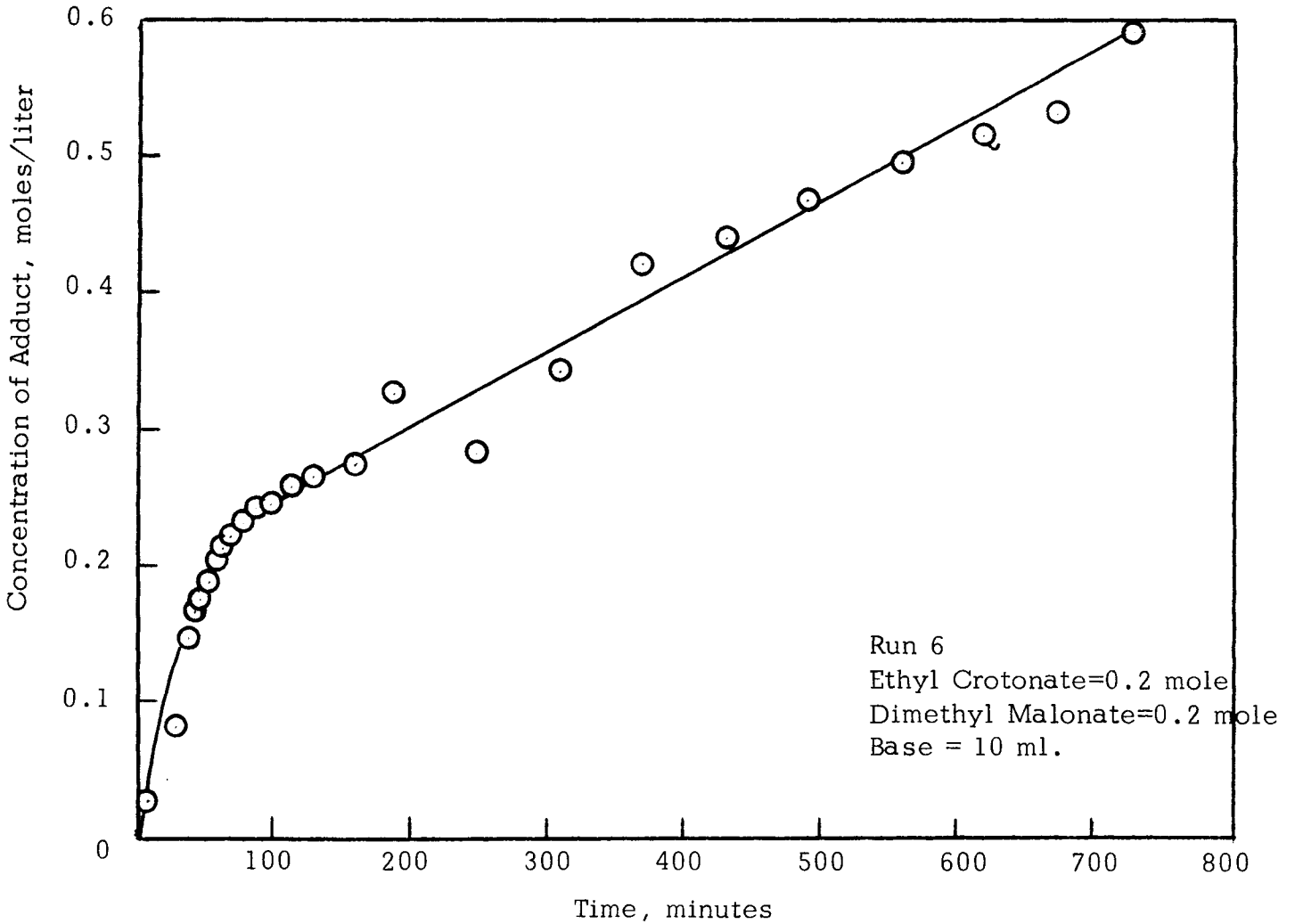


Figure 8. Concentration of Adduct as a Function of Time

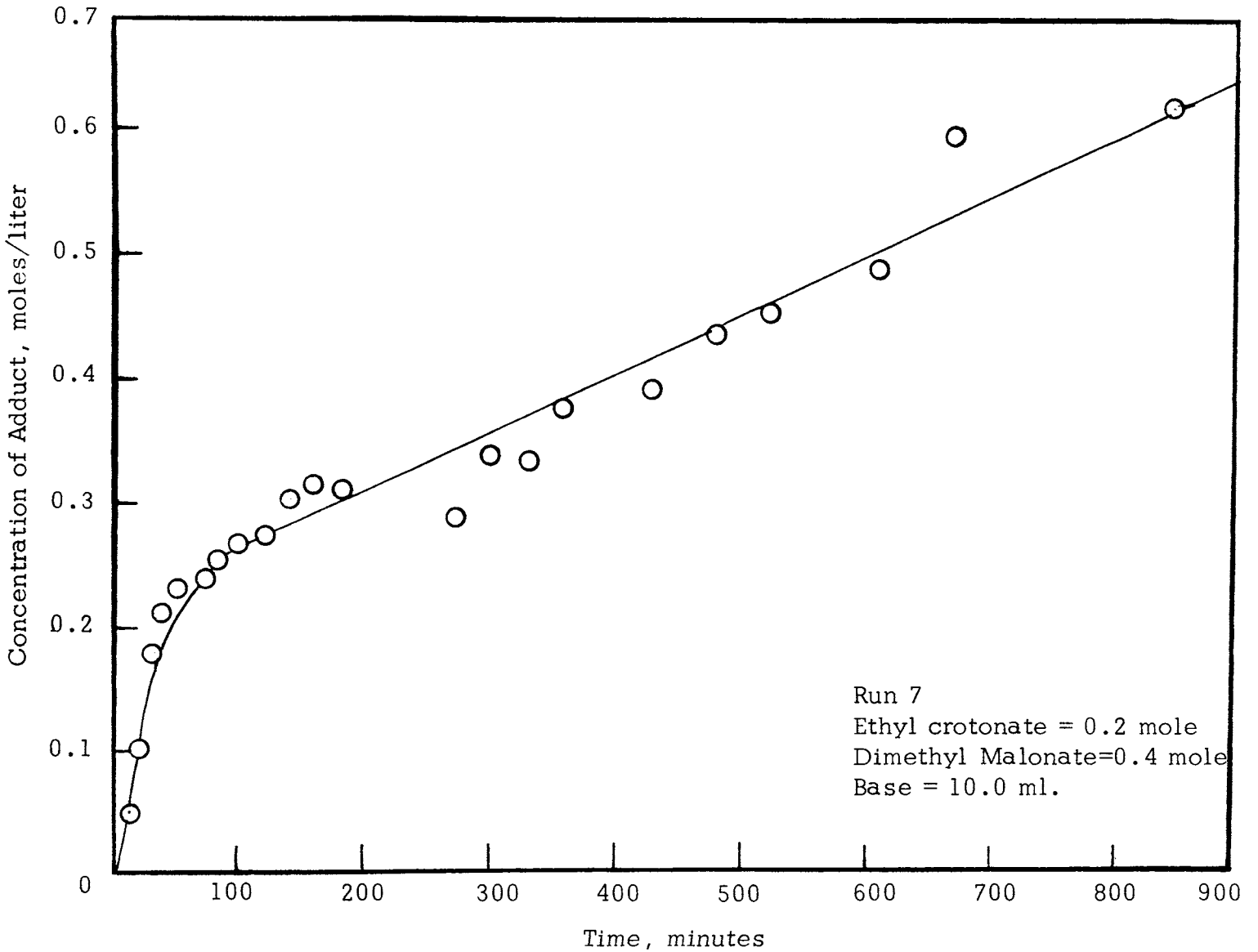


Figure 9. Concentration of Adduct as a Function of Time

VI. CONCLUSIONS

The study of the typical Michael reaction described in this thesis leads to the following conclusions.

A. As proposed by the previous workers (29, 10) the rate of the forward reaction is proportional to the concentration of the crotonate ester and the concentration of malonate anion.

B. The normal Michael reaction takes place by the attack of the malonate anion upon the acceptor to form the adduct anion.

C. The rate is proportional to the amounts of base, crotonate and malonate species.

D. The reaction over the most of the reaction period is pseudo zero-order.

E. The assumed and tested rate expression for the over-all rate is valid.

VII. SUMMARY

A typical Michael reaction has been studied with variations in the initial amounts of reactants. A gas chromatograph was used for the purpose of analyses and mathematical relationships were established for the treatment of data. A general computer program was written for the same purpose.

Under the limitations of low concentration of base used, the rate of reaction was found to be approximately doubled when the crotonate or malonate concentrations were doubled or quantity of base was doubled. After two hours of reaction time, the rate of reaction was constant.

VIII. APPENDICES

APPENDIX A

List of Computer Programs

Program for the Calculations of Adduct-Concentrations

```
C       CALCULATIONS FOR ADDUCT-CONCENTRATIONS.
        DIMENSION T(30),ARASH(30),X(30)
        M=1
        READ 101,VOL,WS,CB
        DO 2 K=1,7
        READ 100,N
        READ 101,GC,GDM,GS,VB
        READ 101,(T(I),ARASH(I),I=1,N)
        PRINT 102,M
        PRINT 103,GC
        PRINT 104,GDM
        PRINT 105,GS
        PRINT 106,CB,VB
        CS=GS/WS*1000.0/VOL
        DO 1 I=1,N
        RASHN=0.8645*ARASH(I)
      1 X(I)=RASHN*CS
        PRINT 108
        PRINT 107,(T(I),X(I),I=1,N)
      2 M=M+1
    100 FORMAT (I4)
    101 FORMAT (6F12.4)
    102 FORMAT (2X,4HRUN=,I1)
    103 FORMAT (2X24HGMS. OF ETHYL CROTONATE=,F7.4)
    104 FORMAT (2X26HGMS. OF DIMETHYL MALONATE=,F7.4)
    105 FORMAT (2X26HGMS. OF PHENYLCYCLOHEXANE=,F7.4)
    106 FORMAT (2X9HAMOUNT OF,F4.3,1HN,5HBASE=,F4.1,1X2HML)
    107 FORMAT (5X,F5.1,F12.4,5X,F5.1,F12.4)
    108 FORMAT (6X4HTIME,5X8HADD-CONC,6X4HTIME,5X8HADD-CONC)
        STOP
        END
```

```
RUN=1
GMS. OF ETHYL CROTONATE=22.7995
GMS. OF DIMETHYL MALONATE=26.4060
GMS. OF PHENYLCYCLOHEXANE=20.0007
AMOUNT OF.106NBASE=10.0 ML
     TIME      ADD-CONC       TIME      ADD-CONC
     10.0        .0203        30.0        .0816
     40.0        .1001        50.0        .1062
     60.0        .1170        75.0        .1243
     90.0        .1278       105.0        .1312
    120.0        .1489       140.0        .1506
    160.0        .1536       180.0        .1679
    210.0        .1718       240.0        .1765
    270.0        .1817       300.0        .1886
```

A Program for the Calculations of Rate and Logarithm of Rate.

```
C     CALCULATIONS FOR RATE VS. XMEAN AND RATE-LOG VS. XMEAN-LOG
      DIMENSION T(30),X(30),Y(30)
      M=1
      DO 5 K=1,4
      PRINT 104,M
      PRINT 103
C     FIRST DATA SHOULD BE A ZERO VALUE
      T(1)=0.0
      READ 100, N
      L=N+1
      READ 101, B1,B2,B3,B4,B5,B6
      DO 21 I=1,3
      X(I)=B1+B2*T(I)+B3*T(I)*T(I)+B4*T(I)*T(I)*T(I)
   21 T(I+1)=T(I)+40.0
      DO 22 I=3,L
      X(I)=B5+B6*T(I)
   22 T(I+1)=T(I)+40.0
      DO 2 I=1,N
      DELX=X(I+1)-X(I)
      DELT=T(I+1)-T(I)
      Y(I)=DELX/DELT
      XM=(X(I)+X(I+1))/2.0
      RATEL=LOGF(Y(I))
      XML=LOGF(XM)
    2 PRINT 102,XM,Y(I),XML,RATEL
    5 M=M+1
  100 FORMAT(I4)
  101 FORMAT (4E18.8)
  102 FORMAT (7X,F5.4,5X,E10.4,2X,E18.8,2X,E18.8)
  103 FORMAT(7X5HXMEAN,8X4HRATE,11X9HXMEAN-LOG,11X8HRATE-LOG)
  104 FORMAT(7X,4HRUN=,I1)
      STOP
      END
```

RUN=1

XMEAN	RATE	XMEAN-LOG	RATE-LOG
.0370	0.3059E-02	-0.32977187E+01	-0.57896546E+01
.1191	0.1047E-02	-0.21279737E+01	-0.68622986E+01
.1449	0.2427E-03	-0.19319701E+01	-0.83236568E+01
.1546	0.2427E-03	-0.18671032E+01	-0.83236568E+01
.1643	0.2427E-03	-0.18061887E+01	-0.83236568E+01
.1740	0.2427E-03	-0.17487726E+01	-0.83236568E+01
.1837	0.2427E-03	-0.16944749E+01	-0.83236568E+01
.1934	0.2427E-03	-0.16429742E+01	-0.83236568E+01
.2031	0.2427E-03	-0.15939966E+01	-0.83236568E+01
.2128	0.2427E-03	-0.15473062E+01	-0.83236568E+01

.2225	0.2427E-03	-0.15026990E+01	-0.83236568E+01
.2322	0.2427E-03	-0.14599969E+01	-0.83236568E+01
.2419	0.2427E-03	-0.14190439E+01	-0.83236568E+01
.2517	0.2427E-03	-0.13797023E+01	-0.83236568E+01
.2614	0.2427E-03	-0.13418499E+01	-0.83236568E+01
.2711	0.2427E-03	-0.13053783E+01	-0.83236568E+01
.2808	0.2427E-03	-0.12701901E+01	-0.83236568E+01
.2905	0.2427E-03	-0.12361981E+01	-0.83236568E+01
.3002	0.2427E-03	-0.12033236E+01	-0.83236568E+01
.3099	0.2427E-03	-0.11714956E+01	-0.832 6568E+01
.3196	0.2427E-03	-0.11406494E+01	-0.83236568E+01
.3293	0.2427E-03	-0.11107263E+01	-0.83236568E+01
RUN=2			
XMEAN	RATE	XMEAN-LOG	RATE-LOG
.0762	0.5324E-02	-0.25739126E+01	-0.52354964E+01
.2414	0.2932E-02	-0.14214553E+01	-0.58320337E+01
.3103	0.5134E-03	-0.11703045E+01	-0.75744781E+01
.3308	0.5134E-03	-0.11062171E+01	-0.75744776E+01
.3513	0.5134E-03	-0.10459906E+01	-0.75744776E+01
.3719	0.5134E-03	-0.98918630E+00	-0.75744781E+01
.3924	0.5134E-03	-0.93543610E+00	-0.75744776E+01
.4130	0.5134E-03	-0.88442830E+00	-0.75744776E+01
.4335	0.5134E-03	-0.83589650E+00	-0.75744781E+01
.4540	0.5134E-03	-0.78961150E+00	-0.75744776E+01
.4746	0.5134E-03	-0.74537430E+00	-0.75744776E+01
.4951	0.5134E-03	-0.70301130E+00	-0.75744781E+01
.5156	0.5134E-03	-0.66237030E+00	-0.75744776E+01
.5362	0.5134E-03	-0.62331650E+00	-0.75744781E+01
.5567	0.5134E-03	-0.58573080E+00	-0.75744776E+01
.5772	0.5134E-03	-0.54950670E+00	-0.75744776E+01
.5978	0.5134E-03	-0.51454900E+00	-0.75744781E+01
.6183	0.5134E-03	-0.48077230E+00	-0.75744776E+01
.6388	0.5134E-03	-0.44809920E+00	-0.75744776E+01
.6594	0.5134E-03	-0.41646010E+00	-0.75744781E+01
RUN=3			
XMEAN	RATE	XMEAN-LOG	RATE-LOG
.0554	0.4556E-02	-0.28925830E+01	-0.53912106E+01
.1782	0.1581E-02	-0.17249593E+01	-0.64497508E+01
.2194	0.4808E-03	-0.15167878E+01	-0.76399666E+01
.2386	0.4808E-03	-0.14327602E+01	-0.76399661E+01
.2579	0.4808E-03	-0.13552491E+01	-0.76399661E+01
.2771	0.4808E-03	-0.12833161E+01	-0.76399666E+01
.2964	0.4808E-03	-0.12162119E+01	-0.76399661E+01
.3156	0.4808E-03	-0.11533288E+01	-0.76399661E+01
.3348	0.4808E-03	-0.10941672E+01	-0.76399666E+01
.3541	0.4808E-03	-0.10383110E+01	-0.76399661E+01

.3733	0.4808E-03	-0.98541050E+00	-0.76399661E+01
.3925	0.4808E-03	-0.93516850E+00	-0.76399666E+01
.4118	0.4808E-03	-0.88733050E+00	-0.76399661E+01
.4310	0.4808E-03	-0.84167690E+00	-0.76399666E+01
.4502	0.4808E-03	-0.79801680E+00	-0.76399661E+01
.4695	0.4808E-03	-0.75618350E+00	-0.76399661E+01
.4887	0.4808E-03	-0.71603010E+00	-0.76399666E+01
.5079	0.4808E-03	-0.67742690E+00	-0.76399661E+01

RUN=4

XMEAN	RATE	XMEAN-LOG	RATE-LOG
.0661	0.3370E-02	-0.27171654E+01	-0.56928944E+01
.1671	0.1684E-02	-0.17889896E+01	-0.63868588E+01
.2117	0.5433E-03	-0.15527497E+01	-0.75179040E+01
.2334	0.5433E-03	-0.14550191E+01	-0.75179040E+01
.2551	0.5433E-03	-0.13659952E+01	-0.75179040E+01
.2769	0.5433E-03	-0.12842526E+01	-0.75179040E+01
.2986	0.5433E-03	-0.12086896E+01	-0.75179035E+01
.3203	0.5433E-03	-0.11384375E+01	-0.75179040E+01
.3420	0.5433E-03	-0.10727983E+01	-0.75179040E+01
.3638	0.5433E-03	-0.10112037E+01	-0.75179040E+01
.3855	0.5433E-03	-0.95318390E+00	-0.75179040E+01
.4072	0.5433E-03	-0.89834670E+00	-0.75179040E+01
.4290	0.5433E-03	-0.84636090E+00	-0.75179035E+01
.4507	0.5433E-03	-0.79694470E+00	-0.75179040E+01
.4724	0.5433E-03	-0.74985590E+00	-0.75179040E+01
.4942	0.5433E-03	-0.70488500E+00	-0.75179040E+01
.5159	0.5433E-03	-0.66184960E+00	-0.75179040E+01
.5376	0.5433E-03	-0.62059010E+00	-0.75179040E+01

STOP END OF PROGRAM AT STATEMENT 0104 + 01 LINES.

A Program for the Calculations of Rate and Equilibrium Constants

```
C       CALCULATIONS FOR RATE-CONSTANT
        DIMENSION T(95),X(95),Y(95)
        READ 101,AKB,AKM,AKA
        READ 100,TEMP,VOL,WC,WMH,WS,DC,DMH,DS,WTB,CB,DTB
        PRINT 103
        M=1
        DO 5 K=1,7
C       FIRST DATA SHOULD BE A ZERO VALUE
        T(1)=0.0
        READ 102, N
        READ 100,GC,GMH,GS,VB
        L=N+1
        READ 101, B1,B2,B3,B4,B5,B6
        A=GC/WC*1000./VOL
        B=GMH/WMH*1000./VOL
        CS=GS/WS*1000./VOL
        C=CB*VB/VOL
        VTB=VOL-VB-GC/DC-GMH/DMH-GS/DS
        BH=VTB*DTB/(VOL*WTB)*1000.0
        DO 21 I=1,12
        X(I)=B1+B2*T(I)+B3*T(I)*T(I)+B4*T(I)*T(I)*T(I)
   21   T(I+1)=T(I)+10.0
        DO 22 I=13,L
        X(I)=B5+B6*T(I)
   22   T(I+1)=T(I)+10.0
        DO 2 I=1,N
        DELX=X(I+1)-X(I)
        DELT=T(I+1)-T(I)
    2   Y(I)=DELX/DELT
        C1=0.0
        C2=0.0
        C3=0.0
        C4=0.0
        C5=0.0
        DO 3 I=1,N
        XM=(X(I)+X(I+1))/2.0
        PHI=AKM*(B-XM)+AKA*XM+AKB*BH
        P=(A-XM)*(B-XM)
        Z1=P/PHI
        Z2=XM/PHI
        C1=C1+Y(I)*Z1
        C2=C2+Z1*Z1
        C3=C3+Z1*Z2
        C4=C4+Y(I)*Z2
    3   C5=C5+Z2*Z2
        A1=(C3*C4-C1*C5)/(C3*C3-C2*C5)
```

```
      A2=(A1*C2-C1)/C3
      AK1=A1/(AKM*C)
      AK2=A2/(AKA*C)
      AKBL=(AK1*AKM)/(AK2*AKA)
      PRINT 104,M,AK1,AK2,AKBL
    5 M=M+1
  100 FORMAT (6F12.4)
  101 FORMAT (4E18.8)
  102 FORMAT (I4)
  103 FORMAT (7X3HRUN,10X9HK-FORWARD,11X10HK-BACKWARD,10X6HK-EQBL)
  104 FORMAT (8X,I1,11X,E10.4,10X,E10.4,10X,F6.2)
      STOP
      END
```

RUN	K-FORWARD	K-BACKWARD	K-EQBL
1	0.6690E-00	0.4236E+02	1.26
2	0.7675E-00	0.1752E+01	35.05
3	0.4728E-00	0.2697E+02	1.40
4	0.6974E-00	0.2249E+02	2.48
5	0.2002E+01	0.5120E+02	3.13
6	0.1193E+01	0.7920E+01	12.05
7	0.1269E+01	0.6425E+02	1.58

```
STOP END OF PROGRAM AT STATEMENT 0104 + 01 LINES.
```

APPENDIX B

List of Equipment and Materials

Equipment

Gas Chromatograph. F & M. Model 720. Range: 0-500° C., 0-200 milliamperes d-c. Manufactured by: F & M Scientific Corporation, Avondale, Pennsylvania.

Hypodermic Syringes.

1. Size: 10 microliters. Model 701-N. Manufactured by: Hamilton Company, Incorporated., Whitter, California.
2. Size: 2 cc. Manufactured by: Eisele and Company, Nashville, Tennessee.

Heating Mantles. Iron-Constantan, 450° C. maximum, manufactured by: Glas-Col Aparatus Company, Terre Haute, Indiana.

Powerstats. Type: 116, voltage: 120, maximum 7 1/2 amperes. Manufactured by: Superior Electric Company, Bristol, California.

Materials

Ethyl Crotonate: It was prepared in the laboratory. B. P.*: 138° Centigrade at pressure of 748 mm of mercury.

---

*Lange's Handbook of Chemistry (1949).

Dimethyl Malonate: Lot No. 7636; Matheson, Coleman & Bell Co. It was re-distilled at 98° Centigrade and 41 millimeters of mercury pressure.

Phenyl cyclohexane: Grade: Practical; Lot No.: 391075; Matheson, Coleman and Bell Co., Norwood, Ohio.

Tertiary Butyl Alcohol (2-methyl-2-propanol): Lot No. 17, Matheson, Chemical Co.; M.P.: 24.5-25.5° Centigrade.

Potassium t-butoxide solution: It was prepared by dissolving freshly cut potassium metal in t-butyl alcohol.

Potassium Carbonate, Anhydrous: Granular, Lot No. 23088, J. T. Baker Chemical Co., Phillipsburg, New Jersey.

IX. BIBLIOGRAPHY

1. Alexander, E. R., Principles of Ionic Organic Reactions, p. 150, John Wiley and Sons, Inc., New York, New York (1950).

2. Ambrose, D., Gas Chromatography, Van Nostrand, Princeton, New Jersey (1962).

3. Desty, D. H., Editor, Gas Chromatography, Academic Press, New York, New York (1958).

4. Gardner, J. A. and Rydon, H. N.,J. Chem. Soc., 42, 45, 48 (1938).

5. Gould, E. S., Mechanism and Structure in Organic Chemistry, Holt, Rinehart, Winston, New York, New York (1959).

6. Holden, N. E. and Lapworth, A., J. Chem. Soc., 2368 (1931).

7. Ingold, C. K., Structure and Mechanism in Organic Chemistry, p. 692-695, Cornell University Press, Ithaca, New York (1953).

8. James, W. and Martin, D., Biochem. J., 50, 679 (1952).

9. Jones,W., J. Chem. Soc., 105, 1547 (1914).

10. Kamlet, M. and Glover, D., J. Am. Chem. Soc., 77, 4896 (1955).

11. Keulemans, A., Gas Chromatography, Reinhold Publishing Corp., New York, New York (1957).

12. Korst, J. J., Master or Arts Thesis, Dartmouth College, Hanover, New Hampshire (1958).

13. Littlewood, A. B., Gas Chromatography, Academic Press, New York, New York (1958).

14. Michael, A. and Ross, J., J. Am. Chem. Soc., 52, 4598 (1930).

15. Nogare, S., Gas-Liquid Chromatography, Interscience, New York, New York (1962).

16. Ogata, T; Okano, M.; Furuya, Y. and Tabushi, I., J. Am. Chem. Soc., 78, 5426 (1956).

17. Patai, S., Weinstein, S., and Rappoport, Z., J. Chem. Soc., 1741 (1962).

18. Pecsok, R., Principles and Practice of Gas Chromatography, John Wiley and Sons, Inc., New York, New York (1959).

19. Phillips, C., Gas Chromatography, Academic Press, New York, New York (1956).

20. Purnell, H., Gas Chromatography, John Wiley and Sons, Inc., New York, New York (1959).

21. Samuel, D. and Ginsburg, D., J. Chem. Soc., 1288 (1955).

22. Shafer, P. R., Ph. D. Thesis, University of Wisconsin, Madison, Wisconsin (1951).

23. Shafer, P. R., Loeb and Johnson, J. Am. Chem. Soc., 75 5963 (1953).

24. Shimamura, O. and Inamoto, N., Bull. Chem. Soc. Jap., 28, 529 (1955).

25. Shimamura, O., Inamoto, N., and Suehiro, ibid, 27, 221 (1954).

26. Shimamura, O., Suehiro and Inamoto, N., Chem. Abstracts, 11962h (1960).

27. Swan, G., J. Chem. Soc., 1039 (1955).

28. Tsurata, T., Yasuhara, Y., and Farukawa, J., J. Org. Chem., 18, 1246 (1953).

29. Wulfman, D., Master of Arts Thesis, Dartmouth College, Hanover, New Hampshire (1958).

30. Zalukajevs and Klykova, Chem. Abstracts, 61 (1964).

31. Zellers, G., and Levine, R., J. Org. Chem., 13, 911 (1948).

X. ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Dr. D.S. Wulfman for his guidance and encouragement during the course of this work.

Appreciation is also extended to Dr. S.B. Hanna and Dr. R. M. Wellek for their suggestions during the investigation.

Acknowledgement is made to Chemistry Department for the use of the gas chromatographic equipment and for financial aid during the period of September, 1964 to May, 1965.

Acknowledgement is made to Mr. Charles F. Seger III for preparation and purification of a number of reagents.

XI. VITA

The author was born on March 15, 1943. He received his elementary and high school education in Bombay, India.

After graduation from high school, he attended St. Xavier's College for two years. In January, 1962, he came to the United States, attended the Missouri School of Mines and Metallurgy (the name was changed to University of Missouri at Rolla in July, 1964.) and received a B.S. degree in Chemical Engineering in May, 1964.

In June, 1964, he enrolled in the graduate school. During the period of September to May, 1964, he was employed as a student assistant by the Chemistry Department.