

Open Research Online

The Open University's repository of research publications and other research outputs

Kinetic study of the gas phase pyrolysis of cis-1-chloro-2-butene

Thesis

How to cite:

Lee, Yok-Chin (1980). Kinetic study of the gas phase pyrolysis of cis-1-chloro-2-butene. MPhil thesis The Open University.

For guidance on citations see [FAQs](#).

© 1979 The Author

Version: Version of Record

Link(s) to article on publisher's website:
<http://dx.doi.org/doi:10.21954/ou.ro.0000fc90>

Copyright and Moral Rights for the articles on this site are retained by the individual authors and/or other copyright owners. For more information on Open Research Online's data [policy](#) on reuse of materials please consult the policies page.

oro.open.ac.uk

UNRESTRICTED

Kinetic study of the gas phase pyrolysis

of cis-1-chloro-2-butene

by

Yok-Chin Lee, B.Sc., M.Sc

Faculty of Science

The Open University

September, 1979

Submitted as a requirement for the degree of

Master of Philosophy

in the discipline of Chemistry

Date of submission: 1-9-79

Date of award: 4-7-80

ProQuest Number: 27777442

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent on the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest 27777442

Published by ProQuest LLC (2020). Copyright of the Dissertation is held by the Author.

All Rights Reserved.

This work is protected against unauthorized copying under Title 17, United States Code
Microform Edition © ProQuest LLC.

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 - 1346

Acknowledgement

The author wishes to thank Professor L. J. Haynes for the facilities in Chemistry laboratory of the Open University and for his interest in work.

She is particularly grateful to Dr. C. J. Harding for his patient guidance, devotion and encouragement during the course of this work.

Sincere thanks are given to Dr. A. Bassindale and Dr. M. Kanjia for their useful suggestions and valuable discussion.

Thanks are due to Mr. G. Jeffs and Mr. A.J. Leslie for their help in the construction of equipment, and the invaluable assistance of Mrs. M. Golden for the typing of this thesis.

She also wishes to thank the Open University for the grant received during the course of this work.

Finally, she is indebted to the member of her family, especially to her husband Yue Wah, for their never ending support.

Abstract

The pyrolysis of cis-1-chloro-2-butene has been studied in the temperature range 564 - 617 K. The predominant reaction is the elimination of HCl by a pathway that is believed to be homogeneous and unimolecular. The Arrhenius parameters suggests a six-centred activated complex :

$$\log \frac{k_1}{s^{-1}} = 12.81 + 0.77 - \frac{181800 + 8700 \text{ J mol}^{-1}}{2.303 \text{ RT}}$$

This reaction is accompanied by a relatively slow isomerisation, cis→trans, which is shown to be heterogeneous. Subsequent polymerisation of the product, butadiene also occurs.

Comparisons of the rate data for the elimination reaction with that of structurally similar compounds and with alkyl halides can be made. It appears that in the six-centred mechanism the hydrogen plays a more important role in the formation of the incipient hydrogen halide molecule than it is generally thought to do in the more usual four-centred mechanism. Nevertheless, electron-releasing groups have a large effect on the rate, similar to that observed in ester pyrolysis, and hence it is inferred that there is substantial development of polarity in the six-centred mechanism.

Contents

Chapter 1	Page
Introduction	1
1.1. Gas phase elimination reactions	2
1.1.1 The radical non-chain mechanism	2
1.1.2 The radical chain mechanism	2
1.1.3 The molecular mechanism	5
1.2 The pyrolysis of alkyl halides	6
1.3 The transition state in molecular gas phase elimination reactions	10
1.4 Substituent effects as a measure of the polarity of gas phase reactions	17
1.5 Multi-centre elimination reactions	18
1.5.1 Three-centre elimination reactions	18
1.5.2 Four-centre elimination reactions	20
1.5.3 Six-centre elimination reactions	20
1.6 Interpretation of activation parameters for gas phase reaction	23

Chapter 2		Page
2.1	Description of apparatus	25
2.1.1	The furnace and control	25
2.1.2	The vaccum line	27
2.1.3	Gas chromatography	28
2.2	Preparation of materials	31
2.2.1	3-bromopropene	31
2.2.2	Cyclohexene	31
2.2.3	But-2-yn-1-ol	31
2.2.4	<u>cis</u> -but-2-en-1-ol	32
2.2.5	<u>cis</u> -1-chloro-2-butene	32
2.3	Experimental technique	35
2.3.1	Seasoning of the reaction vessel	35
2.3.2	Procedure for a typical run	35
2.3.3	Analytical technique	37

Chapter 3

3.1	Stoichiometry of the reaction	39
3.2	Order of the reaction	45

	Page
3.3 Homogeneity	47
3.4 Effect of added inhibitor	49
3.5 Arrhenius parameters	53
Chapter 4	
Discussion	
4.1 Pyrolysis of cis-1-chloro-2-butene	56
4.2 Nature of the transition state	59
4.3 Polarity of the transition state	63
Appendix 1	70
Appendix 2	71
References	74

Chapter 1

INTRODUCTION

The main purpose of this kinetic study is to investigate the mechanism of the decomposition of 1-chloro-2-butene in the gas phase. In the pyrolysis, the compound has been found to decompose by the expected elimination reaction and to undergo some isomerisation. The effect of temperature on the rate constant, k_1 , of the elimination reaction has been studied and found to obey an Arrhenius equation. The activation parameters have been evaluated. From the interpretation of the rate of reaction and its response to a variable environment, the mechanism of the pyrolysis reactions have been inferred.

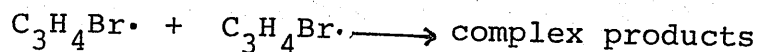
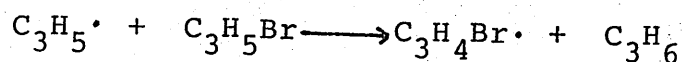
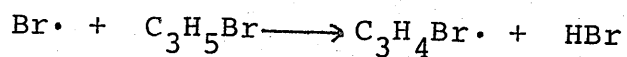
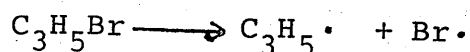
1.1 Gas phase elimination reactions

Elimination reactions of alkyl halides proceed by a variety of mechanisms. This was first pointed out in 1939 by Daniels and Veltman⁽¹⁾. They proposed that there were three possible mechanisms of homogeneous decomposition of alkyl halides, namely, radical non-chain, radical chain and unimolecular reactions.

1.1.1 The radical non-chain mechanism

An example of a radical non-chain reaction is given by the thermolysis of allylbromide (3-bromopropene) in a seasoned vessel⁽²⁾.

The mechanism was proposed to be:

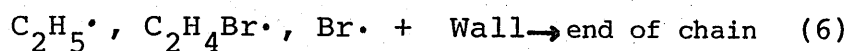
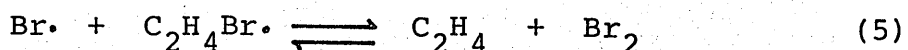
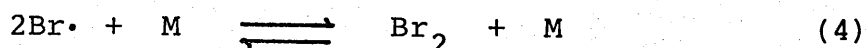
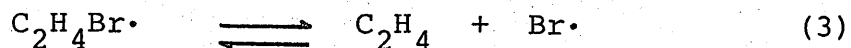
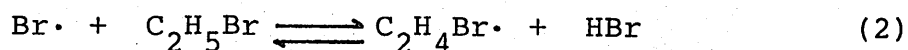
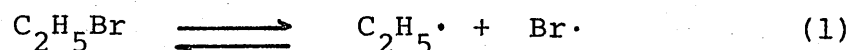


The radical non-chain mechanism in this case is confirmed by the fact that the activation energy ($189.7 \text{ kJ mol}^{-1}$) is in close agreement with the homolytic bond dissociation energy of the C-Br bond in allyl bromide⁽²⁾ ($190.2 \text{ kJ mol}^{-1}$).

1.1.2 The radical chain mechanism

A possible radical chain mechanism for the pyrolysis of

bromoethane⁽²⁾ is shown below:



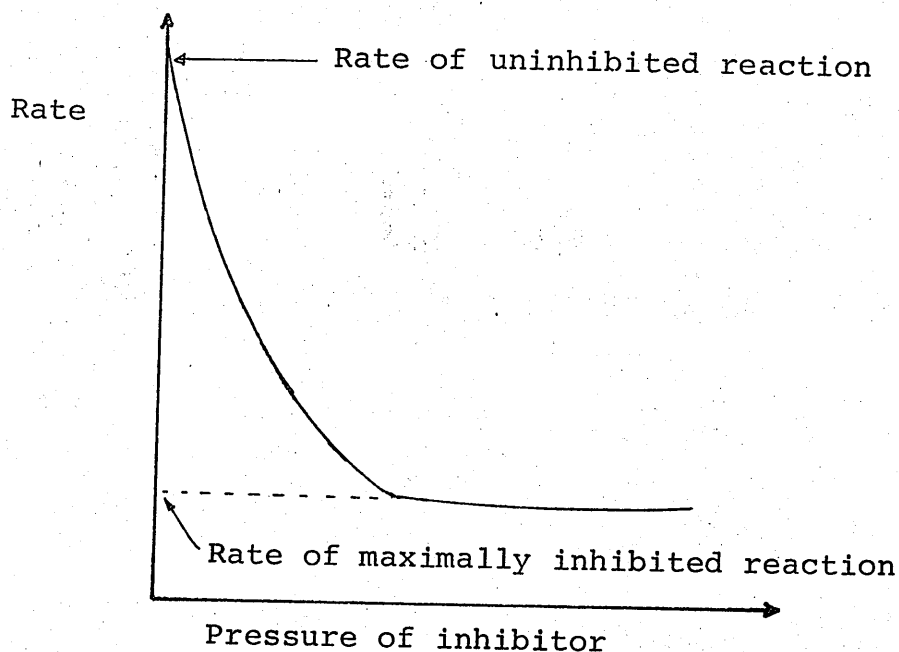
In this mechanism, (1) is the initiating step, (2) and (3) are the propagating steps, and (4), (5), (6) are possible chain-ending steps. The bromine-catalysis of this reaction can be explained in terms of steps (4), (2) and (5).

The radical chain mechanism is often recognised by the use of radical chain inhibitors, such as cyclohexene, propene or nitric oxide. Thus if the rate of a homogeneous gas-phase reaction is reduced in the presence of inhibitor, then it can be said that at least part of the reaction proceeds by a radical mechanism.

The effect of an inhibitor on many radical reactions is to reduce the rate (or rate constant) to some value which is then independent of further addition of inhibitor (Fig. 1.1).

Although Hinshelwood^(3,4,5) proposed that in the region of maximal inhibition, a molecular mechanism was operating in

Figure 1. Effect of an inhibitor



the decomposition of alkanes, aldehydes and ethers, this has been disproved by several workers. The main objection to this proposal has come from studies of isotopic mixing. Rice and Varnerin⁽⁶⁾ decomposed C_2D_6 in the presence of CH_4 . They found that the ratio of CH_3D to CH_4 formed was independent of the concentration of nitric oxide. The Hinshelwood mechanism predicts that this ratio should be zero at maximum inhibition and is therefore in direct conflict with experiment. Amongst the alkyl halides, however, the observation of a maximally inhibited reaction in the normal bromoalkanes has been interpreted as a molecular process⁽⁷⁾. Thus Capon has studied the pyrolysis of mixed bromoethane and chloroethane in the presence of cyclohexene and found that there was no interaction

between bromoethane and chloroethane.

1.1.3 The molecular mechanism

The majority of elimination reactions of alkyl halides proceed by a molecular mechanism. Evidence for this assertion comes from the agreement between the results obtained by the variety of methods used in the study of these reactions. These include static, flow⁽⁸⁾, single-pulse shock tube⁽⁹⁾ and chemical activation⁽¹⁰⁾. The static method has been used in the present work and is described in more detail in Chapter 2. Table 1.1 shows a comparison of results obtained by static methods and by shock tube studies; the agreement is excellent.

Table 1.1

Comparison of results by static and shock tube techniques

Compound	Static system			Shock tube system		
	$\frac{T}{C}$	$\log \frac{A}{s^{-1}}$	$\frac{E_A}{kJ mol^{-1}}$	$\frac{T}{C}$	$\log \frac{A}{s^{-1}}$	$\frac{E_A}{kJ mol^{-1}}$
chloroethane	420-500	13.63	237.8	550-730	13.16	235.8
2-chloropropane	370-410	13.40	211	480-680	13.64	213.6
2-chloro-2 methyl propane	290-330	13.72	188	480-680	13.73	186.8

Although no sufficient condition exists to test for a

unimolecular reaction in static systems, a set of requirements for a molecular mechanism can be stated:

- (i) first order kinetics at high pressure
- (ii) fall-off behaviour at low pressure
- (iii) absence of induction periods
- (iv) lack of effect of inhibitor added
- (v) lack of effect of increase in surface area

In the present work these criteria, with the exception of (ii), have been used to indicate the molecularity of the reaction.

1.2 The pyrolysis of alkyl halides

Since 1939 the elimination of hydrogen halides from alkyl halides to yield the corresponding alkenes has been studied in some detail. The nature of the reaction which occurs upon pyrolysis of an alkyl halide, i.e. whether unimolecular or free radical, homogeneous or heterogeneous, depends upon the halogen involved and upon the structure of the alkyl group concerned.

For fluoroalkanes, it was first thought that direct investigation of the pyrolysis reaction could not be studied using static or dynamic systems. This is because the liberated hydrogen fluoride attacks the carbonaceous coating and subsequently, the glass walls of the reaction vessel. Initially shock tube⁽¹¹⁾ and chemical activation⁽¹⁰⁾

methods were used successfully in the study of thermal decompositions of fluoroalkanes. But more recently, kinetic studies have been made in conventional static systems⁽¹²⁾. The pyrolyses are reported to be clean unimolecular reactions in vessels seasoned with fluoroethane⁽¹²⁾.

In most of the chloroalkane pyrolyses the rate appears to be unaffected by the addition of known radical scavengers and there are no induction periods. With a few exceptions, e.g. 1,2-dichloroethane, 3-chloro-1-propane, the chloroalkanes appear to decompose by a molecular mechanism.

As evidence for the mechanism of the process, the activation parameters of chloroethane decomposition obtained by previous workers, are set out in Table 1.2. It can be seen from the reproducibility obtained by different methods that the molecularity of the reaction is not in doubt.

Table 1.2

The Arrhenius parameters for chloroethane decomposition

$\log \frac{A}{s^{-1}}$	$\frac{E_A}{kJ\ mol^{-1}}$	Techniques	Ref.
13.63	237.8	static	13
13.16	236.2	shock tube	9
13.51	236.6	static	14
12.37	229.9	chemical activation	15

The behaviour of bromoalkanes is more diverse, although they can in general be classified into two groups. The addition of inhibitor reduces the rate of decomposition of primary bromoalkanes to a minimum value, and further addition of inhibitor up to high concentration does not produce an induced reaction. Secondary and tertiary bromides are not affected by the addition of inhibitors. This indicates that the decomposition of primary bromides is a mixture of unimolecular and radical chain reactions, while secondary and tertiary compounds decompose by unimolecular reactions.

The activation parameters of some bromoalkane decompositions, reported by previous workers, are listed in Table 1.3.

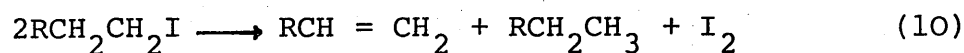
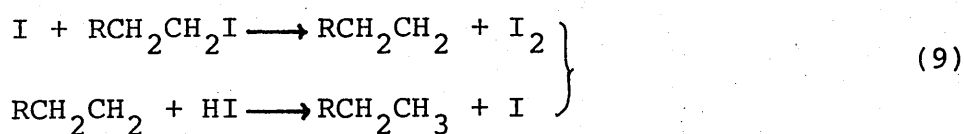
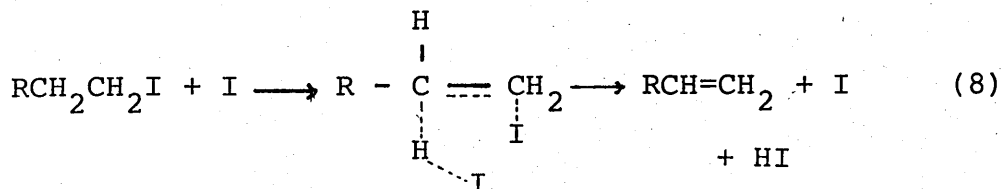
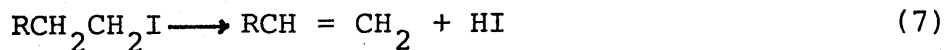
Table 1.3

The Arrhenius parameters for some bromoalkane pyrolyses

Compound	$\log \frac{A}{s^{-1}}$	$\frac{E_A}{kJ mol^{-1}}$	Ref.
bromoethane	12.86	218.6	8
	13.19	224.5	9
2-bromopropane	13.62	199.8	16
	13.60	199.4	8

In iodoalkane pyrolyses the unimolecular elimination (7) is complicated by an iodine-atom-catalysed elimination which may be a concerted process (8) and by the

iodine-atom-catalysed reduction by hydrogen iodide (9). The scheme proposed is represented by reactions (7) to (9).



The overall stoichiometry of iodoalkane pyrolysis is thus represented by (10). Benson⁽¹⁷⁾ regards the pyrolysis of iodoalkanes as effectively rate-controlled by the elimination of HI either via a direct four-centre route or via an iodine-atom-catalysed path. The Arrhenius parameters for the pyrolyses of a number of iodoalkanes are listed in Table 1.4.

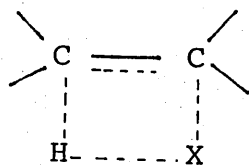
Table 1.4

The Arrhenius parameters for iodoalkanes pyrolyses

Compound	$\log \frac{A}{\text{s}^{-1}}$	$\frac{E_A}{\text{kJ mol}^{-1}}$	Ref.
iodoethane	13.53	206.1	18
	13.60	209	19
2-iodopropane	13.44	183.9	20
	13.67	188.5	9

1.3 The transition state in molecular gas phase elimination reactions

Before the mid 1950's, it was generally accepted that all gas-phase reactions, whether radical or molecular, were in principle homolytic. Thus the decomposition of alkyl halides in the gas phase could be considered to proceed through a homopolar four-centre transition state I



I

However, in 1953, Maccoll, et al⁽²¹⁾ observed that in the elimination of bromoalkanes, α -methylation produced a large increase in rate whereas β -methylation produced only a small increase. They concluded that the carbon-bromine bond strength was the main factor in determining the rate. Moreover, since the effect of changing the β -carbon from primary to tertiary was small, then the influence of the β -carbon-hydrogen bond on the rate was correspondingly slight.

In the elimination reactions of alkyl halides, the effects of many substituents have been investigated and all have been found to support an ionic transition state. This observation has been summarised by Maccoll⁽²²⁾: electron releasing groups in the α -position produce a large increase in rate and in the β -position a small increase in rate. The effects of α -methyl and β -methyl substitution for a number of alkyl halides⁽²³⁾ are shown in Tables 1.5 and 1.6.

Table 1.5

 α -methylation: relative rates of decomposition

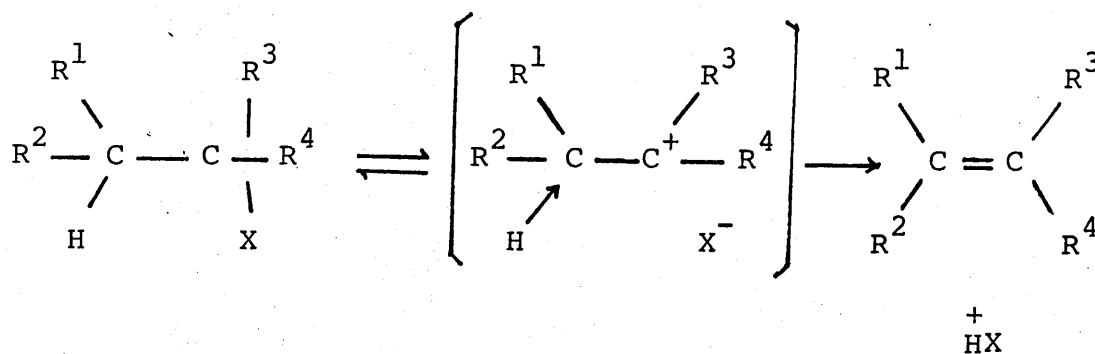
	T / °C	Ethyl	i-Propyl	t-Butyl
chloride	360	1	143	25,900
bromide	320	1	292	61,000
iodide	280	1	117	28,800

Table 1.6

 β -methylation: relative rates of decomposition

	T / °C	Ethyl	n-Propyl	i-Butyl
chloride	437	1	3.3	3.2
bromide	405	1	3.7	6.7

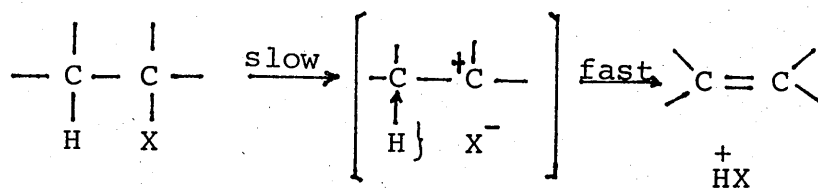
Further studies on substituent effects led Maccoll and Thomas⁽²⁴⁾ to point out that an analogy existed between these gas phase elimination reactions and S_N1 and $E1$ reactions in polar solvents, and they postulated a 'quasi'-heterolytic mechanism involving a very polar, intimate, ion-pair transition state as depicted in II.



II

The polar character of the transition state is depicted to develop mainly in the C - X bond as consistent with the substituent effects.

The α -hydrogen was suggested to possess the role similar to that of the solvent in a polar reaction in solution. Ingold⁽³⁵⁾ went further to suggest "a rate-determining step involving halogen heterolysis but no hydrogen loosening of any kind" and represented this by III.



III

Other electron releasing groups have also been reported to increase the rate of elimination. α -phenylation produces an increase in rate equal roughly to the effect of between one and two α -methyl groups, and β -phenylation is only roughly equal to β -methylation. The concept of an ionic transition state is also supported strongly by the effect of p-substituents in the ring in the

α -phenylchloroethanes⁽²⁵⁾. The effects of α - and β -halogenosubstitution have also been investigated⁽²³⁾, and relative rates are shown in Table 1.7. It is seen that whereas α -halogenosubstitution increases the rate of elimination, β -halogenosubstitution decreases it, which again parallels the effects observed in solvolysis⁽²⁶⁾.

Table 1.7

The effects of α - and β -halogen substitution

X = Bromine

T / °C	Relative elimination rates			
	CH ₃ CX ₃	CH ₃ CHX ₂	CH ₃ CH ₂ X	CH ₂ XCH ₂ X
416	--	9.6	1	0.25
437	32	8.2	1	0.55

Thomas⁽²⁷⁾ has investigated the substance 1-chloroethyl methyl ether which provides an extreme example of an electron releasing group, the methoxy group. In this study $E_A = 139$ (237) kJ mol⁻¹ and $\log \frac{A}{s^{-1}} = 11.46$ (13.43), the values in brackets being those for chloroethane. At 330 °C, the rate constant relative to chloroethane is 7×10^6 , mainly as a result of a decrease of 98 kJ mol⁻¹ in the activation energy. Thus the α -methoxyl group markedly enhances the rate of elimination.

The proposal of a heterolytic transition state is further supported by the relation between the activation energy and the heterolytic bond dissociation energy. Maccoll

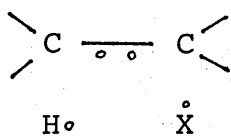
and Thomas⁽²⁴⁾ have observed that there is a general correlation between the activation energy and the heterolytic bond dissociation energy, i.e. $D(R^+ X^-)$, for a range of RX, while a less general correlation exists with the homolytic bond dissociation energy $D(R-X)$. The observed activation energy $E_A(HX)$ for elimination was found to be linearly related to the heterolytic bond dissociation energy. The relationship obtained was

$$E_A(HX) = 0.29 D(R^+ X^-)$$

A plot of $E_A(HX)$ against $D(R^+ X^-)$ is shown in Figure 1.2

A modification of the polar representation of the transition state proposed by Maccoll has been suggested by Benson and Bose⁽²⁸⁾ who postulated a semi-ion pair transition state for gas-phase elimination represented by IV.

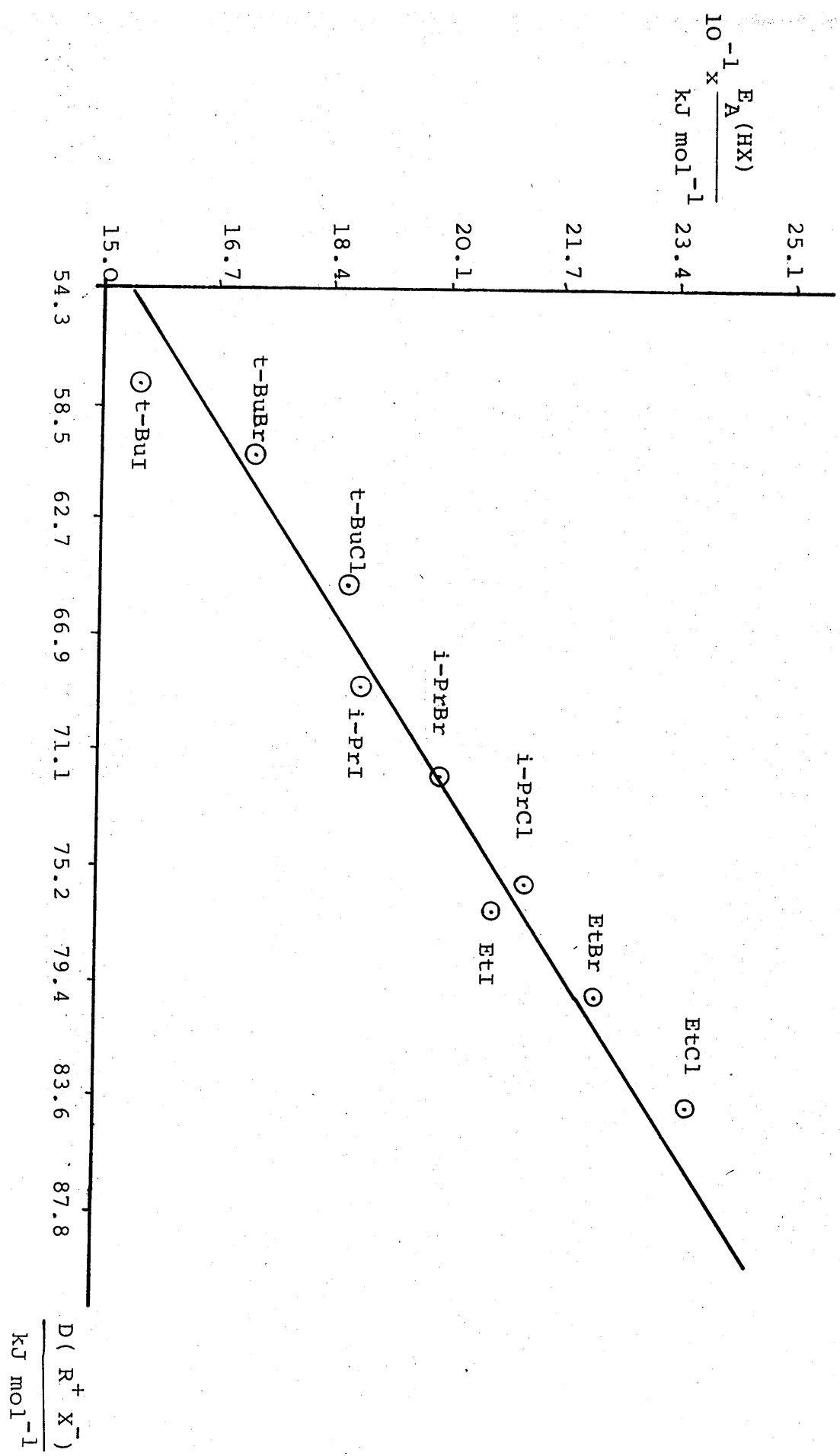
Using this model, good

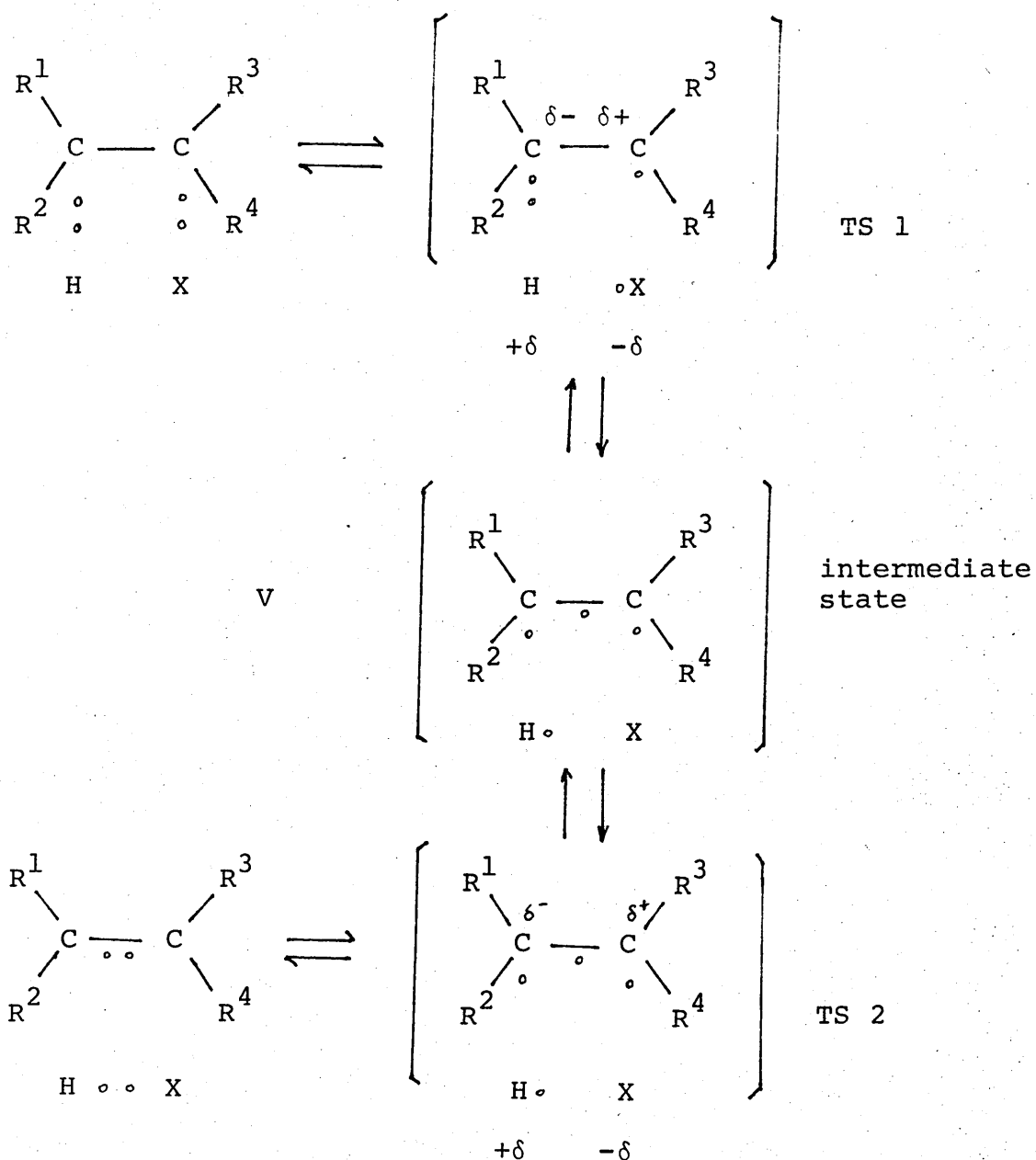


IV

agreement was observed between the experimental activation energies and those calculated from electrostatic interaction theory. Subsequently Benson and Haugen⁽²⁹⁾ depicted the transition state as quadrupolar structure, symbolised in V.

Figure 1.2 Plot of E_A (HX) against $D(R^+ X^-)$





In this model, the transition state is formed by an intimate association of two semi-ion pairs into a four-centre quadrupole with the formal charge separation of $\frac{1}{2}$ electron on each centre.

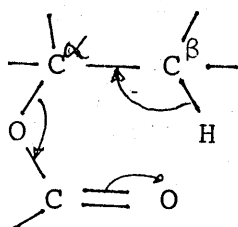
Recently, a model of the transition state has been proposed on the basis of the chlorine heavy atom kinetic isotope effect⁽³⁰⁾ in the elimination reaction of chloroethane. This model gives support to an extension

of the C-Cl bond together with a contraction of the C-C bond and an increase in the C-C-Cl bond angle in the activated complex, and appears to add support to the polar formulation shown in II.

1.4 Substituent effects as a measure of the polarity of gas-phase reactions

The effects of α -methyl substituent on the rate of gas phase reactions have been interpreted as a measure of the degree of polarity which develops in the transition state. For example, reactions which are non-polar and do not respond to changes in the polarity of the environment also fail to respond to methyl substitution; e.g. the decomposition of cyclobutanes reported by Frey and Walsh⁽³¹⁾. At the other extreme lie the chloroalkanes, where α -methyl substitution increases the rate by a factor of 150. In between one finds the esters where a factor of about 25 results from α -methyl substitution.

The heterolytic character of the transition state in gas phase reactions is not confined to alkyl halides. For instance, esters such as formates and acetates are found to decompose unimolecularly through a six-centred transition state and are strongly affected by electron-releasing substituents. Here α -methylation produces a rate increase by a factor of about 30 which is consistent with the redistribution of charge in the transition state shown in VI (e.g. see Ref. 32).



VI

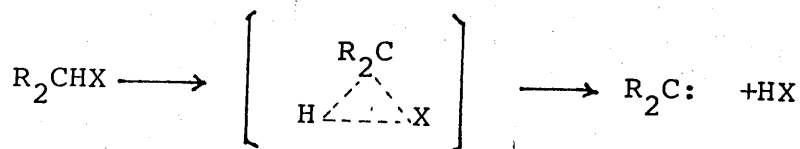
In this work the effects of methyl substitution on the rate of elimination of chloroalkenes is investigated.

1.5 Multicentre elimination reactions

Many studies show that a large number of gas-phase unimolecular reactions take place via multi-centre cyclic activated complexes. The Arrhenius parameters for these reactions often provide clues to the geometry of the activated complex. Activation energies are always lower than the bond dissociation energies of the weakest bonds in the molecule (indicative of concerted, bond-breaking-bond-forming processes) and activation entropies are usually quite negative.

1.5.1 Three-centre elimination reactions

The only likely route for the pyrolysis of halogenated methane is the elimination of hydrogen halide to give a carbene VII



VII

This has been shown to be the only mode of molecular decomposition of trifluoromethane^(33,34) and difluorochloromethane^(35,36) together with a competitive pathway by a radical route initiated by carbon-bromine fission in the case of difluorobromomethane⁽³⁷⁾. All these decompositions yield difluorocarbene which rapidly dimerizes. The α -elimination of HCl to give dichlorocarbene has been proposed in the pyrolysis of trichloromethane⁽³⁸⁾, but it is likely that this pathway is less important than the radical route. The Arrhenius parameters for α -elimination from the difluorohalomethane are given in Table 1.8. For the three-centre transition state suggested, the A factors would be expected to lie between 10^{13} s^{-1} and 10^{14} s^{-1} . There is little difference in the rates of elimination of hydrogen chloride and hydrogen bromide whereas hydrogen fluoride elimination is a much slower process.

Table 1.8

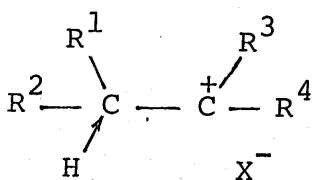
 α -hydrogen halide elimination from halomethane

	$\log \frac{A}{\text{s}^{-1}}$	$E_A/\text{kJ mol}^{-1}$	Ref.
$\text{CF}_2\text{HF} \rightarrow \text{:CF}_2 + \text{HF}$	12.2	249	33
	11.8	244	34
$\text{CF}_2\text{HCl} \rightarrow \text{:CF}_2 + \text{HCl}$	13.8	233	35
	12.6	221	36
$\text{CF}_2\text{HBr} \rightarrow \text{:CF}_2 + \text{HBr}$	14.3	232	37

It can be seen that agreement between different workers is poor, and the wide range of values of A factors does not help to illuminate the detailed mechanism of this 1,3 elimination.

1.5.2 Four-centre elimination reaction

In the earliest studies of the unimolecular elimination of HX from alkyl halides, the four-centre nature was already known, although the 'ionic' character of the reaction and its mechanistic importance were not realised until Maccoll and Thomas first proposed a 'quasi-heterolytic' reaction path (see Section 1.4). The concept of a highly polar or quasi-ionic activated complex II involved in this cis-elimination process has generally been accepted in view of the large amount of experimental data discussed earlier.

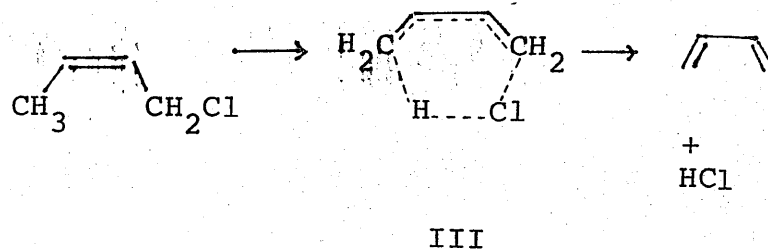


II

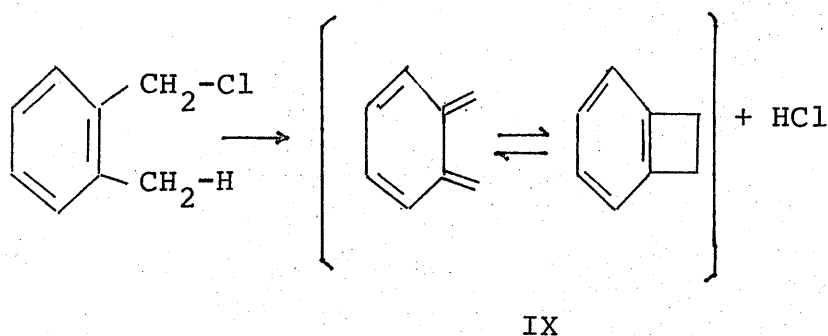
1.5.3 Six-centre elimination reaction

Some work on six-centre transition states in reactions involving halogen compounds has been communicated⁽³⁹⁾. In a study of the pyrolysis of 1-chloro-2-butene, Rodgers⁽⁴⁰⁾ observed fast starts, which were later interpreted by Harding⁽⁴¹⁾ as the rapid decomposition of a small amount of the cis-isomer in a mixture dominated

by the trans isomer. It was thus suggested that a six-centred transition state VIII is plausible for the elimination of cis-1-chloro-2-butene



In 1968, Wong⁽⁴²⁾ observed elimination of hydrogen chloride from o-chloro-o-xylene IX

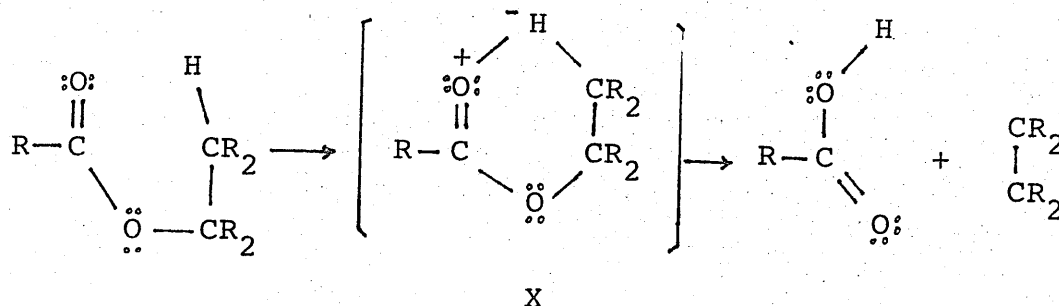


and concluded that in the formation of benzocyclobutene, o-quinodimethane was first produced. The mechanism involved a similar six-centred transition state to that suggested for cis-1-chloro-2-butene which at that time had not been studied in a pure form in kinetic runs. Harding⁽⁴¹⁾ in his study of 1-chloro-3-methyl-2-butene pyrolysis, found that the rate of reaction was appreciably faster than that of 3-chloro-3-methyl-2-butene pyrolysis, indicating that former compounds followed a six-centred reaction

path which is not accessible to the latter compound. Walsh⁽⁴³⁾ has also observed elimination of HI from cis-1-iodo-but-2-ene through a six-centred reaction path.

Recently, Robinson and coworkers⁽⁵⁸⁾ have studied the thermal decomposition of cis-4-chloro-pent-2-ene. The very low A factor is consistent with the expected loss of internal rotation in the transition state, although it is rather low in comparison with other six-centred mechanisms and with estimates of the A factor such as those made by Benson⁽⁴⁴⁾ and Umana⁽⁴⁵⁾.

Apart from suitable substituted allylchlorides, other compounds such as esters which possess a β -hydrogen in the alkyl group, may decompose into acid and alkenes via a six-centred transition state⁽⁴⁶⁾ X



The work described in this thesis is in connection with the gas-phase elimination of HCl from cis-1-chloro-2-butene which is also supposed to undergo a six-centre elimination of HCl. The conclusions drawn from this work depend, as do most of the studies of six-centre mechanisms on the

interpretation of 'low' A factors, and on the relative values of activation energies.

1.6 Interpretation of activation parameters for gas phase reaction

A simple interpretation of transition state theory for a unimolecular reaction is given by

$$A = \frac{ekT_m}{h} \exp \left\{ \frac{\Delta S^\ddagger}{R} \right\} \quad (11)$$

Calculation of A factors requires estimates of ΔS^\ddagger , the entropy of activation. Benson and coworkers⁽²⁹⁾ have, on the basis of transition state theory, combined with relatively simple valence bond and electrostatic semi-empirical concepts, derived a method of semi-qualitative predictions of activation energies and entropies for a few classes of compounds.

For multicentre unimolecular concerted reactions, O'Neal and Benson⁽⁴⁴⁾ derived a method for calculating entropies of activation ΔS^\ddagger which served to predict log A, by assigning bending, stretching and torsion frequencies to one and three electron bonds in the transition state.

A recent approach to the interpretation of activation energies has been developed by Woodward and Hoffmann⁽⁴⁹⁾ involving the conservation of orbital symmetry. They predicted that reactions which occur with conservation of orbital symmetry would have activation energies much lower than related reactions which occur without

conservation of orbital symmetry. The ease with which 1,4-elimination and 1,4-addition of HX to 1,3-alkadienes occurs is consistent with the deduction that such 1,4-processes are symmetry allowed. By contrast, the 1,2-elimination reactions are symmetry forbidden, and it has been suggested⁽⁴⁹⁾ that the polar nature of the transition state imparts some degree of allowedness to these reactions, although their activation energies are still relatively high.

Pro

Anal

Chapter 2

2.1 Description of apparatus

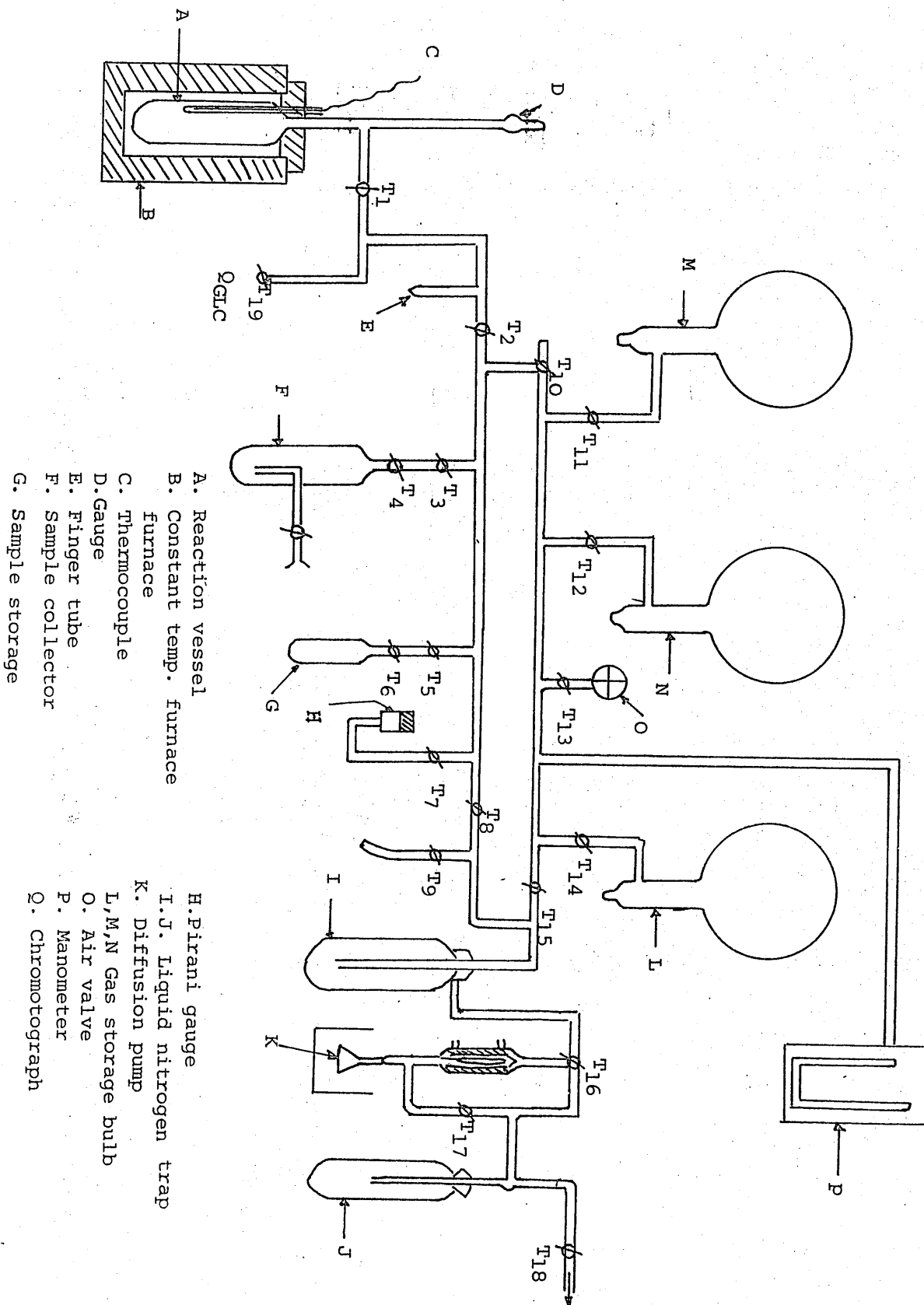
The vacuum line was built as shown in Figure 2.1. The reaction vessel was a Pyrex glass tube with hemispherical ends. It was 5.2 cm in diameter and 14 cm long, giving a volume of approximately 300 cm³. It was situated in a thermostatted furnace. A thin glass diaphragm pressure gauge was mounted above the vessel to enable pressure measurements to be carried out without contact of the reactants and products with the manometric liquid.

2.1.1 The furnace and control

The furnace consisted of a cylindrical aluminium block and was surrounded by an asbestos box containing micafill and glass fibre wool for minimising heat losses. The block was bored out centrally to accommodate the reaction vessel. The block was heated with a nichrome element wound on sheets of mica around the block; the windings being more closely spaced at the top, in order to compensate for the heat loss through the insulation on the top of the furnace.

Temperature was measured using a chromel-alumel thermocouple which was placed in a glass tube, previously sealed into the reaction vessel. The hot junction was placed in the thermocouple sleeve and the cold junction was immersed in a vacuum flask filled with wet, crushed

Figure 2.1 Apparatus for kinetic measurement



ice. The thermocouple potential was measured to within 0.0001 millivolts with a potentiometer, Type P10⁻⁷ (Croydon Precision Instrument). The temperature of the furnace was controlled by a Versicon Type 101 (C.N.S. Instrument Ltd.) controller coupled to a platinum resistance thermometer which was inserted into a hole in the metal block.

To prevent heat losses from the tubes connecting the reaction vessel, heating tape and asbestos paper were wound onto these sections.

2.1.2 The vacuum system

The vacuum system is shown diagrammatically in Figure 2.1.

The reaction vessel A was cylindrical with a capacity of about 300 cm³. The sleeve C housed the hot junction of the thermocouple which was used to measure the temperature of the reacting system. A second vessel of a similar design contained four concentric glass cylinders. This was the packed vessel used for the homogeneity tests.

The vessel was connected by heated capillary tubing to the pressure gauge D and by heated tubing to the sample valve of the gas chromatography and to 'finger' E.

Finger E was used to condense the reactant before it was introduced into the vessel. Tap T2 isolated the vessel from the rest of the vacuum system. The capillary tubing between T2 and the vessel A constituted the 'dead space', which was wound with nichrome wire and heated to a

temperature above 100 °C to prevent condensation. Taps T1 and T2 were mounted as close as possible to the vessel in order to minimise the dead space. Trap F, which was removable, was used for condensing the reaction products for analyses for HCl. Tube G was used for storing liquid reactants. Reservoirs L, M, N were used for gas storage.

The pressure gauge on the top side of the reaction vessel was connected to a Ferranti Minicom transducer.

The reaction system was evacuated by a rotary oil pump and a mercury diffusion pump K. A pirani gauge H was used to determine the pressure in the vacuum system, which could be reduced to approximately 10^{-4} torr with the pumping system.

2.1.3 Gas chromatography

All quantitative analyses were made by gas chromatography using a Varian 1400 gas chromatograph with a flame ionisation detector. A number of columns were made for this work. The procedure employed is described in the literature⁽⁵⁰⁾. The columns are listed below (Table 2.1), and the retention times under the operating conditions are listed in Table 2.2

Column 4 consisted of two stationary phases connected in series. The squalene was added because, on column 3, vinyl cyclohexene, a dimerisation product of 1,3-butadiene,

Table 2.1
Columns for gas chromatography

Column No.	Liquid phase	Concentration	Support	Length
1	Di-lauryl-phthalate	5%	80-100 chrom. W A.W. DMCS	6 ft
2	β,β -Dithiopropionitrile	10%	80-100 chrom. W A.W. DMCS	10 ft
3	β,β -Dithiopropionitrile	20%	80-100 chrom. G A.W. DMCS	20 ft
4	β,β -Dithiopropionitrile	20%	80-100 chrom. G A.W. DMCS	20 ft
	Squalene	20%	80-100 chrom. G A.W. DMCS	1 ft

had a retention time between those of cis- and trans-1-chloro-2-butene, while cyclohexene had a retention time between 1,3-butadiene and 3 chloro-1-butene.

Quantitative analysis of the reaction products was made using column 4. The relative response of the flame ionisation detector to the reactants and products was established by analysing mixtures of known composition. It was found that the response to each of the chlorobutenes was equal, but that to 1,3-butadiene was higher:

$$\text{butadiene} : \text{chlorobutene} = 1.20 : 1.00$$

This ratio was subsequently used in the determination of the partial pressures of chlorobutenes and 1,3-butadiene in the reaction mixture. Peak areas were measured by triangulation.

Table 2.2

Column 1 : $T/^{\circ}\text{C} = 85$	
Flow Rate / $\text{ml min}^{-1} = 25$	
Substance	Retention time/min
propyn-3-ol	3.2
but-2-yn-1-ol	8.7
iodomethane	0.9

Column 2 : $T/^{\circ}\text{C} = 70$	
Flow rate / $\text{ml min}^{-1} = 25$	
Substance	Retention time/min
Butanol	12.5
<u>trans</u> but-2-en-1-ol	22.2
<u>cis</u> -but-2-en-1-ol	30.9
3 buten-1-ol	17.1

Column 3 : $T/^{\circ}\text{C} = 50$	
Flow rate / $\text{ml min}^{-1} = 25$	
Substance	Retention time/min
3 chloro-1-butene	15.1
<u>trans</u> -1-chloro-2-butene	31.2
<u>cis</u> -1-chloro-2-butene	34.4

Column 4 : $T/^{\circ}\text{C} = 50$	
Flow rate / $\text{ml min}^{-1} = 25$	
Substance	Retention time/min
1,3 butadiene	5.1
3-chloro-1-butene	16.6
<u>trans</u> -1-chloro-2-butene	34.2
<u>cis</u> -1-chloro-2-butene	38
4-vinylchlorohexene	50

2.2 Preparation of materials

2.2.1 Alkyl bromide

High purity allylbromide was obtained by repeated distillation.

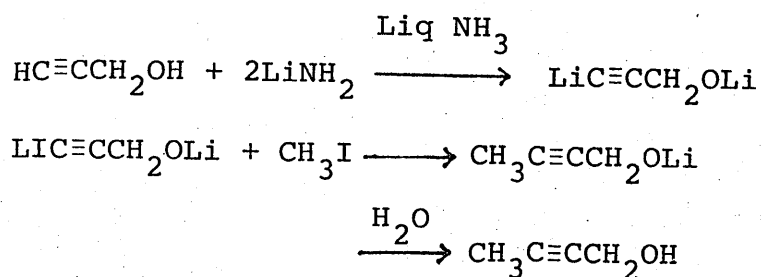
2.2.2 Cyclohexene

A commercial sample was shaken with ferrous sulphate to remove peroxides. It was dried over calcium sulphate and distilled in an atmosphere of nitrogen.

2.2.3 2-Butyn-1-ol

The method followed is that described in reference 51.

The following reactions were followed:



The 2-Butyn-1-ol was prepared by adding 2 moles of propyn-3-ol into a suspension of 4 moles of LiNH_2 vigorously stirred in 2.5 litre of liquid ammonia. The suspension became very thin after the addition.

Subsequently 2 moles of iodomethane was added to the mixture while nitrogen was bubbled through the flask. At the end of the reaction, the ammonia was allowed to evaporate overnight. The solid residue remaining was

dissolved in 1 litre of cold water ($^{\circ}\text{C}$). The resulting solution was subjected to continuous extraction with ether for 40 hours. (A perforator of sintered glass was used, shown in Figure 2.2.). The ethereal solution was dried over 100 g of magnesium sulphate. After the greater part of ether had been distilled off, the residue was carefully fractionated through a 30 cm long vigreux column at reduced pressure.

The compound $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{OH}$ had $T_b = 48^{\circ}\text{C}$ (15 torr)

The yield was 76-80%

2.2.4 cis-but-2-en-1-ol

The cis-but-2-en-1-ol was prepared by hydrogenation of but-2-yn-1-ol. 290 ml of methyl alcohol, 8 g of palladium on barium sulphate and 25 g (0.357 mole) of but-2-yn-1-ol were stirred in contact with hydrogen for three hours in a 1 litre flask. In this time 0.357 mol of H_2 was consumed, after which the methanol was removed by distillation through a 30 cm long vigreux fractionating column. The cis-2-buten-1-ol was then distilled through the same column at reduced pressure.

The compound $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$ had $T_b = 63^{\circ}\text{-}64^{\circ}\text{C}$ (60 torr)

The yield was typically about 75%.

2.2.5 cis-1-chloro-2-butene

A mixture of 2 moles of cis-2-buten-1-ol obtained as above and 44.5 g of pyridine was added slowly to 0.8 mole of phosphorous trichloride. The reaction flask was

Figure 2.2 Apparatus
for continuous extraction

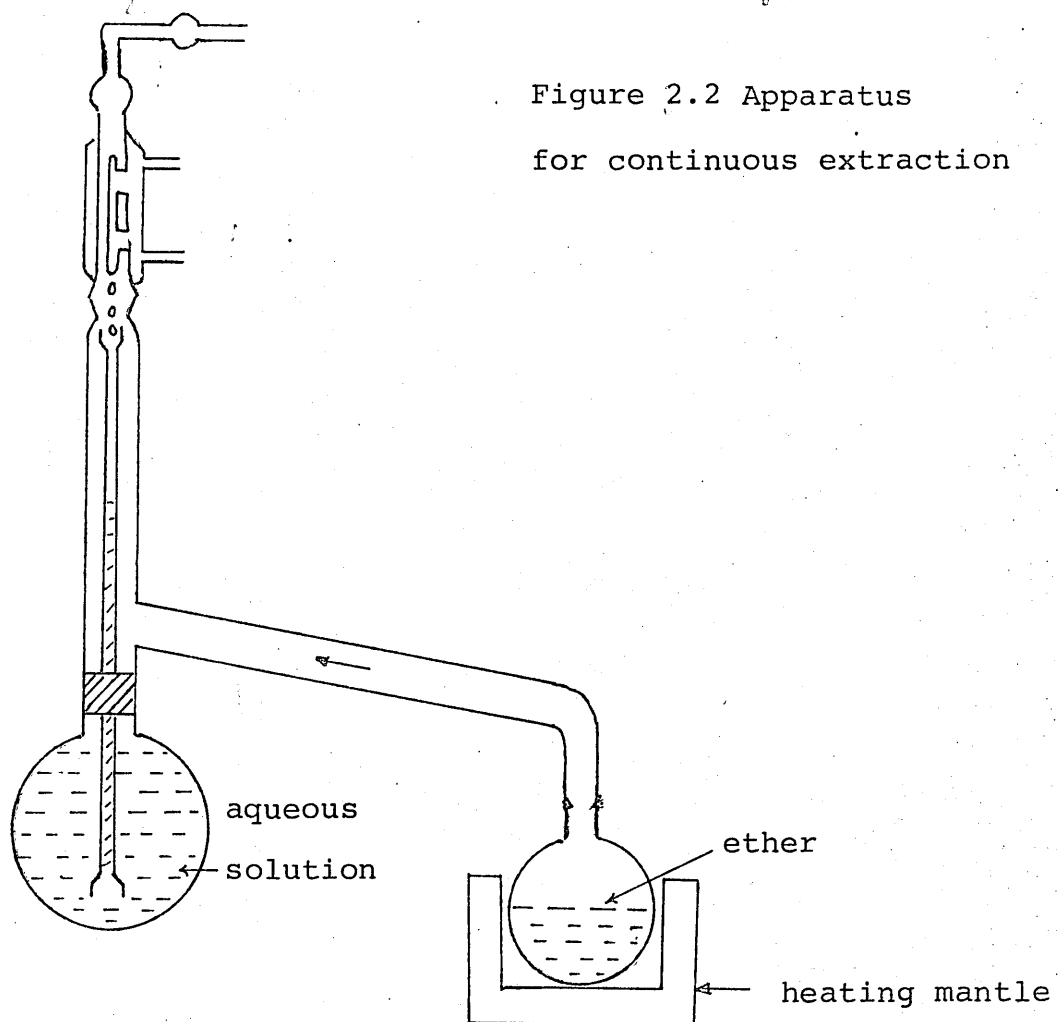
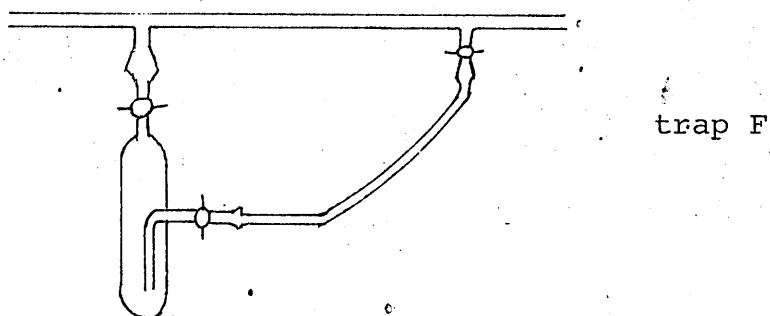


Figure 2.3 Trap for HCl analysis



surrounded by iced/water during this addition. When all the alcohol had been added, a liquid-nitrogen trap was connected directly to the reaction flask and the system was maintained at a pressure of 100 torr. The reaction flask was then placed in a water-bath at 50 °C and the cis-2-buten-1-ol distilled into the trap. The distillate was washed with dilute sodium carbonate solution to remove traces of hydrogen chloride and then placed over anhydrous potassium carbonate to dry overnight. The organic chloride was decanted from the potassium carbonate and distilled through a 30 cm long vigreux column.

The compound cis-CH₃CH = CHCH₂Cl had T_b = 84.1 °C (758 torr) The yield was usually about 50%.

GLC analysis showed that the compound usually contained an isomeric mixture of the following composition* .

3 CB	~	3.5%
<u>trans</u> 1C2B	~	95%
<u>cis</u> 1C2B	~	1.5%

*It is convenient to refer to the three isomers using a shorthand notation:

3ClB = 3-chloro-1-butene

cis 1C2B = cis-1-chloro-2-butene

trans 1C2B = trans-1-chloro-2-butene

The compound was normally prepared a day before the kinetic runs were performed because isomerisation tended to occur if the compound was kept, even at 0°C.

2.3 Experimental technique

2.3.1 Seasoning of the reaction vessel

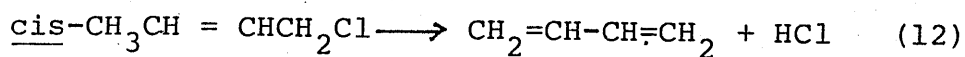
It has been found from early studies that the decomposition rate of many compounds when studied in a clean glass vessel are fast and irreproducible. The decomposition, however, usually becomes reproducible and proceeds at a slower rate if the surface of the vessel is coated with a carbonaceous film. Maccoll⁽²⁾ has shown that allylbromide yields a useful carbonaceous coating, and in this work allylbromide was the source of the coating for all the runs.

2.3.2 Procedure for a typical run

The material to be pyrolysed was placed in a specially made tube G (Figure 2.1) which was fitted to one of the sockets on the vacuum line. The material was degassed, and a small amount (0.1 to 0.5 cm³ depending on the required initial pressure) was then distilled into the finger E and tap T2 was closed. By heating E with a stream of hot air, the reactant was vaporised through T1 into the reaction vessel. Tap T1 was then closed immediately. From this moment, the pressure was recorded on a chart recorder connected to the gauge meter.

Before the end of the run, the section of the line between taps T2 and T19 was evacuated and T2 was then closed. The vessel tap T1 was opened and a small sample of product was injected into the GLC for analysis and the rest of the product was trapped in tube F for titration of hydrogen chloride. The amount used for gas chromatographic analysis was about 2 cm³ in volume, i.e. less than 1% of the total reactor volume. Therefore no correction was necessary to the analysis of hydrogen chloride.

The main interest of this work is the determination of the Arrhenius parameters for reaction (12), the elimination. The rate constant for this reaction was estimated from the HCl reaction profile which was measured over a range of temperatures. At three temperatures in this range, a complete reaction profile of elimination and isomeric products was determined to examine the extent of the competing isomerisation reactions. Only in these three extensive studies was gas chromatographic analysis carried out.



For the runs to which inhibitor was added, the inhibitor was introduced into the reaction vessel before the reactant. Care was taken to open the vessel tap for only a very short time to ensure that the reactant entered the vessel without releasing any inhibitor into the line.

2.3.3 Analytical techniques

(a) Calibration of the reactor volume

Before the estimation of the partial pressure of hydrogen chloride in the products was made, it was necessary to find the volume of the reaction vessel. This was done separately by relating the pressure of hydrogen chloride in the vessel to the volume of standard alkali solution required to neutralise the hydrogen chloride. A certain pressure of hydrogen chloride was admitted to the vessel from the storage bulb and this pressure was recorded using the pressure gauge. The vessel was then opened to a trap F which was attached to one of the sockets as shown in Figure 2.1. This trap was cooled by liquid nitrogen and the gas condensed quantitatively into it. After removal of the trap, about 20 cm³ of water were introduced through the upper end of the trap and the trap was shaken to dissolve the hydrogen chloride. The acid solution was transferred into a conical flask and titrated with sodium ethoxide solution using phenolphthalein as indicator. The procedure was repeated several times with good agreement. The volume of the reaction vessel was then calculated on the assumption that at the temperature and pressure concerned, HCl obeys the ideal gas law.

(b) Determination of amount of hydrogen chloride from a run

The procedure of trapping the reaction products for hydrogen chloride analysis was as follows:

Approximately 20 cm³ of A.R. acetone was put into the trap, degassed and cooled to -196 °C by liquid nitrogen. At the end of the run, the reaction products were condensed into this trap and dissolved in the acetone. The trap was shaken thoroughly to dissolve the hydrogen chloride. This solution was transferred into a conical flask and titrated with sodium ethoxide solution using phenolphthalein as indicator. This analytical technique was tested to show that solvolysis of the organic chloride did not happen during the titration. Tests were also made to show that no addition of hydrogen chloride to the alkene occurred in the sampling procedure.

(c) Gas-liquid chromatographic analyses

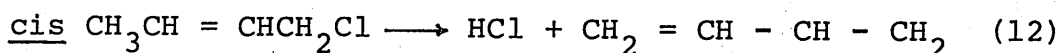
The gas chromatograph was connected to the vacuum system as shown in Figure 2.1. At the end of the run, the vessel tap T1 was opened (tap T2 was closed) and the products allowed to expand into the sample loop. This sample was then injected from the sample loop into the GLC and the analysis was performed. Tests were performed on the chloroalkenes and mixtures of HCl and butadiene to examine whether isomerisations or addition occurred during sampling. No isomerisation was found to occur, and the extent of addition was less than 1% of an equimolar mixture of HCl and butadiene.

CHAPTER 3

Pyrolysis of cis-1-chloro-2-butene

3.1 Stoichiometry of the reaction

cis-1-chloro-2-butene was pyrolysed in the temperature range 291 - 344 °C. By analogy with the decomposition of other unsaturated organic chlorides previously studied, it was expected that the predominant reaction would be the elimination of hydrogen chloride (12), although it was also expected that as with other chloroalkenes, isomerisation would occur⁽⁴⁰⁾. This reaction would be followed by a much slower dimerisation of the alkene product, butadiene under the studied temperature range⁽⁵²⁾.



According to equation (12), during the pyrolysis of cis-1-chloro-2-butene, the total pressure should increase smoothly and the ratio of the final pressure to the initial pressure should be two. However, by comparing the extent of the reaction measured by the pressure gauge and by hydrogen chloride analysis (shown in Table 3.1), it was apparent that the pressure increase as measured by the gauge was always less than the partial pressure of HCl. This was due to the subsequent polymerisation of the elimination product, butadiene, mainly to form

vinylcyclohexene⁽⁵²⁾, at long reaction times. It was also found that pressures measured with the gauge were less reproducible than partial pressure measurements made by titration of HCl. It was therefore decided to measure hydrogen chloride using titration instead of by measurement pressure increase.

An extreme study of the pyrolysis of the compound was carried out at three temperatures and the reaction profiles were obtained.

In the extensive study, GLC was used to measure the relative concentrations of butadiene, cis-1-chloro-2-butene, trans 1-chloro-2-butene and 3-chloro-1-butene. Hydrogen chloride was measured separately by titrating with a standard alkali solution. The relative concentrations of the organic substances listed were converted to partial pressures using the total pressure and the partial pressure of HCl. This procedure ignores the polymerisation of butadiene, but since the kinetic measurements were based mainly on the first 50% of the elimination reaction when the extent of polymerisation is very low⁽⁵²⁾, then this assumption does not affect the reaction profile substantially. The partial pressure of HCl is, in any case, unaffected.

The results of the extensive studies (reaction profiles) are shown in Figures 3.1, 3.2 and 3.3. The vertical axes of Figures 3.1, 3.2 and 3.3 are graduated in relative pressure units based on p_0 (total) = 1.

Figure 3.1 Pyrolysis of cis-1-chloro-2-butene at 609 K

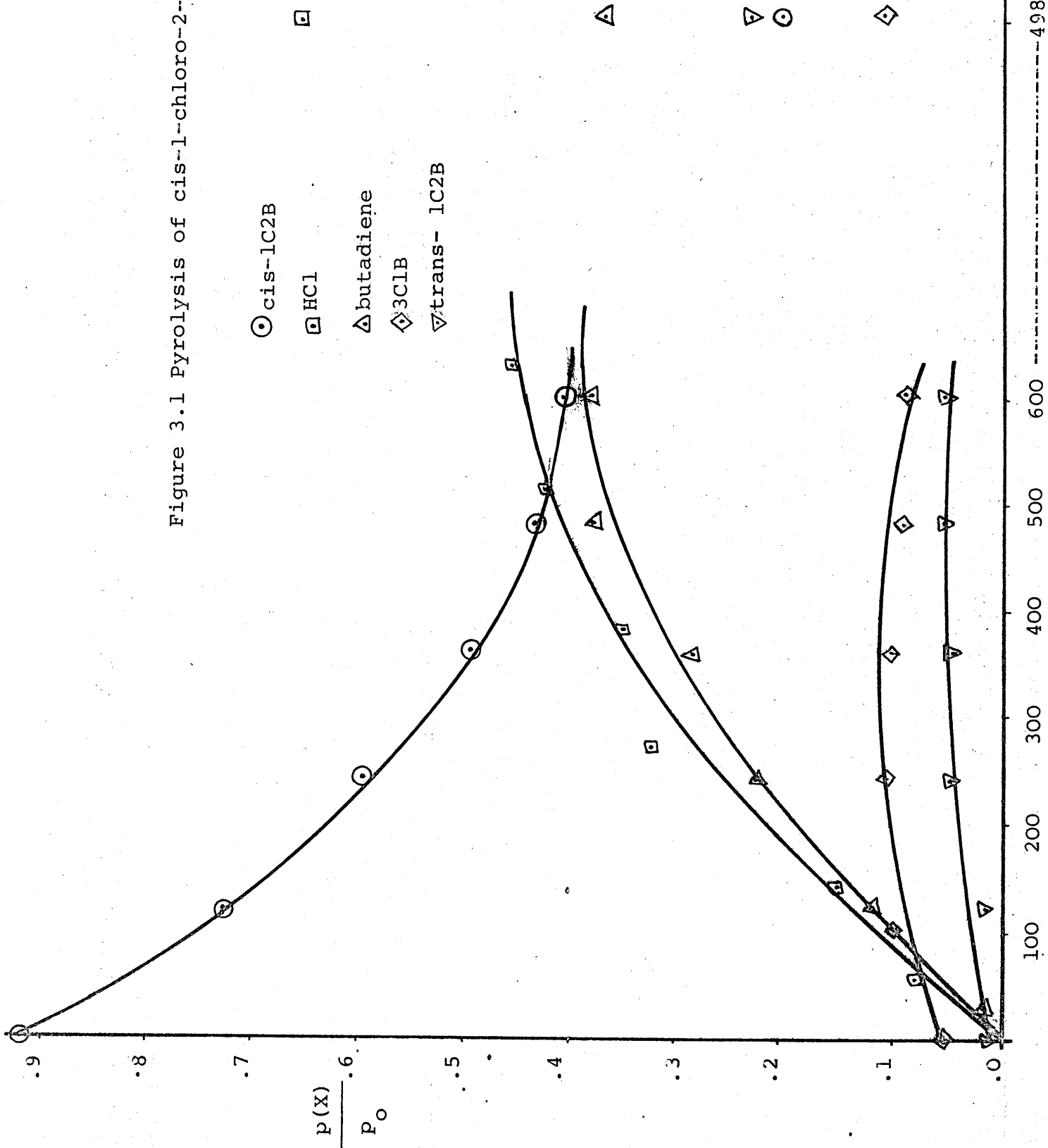


Figure 3.2 Pyrolysis of cis-1-chloro-2-butene
at 573.65 K

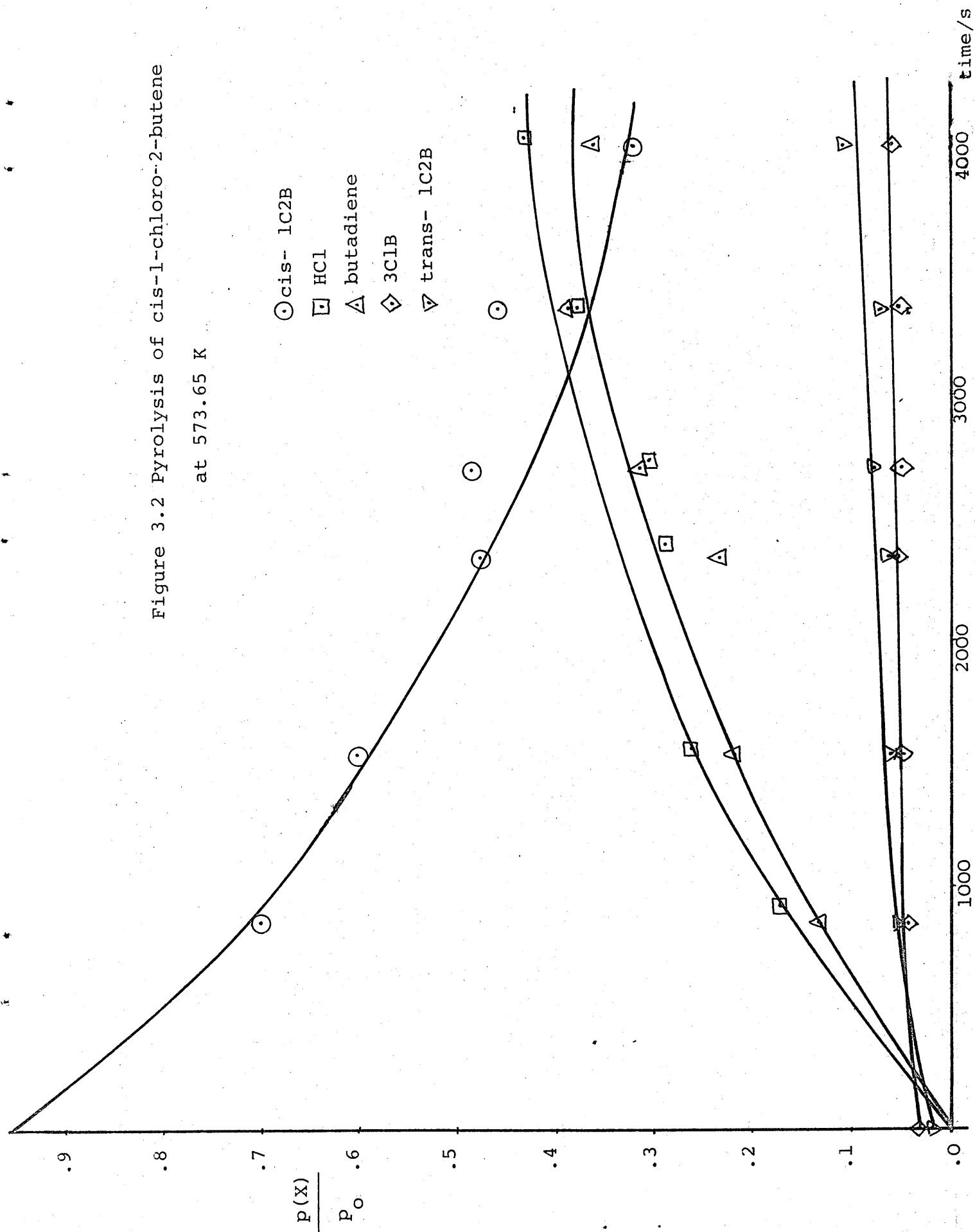
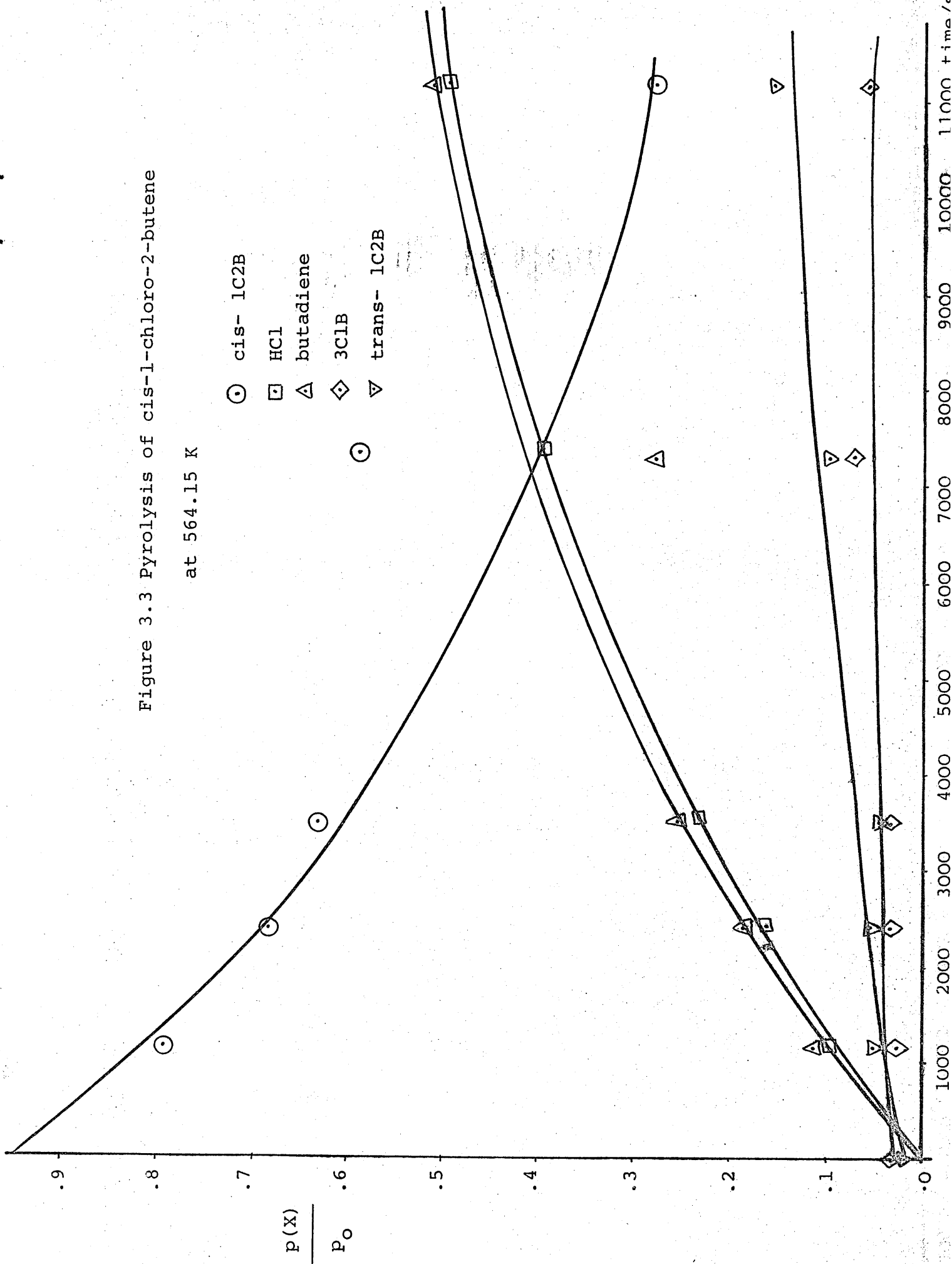


Figure 3.3 Pyrolysis of cis-1-chloro-2-butene

at 564.15 K

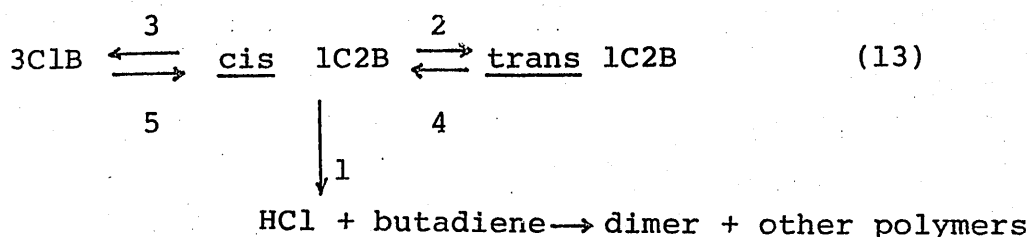
- cis- 1C2B
- HCl
- △ butadiene
- ◇ 3C1B
- ▽ trans- 1C2B



The diagrams show clearly the smooth disappearance of cis-1-chloro-2-butene and the formation of hydrogen chloride and butadiene at approximately the same rate. The increasing difference with time between hydrogen chloride and butadiene can be attributed to the dimerisation of butadiene. The 3-chloro-1-butene and trans-1-chloro-2-butene only contributed a very small amount to the total pressure.

The possibility that the elimination reaction was reversible was ruled out on the following evidence. The pressure of an equimolar mixture of butadiene and hydrogen chloride was found to decrease at exactly the same rate as that of butadiene alone. An analysis showed that no organic chlorides were produced after an equimolar mixture of butadiene and hydrogen chloride was left in the reaction vessel for several half-lives of the elimination reaction. Furthermore, no reactant remained in runs taken for a very large number of half-lives of the elimination reaction. These experiments convincingly prove that the isomerisation observed must have occurred by route 2 and 3 and did not occur by the reversal of route 1.

The reaction scheme is therefore:



Reactions 4 and 5 are included because they have been reported to play a prominent part in the pyrolysis of 3ClB and trans 1C2B, at only slightly higher temperatures than are used in this work⁽⁴⁰⁾.

Table 3.1

T = 598.7K

Partial pressure/torr

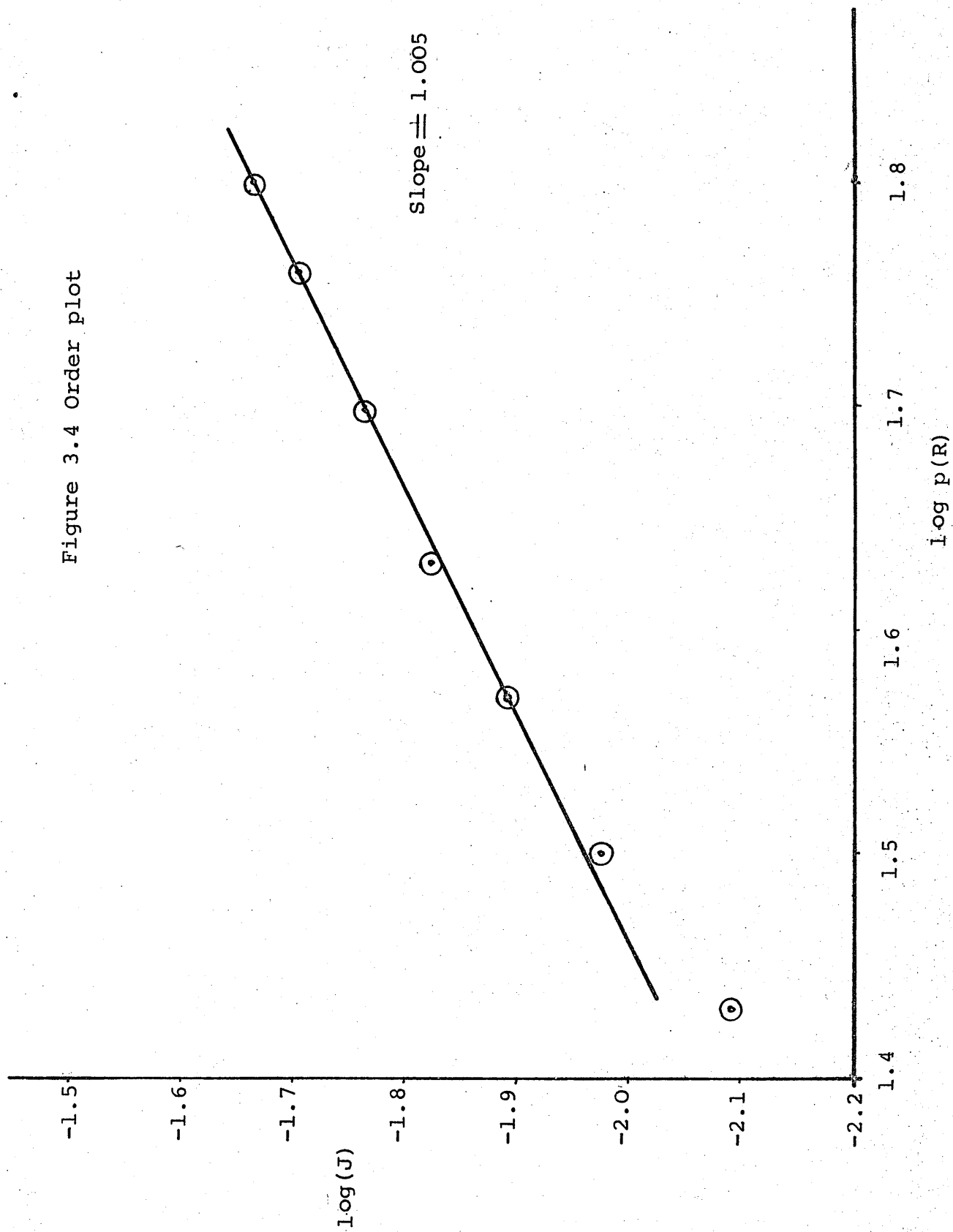
by HCl analysis	24.3	14.2	9.5	60.3
by pressure gauge	23.4	13.3	9.7	57

3.2 Order of the reaction

In the pyrolysis of cis-1-chloro-2-butene, the production of hydrogen chloride is described by the reaction profile showing partial pressure by HCl (Figures 3.1, 3.2, 3.3). After about one half-life of the elimination reaction, the partial pressure of the isomeric chlorides increased by about 5% of the total pressure. This relatively slow isomerisation did not significantly affect the kinetic behaviour of the reaction.

A series of decompositions were carried out in the temperature range 291 - 344 °C. When examined, the runs gave good first order log plots: the typical order plot was obtained by plotting $\log \left[\frac{dp(\text{HCl})}{dt} \right]$ against $\log p(\text{R})$ (Figure 3.4), where $p(\text{R})$ is the partial pressure of the reactant at time t , and $\frac{dp(\text{HCl})}{dt}$ is the slope of

Figure 3.4 Order plot



1.005. The result clearly indicates that reaction (12) is a first order reaction. The data used to obtain the order plot are listed in Appendix 1.

It was also found that the first order integrated rate equation (12) was closely obeyed up to about 50% reaction. Beyond this time, the dimerisation of butadiene and the isomerisation combined to produce a deviation from linearity. Figure 3.5 shows a typical plot of $\ln \frac{p_0(C) - p(HCl)}{p_0(C)}$ against time, where $p_0(C)$ is the purity of reactant and $p(HCl)$ is the partial pressure of HCl expressed as a fraction of the initial pressure of reactant. The slope gave the rate constant, k_1 . It was also observed that there was no variation of the rate constant over the pressure range 40 - 120 torr.

3.3 Homogeneity

It was found that in a coated glass vessel, the rate of decomposition of cis-1-chloro-2-butene was reproducible. To test for homogeneity, runs were carried out in a packed vessel, having surface-to-volume ratio of about 3.0 cm^{-1} compared with about 1.0 cm^{-1} for the unpacked vessel. After thorough seasoning of these vessels as mentioned before (Chapter 2), the rates of decomposition of cis-1-chloro-2-butene were found to be independent of the surfact - to - volume ratio within experimental error, as shown in the Table 3.2

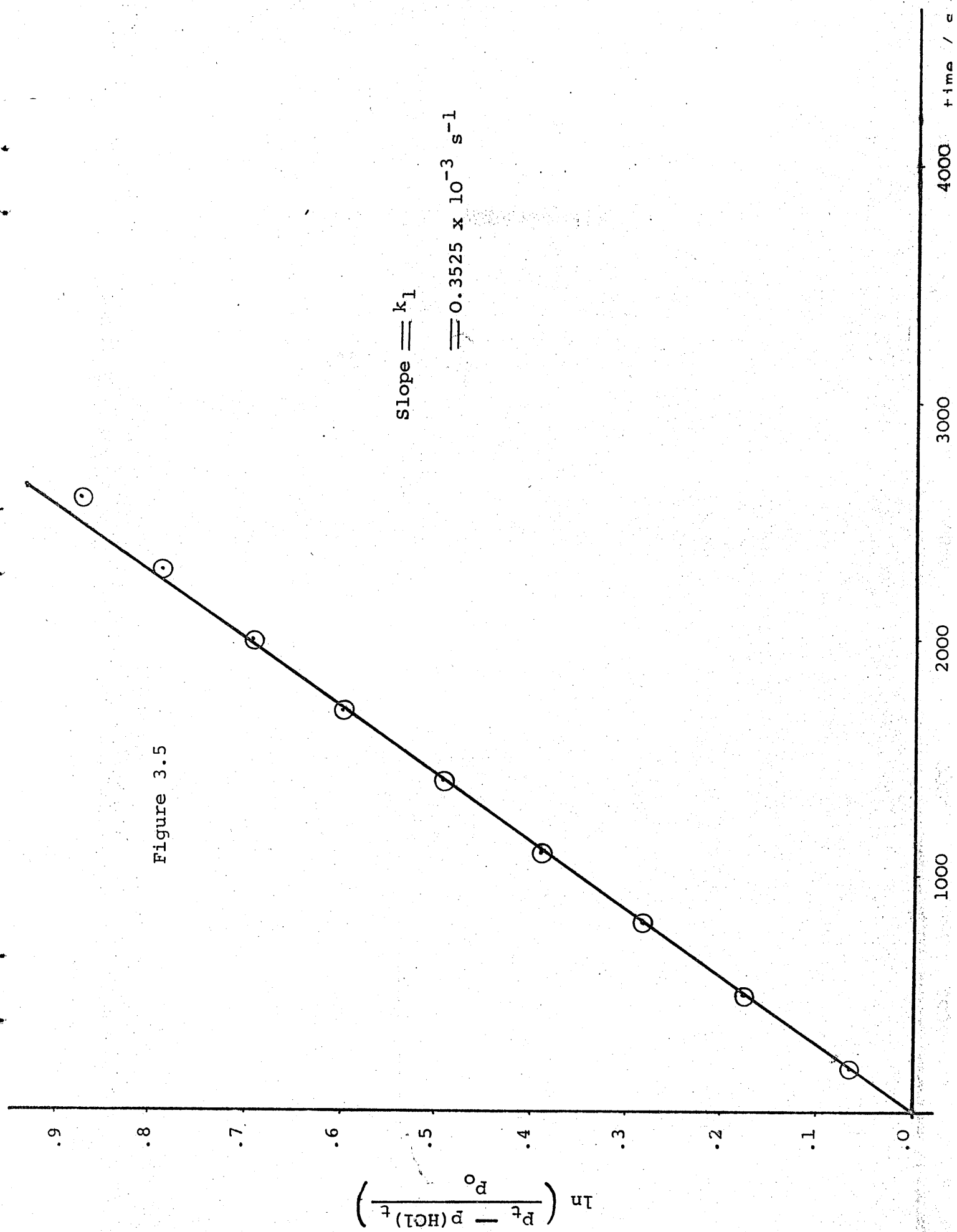


Figure 3.5

Slope = k_1
 $= 0.3525 \times 10^{-3} \text{ s}^{-1}$

Table 3.2

Comparison of rate constants for unpacked and packed vessels

T/K	$10^3 \times k_1/s^{-1}$ (packed vessel)	$10^3 \times k_1/s^{-1}$ (unpacked vessel)
609	1.445	1.491
573.65	0.211	0.223

It was observed that rates of isomerisation depended heavily on surface-to-volume ratio as shown in Figure 3.6.

3.4 Effect of added inhibitor

To investigate the effect of added inhibitor, two series of kinetic runs were carried out in the presence of cyclohexene. The results are plotted in Figure 3.7 and Figure 3.8. By comparing the runs obtained without cyclohexene, it can be said that the addition of the known inhibitor in varying amounts has no effect on the rate of the reaction. A summary of the runs is shown in Table 3.3 where p_i denotes the pressure of inhibitor and p_o denotes the initial pressure of reactant. The differences in k_i in the presence and absence of inhibitor, are within the reproducibility of the experiments.

Table 3.3

Effect of added inhibitor on k_1

T/K	inhibitor	p_i /torr	p_o /torr	$10^3 k_1/s^{-1}$	$10^3 k_1/s^{-1}$ (in absence of inhibitor)
598.7	cyclohexene	57	65	0.98	0.883
609	cyclohexene	43	53	1.511	1.491

Figure 3.6 Isomerisation of cis-1-chloro-2-butene

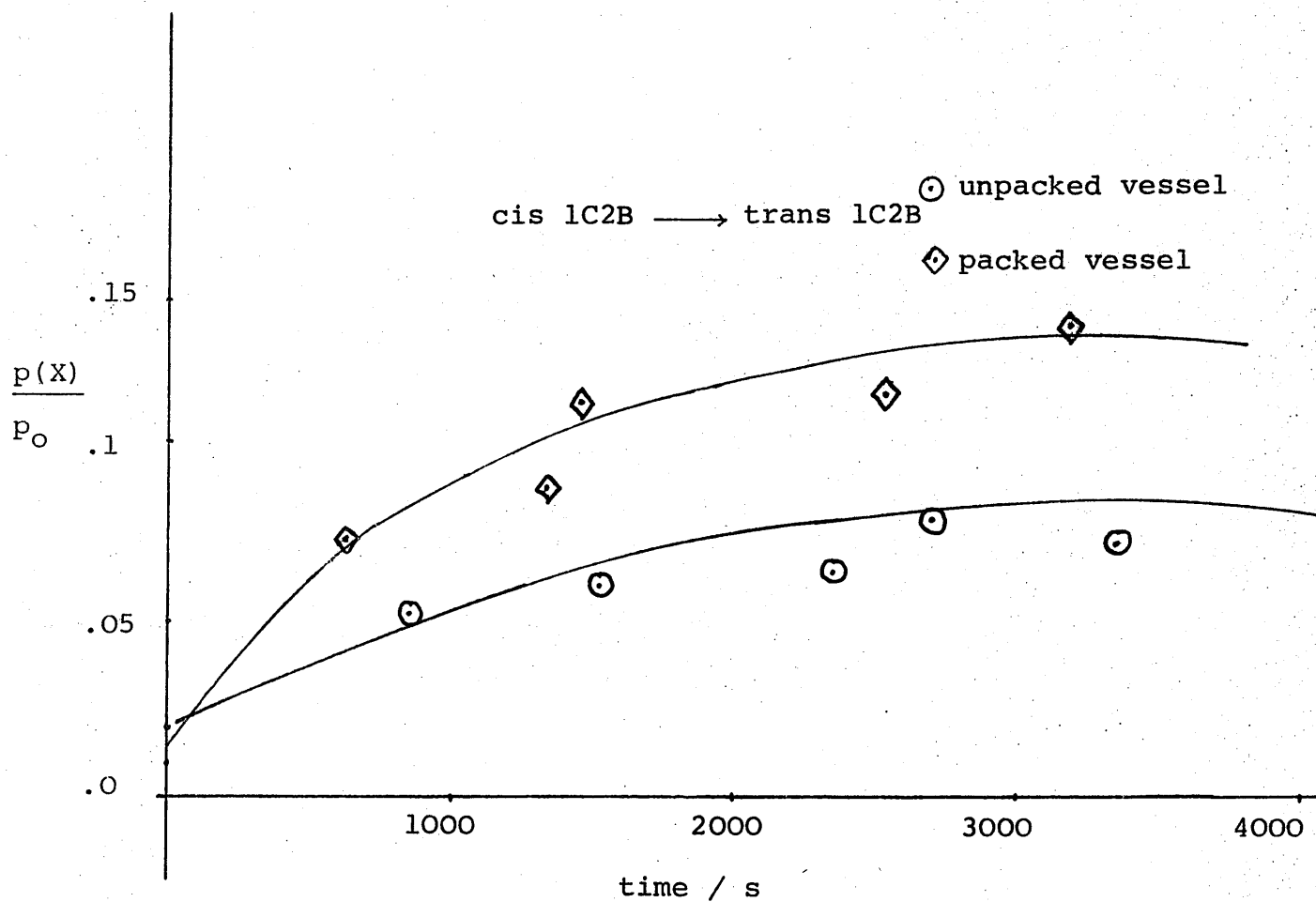
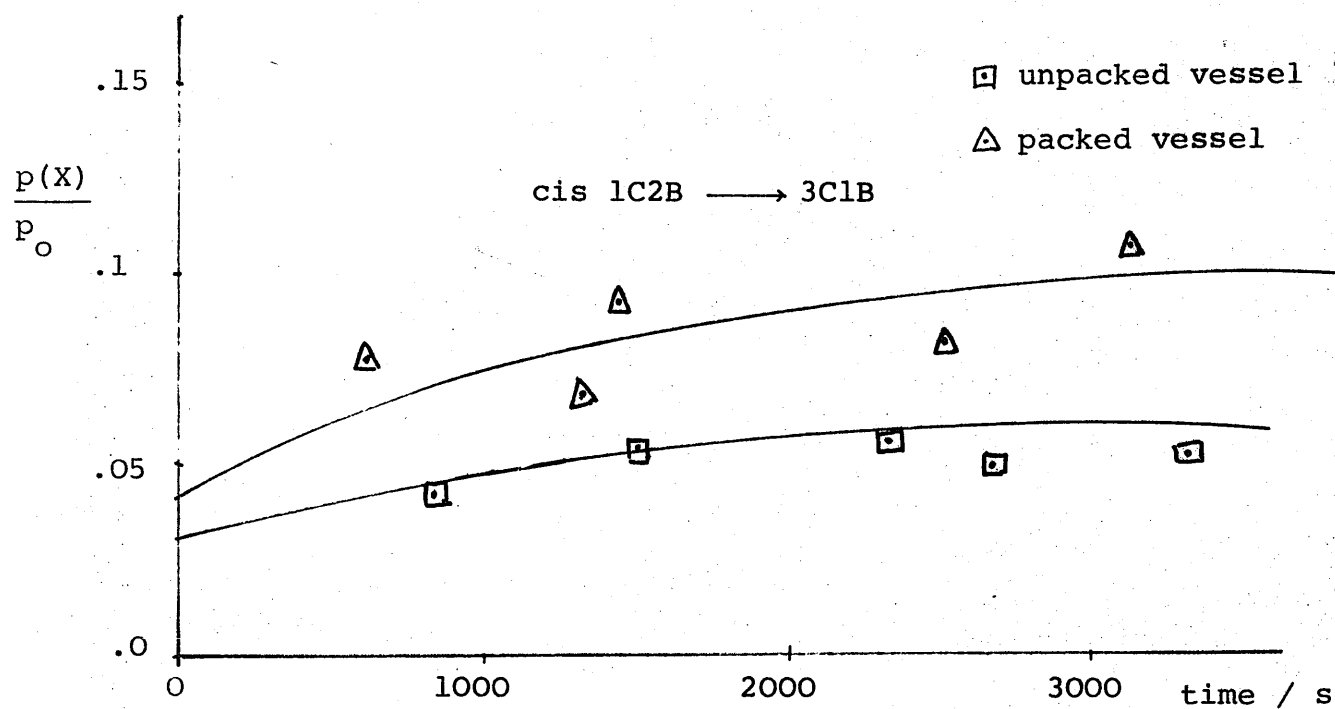


Figure 3.7 Pyrolysis of cis-1-chloro-2-butene in the presence of inhibitor at 598.7 K

○ without cyclohexene

△ with cyclohexene

$\frac{p(x)}{P_0}$

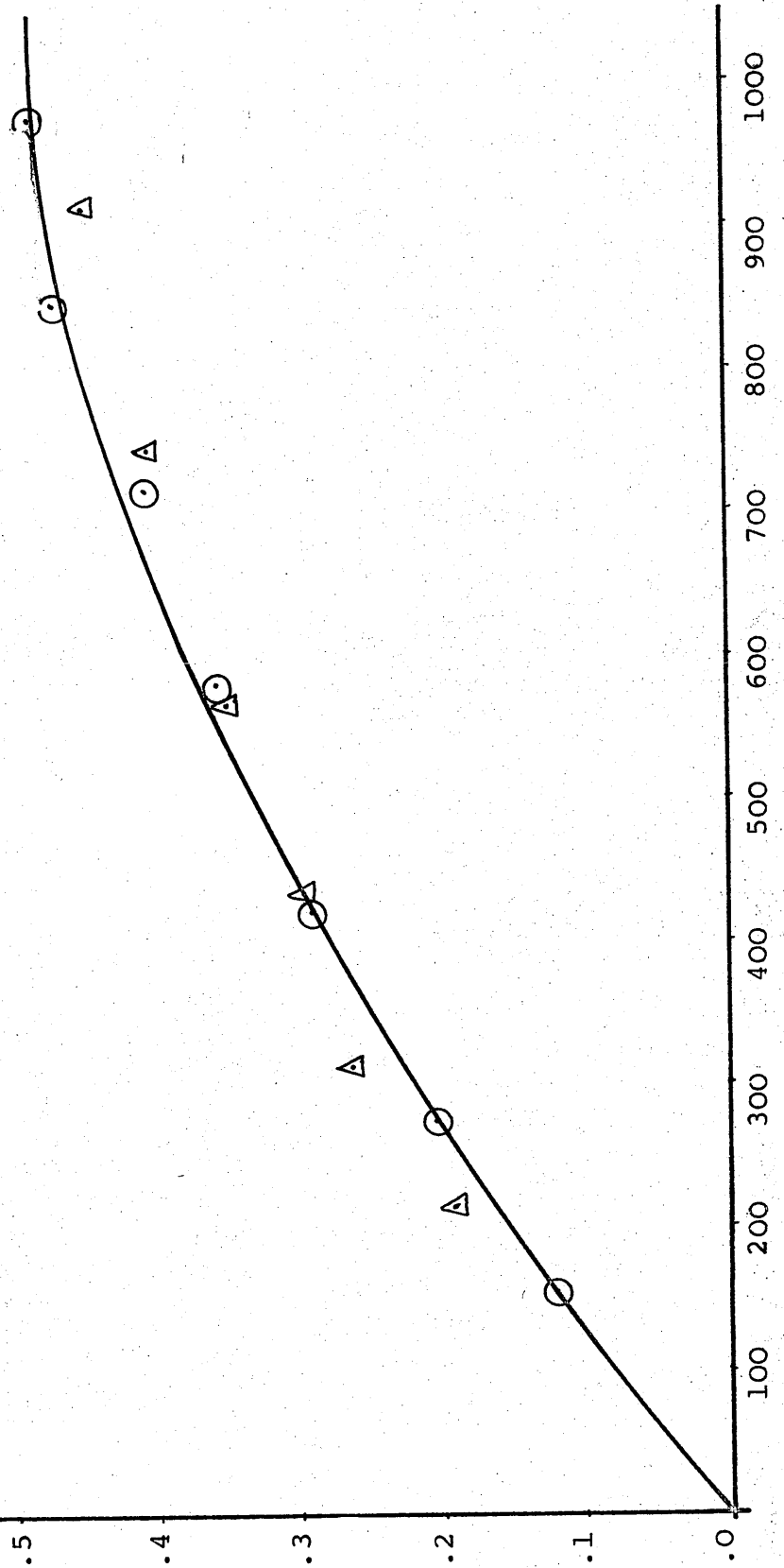
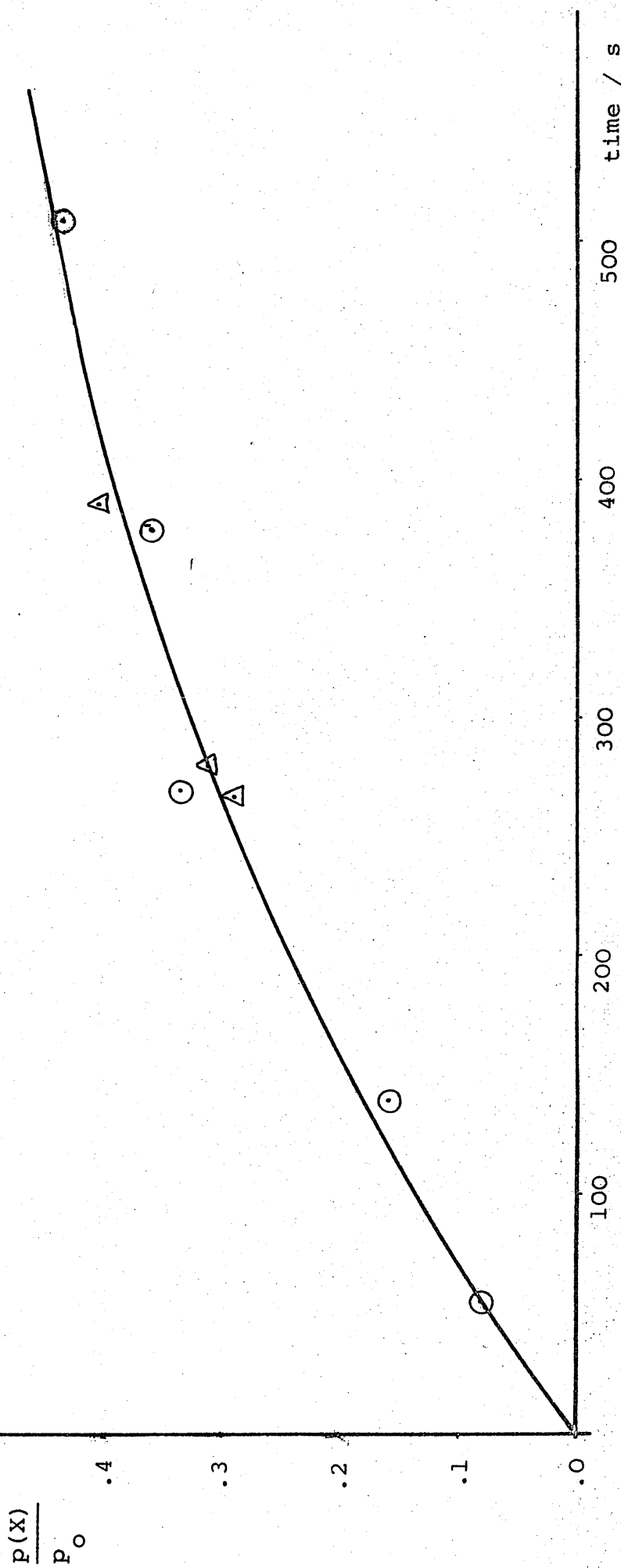


Figure 3.8 Pyrolysis of cis -1-chloro-2-butene in the presence of inhibitor at 609 K

△ with cyclohexene
○ without cyclohexene



3.5 Arrhenius parameters

A series of experiments was conducted at each of seven different temperatures ranging from 291 - 344 °C. About seven runs were needed to obtain a complete reaction profile for the formation of hydrogen chloride. To obtain the rate constant k_1 , a graph of $\ln \frac{p_0(C) - p(HCl)}{p_0(C)}$

against time was then plotted similar to that shown in Figure 3.5. The results of the experiments are summarised in Table 3.4. Full details of the kinetic runs are given in Appendix 2.

Table 3.4

Temperature dependence of k_1

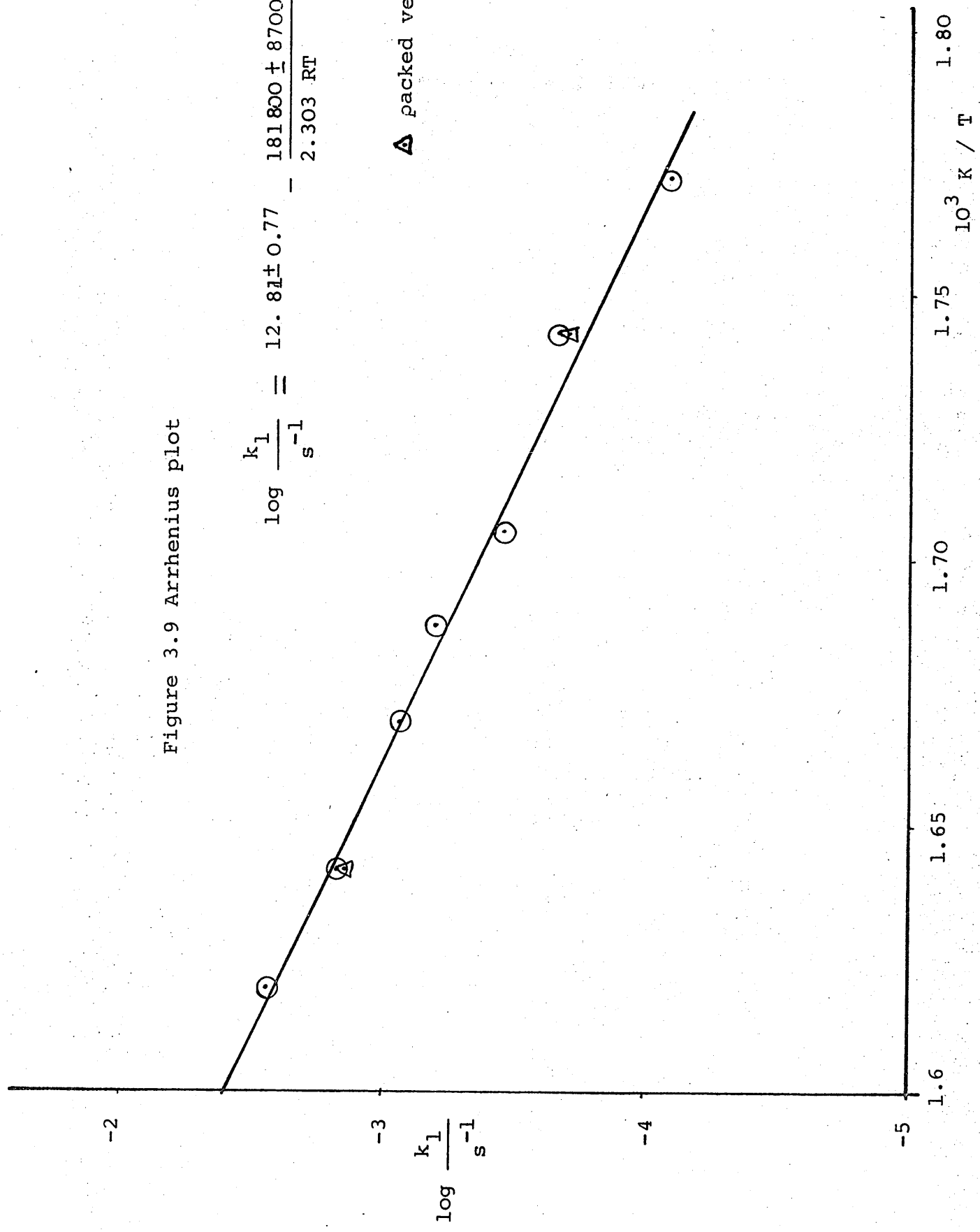
T/K	No. of runs	$10^3 k_1 / s^{-1}$
617.4	8	2.788
609.0	6	1.491
598.7	7	0.883
592.5	7	0.647
586.0	7	0.353
573.65	5	0.223
564.15	5	0.083

The results are plotted in Figure 3.9 as a graph of the logarithm of the rate constant versus the reciprocal of the absolute temperature and include the results for the packed vessel study.

Figure 3.9 Arrhenius plot

$$\log \frac{k_1}{s^{-1}} = 12.81 \pm 0.77 - \frac{181800 \pm 8700 \text{ J mol}^{-1}}{2.303 RT}$$

Δ packed vessel study



A least squares analysis was made of the rate constants and the Arrhenius equation, including standard errors, obtained is:

$$\log \frac{k_1}{s^{-1}} = 12.81 \pm 0.77 - \frac{181800 + 8700 \text{ J mol}^{-1}}{2.303 \text{ RT}}$$

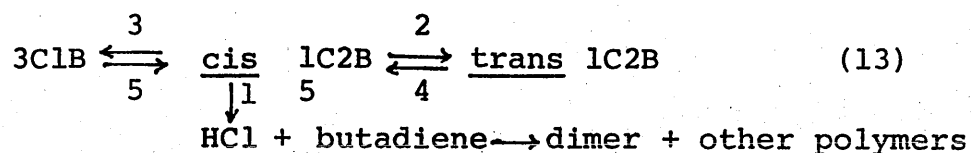
CHAPTER 4

Discussion

4.1 Pyrolysis of *cis*-1-chloro-2-butene

When *cis*-1-chloro-2-butene is pyrolysed in the temperature range 564-617K, the predominant reaction is the elimination of hydrogen chloride, while a small amount of isomerisation occurs. A relatively slow polymerisation of the butadiene follows.

The reaction scheme is:



For the predominant reaction, the elimination, the homogeneity was tested by varying the surface-to-volume ratio as pointed out in Section 3.3. Heterogeneous processes can start on the walls of a clean glass vessel. To prevent this occurring, a suitable coating of the reaction vessel was produced by the decomposition of allyl bromide. The rate constants determined at two temperatures in the seasoned packed vessel, compared with those in the seasoned unpacked vessel, are summarised in Table 3.2. In view of the large increase of surface-to-volume ratio, the small increase in rate indicates that the reaction is predominantly homogeneous. This test alone does not rule out a mechanism such as the one proposed by Laidler⁽⁵³⁾ who suggested that the coating of the reaction vessel may increase the number

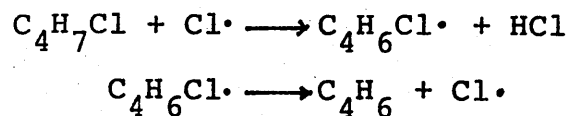
of active sites above the number on a clean glass surface. However, this seems an unlikely mechanism for hydrogen chloride elimination when other techniques e.g. shock tube studies, have been used to demonstrate that this type of reaction is homogeneous⁽⁹⁾.

Figure 3.4 shows a plot of the logarithm of the pressure change against the logarithm of the partial pressure of the reactant. A linear relationship exists for the first 60% of the reaction, where the secondary reactions are negligible. As the slope of the linear region is 1.005, it can be concluded that the predominant reaction is first order.

It is usually possible to judge whether a reaction occurs by a radical non-chain mechanism by consideration of the energetics of such a process. However, for cis-1-chloro-2-butene, the homolytic bond dissociation energy is not known. By comparison with 3-chloropropene for which the C-Cl bond dissociation energy has been estimated as 252 kJ mol^{-1} , the value for cis-1-chloro-2-butene is not likely to be less than 210 kJ mol^{-1} . The observed activation energy for elimination of cis-1-chloro-2-butene is about 181 kJ mol^{-1} . Therefore it is possible to rule out a radical non-chain mechanism.

Another pathway for the reaction is a radical chain mechanism. This can be detected by using a radical chain inhibitor, such as cyclohexene. The most likely

propagating steps for such a scheme would be



If this occurred, the addition of cyclohexene would very likely reduce the reaction rate. Since no rate decrease was observed by adding a radical scavenger, it can be concluded that no radical chain process occurs.

Since there was no induction period, no inhibition effects, and the reaction exhibits first order kinetics, it can be said that the reaction under investigation is a unimolecular process.

Apart from the main elimination reaction, isomerisation of the cis-1-chloro-2-butene was also observed. A very small amount of trans isomer was normally present in the reactant at the start of the pyrolysis, and its concentration increased steadily with time. By changing the surface-to-volume ratio using a packed vessel, the rate of increase of this trans isomer was found to be higher, indicating a heterogeneous process.

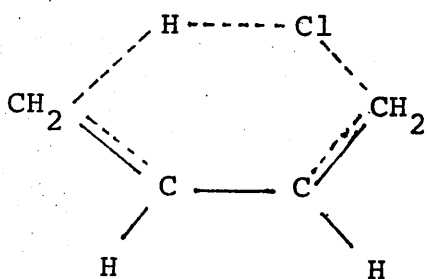
Examination of the extent of this effect (see Section 3.3) shows that for an increase in surface-to-volume ratio from about 1 cm^{-1} to about 3 cm^{-1} , the rate of production of trans isomer increased by about a factor of three. Since the packed and unpacked vessels were of similar volume, there appears to be a linear dependence of this rate on the surface area.

Isomerisation of cis-1C2B to 3C1B was also found, but the rate was observed to be rather slow and could not be measured accurately by the analytical technique used. Thomas⁽⁵⁴⁾ has shown that at the temperature studied the α -isomer does not decompose fast. Although a slight decrease in the concentration of α -isomer was sometimes detected in these experiments, this is probably not significant in view of the errors in analysis. No detailed investigation of the surface reactions was made.

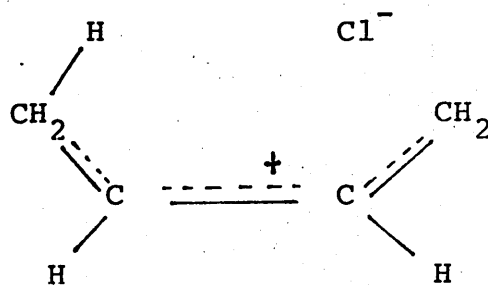
In the studied temperature range (564-617K), it was found, as previously reported⁽⁵⁵⁾, that dimerisation of butadiene to vinylcyclohexene occurred, but was relatively slow. The rest of this discussion is concerned only with the elimination reaction of the cis isomer in the scheme (13).

4.2 Nature of the transition state

The various transition states proposed for the gas phase elimination (Section 1.4) can now be considered in the light of the results of the pyrolysis of cis-1-chloro-2-butene. It has been proposed that elimination in cis-1-chloro-2-butene proceeded through a six-centred transition state which can be represented by (XI) or (XII).



XI

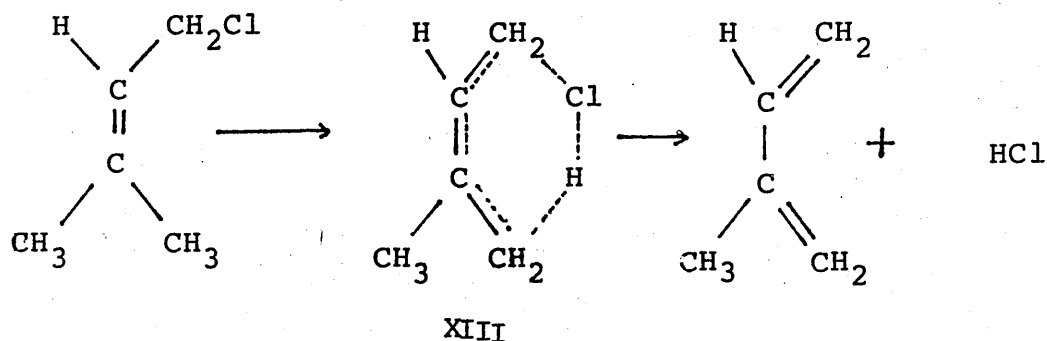


XII

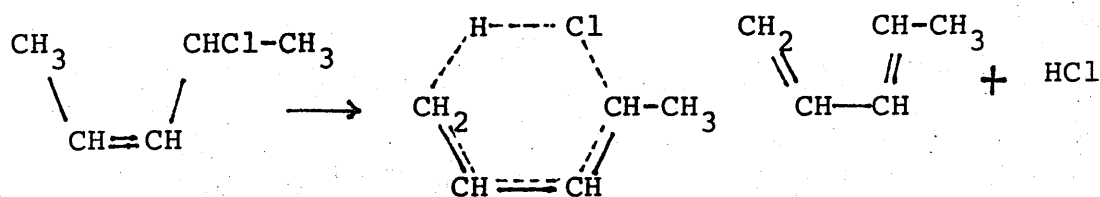
There is a considerable amount of supporting evidence for the proposed cyclic transition state. Neglecting a small amount of isomerisation, the product observed from the elimination reaction of cis-1-chloro-2-butene was butadiene and hydrogen chloride. If a four-centre mechanism occurred, this would involve elimination with a vinyl proton, and would produce methylallene as an initial product, which has not been observed. However, at the temperatures at which this study was made, methylallene would rapidly isomerise to butadiene⁽⁵⁶⁾. Failure to observe methylallene does not, therefore, rule out the four-centre mechanism, although a molecular elimination involving the vinyl proton does not occur in 3-chloropropene⁽⁵⁷⁾.

The most convincing evidence for elimination through a six-centre mechanism comes from a comparison of the A factor observed for this reaction ($\log \frac{A}{s} = 12.81$) with those of other six-centre reactions.

The concept of a six-centre transition state for cis-1-chloro-2-butene has been communicated⁽⁵⁷⁾ together with several other proposed six-centre reactions involving halogens. In the pyrolysis of 1-chloro-3-methyl-2-butene Harding⁽⁵⁸⁾ proposed scheme XIII ($\log A/s = 12.03$)

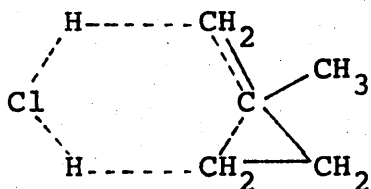


Thermal decomposition of cis-4-chloropent-2-ene has been studied by Robinson⁽⁵⁹⁾ who suggested a mechanism represented by XIV ($\log A/s^{-1} = 9.85$)



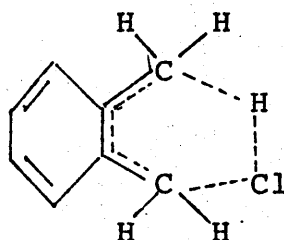
XIV

The hydrogen chloride-catalysed isomerisation of 1,1-dimethyl-cyclopropane produces only 2-methyl-2-butene for which the transition state has been depicted as XV.



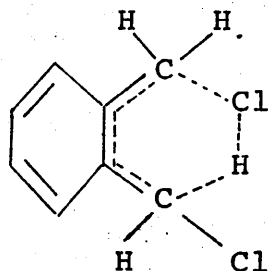
XV

The pyrolysis of α -chloro-o-xylene⁽⁴²⁾ yields benzylcyclobutene, for which XVI has been proposed as the transition state, ($\log A/s^{-1} = 11.47$).



XVI

Similarly Umaña⁽⁴⁵⁾ studied the decomposition of 1,2-bis (chloro-methyl) benzene and proposed the transition state XVII ($\log A/s^{-1} = 11.08$)



XVII

The Arrhenius A factor, according to transition state theory, is given by $A = \frac{ekT_m}{h} \exp \left\{ \frac{\Delta S^\ddagger}{R} \right\}$ where T_m is the mean temperature of the study. The entropy of activation, ΔS^\ddagger in these six-centred processes can be expected to be negative, due to the loss of internal rotation in forming the cyclic transition state. Umaña estimated the A factor using the method of Beason and Bose⁽²⁸⁾ and obtained the values: for 1-chloro-3 methyl-2-butene, $\log A = 11.7$; and for α -chloro-o-xylene, $\log A = 12.0$. Umaña then postulated a pseudo four-centre transition state for the same reaction and estimated $\log A/s^{-1}$ to be 11.9 for both 1.-chloro-3-methyl-2-butene and 1-chloro-o-xylene. While these estimates confirm a "low" value for A factors of cyclic transition state, they fail to agree precisely with the experimental values, and, more seriously, they do not discriminate between the two structures proposed by Umaña. Furthermore, recent criticism of the use of additivity rules in the estimation of thermochemical properties does not add confidence to their use in the type of estimate

made by Umana⁽⁶⁰⁾. Nevertheless it is to be expected that the values discussed lie in the range, $A = 10^{12} \pm 1.0 \text{ s}^{-1}$.

This general expectation is largely borne out by a survey of other analogous six-centre reactions. For ester pyrolyses⁽⁶¹⁾, the range of A factors fall within $10^{11.3}$ to $10^{12.78} \text{ s}^{-1}$. With Cope rearrangements⁽⁶²⁾ the range of A values has been found to be within 10^9 and 10^{10} s^{-1} . And in Claisen rearrangements the range is normally between 10^9 and 10^{10} s^{-1} .

Further evidence for the six-centre nature of the reaction can be inferred from the thermal addition of HI to conjugated dienes as studied by Walsh⁽⁶³⁾. In these reactions, second order kinetics was observed and, on the basis of the Arrhenius parameters, a 1,4 addition of HI was proposed.

4.3 Polarity of transition state

In 1955, Maccoll and Thomas⁽²⁴⁾ noticed a marked correlation between rate sequences in the gas phase and rate sequences in the corresponding S_N1 reactions in polar solvents. Later Maccoll observed that electron releasing groups at the α -position markedly accelerate the rate of reaction, and in the β -position produce only a small increase in rate. The β -hydrogen may stabilize the forming X^- in a manner similar to the polar solvent stabilization in solvolytic reactions. They also pointed out that a general correlation exists

between the activation energy and the homolytic bond dissociation energy. These observations strongly support the concept of an ionic transition state.

The increase in rate produced by the introduction of electron releasing groups at the reaction centre has proved to be a useful measure of the extent of polarity which develops in the transition state. From a number of gas phase reactions, Maccoll⁽⁶⁴⁾ has noted the various effects of α -methylation, and has classified them according to the degree of heterolysis involved in the transition state. The decomposition of esters and alkyl halides are examples where rate increases of about 25 and 150 respectively are observed. The proposed six-centre transition state for cis-1-chloro-2-butene might be expected to involve a smaller degree of polarity than in the four-centre transition state of the alkyl halides. The reason lies in the greater degree of assistance expected from the hydrogen atom in the former compound. The following table shows a comparison of the substituent effects of the above three reaction types.

It can be seen from Table 4.1 that allylic halides and esters have quite similar substituent effects. If the enhancement of the rate by α -methylation is taken as a measure of the polarity of the transition state, the elimination from the chloroalkenes is considerably less polar than the well established four-centre

mechanism in alkyl halides, and compares closely with esters where there is also believed to be substantial polarity but also an involvement (bonding) of the leaving hydrogen in the transition state.

Table 4.1

Effects of methyl substitution on elimination rates:

Relative rates of elimination of alkyl halides, esters and allylic chlorides,
T = 600 K

	Parent	Methyl substituent
alkyl halides	ethyl chloride (64)	iso-propyl chloride (64)
	1	150
chloro alkenes	(a) <u>cis</u> -1-chloro-2-butene	<u>cis</u> -4-chloropent-2-ene (59)
	1	28
esters	ethyl acetate (64)	iso-propyl acetate (64)
(a) this work	1	25

Examination of the Arrhenius parameters should also cast light on the detailed mechanism of the reaction. However, the A factor cis-4-chloropent-2-ene observed by Robinson⁽⁵⁹⁾ is found to be very low compared with other six-centre reactions. Direct comparison of Arrhenius parameters for allylic compounds with alkyl halides therefore appears to be difficult. However recalculation of the activation energy is possible by selecting an "average" A factor ($A = 10^{12.5} \text{ s}^{-1}$).

There is some justification for such a comparison while the Arrhenius parameters are prone to large errors when the kinetic study spans only about 70 K, the rate data are more reliable. The determination of Arrhenius parameters from kinetic studies of an impurity present at a concentration of about 10% inevitably introduces large errors⁽⁵⁹⁾. Without such an assumption about the A factors, comparison of reported activation energies is of doubtful value. Table 4.2 shows the results of recalculation for allylic compounds and the comparison with alkyl halides.

Table 4.2

Recalculated E_A /kJ mol⁻¹, setting $A = 10^{12.5} \text{ s}^{-1}$

<u>cis</u> -1-chloro 2-butene	1-chloro 3-methyl 2-butene	<u>cis</u> -4-chloro pent-2-ene	EtCl*	i-PrCl*
178	165	161	237	212

* not recalculated

It can be seen very clearly that the "six-centre" transition state compounds have smaller activation energies than do the "four-centre" alkyl halides. This can be explained by the more facile six-centre pathway. If, as in the alkyl halides, the rate increase due to α -methylation appears largely in the lowering of the activation energy, this reduction in the energy barrier is about three quarters of that observed in the alkyl halides. By comparing the activation energies of the

above three allylic halides, it can be seen that α -methyl substituent has the effect of lowering E_A . This can be explained by the electron releasing effect of the γ -methyl group i.e. an inductive effect being relayed through the conjugated allylic system.

It was stated earlier that there exists an analogy between gas-phase eliminations from alkyl halides and their S_N1 reactions in polar solvents. It might be expected that the rate sequence for allylic systems in solution would also be roughly parallel to that in the gas phase. Table 4.3 shows the relative rates of unimolecular hydrolysis at 44.6 °C of a number of compounds in 0.5% aqueous formic acid, followed by relative rates of elimination in the gas phase.

Table 4.3

Relative solvolysis rates⁽⁶⁵⁾ (T = 44.6 °C)

3CP	<u>trans</u> -1C2B	3C1B	<u>trans</u> -4C2P	1C3M2B
0.278×10^{-3}	1	1.58	—	0.42×10^4

Relative pyrolysis rates (T = 361.1 °C)

3CP	<u>cis</u> -1C2B	3C1B	<u>cis</u> -4C2P ⁽⁵⁹⁾	1C3M2B ⁽⁴¹⁾
$.026 \times 10^{-3}$	1	0.0756	14.33	10.45

3CP denotes 3-chloropropene

4C2P denotes 4-chloro-2-pentene

1C3M2B denotes 1-chloro-3-methyl-2-butene

As there is no readily available data for *cis*-1-chloro-2-butene in solvolysis, comparison will be made with the *trans* isomer because the isomerism is likely to be far less important in dissociative reactions in solution than in the gas phase molecular process. A methyl group in either the α or the γ -position produces a large increase in reactivity. Thus *cis*-4-chloropent-2-ene and 1-chloro-3-methyl-2-butene are more reactive than the *cis*-1-chloro-2-butene by a factor of about 10^4 . It can be seen too that the substituent effects in the gas phase are in parallel to those observed in solvolysis.

It can be concluded that the elimination of HX from allylic halides containing a *cis*-methyl substituent is a particularly facile reaction. Comparison with well categorised substituent effects in other gas phase elimination and with dissociative reactions in solution indicate a rather polar transition state although one in which the quasi-heterolytic description applied to four-centre elimination from saturated alkyl halides is less valid.

This difference between four- and six-centred mechanisms has recently been interpreted according to symmetry rules. Thermally, four-centre reactions are normally "not allowed". But it has been suggested by Pearson⁽⁴⁸⁾ that the polar nature of the transition state destroys the symmetry and therefore the elimination reaction of alkyl halides becomes partially allowed, although the

activation energy is still rather high. For example, chloroethane has an activation energy of 237 kJ mol^{-1} . For the six-centre mechanism, the reaction is "allowed" according to symmetry rules. Thus for cis-1-chloro-2-butene the activation energy is: 181 kJ mol^{-1} .

This may account for the extreme polar nature of the transition state in alkyl halides, but it does not aid the interpretation of the elimination from the chloroalkenes except to add further weight to the convincing arguments for a six-centre mechanism.

Appendix 1

Data for order plot

$p(R)/\text{ torr}$	$\log p(R)/\text{ torr}$	$J/\text{ torr s}^{-1}$	$\log J/\text{ torr s}^{-1}$
65.1	1.813	0.023835	-1.62278
63.0	1.799	0.0217	-1.6635
56.9	1.76	0.01981	-1.703
49.4	1.69	0.01729	-1.762
42.91	1.63	0.01512	-1.820
37.2	1.57	0.01281	-1.8925
32.6	1.51	0.010605	-1.9744
26.95	1.43	0.00805	-2.0942
21.28	1.33	0.006545	-2.184

Appendix 2

Data for calculation of rate constants k_1

1. $T = 617 \text{ K}$ $k_1 = 2.788 \times 10^{-3} \text{ s}^{-1}$

t / s^{-1}	p_0 / torr	$p(\text{HCl}) / \text{torr}$
70	77.8	13.32
99	60.0	13.72
156	77.0	23.81
180	69.5	23.54
234	57.5	24.48
267	73.5	32.96
342	46.0	24.48
388	136.0	78.56

2. $T = 609 \text{ K}$ $k_1 = 1.491 \times 10^{-3} \text{ s}^{-1}$

t / s^{-1}	p_0 / torr	$p(\text{HCl}) / \text{torr}$
55	59.0	4.6
140	92.5	13.7
270	46.5	14.8
380	63.5	21.0
510	70.0	29.3
625	85.5	39.3

3. $T = 598.7 \text{ K}$ $k_1 = 0.883 \times 10^{-3} \text{ s}^{-1}$

t / s^{-1}	p_0 / torr	$p(\text{HCl}) / \text{torr}$
153	77.8	9.55
273	69.2	14.19
420	52.8	15.49
580	69.3	24.52
714	70.0	28.65
845	51.3	24.26
975	123.0	60.26

4. $T = 592.45 \text{ K}$ $k_1 = 0.647 \times 10^{-3} \text{ s}^{-1}$

t / s^{-1}	p_0 / torr	$p(\text{HCl}) / \text{torr}$
300	59.8	10.22
426	40.5	10.22
660	96.0	27.74
830	73.8	28.11
984	53.5	23.26
1410	58.2	27.86
1674	98.7	49.08

5. $T = 586 \text{ K}$ $k_1 = 0.3525 \times 10^{-3} \text{ s}^{-1}$

t / s^{-1}	$p_{\text{O}} / \text{torr}$	$p(\text{HCl}) / \text{torr}$
414	58.5	7.59
780	74.0	16.69
1290	80.0	27.20
1860	75.3	33.25
2530	123.0	64.00
3000	76.0	44.25
3560	70.0	45.26

6. $T = 573.65 \text{ K}$ $k_1 = 0.223 \times 10^{-3} \text{ s}^{-1}$

t / s^{-1}	$p_{\text{O}} / \text{torr}$	$p(\text{HCl}) / \text{torr}$
910	45.0	7.78
1550	62.0	16.38
2400	41.0	11.82
2730	80.5	24.60
3360	74.0	28.00

7. $T = 564.15$ $k_1 = 0.083 \times 10^{-3} \text{ s}^{-1}$

t / s^{-1}	$p_{\text{O}} / \text{torr}$	$p(\text{HCl}) / \text{torr}$
1164	47.2	4.53
2430	50.8	8.20
3552	55.0	12.73
7404	66.0	26.33
11202	68.5	34.53

References

1. F.Daniel and P.L.Veltman, *J.Chem.Phys.* 7, 759, (1939)
2. A.Maccoll, *J.Chem.Soc.*, 965, (1955)
3. D.R.Blackmore and C.N.Hinshelwood, *Proc.Roy.Soc.* A268
21, (1962)
4. G.R.Freeman, C.J.Danby and C.N.Hinshelwood, *ibid*, A245
456 (1958)
5. Idem, *ibid*, A245, 28, (1958)
6. F.O.Rice and R.E.Varnerin, *J.Am.Chem.Soc.*, 76, 324, (1954)
7. N.Capon and R.A.Ross, *Trans. Farad Soc.*, 62, 1560 (1966)
8. A.T.Blades and G.W.Murphy, *J.Am.Chem.Soc.* 74, 6219, (1952)
9. W.Tsang, *J.Chem.Phys.* 40, 1171, 1498 (1964), 41, 2487, (1964)
10. G.E.Millward, R.Hartig and E.Tschurkow-Poux, *Chem.Comm.*
203, (1970)
11. P.Cadman, M.Day, A.W.Kirk and A.F.Trotman-Dickenson,
Chem.Comm. 203 (1970), P.Cadman, M.Day and A.F.Trotman-
Dickenson, *J.Chem. Soc. (A)*, 248, 1356 (1971)
12. M.Day and A.F.Trotman-Dickenson, *J.Chem.Soc. (A)*, 233, (1969)
13. N.Capon, Ph.D Thesis, University of London, (1964)
14. H.Hartmann., H.G.Bosche, and H.Heydtmann, *Z.Phys. Chem.*
(Frankfurt) 42, 329, (1964)
15. P.Cadman, M.Day, A.W.Kirk and A.F.Trotman-Dickenson
Chem.Comm. 203, (1970)
16. P.J.Thomas, *J.Chem.Soc.* 1192, (1959)
17. S.W.Benson, *J.Chem.Phys.* 38, 1945, (1963)
18. A.R.Lee, M.Sc. Thesis, University of London (1959)

19. S.W.Benson and A.N.Bose, J.Chem.Phys,37,1081, (1962)
20. A.N.Bose and S.W.Benson, J.Chem.Phys.37,2935, (1962)
21. J.H.G.Green, G.D.Harden, A.Maccoll and P.J.Thomas
J.Chem.Phys,21, 178 (1953)
22. A.Maccoll,Advances in Physical Organic Chemistry,
3,91, (1965), Academic Press, London
23. A.Maccoll,"Studies in chemical structure and reactivity "
Pg. 53, Methuen, London (1966)
24. A.Maccoll and P.J.Thomas,Nature,176,392 (1955)
25. D.H.Davies, Ph.D Thesis, University of London (1967)
and references quoted therein
26. J.Hine and D.E.Lee, J.Am.Chem.Soc. Vol 73, 22,(1951)
27. P.J.Thomas, J.Chem.Soc. 136, (1961)
28. S.W.Benson and A.N.Bose, J.Chem.Phys,39,3463,(1963)
29. S.W.Benson and G.R.Haugen, J.Am.Chem.Soc,87,4036,(1965)
30. Allen Maccoll and Margaret N.Mruzek,Trans Faraday^I2714(1978)
31. H.M.Frey and R.Walsh. Chem.Rev. 69,103,(1969)
32. R.Taylor, J.Chem Soc. Perkin II, 1025 (1975)
33. E.Tschuikow- Roux, J.Chem.Phys 42,3639,(1965)
34. A.P.Modica and J.E.La.Graff, J.Chem.Phys.44,3375,(1966)
35. J.W.Edward and P.A.Small, Nature,202,1329,(1964)
36. G.R.Barnes, R.A.Cox and R.F.Simmons, J.Chem.Soc (B)
1176, (1971)
37. R.A.Cox and R.F.Simmons, J.Chem.Soc.(B),1625, (1971)
38. A.E.Shilov and R.D.Sabirova, Russ, J.Phys.Chem, 34,408
(1960)

39. J.Shapiro and E.S.Swinbourne, Can.J.Chem in the press
40. P.G.Rodgers, Ph.D Thesis , University of London(1966)
41. C.J.Harding, Ph.D Thesis, University of London (1968)
42. S.K.Wong., Ph.D Thesis, University of London (1968)
43. R.Walsh, University of Reading, England, personal comm.(1971)
44. H.E.O'Neal and S.W.Benson, J.Phys.Chem, 71, 2903, (1967)
45. Mirtha Umaña, Ph.D Thesis, University of London (1972)
46. Hurd, C.D. and F.H. Blunck, J.Am.Chem.Soc. 60, 2419, (1938)
47. R.B.Woodward and R.Hoffmann, The conservation of orbital symmetry, Academic Press, Germany, (1970)
48. R.G.Pearson, Symmetry rule for chemical reaction, J.Wiley New York (1976)
49. R.B. Woodward and R.Hoffmann, The conservation of orbital symmetry, Verlag chemie GmbH, Weinheim/Bergstrasse, 1970
50. L.S.Ettre and A.Zlatkis, The practice of gas chromatography J.Wiley & Sons, New York. 1967
51. L.Brandsma, Preparative acetylenic chemistry, Elsevier (1971)
52. D.Rowley and H.Steiner, J.Chem.Soc. 198 , (1951)
53. K.J.Laidler and B.W. Wojciechowski, Trans. Farad. Soc. 59, 369, (1963)
54. P.J.Thomas, J.Chem.Soc. 1238 (1967B)
55. G.Huybrechts, L.Luyckx. Th. Vandenboom and B.Van.Mele Int J.of chemical kinetic vol IX, 283-293 (1977)
56. R.D.Rossini, J.Res. Natl.Bur. Standards, 42, 225 (1949)
57. A.M.Goodale and K.E.Howlett, J.Chem.Soc. 2596, (1954)
58. C.J.Harding, A.Maccoll and R.A.Ross, J.Chem.Soc.(B) 634, (1969)

59. P.J. Robinson, G.C. Skelhorne, M.J. Waller, J.Chem.Soc. PerkinII, 349, (1978)
60. W. Tsang, Int. J. Chem. Kinet, 821, (1978)
61. C.H. Depuy and R.W. King, Chem. Revs. 60, 431, (1960), J.C. Sheer, E.C. Kooyman and F.L.J. Sixma, Rec. Trav Chim. de Pays-Bas, 82, 1123 (1963)
62. G. Foster, A.C. Cope, and F. Daniel, J. Am. Chem. Soc. 69, 1893, (1947)
63. P.J. Gorton and R. Walsh, J. Chem. Soc. Chem. Comm. , (1972)
64. A. Maccoll and P.J. Thomas, " Progress in reaction kinetics 4, 119, (1967)
65. C.A. Vernon, J. Chem. Soc. 423, (1954)