

KINETICS OF BASE-CATALYZED
ISOMERIZATION AND HYDRATION OF
BUTADIENE SULFONES

by

Wen Man Chang, B. Sc.

Thesis submitted to the Graduate Faculty of the
Virginia Polytechnic Institute
in candidacy for the degree of

MASTER OF SCIENCE

in

CHEMISTRY

APPROVED:

Chairman, Luther K. Brice, Jr.

Alan F. Clifford

Frank A. Vingiello

Paul E. Field

John G. Mason

August, 1966

Blacksburg, Virginia

To my mother and grandmother, without whose sacrifices, moral and financial support, my advanced studies in the United States would be virtually impossible.

ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to
under whose guidance and advice this
research was conducted; and to the members of his committee and the
graduate students of the Chemistry Department for their helpful
suggestions.

Special thanks are due Professor of
Chemistry at the Queen's University of Belfast, Belfast, Northern Ireland,
for measuring the heat of formation of the compounds which are under
this kinetic investigation.

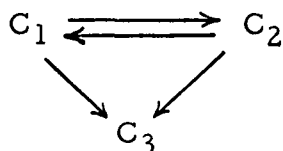
Financial support in the form of a Graduate Teaching
Assistantship during the period of this research was gratefully
received from the Virginia Polytechnic Institute.

TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. NOMENCLATURE	5
III. HISTORICAL	6
A. The Base-Catalyzed Isomerization of the Simple Olefins	6
B. The Base-Catalyzed Isomerization of Butadiene Sulfones'	8
C. Kinetics of Complex Reaction of the Type	10
<pre> graph TD C1 <--> C2 C1 --> C3 C2 --> C3 </pre>	
IV. THE INVESTIGATION	13
A. Preliminary Experiments	13
1. Plan	13
2. Methods	15
B. Experimental	17
1. Materials	17
2. Preparation of Solutions	18
a. α - and β - Butadiene Sulfones	18
b. Base Solution	21
c. Reaction Mixture Solution	21

	Page
d. Acid-Internal Standard Solution	21
e. Standard Solutions for Preparing the Calibration Curves	22
3. Apparatus	23
a. Constant Temperature Bath	23
b. Gas Chromatographic Unit	23
c. Digital Computer	27
4. Kinetic Measurement	27
5. Chromatograms	28
a. Quantitative Measurements	28
b. Effect of Sensitivity of Instrument	29
c. Standard Chromatograms and Calibration Curves	29
d. Chromatograms of Samples from Kinetic Run	32
V. DATA AND RESULTS	35
A. Kinetic Plots	35
1. Concentration-Time Curves	35
2. Reaction Triangle	49
3. Convergence of Reaction Path	51
B. Calculation of Rate Constants	53
1. Relative Rate Constants	53

	Page
a. Direct Calculation	53
b. Method of Wei and Prater	55
2. First-Order Rate Constants	63
a. Direct Calculation	65
b. Graphical Method	66
c. Comparison of the Two Methods	66
3. Second Order Rate Constants	68
VI. DISCUSSION AND CONCLUSION	70
A. Kinetics and Mechanism of Base-Catalyzed Isomeriza- tion and Hydration of Butadiene Sulfones	70
B. Thermodynamic Properties of the Isomerization	73
1. Heat of Isomerization in Aqueous Solution	73
a. $\Delta H(\text{aq})$ from Kinetic Data	75
b. $\Delta H(\text{aq})$ from Thermochemical Data	75
2. Free Energy and Entropy Changes of Isomeriza- tion	77
VII. SUMMARY	78
VIII. APPENDIXES	80
A. Experimental Determination of Relative Rate Constants for the Reaction with the Mechanism	80



	Page
B. Determination of k_{12} by Graphical Method	86
C. Computer Check of the Experimental Data	88
IX. BIBLIOGRAPHY	91
X. VITA	95

LIST OF TABLES

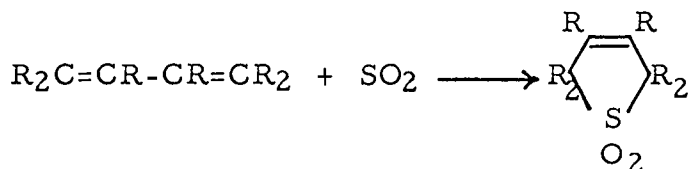
Table	Page
I	Nomenclature 5
II	Kinetic Data for the Isomerization of β -Butadiene Sulfones to α -Butadiene Sulfone Obtained from Spectrophotometric Method 10
III	List of Materials Tested for Use as the Internal Standard Together with Two Butadiene Sulfones 16-17
IV	Chemical Used for the Kinetic Runs 19
V	Chemicals Used for the Preparation of Gas Chromatographic Column 20
VI	Gas Chromatographic Calibration Data 30
VII	Tables of Experimental Data 37-43
VIII	Table of the Initial Composition of the Straight Line Reaction Path and the Limit Value of C_1/C_2 53
IX	Relative Rate Constants Obtained by Direct Calculation... 54-55
X	The Composition Data Used to Evaluate "u" ratio for the β -Butadiene Sulfone - α -Butadiene Sulfone - Alcohol System 61
XI	Table of k_{12} Obtained from Direct Calculation 65
XII	First-Order Rate Constants for the Base-Catalyzed Isomerization and Hydration of the Isomeric Butadiene Sulfones 68
XIII	Second-Order Rate Constants for the Base-Catalyzed Isomerization and Hydration of the Isomeric Butadiene Sulfones 69
XIV	Activation Energies and Frequency Factors 73

LIST OF FIGURES

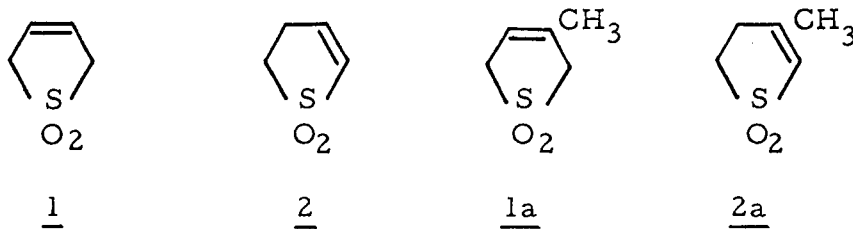
Figure		Page
1.	Calibration Curve	31
2.	A Typical Chromatogram for a Reaction Mixture Obtained from the Reaction Starting with Pure β -Butadiene Sulfone	33-34
3.	The Concentration-Time Curves at 45 °C	45-48
4.	The Reaction Triangle	50
5.	The Convergence of C_1/C_2 from Different Initial Compositions	52
6.	$-\log b_1$ Versus $-\log b_2$ obtained from Pure α - Butadiene Sulfone Initial Concentration	64
7.	A Linear Plot for a First-Order Reaction	67
8.	The Arrhenius Plot	74

I. INTRODUCTION

A subject of recent investigation in this laboratory is the chemical behavior, both of synthetic and physical aspects, of cyclic sulfones which resulted from the modified Diels-Alder sulfur dioxide reaction of 1, 3-dienes with sulfoxide serving as dienophile:



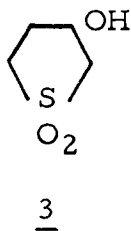
Extensive investigations concerning the reactions and properties of the isomeric dihydrothiophene 1, 1-dioxides such as 2, 5-dihydrothiophene 1, 1-dioxide (1), 2, 3-dihydrothiophene 1, 1-dioxide (2), 3-methyl-2, 5-dihydrothiophene 1, 1-dioxide (1a), and 3-methyl-2, 3-dihydrothiophene 1, 1-dioxide (2a) have been performed by Krug and co-workers.¹⁻⁴ However there has been relatively less



work related to the kinetics of reaction in solution, the reaction mechanism, and the thermodynamic properties.

Brice and co-workers, Chin,⁵ Sullivan,⁶ and Smith⁷ have measured the rate of the reversible base-catalyzed isomerization

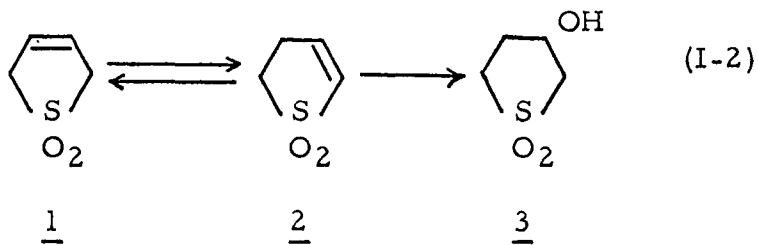
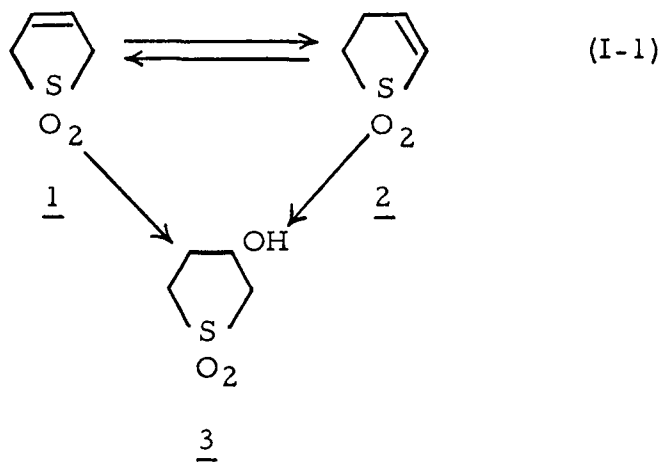
reaction between 1a and 2a by the methods of spectrophotometry, proton magnetic resonance spectroscopy, and gas chromatography. All three methods of analysis gave comparable results, the gas chromatographic method being the most satisfactory. But the kinetic investigation for the same type of reaction between 1 and 2 has not been accomplished by the same methods as used previously because the analytical procedure was complicated by the formation of 3-hydroxytetrahydrothiophene 1, 1-dioxide (3).



The existence of 3 has been proved by both the spectrophotometric and the thin layer chromatographic methods and this compound has also been actually prepared and isolated.⁸⁻¹⁰ Compound 3 is thought not to be an intermediate in the isomerization because the conversion of 3 to 2 cannot be affected under the same conditions as the isomerization of 1.¹¹ Smith⁸ obtained the first-order and second-order rate constants of the reaction from 1 to 2 by assuming that 3 was formed only from 2. This would be predicted from the electronic structures of these three compounds.

Thus, the origin of 3 is still left as a question for lack of

experimental foundation. The problem involved is whether the reaction follows the scheme (I-1) or (I-2):



One object of the present investigation was to determine the value of the rate constants for the four steps in the reaction scheme (I-1). Another object was to obtain the equilibrium composition for the reversible step of this reaction system from which the thermodynamic enthalpy and entropy of isomerization can be calculated.

While many complex reactions have received extensive kinetic study, there are comparatively few references in the literature

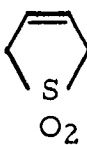
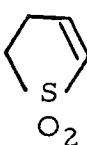
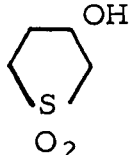
made to the complex reactions of sulfone isomerization. The paucity of data is possibly due to the analytical difficulties. Therefore, this investigation would serve to expand the knowledge in the sulfone field.

II. NOMENCLATURE

The nomenclature in this thesis is that recommended by Chemical Abstracts. Occasionally, for brevity the isomeric dihydrothiophene 1, 1-dioxides (1, 2) will be referred to as the β - or α -isomer respectively, depending on the location of the olefinic linkage and 3-hydroxytetrahydrothiophene (3) will be referred to as the alcohol.

The following table serves to illustrate the nomenclature of the three compounds which constitute the reaction system for this investigation.

TABLE I
Nomenclature

No.	Structural Formula	Systematic Name	Trade Name	Common Name
<u>1</u>		2, 5-dihydrothiophene 1, 1-dioxide	Sulfolene	β -butadiene sulfone (β -isomer)
<u>2</u>		2, 3-dihydrothiophene 1, 1-dioxide	x	α -butadiene sulfone (α -isomer)
<u>3</u>		3-hydroxytetrahydro- thiophene	x	(alcohol)

III. HISTORICAL

In order to understand the principle of base-catalyzed isomerization of diene sulfones, one should first review similar reactions involving simple olefins. In both cases a shift of double bond is observed, but the olefin system having been studied thoroughly will serve as a basis for comparison in the analogous reactions of the diene sulfones.

A. THE BASE-CATALYZED ISOMERIZATION OF THE SIMPLE OLEFINS

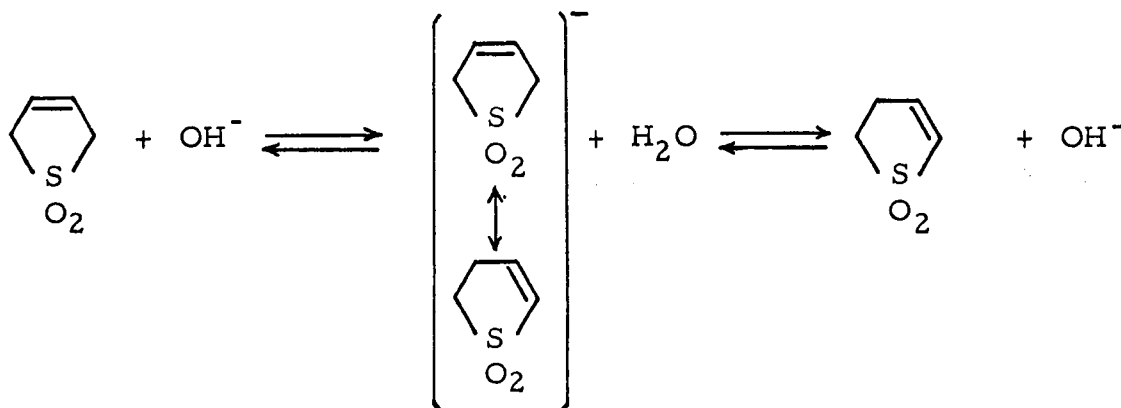
The removal of hydrogen ions from saturated carbon compounds is achieved only with difficulty. This is not the case, however, with compounds where the resulting carbanion can be stabilized by resonance, either by spreading of the negative charge over an unsaturated system or where it involves an electron withdrawing atom or group attached to the carbon atom from which the hydrogen ion is removed. Where this situation arises, the formation of carbanions can be significant and has interesting consequences.

Early investigations of prototropic mobility and the effect of structural variations were hampered by the lack of suitable systems for detailed study.¹² Those compounds, such as propenylbenzenes and propenylammonium salts, which were known to be active in undergoing alkali catalyzed isomerization, either isomerized too rapidly or else had

molecules, especially if the catalyst were a hydrogen bonding solvent such as water.¹²

B. THE BASE-CATALYZED ISOMERIZATION OF BUTADIENE SULFONES

The β -isomer of butadiene sulfone was first synthesized by Staudinger¹⁷ in 1930. However, it was van Zuydewijn¹⁸ who first accomplished the isomerization of the β -isomer to the α -isomer in 1934 by using 0.5 M aqueous potassium hydroxide or ultraviolet radiation. He also suggested that the equilibrium between two isomers is situated roughly at 1/3 α -isomer and 2/3 β -isomer. It was thought that the action of a base brought about the isomerization according to the following mechanism:



In 1937, Boeseken and van Zuydewijn¹⁰ also observed that an alcohol is formed is the isomerization from the β -isomer to the α -isomer is performed in a higher concentration of base. However, no kinetic work concerning this complex reaction was carried out until 1962. Zimmermannová and Procha¹⁹ studied the kinetics of base-

catalyzed isomerization of the β -isomer to the α -isomer and the addition of aliphatic alcohols to the α -isomer. Even though their studies were in an alcoholic solution, it is still worthwhile to mention briefly their results. The isomerization rate increased from methanol to propanol and primary alcohols to tertiary alcohols. The isomerization equilibrium constants showed the high acidity of the 4-position hydrogen atom in the 2, 3-unsaturated sulfone. Concurrently with the isomerization, base-catalyzed addition of alcohol took place at the 3-position of 2, 3-unsaturated sulfone. The rate of addition of alcohol increased from methanol to propanol and decreased from the primary to the tertiary alcohols, which did not add at all.

The earliest kinetic investigation of the isomerization of the β -isomer to the α -isomer in aqueous solution was performed by Wong,²⁰ but poor results were obtained. It has been pointed out previously that the first- and second-order rate constants for the same step of the reaction have been measured successfully by Smith⁸ using a spectrophotometric method. The calculation assumed that the alcohol forms only from the α -isomer. However, he was unable to calculate the other rate constants in reaction scheme (I-1) because only the α -isomer concentration could be measured spectrophotometrically. The following table gives his final results for the isomerization reaction where k_{12} , k'_{12} , $(E_a)_{12}$, and Z_{12} are the first-order rate constant,

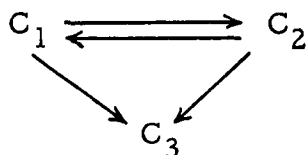
the second-order rate constant, the energy of activation, and the frequency factor, respectively.

TABLE II

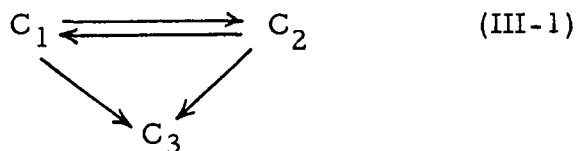
Kinetic Data for the Isomerization of β -Butadiene Sulfone to α -Butadiene Sulfone Obtained from a Spectrophotometric Method

Temp., $^{\circ}\text{C}$	(OH^-) , <u>M</u>	$k_{12} \times 10^2$, min^{-1}	$k'_{12} \times 10^2$, <u>M</u> $^{-1} \text{min}^{-1}$	$(E_a)_{12}$, kcal/mole	Z_{12} , <u>M</u> $^{-1} \text{min}^{-1}$
25	0.300	0.0960	0.320	22.4	9.3×10^{13}
35	0.300	0.351	1.17	22.4	9.3×10^{13}
45	0.300	1.02	3.40	22.4	9.3×10^{13}

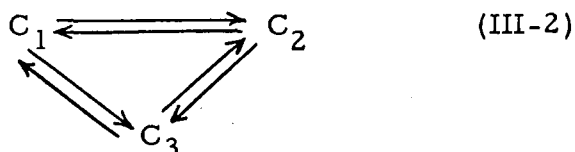
C. A KINETICS OF COMPLEX REACTION OF THE TYPE



The reaction scheme (I-1) can be simply represented by



and this is one of special cases of the reaction system.



The general integrated rate equations for mechanism (III-2) can be readily derived by the methods described in the literatures.²¹⁻²³

However, the integrated forms are complicated and will not be recorded here. The integrated rate expressions for the mechanism (III-2) with the boundary conditions $C_1=C_1^0$, $C_2=0$, and $C_3=0$ at time=0, where superscript zero indicates the initial condition, have been given by Evans;²⁴ while those with the boundary conditions $C_1=C_1^0$, C_2^0 , and $C_3=0$ at time=0 have been given by Alberty and Miller.²⁵

Actual reaction systems with the mechanism (III-1), such as O^{18} -trace experiments on ester hydrolysis, isomerization of 2-butenes, and the reactions of p-phenylene-bis-diazonium ion with water, have been studied by Bender,²⁶⁻²⁸ Hamilton and Burwell,²⁹ and Lewis and Johnson,³⁰ respectively. Lewis and Johnson also derived the explicit expressions for the concentration of each substance as a function of four rate constants, time, and the pH of the solution. However, it should be noted that most of their studies involve either curve-fitting techniques or the method of trial and error to determine the rate constants and the concentration-time curves. As is well known from previous attempts, the behavior of even linear systems containing as few as three reacting species is sufficiently complicated to make their basic dynamic behavior difficult to visualize and the rate constants difficult to evaluate.

Recently, Wei and Prater³¹⁻³⁴ developed a new and powerful method for determining the rate parameters of first-order monomolecular complex reactions that can have an arbitrary number of components. Their result led them to a precise mathematical description of the nature of the reaction. With the mathematical model they developed, one can predict all the paths which such a complex reaction can take in approaching equilibrium. In addition, rates at which each path will be traveled can be predicted.

The model has two special advantages: (i) actual rate studies can be planned to reduce effects of experimental error on rate constants, and (ii) the number of experiments needed to characterize a system is minimized. This has made data interpretation easier and rate study less ambiguous.

The method of Wei and Prater will be used to calculate the relative rate constant of the reaction system (I-1) and compared with the currently developed method.

IV. THE INVESTIGATION

A. PRELIMINARY EXPERIMENTS

One of the problems in this research is how to determine the actual concentrations of the three sulfones which are necessary for determining the rate constants of this complex reaction.

1. Plan

The early experiments by the UV absorption method were discussed in section III-B. This method was repeated to check the reproducibility of previous experimental results. Several corrections were made, especially for the time required for maximum isomerization of the β -isomer to the α -isomer (see section V-B-I-a)

In order to get the actual concentrations of all three components in the reaction system (I-1), at least two of these must be measured. The third one can be obtained by subtracting the summation of the two known concentrations from the total initial concentration. Thus the methods such as thin layer chromatography, gas chromatography, and proton magnetic resonance may be used separately or together with UV absorption method to determine the concentrations.

The thin layer chromatographic method was only qualitative⁸ and this method had already been used in the earlier investigation of this reaction.

Because of the difference in the position of the double bond in the α - and β -isomers, and because of the special environment of the hydroxyl group of the analogous alcohol, the use of proton magnetic resonance (PMR) was at first thought to be applicable. Each compound would have given a characteristic peak in the PMR spectrum, which, when integrated, would have been a good measure of the concentration of the individual molecule. The model A-60 Nuclear Magnetic Resonance Spectrometer made by Varian Associates, Palo Alto, California, was used. It was found, however, that this technique was not suitable because the strong peak from solvent water completely masked all the other resonances³⁵ and this method was abandoned.

All the remaining efforts were devoted to the gas chromatographic method. Brice⁸ did several preliminary experiments in this work to determine which type of column packing material should be used for the best result. Several materials such as Se-30, Se-52, and 6.3% or 15% carbowax 1500 all on Gas Chrom Z substrate had been tested and it was decided that the 6.3% carbowax 1500 would produce the best separation between the α -isomer and β -isomer. The alcohol is apparently too polar to come off the column except at high temperatures.

A gas chromatographic column made by M. F. Burke of this laboratory was decomposed after eight months of use at a column oven

temperature of 145 °C, which was five degrees lower than the critical temperature of carbowax 1500. A second column was prepared and the column oven temperature lowered. More details of this work will be discussed in section IV-B-3-b.

2. Methods

An internal standard is required for this quantitative analysis. This method gives the actual concentrations of α - and β -isomers and also compensates for the minor variations in column operation, since both the internal standard and the sample are influenced to essentially the same extent.

Harvey and Chalkley³⁶ outlined the requirements of an effective internal standard: (i) it should yield a completely resolved peak; (ii) it should be eluted close to the component or components to be analyzed; (iii) the ratio of its peak area to those of components to be measured should be as close to unity as possible. In addition to these requirements, of course, the material used as an internal standard would be better if its molecules had the same skeletal structure as that of the component to be analyzed. Table III shows the materials tested for selecting the most suitable internal standard as well as the retention times of these materials, the α -isomer, and the β -isomer.

TABLE III

List of Materials Tested for Use as the Internal Standard Together with Two Butadiene Sulfones

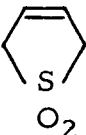
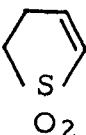
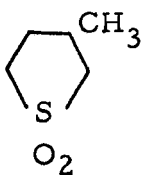
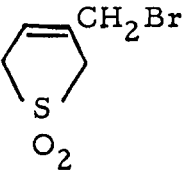
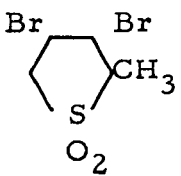
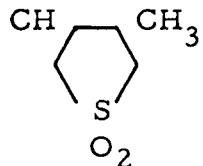
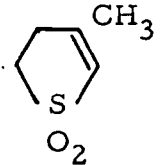
Structural formula	Qualitative solubility in water at room temperature	Retention time in minutes under experimental condition	Remarks
	Good	1.5	x
	Good	4.0	x
	Good	1.5	Overlap with the peak of the α -isomer
	Good	1.7	Overlap with the peak of the α -isomer
	Poor	x	x

TABLE III (Cont'd)

	Good	7.0	Retention time too long
	Good	2.3	Selected internal standard

Calibration with an internal standard is performed by the addition of a constant amount of the standard to a specific volume of several synthetic mixtures containing varying known amounts of solutes under investigation. The range of solute concentration is chosen near to that which exists in the known sample, and the resulting synthetic mixtures are chromatographed. A plot of the ratio of solute/standard peak areas against the ratio of solute/standard concentrations results in the desired calibration curve.

B. EXPERIMENTAL

1. Materials

The β -butadiene used was a crude product from the Special Products Division of Phillips Petroleum Company, Bartlesville,

Oklahoma. The melting point of this sample was found to be 62-64 °C (Lit.³⁷ 63.5-64.5 °C). The crude material was then recrystallized from methanol in several successive recrystallizations^{8, 37} until the melting point was found to be 63.5-64.5 °C. This purified compound was vacuum dried at 15 mm pressure for fifteen hours.

The α -butadiene sulfone was prepared from the commercially available β -isomer by standard laboratory procedures.^{8, 37} The melting point of this compound after recrystallization and vacuum drying was found to be 47-48 °C (Lit.³⁷ 48-49 °C).

The compound 2-methyl-4,5-dihydrothiophene 1,1-dioxide was obtained from J. A. Rigney³⁸ in this laboratory. It had a melting point of 69.5-70 °C (Lit.^{39, 40} 68-69 °C), indicating a high purity.

The description of all the other compounds and reagents used for the kinetic runs and gas chromatographic column are listed in Table IV and Table V, respectively.

2. Preparation of Solutions

All volumetric glassware, except burets, used for preparing the solution were of Kimax quality and were used without calibration. The burets were Exax.

a. α -and β -butadiene Sulfones

For this investigation, it was found that a convenient concentration of these two sulfones was 0.200 M which was equivalent to

TABLE IV
Chemicals Used for the Kinetic Runs

Name	Manufacturer	Description
Absolute Ethanol	U. S. Industrial Chemical Co.	Reagent grade
Activated Carbon	J. T. Baker Chemical Co.	Mesh size: 50/200
Benzene	J. T. Baker Chemical Co.	Reagent grade
Chloroform	Fisher Scientific Co.	Reagent grade
Hydrochloric Acid	J. T. Baker Chemical Co.	Reagent grade, 37.2%
Methanol	Fisher Scientific Co.	Reagent grade
Petroleum Ether	J. T. Baker Chemical Co.	Reagent grade
Potassium Dichromate	J. T. Baker Chemical Co.	Reagent grade
Sodium Hydroxide	J. T. Baker Chemical Co.	Reagent grade, 50.7%
Sulfuric Acid	J. T. Baker Chemical Co.	Reagent grade, 97%
Water	Chemistry Dept., V. P. I.	Doubly distilled and carbonate free

TABLE V

Chemicals Used for the Preparation of Gas Chromatographic Column

Name	Manufacturer	Description
Acetone	Fisher Scientific Co.	Reagent grade
Carbowax 1500	F & M Scientific Corp.	<ol style="list-style-type: none"> 1. Liquid Phase 2. Polyethylene glycol polymers 3. Average molecular weight: 1500 4. Temperature limit: 150 °C
Gas Chrom Z	Applied Science Laboratories, Inc.	<ol style="list-style-type: none"> 1. Diatomaceous solid support 2. Mesh size: 80/100 3. Silanized, i. e. the hydroxyl groups on the surface had been reacted with hexamethyldisilazene to produce a more inert substrate⁴¹
Methylene Chloride	Fisher Scientific Co.	Reagent grade

2.3632 g per 100.0 ml of water. Stock solutions of twice of this concentration were prepared and kept at 4-5 °C.

b. Base Solution

A carbonate free 0.600 M sodium hydroxide solution was used as the stock solution for all the following kinetic experiments and stored in a clean polyethylene bottle. This base solution was standardized three times with 0.200 M potassium hydrogen phthalate using phenolphthalein as an indicator. Care must be taken that due to the very sensitive influence of concentration of base on the reaction rate measurements, the molarity must be adjusted as accurately as possible.^{6, 8}

c. Reaction Mixture Solution

All reaction mixtures were prepared by mixing 7.00 ml of pure stock sulfone solution or the appropriate mixture of α - and β -isomer solutions of total concentration 0.400 M with the same amount of stock sodium hydroxide solution.

d. Acid-Internal Standard Solution

Since the neutralization method was used to quench the isomerization reaction and the internal standard method was employed in the gas chromatographic analysis, a solution containing both acid and internal standard was prepared and used as a quenching reagent. Quenching was accomplished by mixing the sample of basic reaction mixture with this reagent in the volume ratio of 1:1. The more details about

sampling and quenching procedures will be discussed in section IV-B-4.

For the gas chromatographic analysis, a suitable concentration of the internal standard, which was 2-methyl-4,5-dihydrothiophene 1,1-dioxide (MDD), was found to be 0.050 M. Therefore, the internal standard solution, which was 0.320 M with respect to hydrochloric acid and 0.100 M with respect to MDD, was prepared by first dissolving 3.3045 g of MDD in 76.60 ml of 1.045 M hydrochloric acid and diluting to 250.0 ml. The acid concentration was standardized by stock sodium hydroxide solution.

This meant a quenched reaction mixture would be 0.100 M total concentration in α - and β -butadiene sulfones and alcohol, 0.050 M MDD, 0.150 M sodium chloride, and 0.010 M hydrochloric acid. The neutralization of base in the reaction mixture is therefore complete.

e. Standard Solutions for Preparing the Calibration Curves

These solutions were obtained by preparing seven solutions each of which contained the same amount of acid, salt, and internal standard as the quenched reaction mixtures. The total concentration of two sulfone isomers were 0.100 M. No alcohol was present in these standard solutions. The seven solutions contained 0, 10, 30, 50, 70, 90 and 100% of α -isomer and 100, 90, 70, 50, 30, 10 and 0% of β -isomer, respectively.

3. Apparatus

a. Constant Temperature Bath

The kinetic runs were made in a constant temperature bath made by Fisher Scientific Co. The bath was operated by a Fisher unitized bath control unit, and the temperature of water inside the bath was regulated automatically by a Fisher thermoregulator connected to the control unit. The temperature of each bath was adjusted so that the deviation from the set temperature was no more than ± 0.05 °C during any single kinetic run.

b. Gas Chromatographic Unit

The gas chromatograph used was the Aerograph "Moduline" Model 204, a dual-column instrument with an independent dual ionization detector. The instrument was made by Wilkens Instrument and Research, Inc., Walnut Creek, California. Several features are two differential-flow controllers and flowmeters, individual sample injector tubes, and separate detector and column ovens with proportional-temperature control of detector oven. For the gas chromatographic analysis of the samples collected from a kinetic run, only one of these dual systems was used, i. e., the instrument was used as a single column one.

Column: The column used was 1/8 in. OD stainless steel tubing and was coiled with a diameter of approximately 9 in. The length of the column which gave the best separation among each species of a

sample under the experimental conditions was 4 ft. and 4 in. including Swagelok fittings at both ends.

The packing material was 1.53 gm of 6.3% of Carbowax 1500 on Gas Chrom Z with mesh size 80/100. This was prepared by first making a slurry of the liquid phase and solid support in methylene chloride. The solvent was removed by evaporating this slurry under vacuum while stirring it by means of a Morton flask attached to a Roto-Vac evaporator. The slightly damp packing was then dried in an oven at 120 °C for six hours.

In loading the column an even packing is desirable so that the gas flow does not vary either across the column or irregularly along its length. Experience is needed to achieve even packing so as to obtain the best performance. A funnel is attached to one end of column by the 2 in. long Tyco tubing, and the other end plugged with silanized glass wool. A convenient method of filling is to apply suction to the appropriate end of the column while it is vibrated; the vibration is induced by the use of an electric massager. After the loading was finished, the funnel is removed and the silanized glass wool plugged into that end.

The column must be set in the oven at a temperature at least 5 °C higher than the regular experimental oven temperature with helium flow for 24 hours before it is ready for analytical use.

Detector: Three gas streams are required for operation of

flame-ionization detector: carrier gas, hydrogen, and air. When organic matter is burned in the hydrogen flame, electrons and negative ions are released and collected on the anode, thus producing an electrical current in proportion to the amount of matter burned. This current is amplified by an electrometer and applied to a strip-chart recorder for representation as a peak on a chart.

Injector: Sodium chloride was produced after the basic reaction mixture was quenched by the acid and since this salt would contaminate the injector port, cleaning requirements of the injector tube could be minimized if a glass-injector liner is used for flash vaporized injections. The liner also provides a nonreactive surface for components which might decompose.

The glass-injector liner must be cut in such a way that it can be inserted into injector tube as far as possible and with notch pointing upward. The silicone rubber septum which seals the injection port must be changed after each twenty injections in order to avoid the leak of vaporized sample through pierced holes.

Temperatures: The optimum temperature readouts of the instrument were 135, 240, and 175 °C for column oven, detector oven, and injector, respectively.

Carrier Gases and Flow Rates: The carrier gases, helium and hydrogen, used in this work were obtained from the Air Reduction Co.,

Bluefield, West Virginia. The gas pressure was regulated with a two stage pressure regulator and with the second stage set at 40 psi for helium and 32 psi for hydrogen. The column inlet pressure was controlled by a single input on-off valve and a differential flow controller with needle valve and flowmeter. Since a slight change in flow rate would give a considerable change in retention time and the peak shape, a constant flow rate was absolutely required. The helium flow rate was measured with a soap bubble flowmeter with the movement of the bubble being timed with a stop watch and it was found that a better chromatogram was obtained at a flow rate of 10 ml per 13 sec.

The constant air flow at 300 ml per minute was obtained from an Oscar' 66 Aerator made by the Oscar Co., Berkeley, California.

Syringe and Sample Size: A syringe with capacity 10.0 μ l and needle length 2 in. was used. This was obtained from the Hamilton Co., Inc., Whittier, California.

The sample size used for all injections was 1.4 μ l. This sample size with all previous experimental conditions gave the best separations among the three components, each of which appeared with a nice peak shape on the chromatogram.

Recorder: The recorder used for the chromatographic measurements was a potentiometric, 1-millivolt full scale, floating input Model SR recorder made by E. H. Sargent & Co., Chicago, Illinois. The

chart speed was set at medium and corresponding to 1 in. per minute.

c. Digital Computer

Since it would involve a very tedious mathematical operation to integrate the system of three linear simultaneous equations as well as to plot the concentration-time curve of each component from the integrated equation, the IBM 7040 computer was used to obtain the concentration-time data from the experimentally obtained rate constants and the initial condition (see Appendix, page 88).

4. Kinetic Measurements

All measurements of rates were made in a constant temperature bath. The rates were measured at three different temperatures, 35, 45, 55 °C.

For each set of kinetic runs, the sulfone solution was pipeted into a 25-ml Bantam-Ware pear-shaped flask. This flask was used so that most of the sample could be withdrawn from the reaction mixture. Sodium hydroxide solution was then added at the same temperature as that of sulfone solution. Since the reaction was rather slow, instantaneous mixing was not necessary. One milliliter of reaction mixture was withdrawn at a specific time and the reaction was quenched in a test tube which already contained the same amount of acid-internal standard solution. Generally, for the reaction at higher temperature, shorter time intervals were required to collect the sample. The quenched

samples were used directly for gas chromatographic analysis.

5. Chromatograms

The retention times are 1.5, 2.3, and 4 minutes for the β -isomer, the internal standard, and α -isomer, respectively. The separations occurred according to the differences in polarities among the liquid phase and the three components in the sample.

A slight decomposition of the β -isomer on the column was observed. However, this was immaterial since the effect of this decomposition is internally cancelled during the course of calculations.

a. Quantitative Measurements

Two ways of determining peak area were tested: by mechanical integration and by the triangle area method. The integrator used was Model 204 Disc Integrator made by the Disc Instruments, Inc., Santa Ana, California. It was found out that it was difficult to determine the "null point" where the integrator pen would stop and then reverse its direction. As the result, the reproducibility of the ratio of peak areas by this method was poor. The second method was to draw tangents to each side of the peak so as to form a triangle with the base line; the area of this triangle is approximately proportional to the area of the peak. Even though the point of intersection was rather difficult to locate accurately for sharp peaks, the reproducibility of this method was much better than the first one. For all the peak area measurements described

hereafter, the triangle area method was used.

b. Effect of Sensitivity of Instrument

Occasionally, because of the contamination of the detector and/or the drift of the air flow, the response of the detector diminished gradually. It was found even when the sensitivity of the instrument decreased or it changed from its regular position, i.e. $10^2 \times 4$, the ratio of peak areas would not change. To minimize this effect, air flow was checked at least once a day and the detector was cleaned regularly.

c. Standard Chromatograms and Calibration Curves

These chromatograms were obtained by injecting the standard solutions (see section IV-B-2-e) directly in the gas chromatography. Each solution was injected twice. The calibration curves were obtained by plotting the average value of the ratio of peak area of each isomer to that of standard, (A_i/A_s) , against the corresponding ratio of concentrations, (C_i/C_s) . The data are shown in Table VI and Figure 1 where the subscripts $i=1$ and $i=2$ represent the β -isomer and α -isomer, respectively.

TABLE VI
Gas Chromatographic Calibration Data

Sample No.	(C_1/C_s)	(C_2/C_s)	(A_1/A_s) ± 0.008	(A_2/A_s) ± 0.006
1	2.00	0.000	1.48	0.000
2	1.80	0.200	1.30	0.135
3	1.60	0.400	1.13	0.307
4	1.40	0.600	0.963	0.468
5	1.20	0.800	0.808	0.627
6	1.00	1.00	0.673	0.748
7	0.800	1.20	0.540	0.911
8	0.600	1.40	0.407	1.06
9	0.400	1.60	0.266	1.21
10	0.200	1.80	0.123	1.38
11	0.000	2.00	0.000	1.53

To calculate the actual concentration of either isomer, C_i , inside the reaction mixture, the concentration read from the calibration curve should be multiplied by a factor of 2 since the sample withdrawn from the reaction mixture was diluted after it was quenched by the same amount of acid-internal standard solution. This relation can be represented by the following formula:

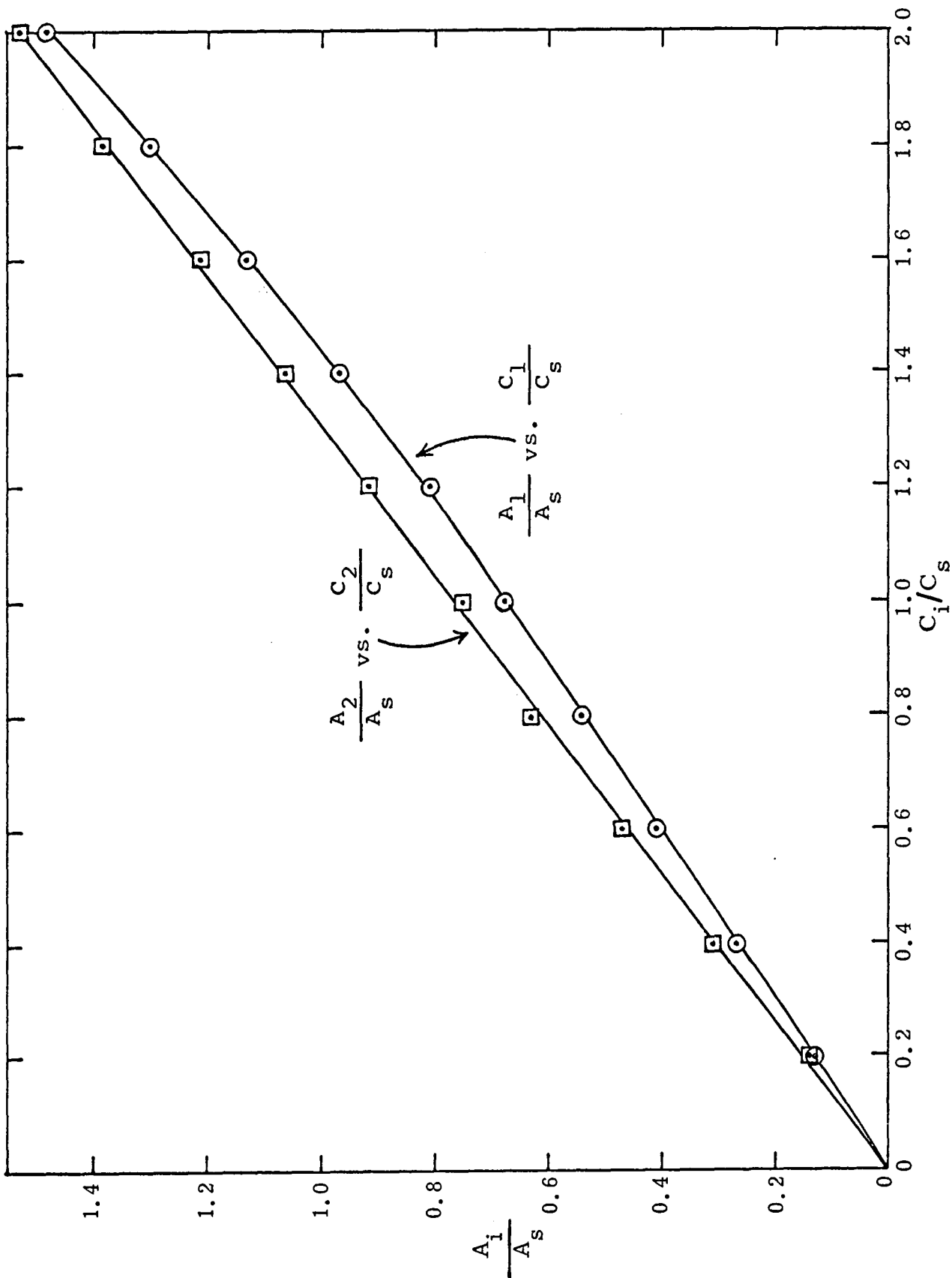


Figure 1. Calibration curves

$$C_i = \left(\frac{C_i}{C_s} \right)_{gc} \times C_s \times 2 \quad (IV-1)$$

where $(C_i/C_s)_{gc}$ is the ratio of the concentration of α - or β -isomer to that of internal standard of the quenched reaction mixture and is read directly from the calibration curve after the gas chromatographic analysis of this mixture. Since $C_s = 0.05 \underline{M}$ (see section IV-B-2-d), equation (IV-1) can be simplified as

$$C_i = \left(\frac{C_i}{C_s} \right)_{gc} \times 0.1 \quad (IV-2)$$

d. Chromatograms of Samples from Kinetic Run

All the samples which came from reaction mixture starting from the pure isomers were analyzed twice. There was a special combination of two isomers in which the ratio of two concentrations would not change as the reaction proceeded (see section V-A). The sample from this reaction mixture was also analyzed twice. All the samples that came from the other reaction mixtures were analyzed only once.

A typical chromatogram for a kinetic run starting with pure β -isomer at 45 °C is shown in Figure 2. As the reaction proceeds, the peak area of the β -isomer decreases and that of the α -isomer goes to maximum and then decreases. However, the peak areas of the internal standard are the same for all injections.

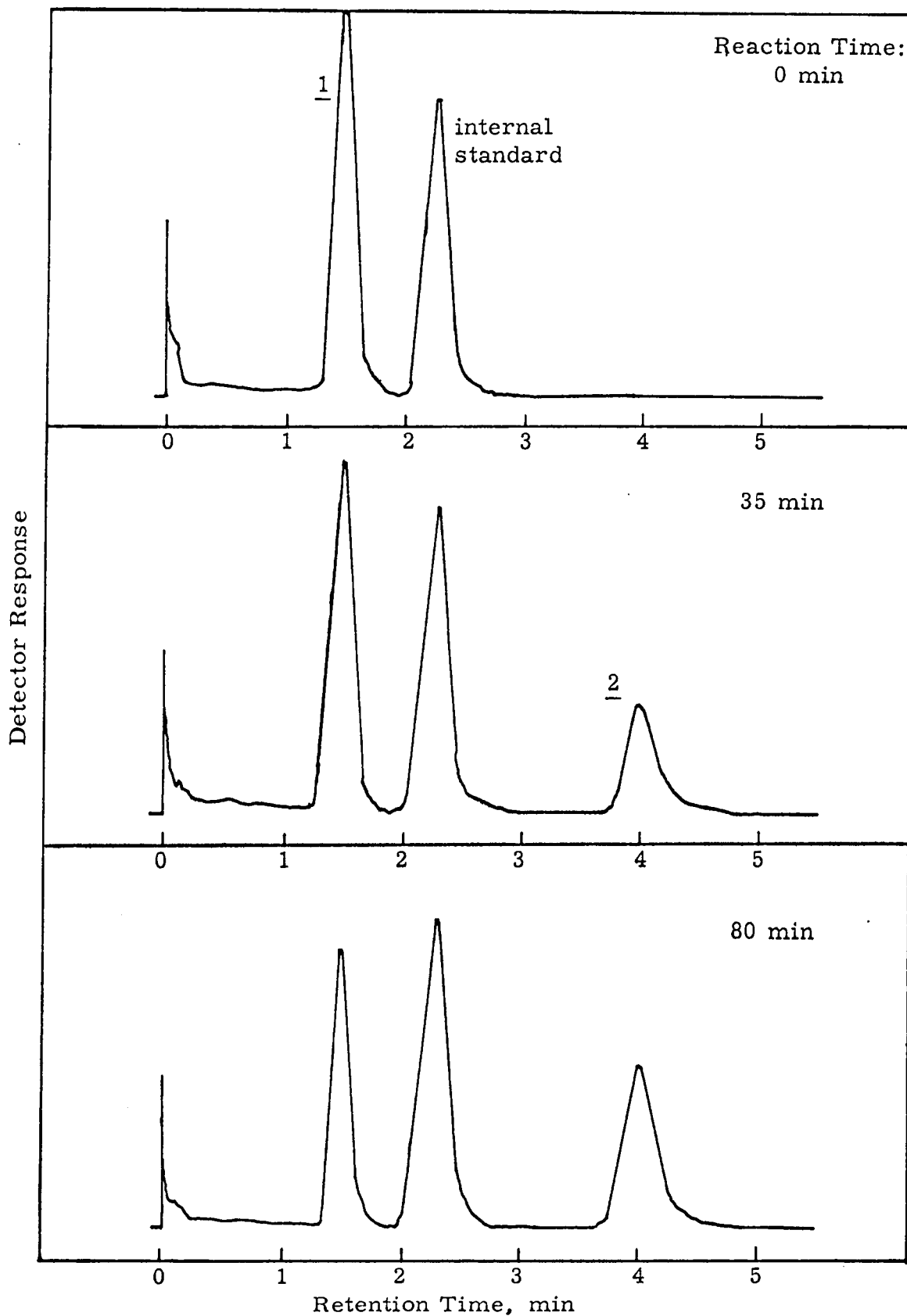


Figure 2. A typical chromatogram for a reaction mixture obtained from the reaction starting with pure β -butadiene sulfone

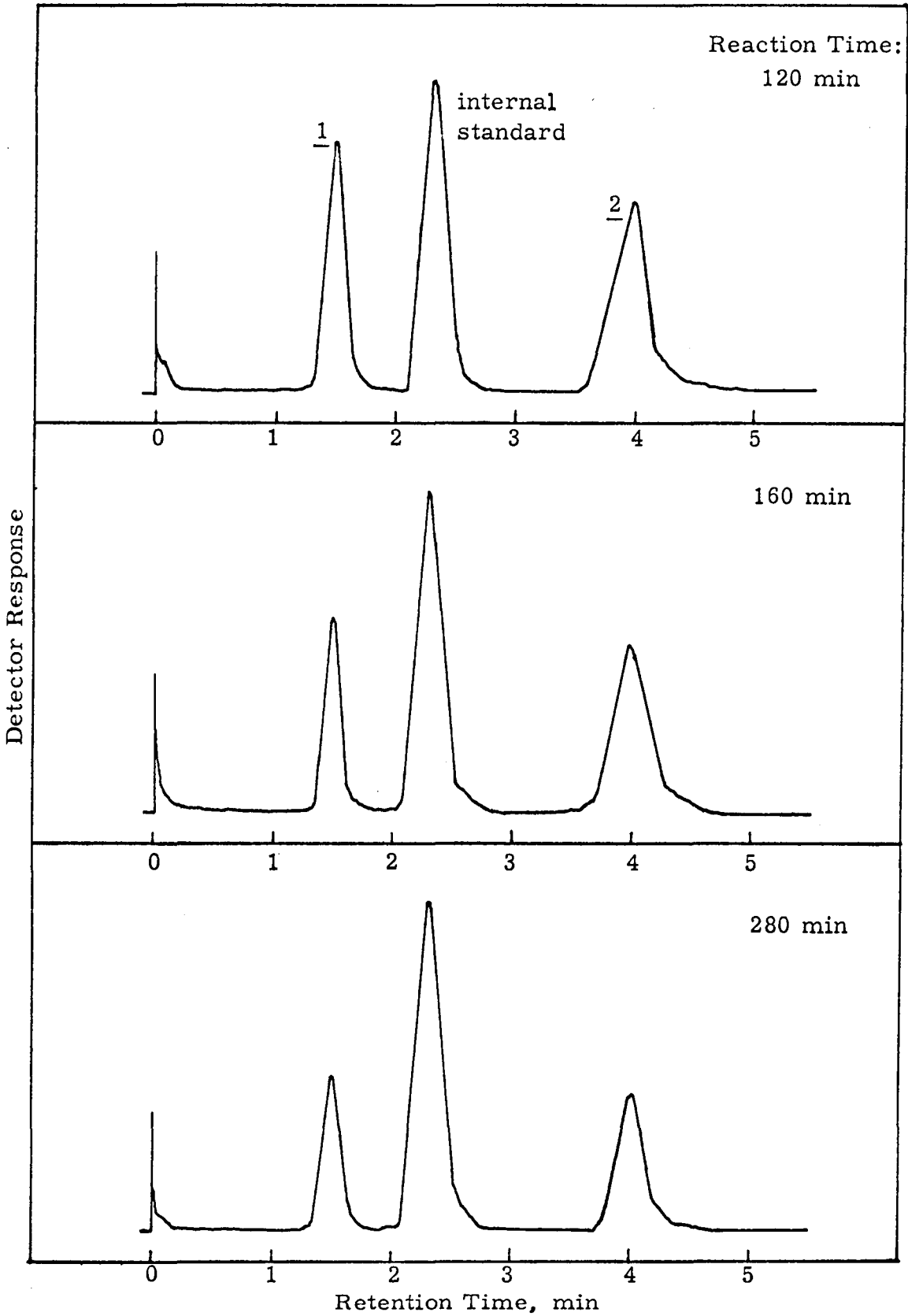


Figure 2. (continued)

V. DATA AND RESULTS

The concentrations of the α - and β -isomers calculated from the method described in section IV-B-5-c are tabulated in Table VII, where (A_1/A_s) and (A_2/A_s) represent the ratio of peak areas of the β -isomer and the α -isomer to the peak area of the standard, respectively, and C_1 is the molar concentration of the β -isomer while C_2 is the molar concentration of the α -isomer at the specific temperature and time. The concentration of alcohol, C_3 , which is not shown in the Table, can be obtained simply by subtracting the sum of C_1 and C_2 from the total initial concentration, which is 0.200 M in all kinetic runs.

A. KINETIC PLOT

Three types of the kinetic plots will be given as follows:

1. Concentration-Time Curve

The most common plot is the plot of the actual concentration of each component versus time on Cartesian coordinates. The experimental concentration-time data obtained from five different initial compositions at 45°C were marked according to these coordinates in Figure 3. The curves were drawn through the calculated concentration-time data which will be discussed in sections V-B-2-c and VIII-C. It should be noted that the concentration-time curves for the reactions starting with the pure isomer were plotted in the same graph (Figure 3-1) for the convenience of comparison.

TABLE VII

Tables of Experimental Data

TABLE VII-1

Run No. 24 Temp. 35 °C Initial Conc.: $C_1^0 = \underline{0.200} \underline{M}$
 $C_2^0 = \underline{0} \underline{M}$

Sample No.	t, Min.	(A_1/A_s) ± 0.002	C_1, \underline{M}	(A_2/A_s) ± 0.002	C_2, \underline{M}	C_1/C_2
1	60	1.11	0.158	0.248	0.0374	4.22
2	120	0.946	0.137	0.401	0.0522	2.63
3	180	0.792	0.116	0.517	0.0675	1.72
4	260	0.652	0.0968	0.575	0.0751	1.29
5	340	0.566	0.0842	0.602	0.0790	1.06
6	400	0.503	0.0750	0.601	0.0794	0.945
7	460	0.460	0.0685	0.595	0.0778	0.881
8	520	0.426	0.0636	0.564	0.0736	0.865
9	640	0.391	0.0570	0.513	0.0670	0.850
10	760	0.325	0.0488	0.455	0.0580	0.842

TABLE VII-2

Run No. 30 Temp. 35 °C Initial Conc.: $C_1^0 = \underline{0.088} \underline{M}$
 $C_2^0 = \underline{0.112} \underline{M}$

Sample No.	t, Min.	(A_1/A_s) ± 0.002	C_1, \underline{M}	(A_2/A_s) ± 0.002	C_2, \underline{M}	C_1/C_2
1	60	0.541	0.0801	0.780	0.102	0.785
2	70	0.492	0.733	0.935	0.0935	0.784
3	180	0.462	0.0680	0.880	0.0880	0.773
4	240	0.429	0.0640	0.815	0.0815	0.785
5	300	0.399	0.0595	0.755	0.0755	0.788
6	360	0.364	0.0545	0.680	0.0682	0.798
7	635	0.288	0.0435	0.544	0.0544	0.798
8	810	0.248	0.0374	0.477	0.0477	0.784
9	930	0.201	0.0305	0.380	0.0380	0.803

TABLE VII-3

Run No. 23 Temp. 35 °C Initial Conc.: $C_1^0 = \underline{0} \text{ M}$
 $C_2^0 = \underline{0.200} \text{ M}$

Sample No.	t, Min.	(A_1/A_s) ± 0.002	$C_1, \text{ M}$	(A_2/A_s) ± 0.003	$C_2, \text{ M}$	C_1/C_2
1	60	0.142	0.0220	1.21	0.159	0.138
2	120	0.229	0.0349	1.04	0.136	0.256
3	182	0.281	0.0430	0.872	0.114	0.377
4	260	0.317	0.0475	0.749	0.0968	0.490
5	340	0.326	0.0490	0.631	0.0830	0.591
6	400	0.325	0.0486	0.575	0.0751	0.647
7	460	0.320	0.0480	0.524	0.0684	0.702
8	520	0.312	0.0468	0.489	0.0635	0.738
9	640	0.282	0.0423	0.428	0.0558	0.768
10	760	0.248	0.0375	0.370	0.0480	0.782

TABLE VII-4

Run No. 12 Temp. 45 °C Initial Conc.: $C_1^0 = \underline{0.200} \text{ M}$
 $C_2^0 = \underline{0} \text{ M}$

Sample No.	t, Min.	(A_1/A_s) ± 0.002	$C_1, \text{ M}$	(A_2/A_s) ± 0.002	$C_2, \text{ M}$	C_1/C_2
1	10	1.32	0.182	0.130	0.0167	10.9
2	20	1.12	0.165	0.258	0.0330	4.98
3	35	0.996	0.144	0.383	0.0500	2.87
4	55	0.832	0.123	0.503	0.0660	0.86
5	80	0.701	0.102	0.582	0.0760	1.34
6	100	0.607	0.0900	0.616	0.0805	1.12
7	120	0.555	0.0825	0.625	0.0815	1.01
8	140	0.498	0.0740	0.614	0.0803	0.922
9	160	0.469	0.0680	0.598	0.0780	0.872
10	220	0.374	0.0560	0.531	0.0692	0.810
11	280	0.302	0.0454	0.453	0.0590	0.770

TABLE VII-5

Run No. 14 Temp. 45 °C Initial Conc.: $C_1^0 = \underline{0.160 \text{ M}}$
 $C_2^0 = \underline{0.040 \text{ M}}$

Sample No.	t, Min.	(A ₁ /A _s)	C ₁ , <u>M</u>	(A ₂ /A _s)	C ₂ , <u>M</u>	C ₁ /C ₂
1	10	1.05	0.150	0.376	0.0480	3.13
2	20	0.952	0.138	0.376	0.0480	2.81
3	35	0.868	0.127	0.510	0.0665	1.91
4	55	0.746	0.113	0.590	0.0760	1.48
5	80	0.648	0.0960	0.620	0.0810	1.19
6	100	0.572	0.0850	0.641	0.0836	1.02
7	120	0.500	0.0745	0.614	0.0804	0.927
8	140	0.463	0.0692	0.606	0.0795	0.870
9	160	0.413	0.0616	0.571	0.0742	0.830
10	220	0.335	0.0503	0.489	0.0635	0.793
11	280	0.269	0.0405	0.405	0.0527	0.769

TABLE VII-6

Run No. 16 Temp. 45 °C Initial Conc.: $C_1^0 = \underline{0.110 \text{ M}}$
 $C_2^0 = \underline{0.090 \text{ M}}$

Sample No.	t, Min.	(A ₁ /A _s)	C ₁ , <u>M</u>	(A ₂ /A _s)	C ₂ , <u>M</u>	C ₁ /C ₂
1	10	0.714	0.106	0.698	0.0912	1.16
2	20	0.661	0.0978	0.706	0.0925	1.06
3	40	0.608	0.0901	0.704	0.0922	0.977
4	60	0.541	0.0791	0.678	0.0888	0.892
5	95	0.453	0.0678	0.623	0.0835	0.812
6	130	0.416	0.0620	0.593	0.0773	0.803
7	181	0.344	0.0517	0.506	0.0660	0.783
8	220	0.304	0.0458	0.452	0.0590	0.777
9	280	0.251	0.0380	0.385	0.0501	0.759

TABLE VII-7

Run No. 18 Temp. 45 °C Initial Conc.: $C_1^0 = \underline{0.086} \underline{M}$
 $C_2^0 = \underline{0.114} \underline{M}$

Sample No.	t, Min.	(A_1/A_s) +0.003 -0.003	C_1, \underline{M}	(A_2/A_s) +0.004 -0.004	C_2, \underline{M}	C_1/C_2
1	10	0.557	0.0826	0.838	0.110	0.754
2	30	0.518	0.0769	0.789	0.103	0.745
3	60	0.469	0.0700	0.702	0.0920	0.761
4	95	0.423	0.0633	0.656	0.0856	0.740
5	130	0.393	0.0585	0.584	0.0764	0.766
6	180	0.341	0.0510	0.514	0.0672	0.759
7	230	0.306	0.0460	0.466	0.0606	0.759
8	280	0.272	0.0412	0.423	0.0556	0.740

TABLE VII-8

Run No. 17 Temp. 45 °C Initial Conc.: $C_1^0 = \underline{0.060} \underline{M}$
 $C_2^0 = \underline{0.140} \underline{M}$

Sample No.	t, Min.	(A_1/A_s)	C_1, \underline{M}	(A_2/A_s)	C_2, \underline{M}	C_1/C_2
1	10	0.420	0.0628	0.950	0.124	0.506
2	20	0.419	0.0626	0.871	0.114	0.549
3	40	0.413	0.0616	0.773	0.101	0.609
4	60	0.403	0.0603	0.708	0.0926	0.651
5	95	0.378	0.0564	0.620	0.0810	0.696
6	130	0.351	0.0526	0.537	0.0700	0.752
7	181	0.304	0.0458	0.471	0.0611	0.750
8	220	0.270	0.0410	0.408	0.0530	0.773
9	280	0.225	0.0345	0.345	0.0450	0.767

TABLE VII-9

Run No. 15 Temp. 45 °C Initial Conc.: $C_1^0 = \underline{0.030} \underline{M}$
 $C_2^0 = \underline{0.170} \underline{M}$

Sample No.	t, Min.	(A_1/A_s)	C_1, \underline{M}	(A_2/A_s)	C_2, \underline{M}	C_1/C_2
1	10	0.241	0.0380	1.19	0.156	0.244
2	20	0.289	0.0435	1.09	0.142	0.306
3	35	0.301	0.0452	1.04	0.137	0.330
4	55	0.345	0.0518	0.820	0.107	0.484
5	80	0.352	0.0530	0.719	0.0940	0.566
6	100	0.357	0.0532	0.613	0.0801	0.664
7	120	0.347	0.0510	0.560	0.0730	0.699
8	140	0.333	0.500	0.513	0.0670	0.744
9	160	0.310	0.0465	0.478	0.0621	0.749
10	220	0.271	0.0410	0.408	0.0530	0.773
11	280	0.220	0.0335	0.344	0.0447	0.749

TABLE VII-10

Run No. 13 Temp. 45 °C Initial Conc.: $C_1^0 = \underline{0} \underline{M}$
 $C_2^0 = \underline{0.200} \underline{M}$

Sample No.	t, Min.	(A_1/A_s) +0.003	C_1, \underline{M}	(A_2/A_s) +0.005	C_2, \underline{M}	C_1/C_2
1	10	0.0711	0.0111	1.39	0.182	0.0612
2	20	0.135	0.0211	1.24	0.162	0.130
3	35	0.210	0.0322	1.08	0.142	0.227
4	55	0.281	0.0425	0.899	0.118	0.361
5	80	0.307	0.0462	0.755	0.102	0.455
6	100	0.326	0.0490	0.697	0.0913	0.537
7	120	0.335	0.0501	0.628	0.0820	0.611
8	140	0.331	0.0498	0.573	0.0750	0.665
9	160	0.325	0.0490	0.533	0.0698	0.702
10	220	0.279	0.0420	0.421	0.0550	0.763
11	280	0.225	0.0345	0.351	0.0457	0.755

TABLE VII-11

Run No. 20 Temp. 55 °C Initial Conc.: $C_1^0 = \underline{0.200} \underline{M}$
 $C_2^0 = \underline{0} \underline{M}$

Sample No.	t, Min.	(A_1/A_s) ±0.002	C_1, \underline{M}	(A_2/A_s) ±0.001	C_2, \underline{M}	C_1/C_2
1	10	1.06	0.152	0.319	0.0411	3.70
2	20	0.802	0.117	0.509	0.0662	1.77
3	35	0.609	0.0902	0.607	0.0795	1.13
4	55	0.470	0.0700	0.603	0.0790	0.885
5	75	0.398	0.0594	0.545	0.0712	0.835
6	95	0.340	0.0508	0.476	0.0620	0.820
7	115	0.283	0.0428	0.411	0.0535	0.800
8	140	0.238	0.0360	0.349	0.0452	0.797
9	165	0.199	0.0304	0.297	0.0382	0.796

TABLE VII-12

Run No. 28 Temp. 55 °C Initial Conc.: $C_1^0 = \underline{0.0876} \underline{M}$
 $C_2^0 = \underline{0.1124} \underline{M}$

Sample No.	t, Min.	(A_1/A_s) ±0.002	C_1, \underline{M}	(A_2/A_s) ±0.003	C_2, \underline{M}	C_1/C_2
1	10	0.526	0.0785	0.772	0.101	0.777
2	25	0.466	0.0696	0.687	0.0898	0.775
3	45	0.409	0.0608	0.598	0.0780	0.780
4	65	0.356	0.0532	0.521	0.0680	0.782
5	90	0.308	0.0461	0.559	0.0598	0.771
6	120	0.249	0.0376	0.363	0.0471	0.798
7	153	0.207	0.0318	0.303	0.0393	0.809
8	180	0.169	0.0256	0.258	0.0332	0.772

TABLE VII-13

Run No. 27 Temp. 55 °C Initial Conc.: $C_1^0 = \underline{0.060} \underline{M}$
 $C_2^0 = \underline{0.140} \underline{M}$

Sample No.	t, Min.	(A_1/A_s)	C_1, \underline{M}	(A_2/A_s)	C_2, \underline{M}	C_1/C_2
1	5	0.418	0.0624	0.965	0.127	0.493
2	15	0.428	0.0640	0.853	0.112	0.572
3	25	0.419	0.0625	0.723	0.0947	0.660
4	45	0.391	0.0582	0.630	0.0822	0.707
5	65	0.352	0.0530	0.542	0.0708	0.748
6	90	0.282	0.0436	0.443	0.0578	0.754
7	120	0.238	0.0362	0.355	0.0462	0.783
8	150	0.193	0.0296	0.292	0.0378	0.783
9	180	0.153	0.0236	0.235	0.0302	0.782

TABLE VII-14

Run No. 19 Temp. 55 °C Initial Conc.: $C_1^0 = \underline{0} \underline{M}$
 $C_2^0 = \underline{0.200} \underline{M}$

Sample No.	t, Min.	(A_1/A_s) + -0.002	C_1, \underline{M}	(A_1/A_s) + -0.002	C_2, \underline{M}	C_1/C_2
1	5	0.119	0.0184	1.308	0.172	0.107
2	22	0.294	0.0444	0.865	0.113	0.392
3	35	0.325	0.0490	0.683	0.0894	0.548
4	55	0.324	0.0485	0.540	0.0702	0.691
5	75	0.288	0.0435	0.447	0.0582	0.748
6	95	0.254	0.0385	0.386	0.0502	0.767
7	115	0.221	0.0336	0.326	0.0422	0.797
8	140	0.184	0.0282	0.279	0.0360	0.784
9	165	0.154	0.0238	0.233	0.0302	0.788

Figure 3. The Concentration-Time Curves at 45 °C

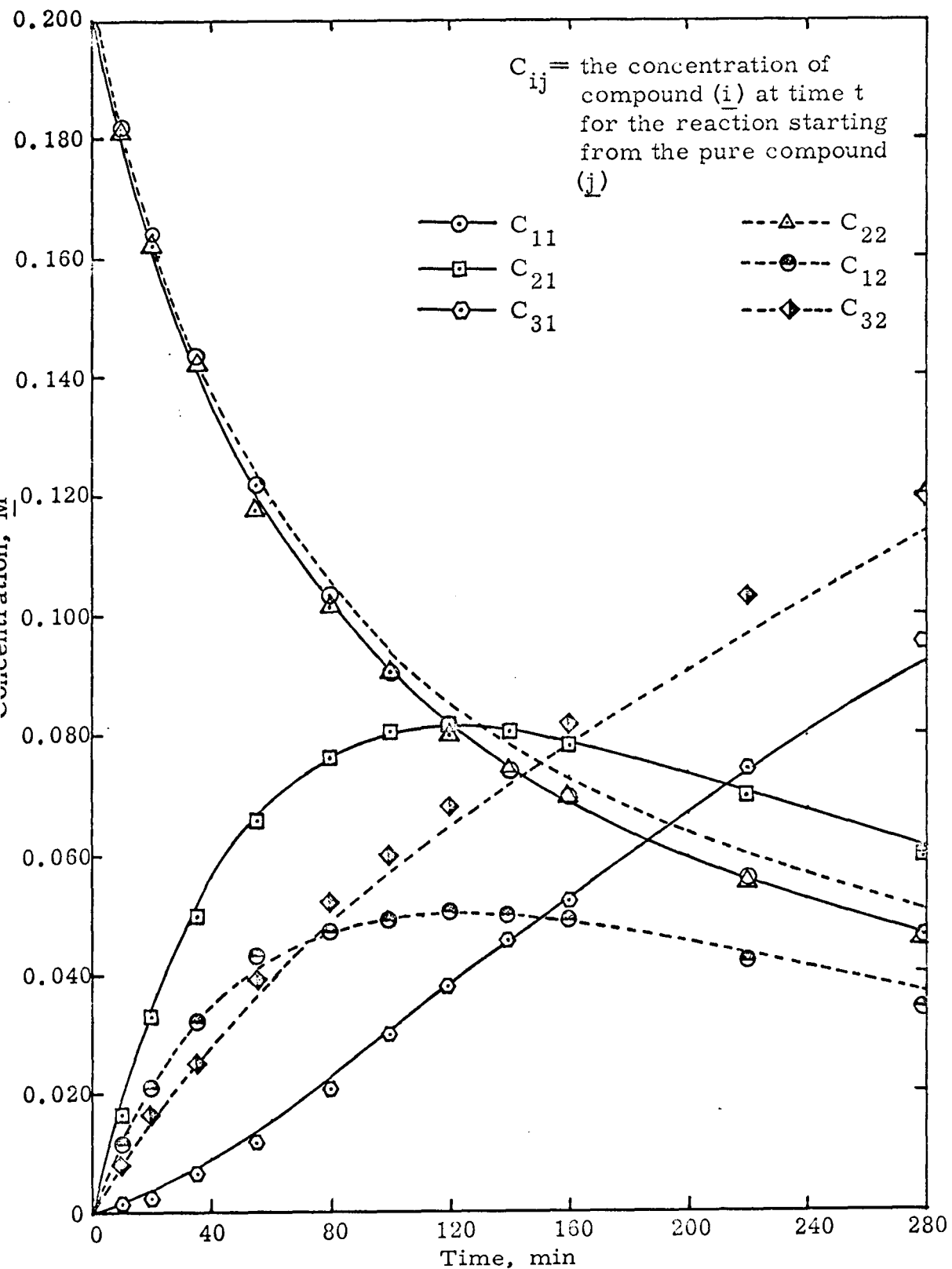


Figure 3-1. The concentration-time curves for the reactions starting from the pure β -butadiene sulfone (1) and the pure α -butadiene sulfone (2)

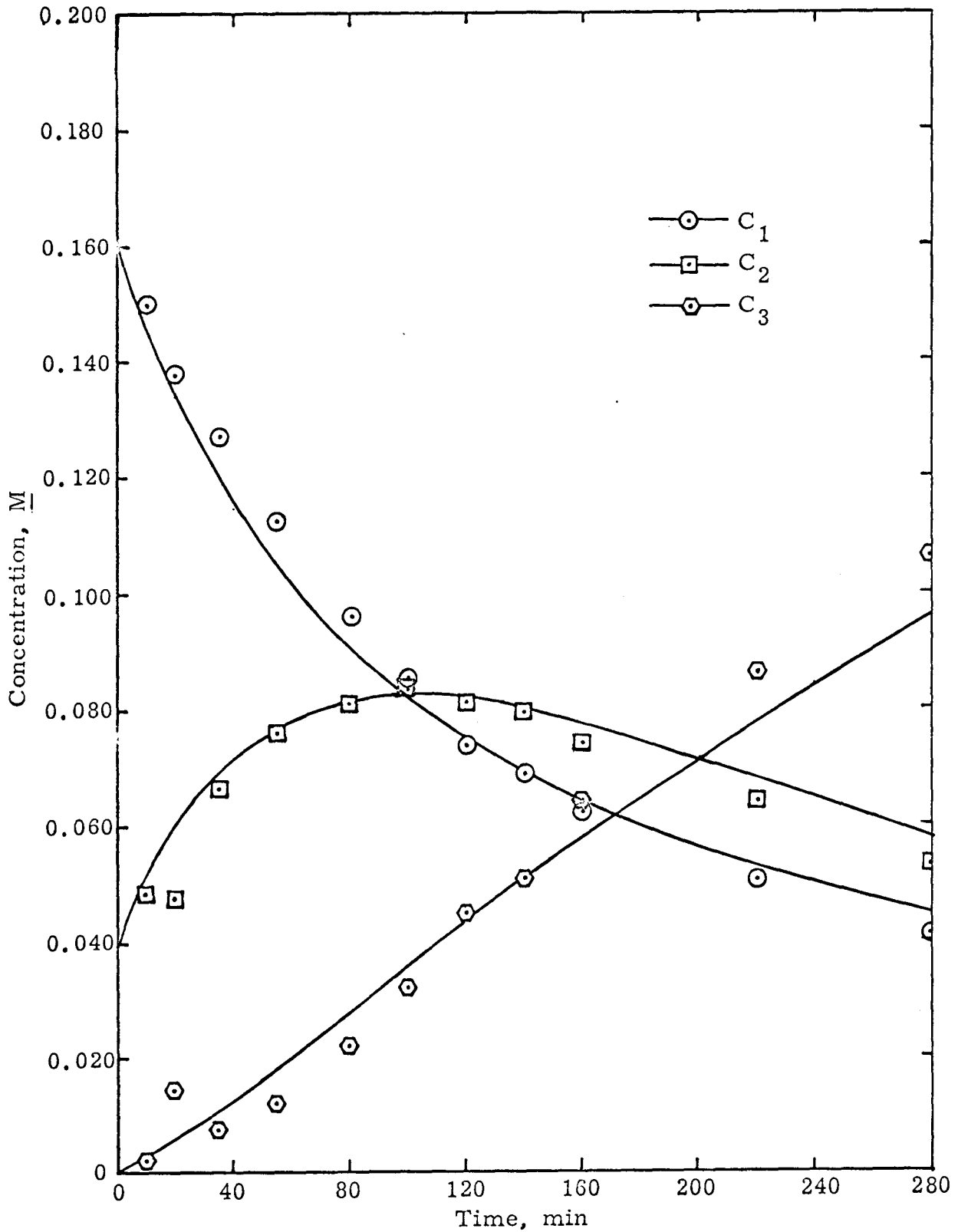


Figure 3-2. The concentration-time curves for the reaction starting from 0.160 M β -butadiene sulfone (1) and 0.040 M α -butadiene sulfone (2)

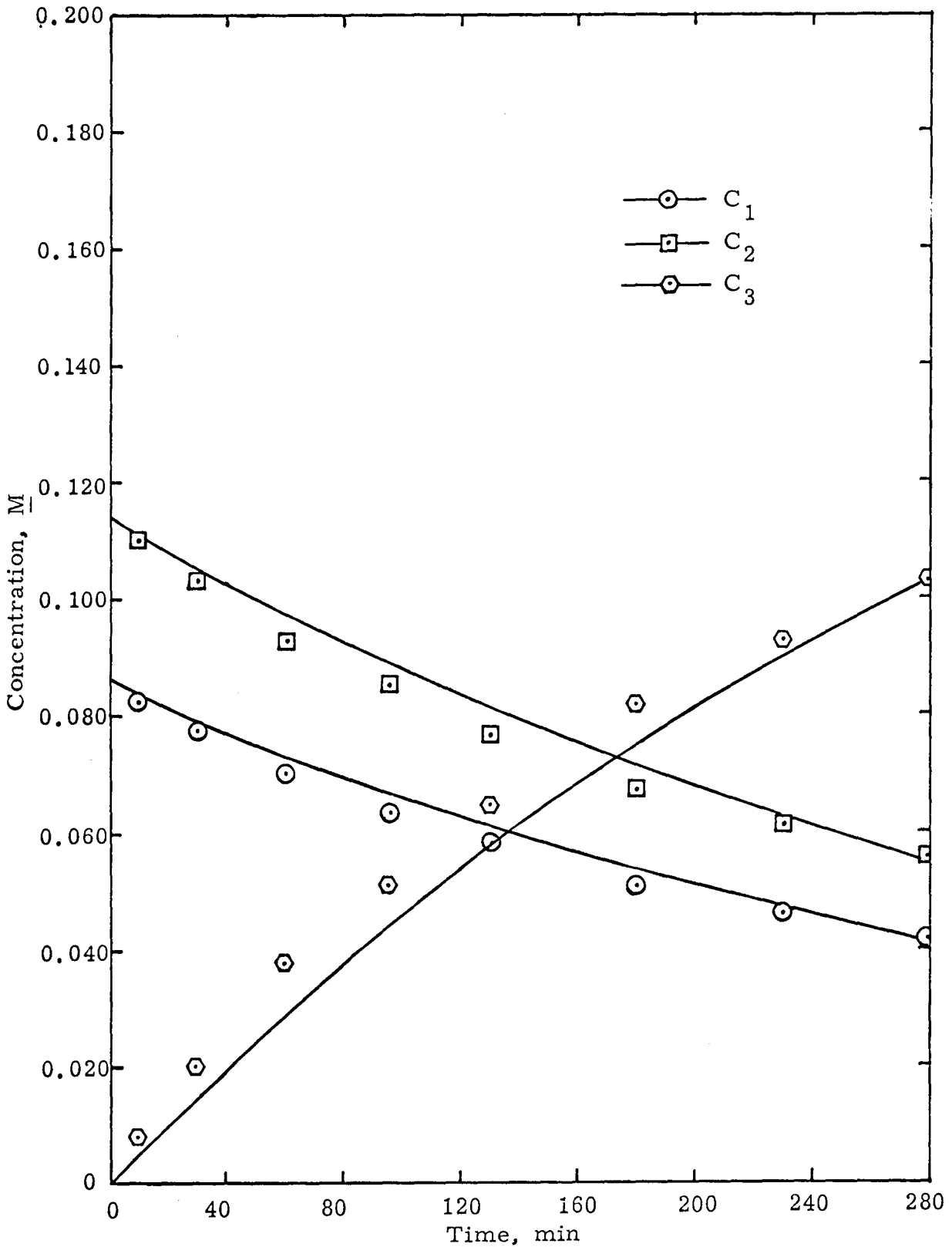


Figure 3-3. The concentration-time curves for the reaction starting from 0.086 M β -butadiene sulfone (1) and 0.114 M α -butadiene sulfone (2)

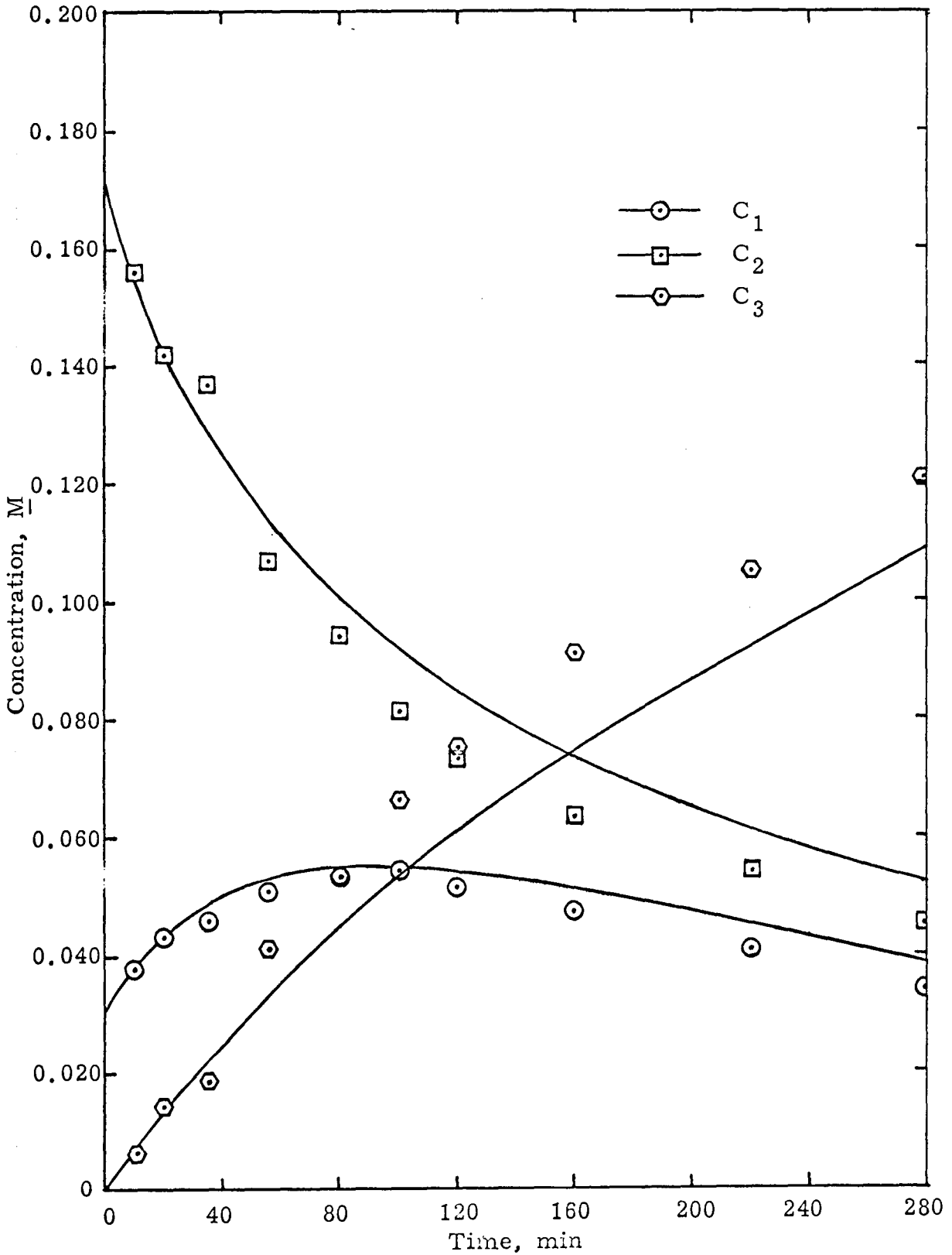


Figure 3-4. The concentration-time curves for the reaction starting from 0.030 M β -butadiene sulfone (1) and 0.170 M α -butadiene sulfone (2)

2. Reaction Triangle

It is possible to describe this three-component system, as shown in Figure 4, on a triangular diagram analogous to a phase diagram of a ternary system. The term "reaction triangle" was first named by Wei and Prater.³¹ It is also called the "reaction simplex."

There are two constraints on this reaction system inside the reaction triangle: (i) the total mass of the reaction system is conserved; and (ii) no negative amounts can arise. It will be convenient to describe the amount of each of these three species in terms of the mole fraction, a_i , so that the condition (i) is given by

$$a_1 + a_2 + a_3 = 1 \quad (\text{V-1})$$

and the condition (ii) is given by

$$a_i \geq 0 \quad (\text{V-2})$$

As the reaction proceeds, the composition point moves along the reaction plane towards pure alcohol and the ratio of the mole fraction of the β -isomer to that of the α -isomer converges to the equilibrium ratio. The five curves corresponding to the five sets of concentration-time curves in Figure 3 are shown in Figure 4. Thus, each curve (reaction path) that the composition point traces out as it goes to alcohol is sufficient to describe the composition change during the course of the reaction. All the curves were also drawn according to the calculated mole fractions. It can be seen from Figure 4 that there is a special

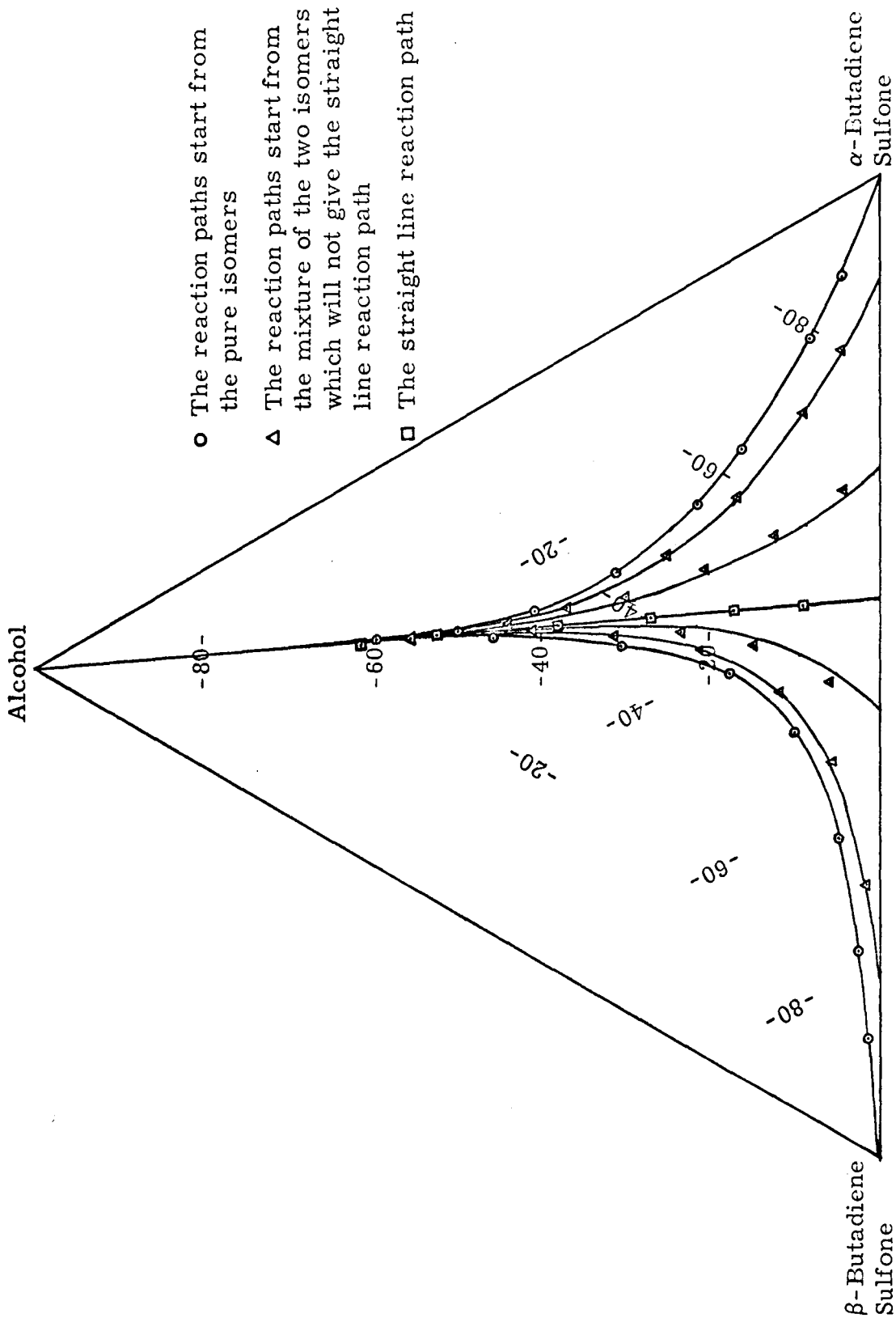


Figure 4. The reaction triangle

straight line reaction path along which the concentration ratio of the β -to α -isomer remains constant throughout the reaction. This was obtained experimentally by extrapolating the approximately straight line portion of the reaction paths near the alcohol vertex back to the opposite side of the reaction triangle.

3. Convergence of the Reaction Paths

The value of the initial concentration of the two isomers which gives the straight line reaction path plays an important role in the calculation of rate constants. Moreover, the ratio of these two concentrations is equal to the corresponding ratio in all reaction mixtures at infinite time.

Bunnett,⁴² in his discussion of the interpretation of rate data, has pointed out that in first-order kinetics the rate constant is most commonly reckoned from the slope of $\log (r_{\infty} - r)$ versus time where r is some property of the system linearly dependent on the extent of the reaction. This practice depends vitally on the accuracy of the infinity value, r_{∞} , which must therefore be determined with care. Sometimes the infinity value drifts with time owing to chemical or physical changes in the infinity solution.

In order to test the accuracy of this infinity value, an alternate plot of the reaction paths at 45 °C is shown in Figure 5. It shows the plots of C_1/C_2 converge to limit values in good agreement with the

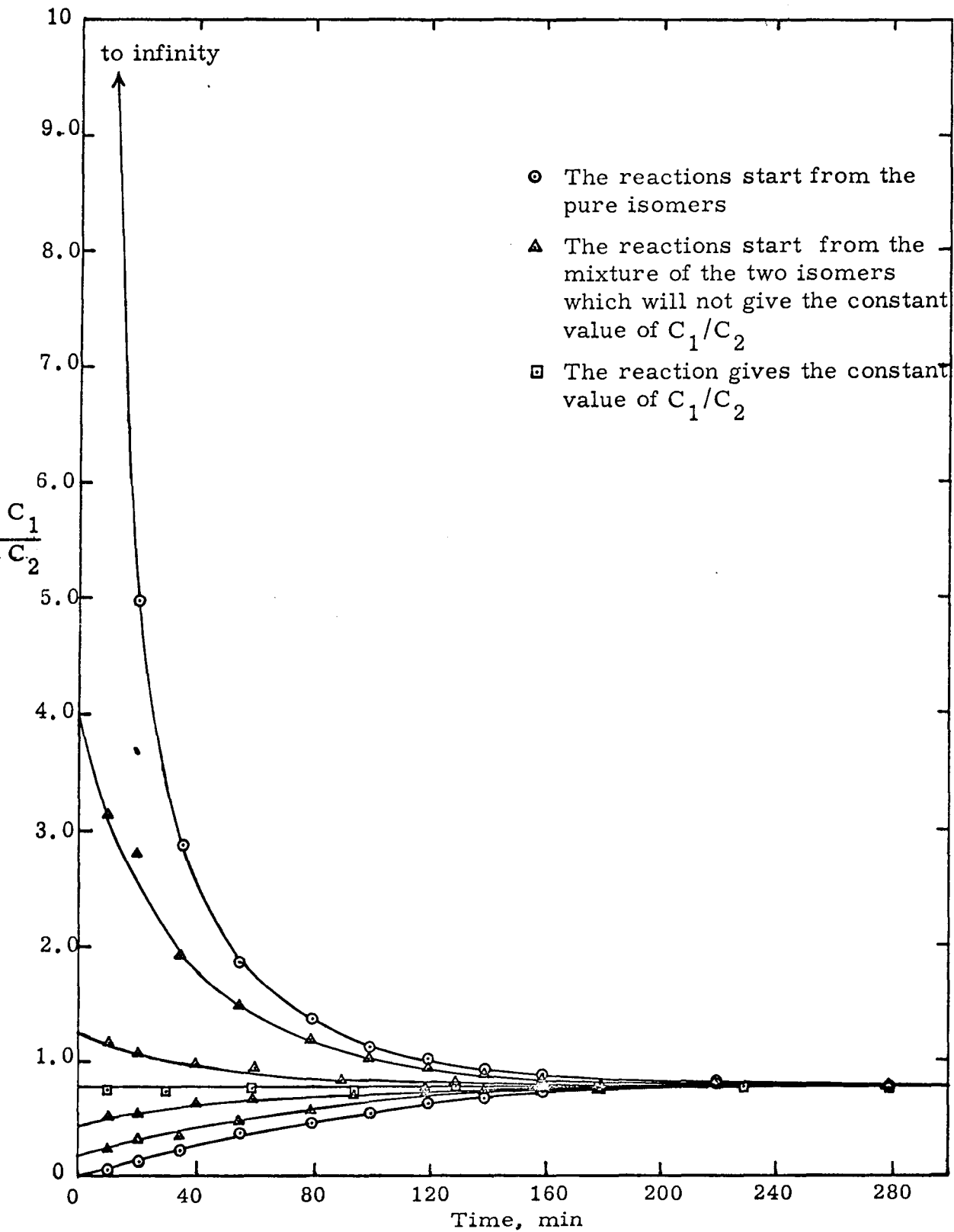


Figure 5. The convergence of C_1/C_2 from different initial compositions

straight line reaction path concentration ratio. Table VIII gives the initial composition of the straight line reaction path as well as the experimental limit value of C_1/C_2 at various temperatures.

TABLE VIII

Table of the Initial Composition of the Straight Line Reaction Path and the Limit Value of C_1/C_2

Temp. °C	Initial Mole Percent composition of straight line reaction path		C_1/C_2	
	α -isomer (100 a_1)	β -isomer (100 a_2)	Initial value for straight line reaction path	Limit value
35	56.0	44.0	0.787	0.787
45	57.0	43.0	0.758	0.758
55	56.3	43.7	0.780	0.780

B. CALCULATION OF RATE CONSTANT

1. Relative Rate Constants

a. Direct Calculation

The mathematical analysis of reaction system (I-1) is provided in the Appendix (page 80) from which one can see that the relative rate constants α , β and γ can be calculated from the equations (VIII-29), VIII-34), and VIII-35) once the concentrations of two isomers at the time of maximum conversion of a pure isomer to the other one are

known,

$$\alpha = \frac{k_{21}}{k_{12}} = \frac{\bar{C}_{12}}{\bar{C}_{21}} \quad (\text{VIII-29})$$

$$\beta = \frac{k_{23}}{k_{12}} = \frac{\bar{C}_{11} - \bar{C}_{12}}{\bar{C}_{21}} \quad (\text{VIII-34})$$

$$\gamma = \frac{k_{13}}{k_{12}} = \frac{\bar{C}_{22} - \bar{C}_{21}}{\bar{C}_{21}} \quad (\text{VIII-35})$$

where C_{ij} is the concentration of species i starting with species j and where the bar indicates the value at \bar{t} , the time of maximum conversion of one isomer to the other. Table IX lists the relative rate constant calculated by this method.

TABLE IX

Relative Rate Constants Obtained by Direct Calculations

Temp. °C	$\bar{C}_{12}, \underline{M}$	$\bar{C}_{21}, \underline{M}$	$\bar{C}_{11}, \underline{M}$	$\bar{C}_{22}, \underline{M}$	$\bar{t}, \text{Min.}$
35	0.0496	0.0798	0.0798	0.0799	350
45	0.0501	0.0815	0.0815	0.0816	120 *
55	0.0498	0.0801	0.0808	0.0801	43

* The value obtained by Simth⁸ is 120 minutes.

TABLE IX (Cont'd)

Temp., °C	Relative rate constant			$\alpha + \beta$
	α	β	γ	
35	0.622	0.379	0	1.00
45	0.615	0.387	0	1.00
55	0.616	0.383	0	1.00

Thus, the criterion of $\gamma = 0$ or $k_{13} = 0$ is that the decay curve of C_{22} cut the curve of C_{21} at \bar{C}_{21} . The fact that the sum of α and β is unity is purely coincidental. Graphically, this means that the decay curves of C_{11} and C_{22} are superimposed (see Figure 3-1).

b. Method of Wei & Prater

All the symbols used in the following operations are listed first. In order to be consistent in the symbols through this work, the notation has been modified from that given by Wei and Prater.³¹ Reference should be made to this for a detailed discussion of this method of calculation of the rate constants.

a_i The amount of the i -th molecular species expressed as mole fraction

a_i^0 The initial value of a_i which gives the composition of the straight line reaction mixture

a_i^* The equilibrium amount of the i -th molecular species

- b_i The amount of the i -th characteristic species in the characteristic coordinate system
- b_i^0 The initial amount of the characteristic species
- $D^{1/2}$ A diagonal matrix with diagonal elements equal to $(a_i^*)^{1/2}$
- $D^{-1/2}$ A diagonal matrix with diagonal elements equal to $(a_i^*)^{-1/2}$
- K^I The relative rate constant matrix in the natural system of coordinates
- K^{II} The relative rate constant matrix in the natural system of coordinates with one element normalized to unity
- u_i The i -th characteristic decay time for a monomolecular system
- U^I The relative rate constant matrix in the characteristic system
- v The composition vector in composition space expressed in the natural system of coordinates
- $v(0)$ The value of the composition vector v at the time $t = 0$
- $v(t)$ The value of the composition vector v at the time t
- $w(t)$ The composition vector expressed in the characteristic system of coordinates at the time t
- x_0 The equilibrium characteristic vector at the time $t = \infty$

- x_i The unit vector in the i -th characteristic direction written in the natural coordinates
- X The $n \times n$ square matrix formed by writing the n -th unit characteristic vector x_i side by side as column matrices
- X^{-1} The inverse of matrix X

The following sample calculation shows how the relative rate constants of this reaction system at 45 °C are evaluated. One notes that, as the reaction proceeds to pure alcohol, the ratio of the β -isomer to the α -isomer converged to the equilibrium ratio. Thus, the characteristic vector $v_{x_1}(0)$ is

$$v_{x_1}(0) = \begin{pmatrix} a_1^o \\ a_2^o \\ a_3^o \end{pmatrix} = \begin{pmatrix} 0.430 \\ 0.570 \\ 0.000 \end{pmatrix} \quad (V-3)$$

In the column matrix v , the order of the components are

$$\begin{pmatrix} \beta\text{-isomer} \\ \alpha\text{-isomer} \\ \text{alcohol} \end{pmatrix} \quad (V-4)$$

The characteristic vector x_o , which corresponds to the composition of

the system at time infinity, is

$$x_0 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad (V-5)$$

and the characteristic vector x_1 is then

$$x_1 = v_{x_1}(0) - x_0 = \begin{pmatrix} 0.430 \\ 0.570 \\ -1.000 \end{pmatrix} \quad (V-6)$$

The equilibrium compositions of this reaction system are those of the subreaction β -isomer \rightleftharpoons α -isomer; hence

$$\frac{a_1^*}{a_2^*} = \frac{\bar{C}_{12}}{\bar{C}_{21}} = 0.614 \quad (V-7)$$

$$a_1^* + a_2^* = 1.00 \quad (V-8)$$

then

$$a_1^* = 0.381$$

$$a_2^* = 0.619$$

Therefore, the matrices $D^{-1/2}$ and $D^{1/2}$ are

$$D^{-1/2} = \begin{pmatrix} (a_1^*)^{-1/2} & 0 \\ 0 & (a_2^*)^{-1/2} \end{pmatrix} = \begin{pmatrix} (0.381)^{-1/2} & 0 \\ 0 & (0.619)^{-1/2} \end{pmatrix}$$

(V-9)

$$D^{1/2} = \begin{pmatrix} (a_2^*)^{1/2} & 0 \\ 0 & (a_2^*)^{1/2} \end{pmatrix} = \begin{pmatrix} (0.381)^{1/2} & 0 \\ 0 & (0.619)^{1/2} \end{pmatrix} \quad (V-10)$$

When transformed by $D^{-1/2}$, the first two elements of x_2 and x_1 must be orthogonal to each other;

$$D^{-1/2} \begin{pmatrix} 0.430 \\ 0.570 \end{pmatrix} = \begin{pmatrix} 0.697 \\ 0.725 \end{pmatrix} \quad (V-11)$$

Interchanging the elements of equation (V-11) and reversing the sign of the second gives

$$\begin{pmatrix} 0.725 \\ -0.697 \end{pmatrix} \quad (V-12)$$

Transforming the matrix (V-12) back to the orthogonal system, one obtains

$$D^{1/2} \begin{pmatrix} 0.725 \\ -0.697 \end{pmatrix} = \begin{pmatrix} 0.447 \\ -0.549 \end{pmatrix} \quad (V-13)$$

Since the sum of the elements of x_2 must be zero, then

$$x_2 = \begin{pmatrix} 0.447 \\ -0.549 \\ 0.102 \end{pmatrix} \quad (V-14)$$

Combining the vectors x_0 , x_1 , and x_2 given by equations (V-5), (V-6), and (V-14), respectively, the matrix X is

$$X = \begin{pmatrix} (x_0) & (x_1) & (x_2) \end{pmatrix} = \begin{pmatrix} 0.000 & 0.430 & 0.447 \\ 0.000 & 0.570 & -0.549 \\ 1.000 & -1.000 & 0.102 \end{pmatrix} \quad (\text{V-15})$$

The inverse of X is

$$X^{-1} = \begin{pmatrix} 1.000 & 1.000 & 1.000 \\ 1.119 & 0.912 & 0.000 \\ 1.161 & -0.877 & 0.000 \end{pmatrix} \quad (\text{V-16})$$

The inverse matrix X^{-1} is used to transform the composition vector $v(t)$ in the natural system to the composition vector $w(t)$ in the characteristic system for a reaction path such as the path from pure α -isomer or pure β -isomer. Applying equation (V-17) to the composition vector $v(t)$ along the reaction path from pure β -isomer, twelve composition points are converted to the characteristic system and are given in Table X.

$$X^{-1} v(t) = X^{-1} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = w(t) = \begin{bmatrix} b_0 \\ b_1 \\ b_2 \end{bmatrix} \quad (\text{V-17})$$

TABLE X

The Composition Data Used to Evaluate "u" Ratio for the

α -Butadiene Sulfone - β -Butadiene Sulfone - Alcohol

System

t, min	v(t)	w(t)	t, min.	v(t)	w(t)
0	$\begin{pmatrix} 1.0000 \\ 0.0000 \\ 0.0000 \end{pmatrix}$	$\begin{bmatrix} 1.0000 \\ 1.1190 \\ 1.1610 \end{bmatrix}$	100	$\begin{pmatrix} 0.4500 \\ 0.4025 \\ 0.1475 \end{pmatrix}$	$\begin{bmatrix} 1.0000 \\ 0.8694 \\ 0.1694 \end{bmatrix}$
10	$\begin{pmatrix} 0.9100 \\ 0.0835 \\ 0.0065 \end{pmatrix}$	$\begin{bmatrix} 1.0000 \\ 1.0903 \\ 0.9828 \end{bmatrix}$	120	$\begin{pmatrix} 0.4125 \\ 0.4075 \\ 0.1800 \end{pmatrix}$	$\begin{bmatrix} 1.0000 \\ 0.8322 \\ 0.1215 \end{bmatrix}$
20	$\begin{pmatrix} 0.8225 \\ 0.1650 \\ 0.0125 \end{pmatrix}$	$\begin{bmatrix} 1.0000 \\ 1.0676 \\ 0.8094 \end{bmatrix}$	140	$\begin{pmatrix} 0.3700 \\ 0.4015 \\ 0.2285 \end{pmatrix}$	$\begin{bmatrix} 1.0000 \\ 0.7802 \\ 0.0775 \end{bmatrix}$
35	$\begin{pmatrix} 0.7170 \\ 0.2500 \\ 0.0330 \end{pmatrix}$	$\begin{bmatrix} 1.0000 \\ 1.0293 \\ 0.6130 \end{bmatrix}$	160	$\begin{pmatrix} 0.3500 \\ 0.3900 \\ 0.2600 \end{pmatrix}$	$\begin{bmatrix} 1.0000 \\ 0.7473 \\ 0.0644 \end{bmatrix}$
55	$\begin{pmatrix} 0.6125 \\ 0.3300 \\ 0.0575 \end{pmatrix}$	$\begin{bmatrix} 1.0000 \\ 0.9842 \\ 0.4220 \end{bmatrix}$	220	$\begin{pmatrix} 0.2800 \\ 0.3460 \\ 0.3740 \end{pmatrix}$	$\begin{bmatrix} 1.0000 \\ 0.6289 \\ 0.0217 \end{bmatrix}$
80	$\begin{pmatrix} 0.5180 \\ 0.3800 \\ 0.1020 \end{pmatrix}$	$\begin{bmatrix} 1.0000 \\ 0.9250 \\ 0.2690 \end{bmatrix}$	280	$\begin{pmatrix} 0.2270 \\ 0.2950 \\ 0.4780 \end{pmatrix}$	$\begin{bmatrix} 1.0000 \\ 0.5230 \\ 0.0048 \end{bmatrix}$

From the equation

$$\ln b_1 = \ln \left[\frac{b_1^o}{(b_1^o)^{u_1/u_2}} \right] + \left(\frac{u_1}{u_2} \right) \ln b_2 \quad (\text{V-18})$$

derived by Wei and Prater³¹, the slope of the plot of $-\log b_1$ versus $-\log b_2$ (Figure 6) is $u_1/u_2 = 0.1330$; hence

$$\begin{aligned} K' &= X U' X^{-1} = X \begin{pmatrix} 0 & 0 & 0 \\ 0 & -\frac{u_1}{u_2} & 0 \\ 0 & 0 & 0 \end{pmatrix} X^{-1} \\ &= \begin{pmatrix} -0.5830 & 0.3398 & 0.0000 \\ 0.5526 & -0.5506 & 0.0000 \\ 0.0304 & 0.2108 & 0.0000 \end{pmatrix} \end{aligned} \quad (\text{V-19})$$

and, making the relative rate constant to the α -isomer in the natural system of coordinates equal to unity, equation (V-19) becomes

$$\begin{aligned}
 K'' &= \begin{pmatrix} -\frac{k_{12}+k_{13}}{k_{12}} & \frac{k_{21}}{k_{12}} & \frac{k_{31}}{k_{12}} \\ \frac{k_{12}}{k_{12}} & -\frac{k_{21}+k_{23}}{k_{12}} & \frac{k_{32}}{k_{12}} \\ \frac{k_{13}}{k_{12}} & \frac{k_{23}}{k_{12}} & \frac{k_{31}+k_{32}}{k_{12}} \end{pmatrix} = \begin{pmatrix} -(1+\gamma) & \alpha & 0 \\ 1 & -(\alpha+\beta) & 0 \\ \gamma & \beta & 0 \end{pmatrix} \\
 &= \begin{pmatrix} -1.055 & 0.615 & 0.000 \\ 1.000 & -0.997 & 0.000 \\ 0.055 & 0.382 & 0.000 \end{pmatrix} \quad (V-20)
 \end{aligned}$$

By performing the similar operations, one can obtain

$$K'' = \begin{pmatrix} -1.038 & 0.622 & 0.000 \\ 1.000 & -1.024 & 0.000 \\ 0.038 & 0.402 & 0.000 \end{pmatrix} \quad (V-21)$$

and

$$K'' = \begin{pmatrix} -1.033 & 0.618 & 0.000 \\ 1.000 & -1.015 & 0.000 \\ 0.033 & 0.397 & 0.000 \end{pmatrix} \quad (V-22)$$

for the reaction at 35 and 55 °C, respectively.

2. First-Order Rate Constants

Since all the relative rate constants have been evaluated, it is then required to determine only one of first-order rate constants, k_{12} ,

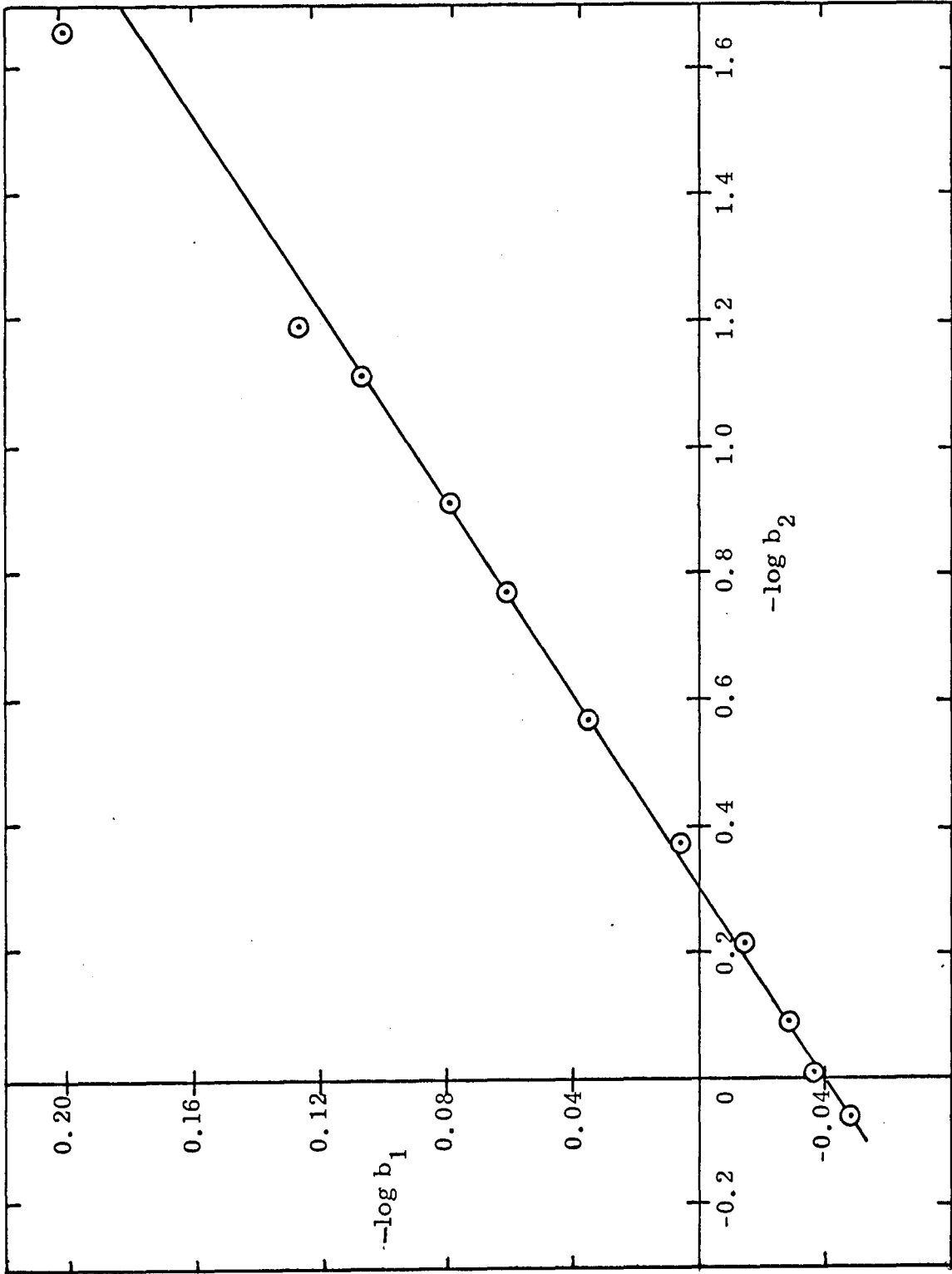


Figure 6. $-\log b_1$ versus $-\log b_2$ obtained from pure β -butadiene sulfone initial composition

in order to obtain all the rest of rate constants k_{21} , k_{13} , and k_{23} .

There are two methods to determine the value of k_{12} :

a. Direct Calculation

The constant k_{12} can be calculated from equations (VIII-14), (VIII-15), and (VIII-26) by using the data in Table IX, equations (V-20), (V-21), and (V-22).

$$P = \frac{1}{2} (1 + \alpha + \beta + \gamma) \quad \text{(VIII-14)}$$

$$Q = \sqrt{P^2 - (\beta + \beta\gamma + \alpha\gamma)} \quad \text{(VIII-15)}$$

$$k_{12} = \frac{1}{Q \bar{t}} \tanh^{-1}\left(\frac{Q}{P}\right) \quad \text{(VIII-26)}$$

The value of k_{12} calculated from the two sets of the relative rate constants for each specific temperature are tabulated in the following table:

TABLE XI

Table of k_{12} 's Obtained from Direct Calculation

Temp., °C	Using α, β , and γ obtained from direct calculation			Using α, β , and γ obtained from method of Wei & Prater		
	P	Q	$k_{12} \times 10^2,$ min ⁻¹	P	Q	$k_{12} \times 10^2,$ min ⁻¹
35	1.001	0.788	0.386	1.031	0.788	0.366
45	1.000	0.784	1.12	1.026	0.784	1.07
55	0.999	0.785	3.14	1.024	0.785	2.99

b. Graphical Method

One can see from equation (VIII-39) that k_{12} can also be calculated from the slope of the straight line yielded by plotting the left-hand side of this equation against time.

$$\log \left[1 + \frac{2 Q}{\left(\frac{C_{11}}{C_{21}}\right)_t - \left(\frac{C_{11}}{C_{21}}\right)_\infty} \right] = \left(\frac{2 Q}{2.303} k_{12} \right) t \quad (\text{VIII-39})$$

Using the experimental value of $(C_{11}/C_{21})_\infty^*$ (see Table VIII), the sample plot for the reaction at 45 °C is shown in Figure 7. By this method, the value of k_{12} are found to be 0.353×10^{-2} , 1.07×10^{-2} , and $3.17 \times 10^{-2} \text{ min}^{-1}$ at 35, 45, and 55 °C, respectively. It should be noted that there is only one set of k_{12} from the graphical method since the values of Q listed in Table XI are the same for each temperature.

c. Comparison of the Two Methods

Even though the results calculated from the different method are in good agreement within the experimental error, the computed concentration-time data (see section VIII-C) show that the relative rate constants calculated by the method of Wei and Prater, and k_{12} obtained

* $(C_{11}/C_{21})_\infty$ can also be calculated from equation (VIII-38), $(C_{11}/C_{21})_\infty = P + Q - \gamma - 1$. The results are comparable to those given in Table VIII at the corresponding temperatures.

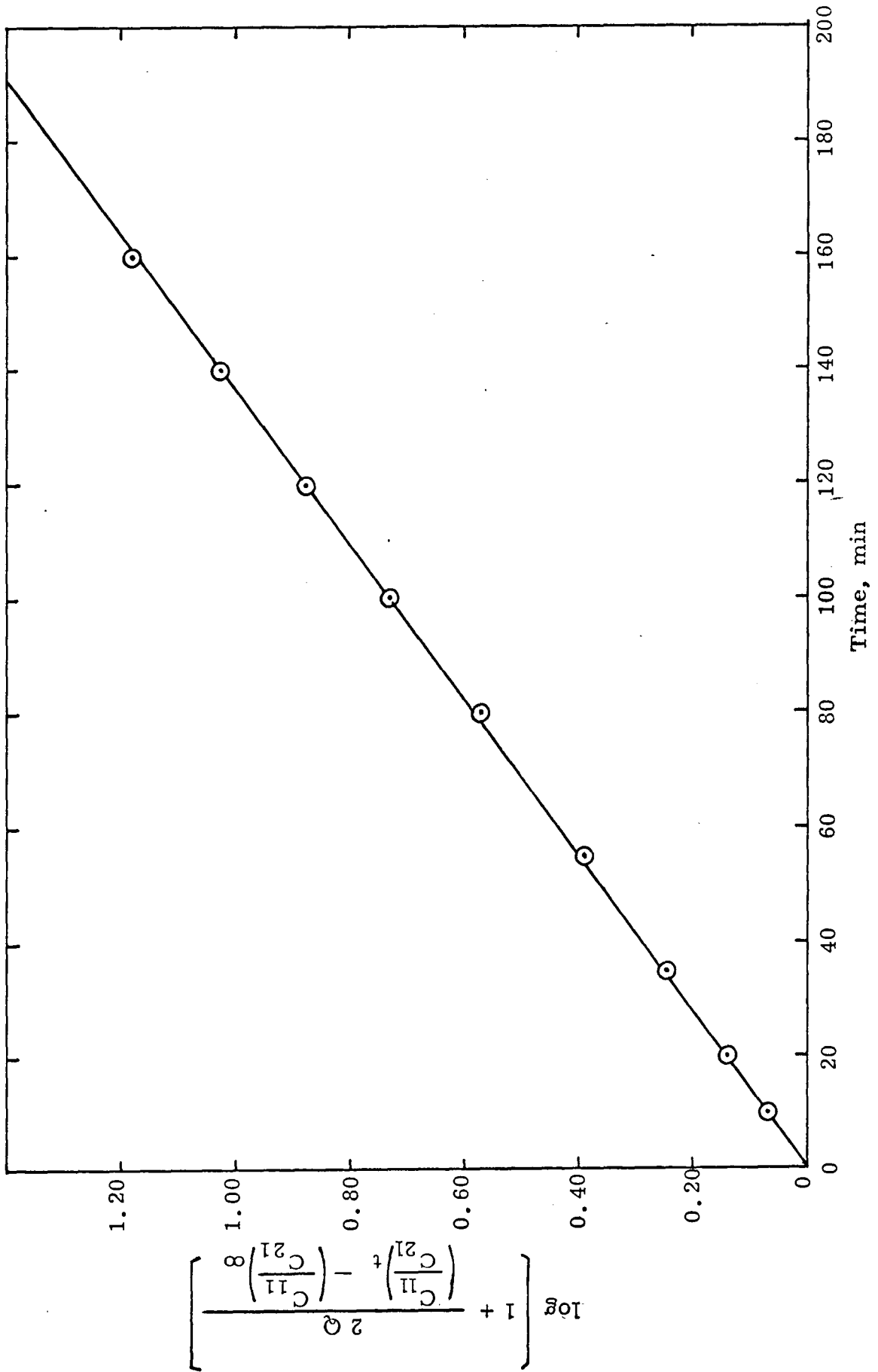


Figure 7. A linear plot for a first-order reaction

from the direct calculation give the best fit to the experimental concentration-time data (see Figures 3 and 4).

Table XII shows the compilation of all of the four first-order rate constants for reaction system (I-1) as calculated by the method of Wei and Prater and equation (VIII-26).

TABLE XII

First-Order Rate Constants for the Base-Catalyzed

Isomerization and Hydration of the Isomeric Butadiene Sulfones

Temp., °C	α	β	γ	$k_{ij} \times 10^2, \text{ min}^{-1}$			
				k_{12}	k_{21}	k_{23}	k_{13}
35	0.622	0.402	0.038	0.366	0.228	0.147	0.014
45	0.615	0.382	0.055	1.07	0.658	0.408	0.059
55	0.618	0.397	0.033	2.99	1.85	1.18	0.099

3. Second-Order Rate Constants

Smith⁸ has shown that the isomerization reactions are first-order in hydroxide ion. Assuming that the hydration reactions are also first-order in hydroxide ion, the second-order rate constants can be calculated from the equation

$$k_{ij}' = \frac{k_{ij}}{C_{\text{OH}^-}} \quad (\text{V-23})$$

where k_{ij}' and C_{OH^-} are second-order rate constant and the base

concentration, respectively. Using the data of k_{ij} in Table XII and $C_{OH^-} = 0.300 \text{ M}$ (see sections B-2-b and B-2-c), the results tabulated in Table XIII were obtained.

TABLE XIII

Second-Order Rate Constants for the Base-Catalyzed
Isomerization and Hydration of the Isomeric Butadiene Sulfones

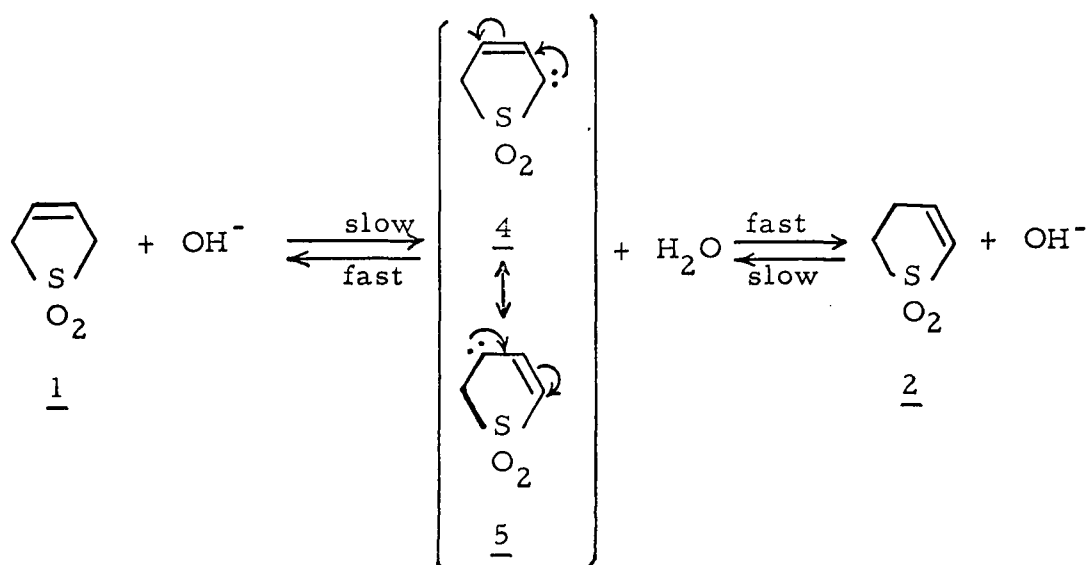
Temp., °C	$k_{ij}' \times 10^2, \text{ M}^{-1} \text{ min}^{-1}$			
	k_{12}'	k_{21}'	k_{23}'	k_{13}'
35	1.22	0.760	0.490	0.046
45	3.57	2.19	1.36	0.19
55	9.97	6.17	3.94	0.33

VI. DISCUSSION AND CONCLUSION

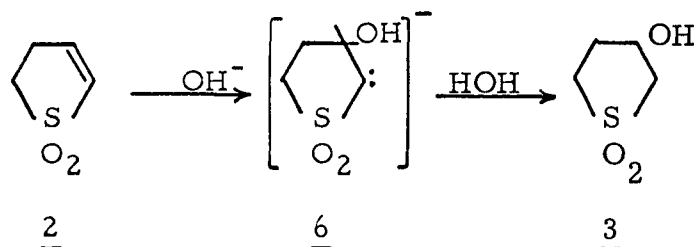
A. KINETICS AND MECHANISM OF BASE-CATALYZED ISOMERIZATION AND HYDRATION OF BUTADIENE SULFONES

The agreement between the experimental rate constant, either k_{12} or k_{12}^1 , at a specific temperature, of this investigation and Smith's (See Tables II, XII, and XIII) gives strong support to his conclusion that this reaction is first-order with respect to β -isomer and to base, and second-order overall. By comparing the concentration-time curves (see Figure 3-1) of the kinetic runs, starting with pure α -isomer and pure β -isomer at the same temperature, one can conclude that the reaction is also first-order with respect to α -isomer. It should be noted again that the reaction is second-order overall, since in a given run the base concentration remains constant.

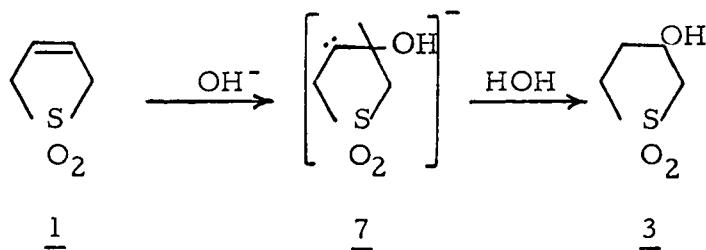
The variation of k_{12} with the base concentration observed by Smith⁸ is consistent with the rate law which would be obtained for a general base catalysis.⁴³ This isomerization reaction is therefore B-S_E 1' involving a slow ionization of substrate followed by a rapid reaction of the anion to give the products:



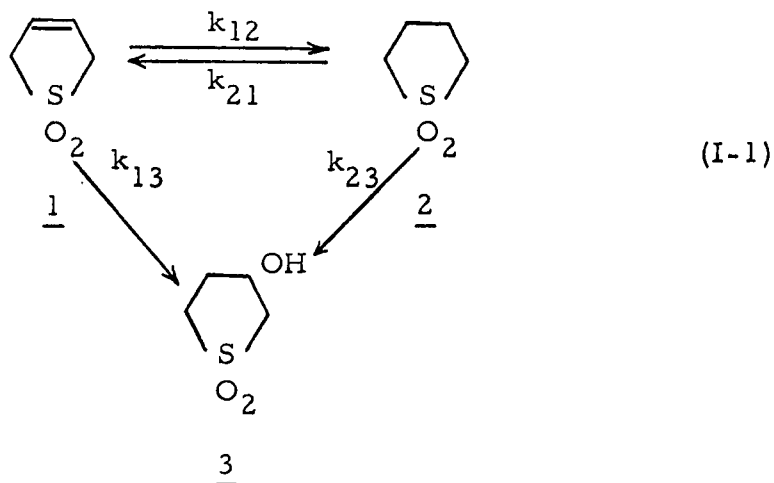
The result which shows that k_{13} is small compared to k_{23} also indicates that the alcohol (3) must come mostly from α -isomer. This can be explained mechanistically by the electronic structure of these compounds and the reaction intermediates. The electron withdrawing group, $=\text{SO}_2$, being nearer to the double bond position in the α -isomer than in β -isomer, creates a greater partial positive charge at the 3-position of the α -isomer. This results in a nucleophilic attack of base at that position followed by an attack of an acidic hydrogen from a water molecule to yield the alcohol. Such a reaction would appear feasible in view of the stabilizing effect upon the carbanion (6) by the adjacent $=\text{SO}_2$ group.



The formation of alcohol from the β -isomer is consistent with the following mechanism:



Thus, the overall reaction scheme of this system is



with $k_{23} \gg k_{13}$.

By referring to the rate constants in Table XIII, the activation energies and frequency factors can be evaluated for the reaction system (I-1). The energy of activation, $(E_a)_{ij}$, of each reaction of this complex system can be obtained from the Arrhenius equation,

$$k_{ij} = Z_{ij} \exp \left[-\frac{(E_a)_{ij}}{R T} \right] \quad (\text{VI-1})$$

where Z_{ij} and R are the frequency factor and the gas constant, respectively. The plot of $\log k_{ij}^1$ versus the reciprocal of the absolute temperature, $1/T$, (Figure 8) was made and $(E_a)_{ij}$ was calculated from the slope of the straight line obtained. Z_{ij} can also be calculated once the value of $(E_a)_{ij}$ is available. Table XIV shows the calculated results.

TABLE XIV
Activation Energies and Frequency Factors

Reaction	E_a , kcal/mole	Z , $\underline{M}^{-1} \text{Min.}^{-1}$
<u>(1)</u> \longrightarrow <u>(2)</u>	21.1 ± 0.1	1.0×10^{13}
<u>(2)</u> \longrightarrow <u>(1)</u>	21.2 ± 0.2	7.7×10^{12}
<u>(2)</u> \longrightarrow <u>(3)</u>	21.2 ± 0.2	4.8×10^{12}
<u>(1)</u> \longrightarrow <u>(3)</u>	20.0 ± 7.7	8.1×10^{10}

The large error of E_a for the reaction from 1 to 3 is due to the fact that the relative rate constant γ is so small and, consequently, the error of its value is large as it is calculated from Wei and Prater's method (see section V-B-1-b).

B. THERMODYNAMIC PROPERTIES OF THE ISOMERIZATION

1. Heat of Isomerization in Aqueous Solution

Two methods were used to calculate the heat of isomerization in aqueous solution, $\Delta H(\text{aq})$.

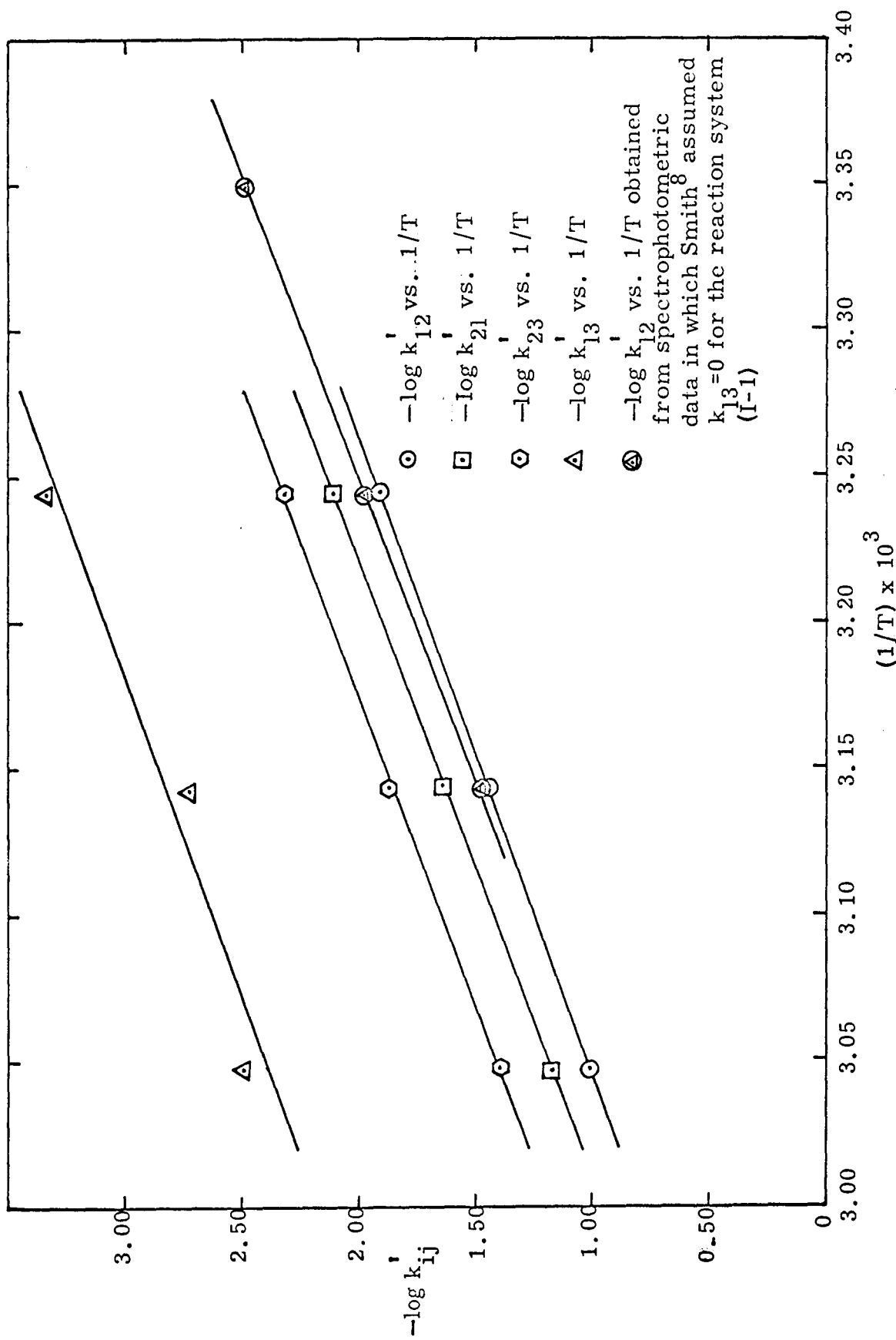


Figure 8. The Arrhenius plot

a. $\Delta H(aq)$ from Kinetic Data

The heat of isomerization in solution can be calculated from the temperature coefficient of the equilibrium constant (van't Hoff equation):

$$\frac{d \ln K_c}{d T} = \frac{\Delta E}{R T^2} = \frac{\Delta H(aq)}{R T^2} \quad (VI-2)$$

where K_c is an equilibrium constant expressed in terms of concentration at temperature T and ΔE is the change in the internal energy of the system. Since

$$K_c = \frac{k_{12}}{k_{21}} = \frac{1}{\alpha} \quad (VI-3)$$

the equation (VI-2) becomes

$$\frac{d \ln \left(\frac{1}{\alpha} \right)}{d T} = \frac{\Delta H(aq)}{R T^2} \quad (VI-4)$$

From Table XII and Figure 8, it is evident that the value of $1/\alpha$ is approximately constant over the temperature range 25 to 55 °C. Thus the left hand term in equation (VI-4) vanishes and $\Delta H(aq) = 0$. This is consistent with the difference in the activation energies of isomerization from which $\Delta H(aq) = \Delta E = E_{21} - E_{12} = 0.1 \pm 0.3$ kcal.

b. $\Delta H(aq)$ from Thermochemical Data

The heat of reaction can be calculated from the following

thermodynamic formula:

$$\Delta H(\text{aq}) = \left[\Delta H_f^\circ (1) - \Delta H_f^\circ (2) \right] + \left[\Delta H_{\text{soln}} (1) - \Delta H_{\text{soln}} (2) \right] \quad (\text{VI-5})$$

where ΔH_f° is the standard heat of formation at 25 °C and ΔH_{soln} is the heat of solution in water at the same temperature.

Mackle^{44, 45} has shown that $\Delta H_f^\circ (1)$ and $\Delta H_f^\circ (2)$ are -76.1 ± 0.6 and -77.2 ± 0.6 kcal, respectively. Although the heats of solution are not known, their difference is probably small and of the same order of magnitude as that of the difference in ΔH_f° . Evidence for the assumption that the difference in ΔH_{soln} is small is obtained by comparison with the isoprene sulfone system,^{8, 45} in which the differences in ΔH_f° and ΔH_{soln} for the two isomers are 0.9 ± 1.6 and -0.26 kcal/mole, respectively. The difference in chromatographic retention times for α - and β -isoprene sulfone is 5.2 minutes whereas that for α - and β -butadiene sulfone under the same conditions is 5.5 minutes, indicating that differences in polarity and therefore difference in

ΔH_{soln} are comparable. Using Mackle's values an approximate calculation shows $\Delta H(\text{aq}) = -0.9 \pm 1.2$ kcal by assuming that the contribution of the difference in ΔH_{soln} can be neglected.

Comparison of the results from the two methods of calculation of $\Delta H(\text{aq})$ shows they are in good agreement and also shows the heat of isomerization is zero within the experimental error.

2. Free Energy and Entropy Changes of Isomerization

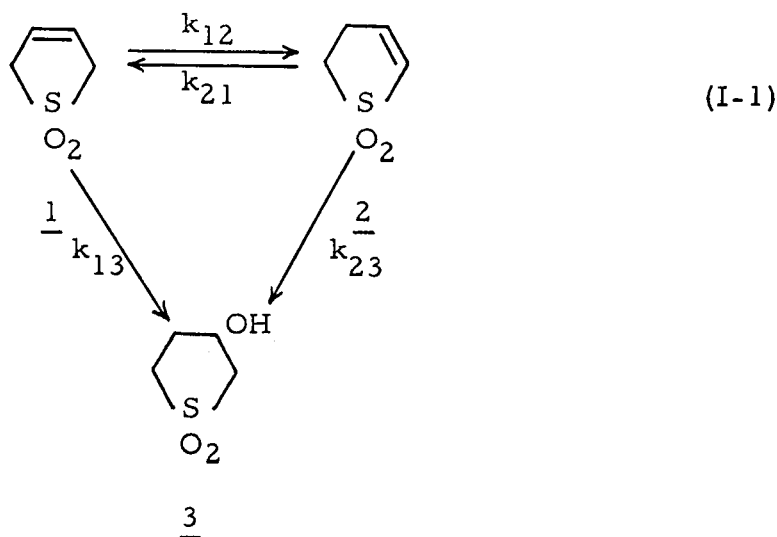
The standard free energy change, ΔG° , for a standard state of 1 M, is $-RT \ln K_c$; hence $\Delta G^\circ = -0.3 \pm 0.01$ kcal/mole at 45 °C.

From the equation $\Delta G^\circ = \Delta H(\text{aq}) - T \Delta S^\circ$, it is calculated that

$T \Delta S^\circ = 0.2 \pm 0.2$ kcal/mole. $\Delta G^\circ = 0$ results from both $\Delta H(\text{aq})$ and ΔS being nearly zero.

VII. SUMMARY

(1) Rate constants have been obtained for the base-catalyzed isomerization and hydration of the isomeric butadiene sulfones (1, 2),



at the temperatures 35, 45, and 55 °C. The kinetic study was carried out by the gas-liquid partition chromatographic technique.

(2) The reaction for the complex system (I-1) was shown to be first-order with respect to 1, 2, and alcohol (3), first-order with respect to base,⁸ and second order over all.

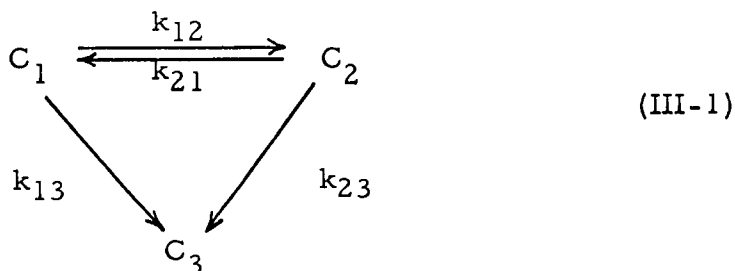
(3) Plausible mechanisms have been proposed for the formation of 3 from 1 as well as the formation of 3 from 2. Equations (VIII-29), VIII-34), and (VIII-35) give approximate values of the relative rate constants of the reaction system (I-1) while the method of Wei and

Prater gave more accurate values of the relative rate constants.

(4) The equilibrium constant obtained for the base-catalyzed isomerization of 1 to 2 was found to be independent of temperature within experimental error in the range of 35 to 55 °C. These equilibrium constants were used to calculate the heat of isomerization in aqueous solution, the entropy change, and the Gibbs free energy change. The heat of isomerization was shown to be in good agreement with an estimated value which was obtained from thermochemical experiments.^{44, 45}

(5) The agreement between the experimental and calculated concentration-time curves is satisfactory except for those curves obtained from the reaction which started from the mixture of 1 and 2 excluding the mixture for the straight line reaction path at 45 °C.

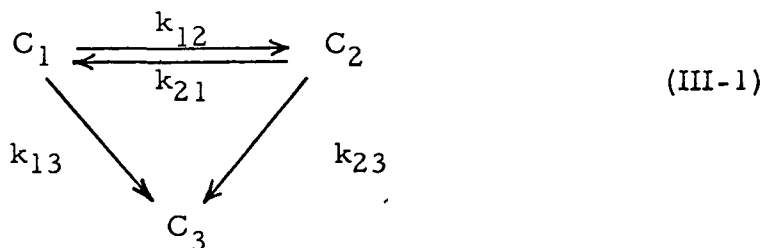
(6) The complicated mathematical description for the complex reaction system of the type



has been simplified from previous work. Also, the new formulas for obtaining the relative rate constants and the rate constant k_{12} have been developed.

VIII. APPENDIXES

A. EXPERIMENTAL DETERMINATION OF RELATIVE RATE
CONSTANTS FOR THE REACTION WITH THE MECHANISM



The rates of these reactions may be written as the following three linear simultaneous equations:

$$\frac{dC_1}{dt} = -k_{12}C_1 + k_{21}C_2 - k_{13}C_1 \tag{VIII-1}$$

$$\frac{dC_2}{dt} = -k_{21}C_2 + k_{12}C_1 - k_{23}C_2 \tag{VIII-2}$$

$$\frac{dC_3}{dt} = k_{13}C_1 + k_{23}C_2 \tag{VIII-3}$$

The secular equation of this system of equations has been given by Lewis and Johnson³⁰ as

$$\begin{vmatrix}
 k_{12} + k_{13} - \lambda & & -k_{21} & 0 \\
 -k_{12} & & k_{21} + k_{23} - \lambda & 0 \\
 -k_{13} & & -k_{23} & -\lambda
 \end{vmatrix} = 0 \tag{VIII-4}$$

where λ is a parameter in the integrated differential equations to be determined. The roots of equation (VIII-4) are given below as equations (VIII-5), (VIII-6), and (VIII-7).

$$\lambda_1 = 0 \quad \text{(VIII-5)}$$

$$\lambda_2 = \frac{1}{2} \left[(k_{12} + k_{13} + k_{21} + k_{23}) + \sqrt{(k_{12} + k_{13} + k_{21} + k_{23})^2 - 4(k_{12}k_{23} + k_{13}k_{21} + k_{13}k_{23})} \right] \quad \text{(VIII-6)}$$

$$\lambda_3 = \frac{1}{2} \left[(k_{12} + k_{13} + k_{21} + k_{23}) - \sqrt{(k_{12} + k_{13} + k_{21} + k_{23})^2 - 4(k_{12}k_{23} + k_{13}k_{21} + k_{13}k_{23})} \right] \quad \text{(VIII-7)}$$

The relative rate constants with respect to k_{12} are defined by the following expressions:

$$\alpha = \frac{k_{21}}{k_{12}} \quad \text{(VIII-8)}$$

$$\beta = \frac{k_{23}}{k_{12}} \quad \text{(VIII-9)}$$

$$\gamma = \frac{k_{13}}{k_{12}} \quad \text{(VIII-10)}$$

Thus, equations (VIII-5), (VIII-6), and (VIII-7) can be simplified as

$$\lambda_1 = 0 \quad (\text{VIII-11})$$

$$\lambda_2 = k_{12}(P+Q) \quad (\text{VIII-12})$$

$$\lambda_3 = k_{12}(P-Q) \quad (\text{VIII-13})$$

where

$$P = \frac{1}{2}(1+\alpha + \beta + \gamma) \quad (\text{VIII-14})$$

$$Q = \sqrt{P^2 - (\beta + \beta\gamma + \alpha\gamma)} \quad (\text{VIII-15})$$

Evans²⁴ has shown that the integrated rate equations for the equations (VIII-1), (VIII-2), and (VIII-3) with the boundary conditions $C_1 = C_1^0$, $C_2 = 0$, and $C_3 = 0$ are

$$C_{11} = C_1^0 \left(\frac{k_{12} + k_{13} - \lambda_3}{\lambda_2 - \lambda_3} e^{-\lambda_2 t} - \frac{k_{12} + k_{13} - \lambda_2}{\lambda_2 - \lambda_3} e^{-\lambda_3 t} \right) \quad (\text{VIII-16})$$

$$C_{21} = C_1^0 \frac{(k_{12} + k_{13} - \lambda_2)(k_{12} + k_{13} - \lambda_3)}{k_{21}(\lambda_2 - \lambda_3)} (e^{-\lambda_2 t} - e^{-\lambda_3 t}) \quad (\text{VIII-17})$$

where C_{ij} means the concentration of compound (i) at time = t when the reaction is started from compound (j).

It is possible to represent the mole fractions C_{11}/C_1^0 in terms of k_{12} and the relative rate constants α , β , and γ by the following algebraic operations:

$$\lambda_2 - \lambda_3 = 2Qk_{12} \quad (\text{VIII-18})$$

$$\frac{C_{11}}{C_1^0} = \frac{1}{2Q} \left\{ \left[1 + \gamma - (P-Q) \right] e^{-k_{12}(P+Q)t} - \left[1 + \gamma - (P+Q) \right] e^{-k_{12}(P-Q)t} \right\}$$

(VIII-19)

$$\frac{C_{21}}{C_1^0} = \frac{1}{2Q} \left[1 + \gamma - (P+Q) \right] \left[\frac{1}{\alpha} + \frac{\gamma}{\alpha} - \frac{(P-Q)}{\alpha} \right] \left[e^{-k_{12}(P+Q)t} - e^{-k_{12}(P-Q)t} \right]$$

(VIII-20)

By applying the following three identities:

$$\sinh (Qk_{12}t) = \frac{e^{Qk_{12}t} - e^{-Qk_{12}t}}{2},$$

$$\cosh (Qk_{12}t) = \frac{e^{Qk_{12}t} + e^{-Qk_{12}t}}{2},$$

$$\text{and } - \left[1 + \gamma - (P+Q) \right] \left[\frac{1}{\alpha} + \frac{\gamma}{\alpha} - \frac{(P-Q)}{\alpha} \right] = 1;$$

equations (VIII-19) and (VIII-20) are reduced to equations (VIII-21) and (VIII-22), respectively.

$$\frac{C_{11}}{C_1^0} = \frac{e^{-k_{12}Pt}}{Q} \left[(-1 + \gamma + P) \sinh (k_{12}Qt) + Q \cosh (k_{12}Qt) \right]$$

(VIII-21)

$$\frac{C_{21}}{C_1^0} = \frac{e^{-k_{12}Pt}}{Q} \sinh (k_{12}Qt)$$

(VIII-22)

In a similar way, one can derive the expression of C_{12}/C_2^0 in terms of k_{12} and the relative rate constants.

$$\frac{C_{12}}{C_1^0} = \frac{e^{-k_{12}Pt}}{Q} \propto \sinh(k_{12}Qt) \quad (\text{VIII-23})$$

To obtain the maximum concentrations of C_2 and C_1 when the reaction started from pure C_1 and C_2 , respectively, are simply to take the first derivatives of equations (VIII-22) and (VIII-23) and to set them equal to zero. Thus,

$$k_{12}Q\bar{t}_{12} = \tanh^{-1} \left(\frac{Q}{P} \right) \quad (\text{VIII-24})$$

$$k_{12}Q\bar{t}_{21} = \tanh^{-1} \left(\frac{Q}{P} \right) \quad (\text{VIII-25})$$

where \bar{t}_{ij} represents the time required for maximum conversion of compound (j) to compound (i). It is clear that $\bar{t}_{12} = \bar{t}_{21}$, i.e., the time required for maximum conversion of C_2^0 to C_1 is the same as that of C_1^0 to C_2 at a specific temperature. For simplicity, set $\bar{t}_{12} = \bar{t}_{21} = \bar{t}$, then both of equations (VIII-24) and (VIII-25) can be represented by

$$k_{12}Q\bar{t} = \tanh^{-1} \left(\frac{Q}{P} \right) \quad (\text{VIII-26})$$

Substitution of \bar{t} from equation (VIII-26) to equations (VIII-22) and (VIII-23) gives the maximum concentration, \bar{C} , of C_1 and C_2 at \bar{t} , respectively.

$$\bar{C}_{21} = C_1^0 e^{-\frac{P}{Q} \tanh^{-1} \left(\frac{Q}{P} \right)} \frac{1}{\sqrt{P^2 - Q^2}} \quad (\text{VIII-27})$$

$$\bar{C}_{12} = C_2^0 \alpha e^{-\frac{P}{Q} \tanh^{-1} \left(\frac{Q}{P} \right)} \frac{1}{\sqrt{P^2 - Q^2}} \quad (\text{VIII-28})$$

The relative rate constant α can therefore be obtained from the experimental data \bar{C}_{21} and \bar{C}_{12} by the following formula:

$$\alpha = \frac{\bar{C}_{12}}{\bar{C}_{21}} \quad (\text{VIII-29})$$

if $C_1^0 = C_2^0$.

To obtain the value of β as well as γ from the experiment, the following derivations are required. Equations (VIII-1) and (VIII-2) are first written as

$$\frac{dC_{12}}{dt} = -k_{12}C_{12} + k_{12}C_{22} - k_{12}C_{12} \quad (\text{VIII-30})$$

$$\text{and} \quad \frac{dC_{21}}{dt} = -k_{12}C_{21} + k_{12}C_{11} - k_{12}C_{21} \quad (\text{VIII-31})$$

and since dC_{12}/dt and dC_{21}/dt vanish at \bar{t}^* ; hence

* dC_{31}/dt or dC_{32}/dt would not vanish at \bar{t} for the reaction scheme

(I-1).

$$-1 + \alpha \frac{\bar{C}_{11}}{\bar{C}_{12}} - \gamma = 0 \quad (\text{VIII-32})$$

$$1 - \alpha \frac{\bar{C}_{21}}{\bar{C}_{11}} - \beta \frac{\bar{C}_{21}}{\bar{C}_{11}} = 0 \quad (\text{VIII-33})$$

where \bar{C}_{ii} represents the concentration of compound (i) at \bar{t} when the reaction started from pure compound (i).

The expressions for the relative rate constants β and γ in terms of experimentally available data can be obtained by solving equations (VIII-29), (VIII-32), and (VIII-33) simultaneously. These are given as

$$\beta = \frac{\bar{C}_{11} - \bar{C}_{12}}{\bar{C}_{21}} \quad (\text{VIII-34})$$

$$\gamma = \frac{\bar{C}_{22} - \bar{C}_{21}}{\bar{C}_{21}} \quad (\text{VIII-35})$$

B. DETERMINATION OF k_{12} BY GRAPHICAL METHOD

The ratio of the concentrations of C_1 and C_2 for the reaction starting from pure C_1 , C_1^0 , can be expressed in terms of k_{12} and the relative rate constants as shown in equation (VIII-36) which is obtained from dividing equation (VIII-21) by equation (VIII-22).

$$\left(\frac{C_{11}}{C_{21}}\right)_t = (P - \gamma - 1) + \frac{Q}{\tanh(k_{12}Qt)} \quad (\text{VIII-36})$$

Furthermore, since $\tanh(k_{12}Qt) = \frac{e^{k_{12}Qt} - e^{-k_{12}Qt}}{e^{k_{12}Qt} + e^{-k_{12}Qt}}$, equation

(VIII-36) can be represented in the exponential form which is

$$\left(\frac{C_{11}}{C_{21}}\right)_t = (P+Q - \gamma - 1) + \frac{2Q}{e^{2Qk_{12}t} - 1} \quad (\text{VIII-37})$$

Two special cases arise from this equation. First, at $t=0$, $(C_{11}/C_{21})_0 = \infty$, which corresponds to the initial condition. Second, at $t = \infty$,

$$\left(\frac{C_{11}}{C_{21}}\right)_\infty = P + Q - \gamma - 1 \quad (\text{VIII-38})$$

i. e., the limit value of the ratio, C_{11}/C_{21} , equation (VIII-37) then becomes

$$\left(\frac{C_{11}}{C_{21}}\right)_t = \left(\frac{C_{11}}{C_{21}}\right)_\infty = \frac{2Q}{e^{2k_{12}Qt} - 1}$$

Upon rearrangement, the last expression is transformed to

$$\log \left[1 + \frac{2Q}{\left(\frac{C_{11}}{C_{21}}\right)_t - \left(\frac{C_{11}}{C_{21}}\right)_\infty} \right] = \left(\frac{2Q}{2.303} k_{12} \right) t \quad (\text{VIII-39})$$

Thus, a plot of the left-hand side of equation (VIII-39) versus time should yield a straight line with the slope $(2Q/2.303)k_{12}$ from which k_{12} can be calculated.

C. COMPUTER CHECK OF THE EXPERIMENTAL DATA

It has been mentioned that the integrated rate equations for the set of differential equations (VIII-1), (VIII-2), and (VIII-3) with the boundary condition $C_1 = C_1^0$, $C_2 = C_2^0$, and $C_3 = 0$ have been obtained by Alberty and Miller²⁵ (see page 10). These are given as

$$C_1 = \frac{(k_{12} + k_{13} - \lambda_3) C_1^0 - k_{21} C_2^0}{\lambda_2 - \lambda_3} e^{-\lambda_2 t} - \frac{(k_{12} + k_{13} - \lambda_2) C_1^0 - k_{21} C_2^0}{\lambda_2 - \lambda_3} e^{-\lambda_3 t} \quad (\text{VIII-40})$$

$$C_2 = \frac{(k_{12} + k_{13} - \lambda_2) (k_{12} + k_{13} - \lambda_3) C_1^0 - k_{21} C_2^0}{k_{21} (\lambda_2 - \lambda_3)} e^{-\lambda_2 t} - \frac{(k_{12} + k_{13} - \lambda_3) (k_{12} + k_{12} - \lambda_2) C_1^0 - k_{21} C_2^0}{k_{21} (\lambda_2 - \lambda_3)} e^{-\lambda_3 t} \quad (\text{VIII-41})$$

and are the general solutions for the reaction system (I-1). If one sets $C_2^0 = 0$ in equations (VIII-40) and (VIII-41), they are reduced to equations (VIII-16) and (VIII-17), respectively.

After the transformations by using equations (VIII-8) to (VIII-15), the left-hand terms of equations (VIII-40) and (VIII-41) can also be represented in terms of k_{12} and the relative rate constants α , β , and γ :

$$C_1 = \frac{[1 + \gamma - (P+Q)] C_1^0 - \alpha C_2^0}{2Q} e^{-k_{12}(P+Q)t} - \frac{[1 + \gamma - (P-Q)] C_1^0 - \alpha C_2^0}{2Q} e^{-k_{12}(P-Q)t} \quad (\text{VIII-42})$$

$$C_2 = \frac{[1 + \gamma - (P+Q)] \left\{ [1 + \gamma - (P-Q)] C_1^0 - \alpha C_2^0 \right\}}{2 \alpha Q} e^{-k_{12}(P+Q)t} - \frac{[1 + \gamma - (P-Q)] \left\{ [1 + \gamma - (P+Q)] C_1^0 - \alpha C_2^0 \right\}}{2 \alpha Q} e^{-k_{12}(P-Q)t} \quad (\text{VIII-43})$$

A computer program for equations (VIII-42), (VIII-43), and $C_3 = (C_1^0 + C_2^0) - (C_1 + C_2)$ was written in Fortran IV machine language.⁴⁶ The different sets of the relative rate constants and k_{12} obtained from the different methods of calculations (see section IV-B) and combined with the initial conditions enable the machine to calculate the

corresponding concentration-time data. The set which gives the best agreement with the experimental data is taken as giving the best values of the rate constants.

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ABSTRACT

The kinetics of base-catalyzed isomerization and hydration of butadiene sulfones has been studied by using the gas chromatographic method. The reaction has been shown to be first-order with respect to each of the three components, i. e., α -butadiene sulfone, β -butadiene sulfone, and alcohol, in this complex reaction system. It is also first-order with respect to base, and second-order overall.

The rate constants and relative rate constants of this reaction system have been obtained in the range of 35 to 55° C. The thermodynamic quantities of the reversible isomerization of β -butadiene sulfone to α -butadiene sulfone have been evaluated. The heat of isomerization obtained in this investigation is consistent with an independent thermochemical measurement.