THE UNIVERSITY OF ALBERTA

THE PYROLYSIS OF EPISULPHIDES

by

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FACULTY OF GRADUATE STUDIES AND RESEARCH

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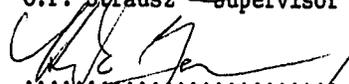
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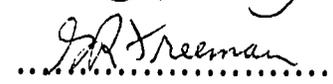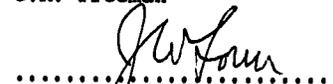
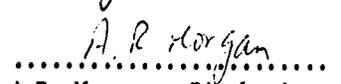THE PYROLYSIS OF EPISULPHIDES

submitted by

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in partial fulfilment of the requirements for the degree of Doctor

of Philosopy

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ABSTRACT

The pyrolysis of ethylene, propylene and butene-2

episulphides was studied in a static system at temperatures below

$250^{o}C$. The only decomposition products were the olefin of the parent

episulphide and polymeric sulphur. An investigation into the surface

effect showed that the reaction is essentially homogeneous and that a

heterogeneous component only occurs in the case of ethylene episulphide

decomposition at low temperatures and pressures. Extensive studies of

the order of reaction for the three episulphides suggest that the

thermal activation follows unimolecular kinetics. This conclusion is

lent further support by the effect of inert diluent gases which

readily accelerate the rate of decomposition at low pressures of

ethylene episulphide and only inefficiently at higher substrate

pressures. Propylene episulphide decomposition is virtually unaffected

by inert gas, since decomposition essentially occurs in the high

pressure region.

The experimental activation energies for ethylene, propylene

and trans-butene episulphide decomposition are 40.2, 38.7 and 35.7

kcal/mole respectively and the log A-factors are 12.52, 12.57 and

12.08 $[sec^{-1}]$.

It is shown that the low activation energies are due to the

reaction proceeding via a low-lying non-vertical triplet excited state

of the episulphide which in turn reacts with a ground state molecule to

yield products. The experimental results are consistent with theoretical

studies which predict that the geometry of the excited state is one of

a ring relaxed species which retains considerable interaction between the CH_2 and S moieties. The A-factors are consistent with a mechanism involving a triplet state and a tightly bound transition state. The findings of the present work are compared with the chemistry of cyclopropane, epoxides and episulphoxides.

A study of the secondary deuterium kinetic isotope effect for the decomposition of C_2H_4S and C_2D_4S shows a normal isotope effect. A calculation of the isotope effect using a ring-distorted episulphide as a model is found to reproduce the experimental isotope effect.

The effect of olefins on episulphide pyrolysis is also investigated. Olefins are found to exhibit a strong quenching effect on the decomposition reaction. A kinetic scheme is proposed to explain this behavior and it is concluded that olefins intercept the excited triplet episulphide intermediate very efficiently. It is also shown that in the presence of cis-butene, triplet episulphide catalyzed isomerization of the olefin also occurs.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

TABLE OF CONTENTS (CONT'D)

TABLE OF CONTENTS (CONT'D)

LIST OF TABLES

LIST OF TABLES (CONT'D)

LIST OF TABLES (CONT'D)

LIST OF TABLES (CONT'D)

LIST OF TABLES (CONT'D)

LIST OF FIGURES

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CHAPTER I

INTRODUCTION

The behavior of small cyclic molecules and especially of
cyclopropane has attracted considerable interest in chemical kinetics.
This has in part been due to the fact that cyclopropane has long been re-
garded as a model system of unimolecular decompositions and as such
has played a considerable role in the development of unimolecular rate
theories. The thermal decompositions of epoxides and episulphoxides
have also been investigated to some extent but those of the episulphides
have remained unexplored. On the other hand, a considerable volume
of work has been expended on the reactions of sulphur atoms with
olefins which yield the appropriate episulphide as the final product.
This process can formally be regarded as the reverse of the pyrolysis
of episulphides. In this chapter a brief review will be given of the
chemistry of cyclopropane, epoxides and episulphoxides, and the
reactions of sulphur atoms with olefins. A brief survey of unimolecular
rate theory and secondary kinetic isotope effects will also be presented.

1) The Isomerization of Cyclopropane

The isomerization of cyclopropane

$$CH_2 \underset{CH_2}{\overset{\displaystyle CH_2}{\diagdown \diagup}} \rightarrow CH_3CH_2 = CH_2 \qquad [1]$$
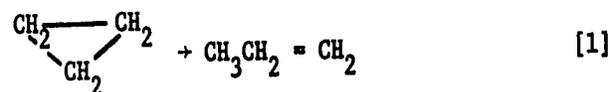
is one of the few processes which follows unimolecular kinetics and is
analytically simple enough for precise quantitative work. Chambers
and Kistiakowksy (1) were amongst the first to study the reaction

and to observe a significant fall-off in the specific rate at low substrate pressures. Pritchard, Sowden and Trotman-Dickenson (2) carried out a more detailed investigation of the reaction. They found that at low substrate pressures, addition of chemically inert gases markedly increased the rate of reaction, a result predicted by simple unimolecular theory.

Two mechanistic models have been proposed for the reaction. In the one case, reaction is visualized as an initial C-C bond cleavage followed by H atom transfer and the other case as reaction occurring by H atom transfer from one carbon atom accompanied by rupture of the opposite C-C bond.

Experimental evidence distinguishing between the two mechanisms of the cyclopropane reaction was revealed by the study of Rabinovitch, Schlag and Wiberg (3) on the isomerization of cis-dideuteriocyclopropane. They discovered that geometrical isomerization to trans-dideuterio-cyclopropane occurred more rapidly than structural isomerization to dideuteriopropylene. This result was most readily explained by postulating an initial biradical intermediate:

$$D\diagdown\diagup\diagual\diagdown D$$
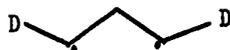
The terminal methylene groups in the biradical would be free to rotate about the carbon-carbon bonds and the biradical could then revert to cyclopropane by ring closure or isomerize to propylene. The Arrhenius parameters for the two isomerizations were

$$k_{structural} = 10^{15.2} e^{-65500/RT} sec^{-1}$$

$$k_{geometric} = 10^{16.0} e^{-64200/RT} sec^{-1} .$$

An alternate mechanism explaining these results was put forward by

Smith (4) who suggested that one C-C bond becomes extended and there

is a twisting of the opposite CH_2 group. RRKM calculations for the

isomerization are also found to be in agreement with the experimental

results when a biradical type activated complex is used as a model (5).

Since the publication of these results, considerable effort has been

exerted to establish the exact mechanism of the reaction.

Thermochemical Analysis of the Cyclopropane Isomerization

A few years after the publication of the results on cis-

dideuteriocyclopropane Benson (6) carried out a more detailed analysis

of the intermediacy of the trimethylene diradical in the isomerization

reaction. The mechanism for the reaction was proposed to be:
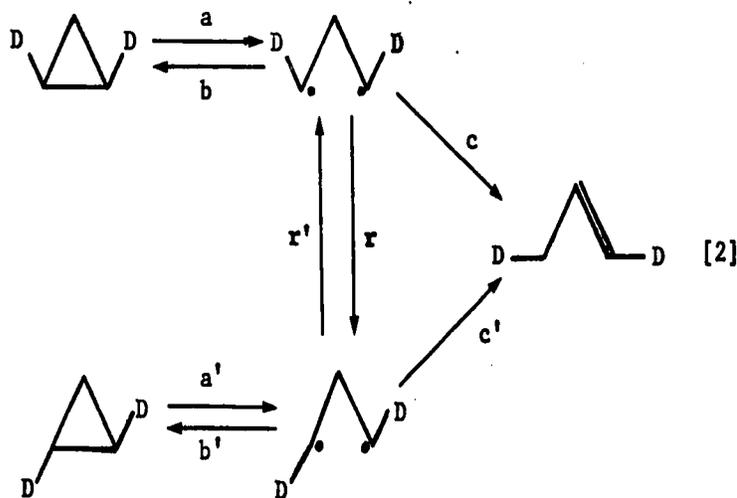
Using thermochemical arguments, Benson was able to assign values for the entropy and enthalpy of formation of the biradical and thereby calculate a value for the equilibrium constant K_{ab}. If $k_r \sim k_{r'} > k_b + k_c$ then the rate expression for propylene formation is

$$\frac{d(p)}{dt} = \frac{k_a \frac{k_c}{k_b}}{1 + \frac{k_c}{k_b}} \quad (\Delta)$$

$$= k_p (\Delta)$$

Rabinovitch and coworkers found that $k_{structural} < k_{geometric}$ and one can therefore assume $k_c/k_b \ll 1$. Thus one obtains

$$k_p = k_a \frac{k_c}{k_b}$$

and identifying k_p and k_a with $k_{structural}$ and $k_{geometric}$ respectively, an expression for k_c/k_b can be derived. Since k_b is obtained from the equilibrium constant K_{ab}, Benson was thus able to calculate an expression for k_c and the Arrhenius expressions for the various rate constants:

$$k_a = 10^{16.0} \exp(-64200/RT)$$

$$k_b = 10^{13.0} \exp(-8200/RT)$$

$$k_c = 10^{12.2} \exp(-9500/RT).$$

From these values one can deduce a schematic representation of a potential energy surface for the isomerization reaction:

8.5 kcal/mole   9.5 kcal/mole

56.0 kcal/mole   62.8 kcal/mole

reaction coordinate
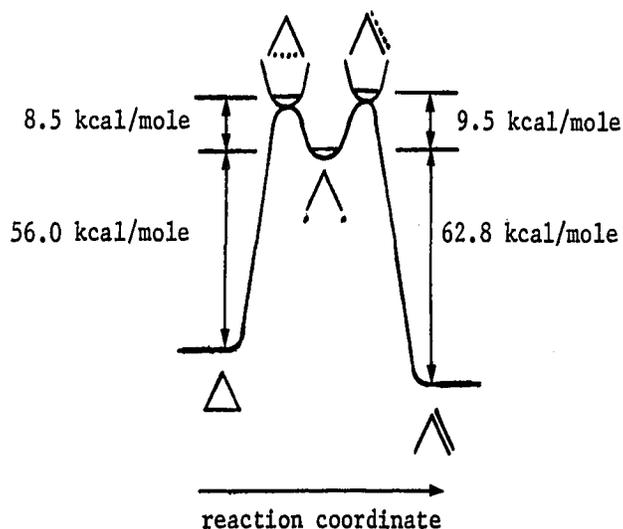
In the same publication, Benson (6) also claimed that Smith's (4)

mechanism was invalid since the energy barrier to a CH_2 twisting mode

would be in excess of 100 kcal/mole, in severe disagreement with

experimental results. The pre-exponential factor for this process

should also be lower than the experimentally determined value. Benson

also suggests that the lifetime of the diradical is less than

$10^{-10.5}$ sec, explaining why attempts to trap it chemically have been

unsuccessful (7).

Evidence in favor of the trimethylene biradical

Many ingenious attempts have been made to clarify the

mechanism of geometric isomerization of cyclopropane. Further

mechanistic insight was sought by studying the geometric isomerization

of optically active 1,2-disubstituted cyclopropanes which also can

undergo racemization.

6
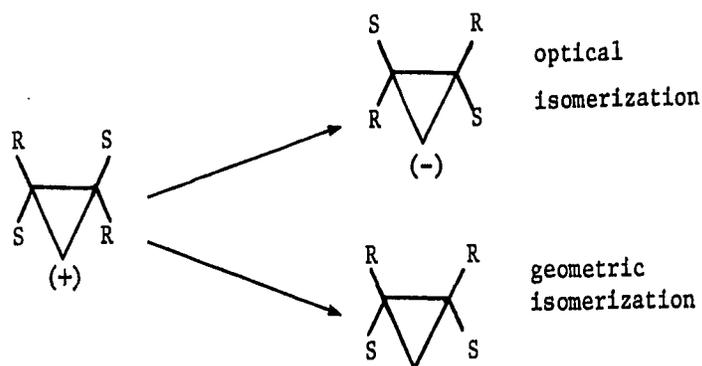
If the RCS groups invert individually, geometric isomerization will predominate, whereas concerted inversion of both RCS groups will lead to racemization of the initial enantiomer. A number of compounds were studied (8) and it was found that a scheme involving biradical intermediates adequately explains the results.

Further evidence supporting the intermediacy of a diradical species comes from studies of vinylcyclopropane pyrolysis (9), which results in isomerization to cyclopentene.
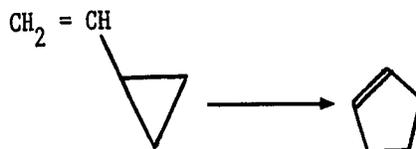
Again a biradical is proposed as an intermediate. The activation energy for this reaction is lower than that of cyclopropane, and this can be interpreted as being due to resonance stabilization of the biradical intermediate. It is noteworthy that the difference in activation energies is equal to the resonance energy of the allyl radical (10):

A great number of other substituted cyclopropanes are believed to decompose via biradical mechanisms (11).

In an effort to ascertain directly the possibility of a trimethylene intermediate, Sims and Yankwitch (12) studied the carbon-13 isotope effect in the structural isomerization of cyclopropane. Their results show a definite isotope effect which is consistent with a mechanism involving considerable ring relaxation.

An attempt to gain further information about the trimethylene biradical was initiated by Crawford and Mishra (13) who investigated the thermolysis of pyrazolines which decompose to form nitrogen and, apparently, a trimethylene biradical:

$$[3]$$
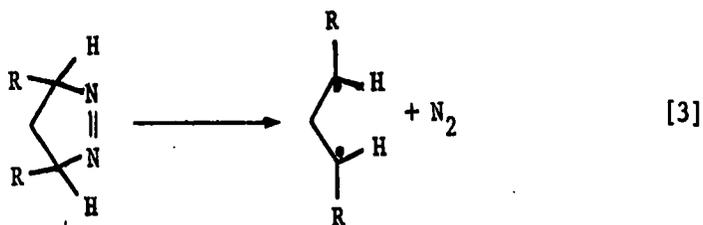
Their results are summarized by the following scheme:
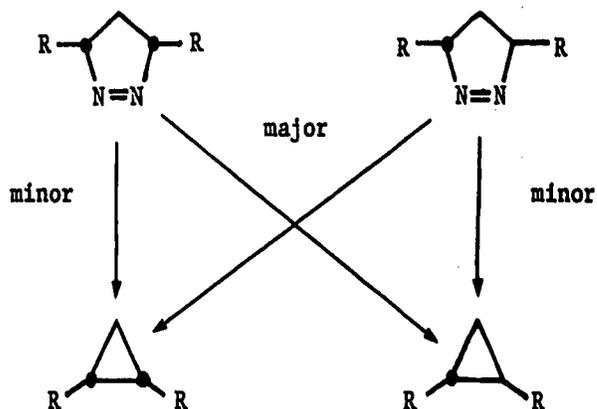
Crawford and Mishra argued that pyrazolines lose N_2 in a concerted
fashion and that the cyclopropane is formed by conrotatory ring
closure of the trimethylene.

Theoretical Calculations on Trimethylene

These experimental results stimulated Hoffmann (14) to perform
a theoretical Extended Hückel Molecular Orbital calculation for
trimethylene. The results of these calculations indeed indicated that
trimethylene, with a conformation where the terminal methylene groups are
coplanar with the carbon skeleton (also called the 0,0 configuration)
was a stable species, and that it would recyclize to cyclopropane in a
conrotatory fashion with a low energy barrier. The most stable CCC
angle for this trimethylene species was predicted to be 125° and the
biradical was calculated to be 44 kcal/mole less stable than
cyclopropane. The trimethylene in Benson's formalism was estimated to
be 54 kcal/mole less stable than cyclopropane. Hoffmann was still able
to identify his calculated trimethylene intermediate with that of
Benson, since the energies in EHMO calculations are usually inexact.

Although the work of Crawford and Mishra, and Hoffmann
provided a great stimulus and new concepts in the development of
cyclopropane chemistry, the recent results of Bergman and coworkers
(15) provide evidence against the intervention of the 0,0 biradical
intermediate. These workers studied the pyrolysis of a pyrazoline
which had a short, two carbon bridge between the central carbon and a
terminal one:

$$R_1, R_2 \quad N{\equiv}N \quad B$$
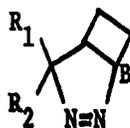
The bridge would prevent rotation of the group at center B in the

intermediate. Pyrolysis of the compound yielded the same amount of

inversion of configuration as in the studies of Crawford and Mishra

on the non-bridged pyrazoline. Since only one group can rotate,

Bergman and coworkers argue that the 0,0 intermediate cannot be implicated

in the decomposition of pyrazoline.

Recent calculations on the trimethylene radical have shed

an entirely new light on cyclopropane isomerization. Hay et al.

(16) using an ab initio Generalized Valence Bond method, and Horsely

et al. (17)using the Self Consistent Field molecular orbital method,

have shown that the geometric isomerization of cyclopropane can be

regarded as a one step process from reactant to product without

invoking a two-step scheme involving a biradical intermediate which would

appear as a minimum in the potential curve. Geometric isomerization

can take place by two paths; (i) rotation of one CH_2 group or

(ii) rotation by both terminal CH_2 groups. The activation energies for

the two processes are found to be essentially identical. The saddle

point for path (i) occurs when one terminal CH_2 group is in the plane

of the carbon skeleton and the other perpendicular to it, but with the

two hydrogens facing into the CCC angle:
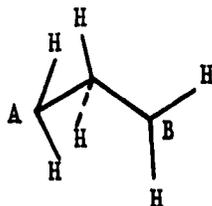
An interesting characteristic of this structure (18) is that

it could also easily isomerize to propylene by rotation of the

central methylene group. This would place one hydrogen in a position

to bond with the terminal group A and put the central carbon in a position to form a π bond with carbon B.

The SCF calculations (17) indicate that path (ii), in which both terminal methylene groups are allowed to rotate would be a disrotatory one and the GVB (16) method predicts that the conrotatory mode is favored slightly over the disrotatory mode.

The above calculations were all performed for the case of singlet trimethylene. While these results indicate that the singlet potential surface for the cyclopropane reaction has no minimum, the situation regarding the triplet trimethylene surface appears to be entirely different (19) in that the ring expanded triplet biradical corresponds to the region where the energy is the lowest. This minimal region is consistently found to be 3.5 to 4.5 kcal/mole below the singlet surface. If the reactant were to cross to the triplet surface after reaching the transition state, then it could be classed as a reaction intermediate in the usual sense. Salem and Rowland (19) suggest that thermochemical estimates of biradical energies and rate constants remain valid only when applied to the triplet state.

2) The Thermal Decomposition of Epoxides

The pyrolysis of ethylene oxide, which is isoelectronic with cyclopropane, would be expected to proceed by an analogous mechanism yielding acetaldehyde. This product is indeed observed, but the overall mechanism is complicated by the intervention of chain and surface reactions.

The major products of the reaction were CH_4 and CO (20).
An interesting feature of the reaction is that addition of He, CO_2, Ne
and other inert gases inhibited the overall rate of the decomposition
(21). This effect was also observed upon the addition of hydrocarbons
such as CH_4, C_2H_6 and C_3H_8. Another interesting fact discovered by
Mueller and Walters (22) was that the yield of CH_3CHO, which is a minor
product, increased in the early stages of reaction and then decreased,
but could be enhanced by the addition of propylene.

In an effort to clarify the mechanism of the ethylene oxide
decomposition, Benson (23) proposed the following reaction scheme :

$$\overset{\bigtriangledown\!\!\!\diagup}{O} \rightleftharpoons \cdot CH_2CH_2O\cdot$$

$$\cdot CH_2CH_2O\cdot \rightarrow CH_3CHO^*$$

$$CH_3CHO^* \rightarrow CH_3 + CHO$$

$$CH_3CHO^* + M \rightarrow CH_3CHO + M$$
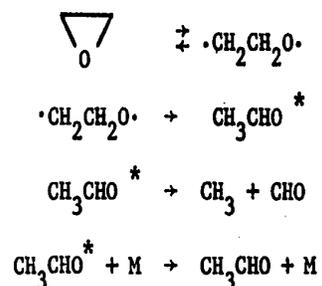
where CH_3CHO^* is a vibrationally hot molecule. CH_3 and CHO react further
producing CH_4 and CO. The effects of inert gases are postulated to be
due to the increased quenching of the hot acetaldehyde molecule.

Support for this mechanism was claimed on the basis of
unimolecular calculations of the rates of ethylene oxide and acetaldehyde
decomposition. The results of this work showed that vibrationally
excited acetaldehyde molecules are indeed primary products of the
pyrolysis of ethylene oxide (24).

Further support for a biradical mechanism in epoxide pyrolysis
was provided by the work of Flowers and Parker (25) who investigated

the reactions of _cis_- and _trans_-2,3-epoxybutane and 1,2-epoxy-2-methylpropane. In the case of the former molecule, _cis-trans_ isomerization was observed and claimed to occur via a biradical intermediate:
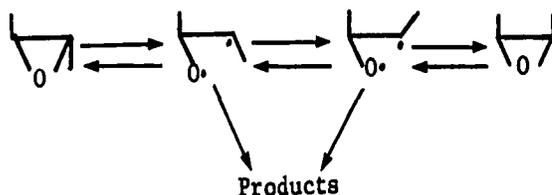
Products

The products butane-2-one and isobutyraldehyde were formed from H-atom and CH_3-group shifts respectively, in the biradical.

Similarly, the pyrolysis of 1,2-epoxy-2-methylpropane was also found to be a homogeneous, first order process not involving free radicals. Isomerization to isobutyraldehyde via a biradical intermediate was the major reaction observed.

A minor process in the decomposition of epoxides is isomerization to produce non-cyclic ethers, which are believed to form via C-C bond cleavage in the substrate.

It is informative to compare the relative rates of ring closure and H-atom migration in the thermolysis of _cis_-dimethyl-cyclopropane and _cis_-2,3-butene epoxide. The ratio of the rate constants in the case of the former molecule is $k_{rc}/k_{H\ mig}=10^{1.32} \exp(2480/RT)$ (27). In the case of the latter molecule the ratio is $10^{0.43} \exp(-2720/RT)$ (25). This clearly illustrates the fact that partially bound oxygen has a much stronger tendency than does carbon to form double bonds.

3) The Thermal Decomposition of Episulphoxides

The episulphoxide molecule presents an example of a small three-membered sulphur containing ring compound. The first report of the decomposition behavior of episulphoxides appears in a study of the preparation of ethylene episulphoxide (28). It was reported that the molecule was fairly unstable at $100^{\circ}C$ and decomposed by dethionylation:

$$\underset{\underset{O}{\overset{\displaystyle CH_2\text{---}CH_2}{\underset{\displaystyle S}{\diagdown\diagup}}}}{} \rightarrow CH_2CH_2 + SO.$$
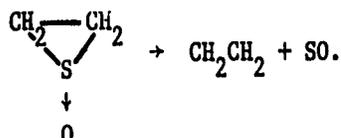
Sulphur monoxide is thermodynamically unstable and presumably disproportionates to elemental sulphur and sulphur dioxide. Experiments with ethylene episulphoxide in solution indicated first order decomposition kinetics with an activation energy of 35 kcal/mole. In a subsequent study of the pyrolysis of cis- and trans-butene episulphoxides, Hartzell and Paige (29) found that the cis isomer yielded 89% cis-butene and the trans isomer yielded 58% trans-butene. The results were taken as evidence for a two step mechanism in which an initial cleavage of just one C-S bond occurs, followed by loss of the sulphur monoxide. These results were confirmed by Baldwin et al. (30) who proposed that decomposition to butene and SO proceeds via a biradical intermediate. It was shown that under favorable stereochemical conditions the molecule could also isomerize to sulphenic acid.

Kondo, Matsumoto, and Negishi recently reported their findings on the pyrolysis of cis- and trans-stilbene episulphoxides, which decompose to stilbene and sulphur monoxide (31):

$$C_6H_5 \overbrace{\underset{S}{\bigtriangleup}} C_6H_5 \rightarrow C_6H_5-CH=CH-C_6H_5 + SO$$

Decomposition of <u>trans</u>-stilbene episulphoxide is stereospecific, while that of the <u>cis</u> isomer is not, and the <u>cis/trans</u>-stilbene product ratio is temperature dependent. When di-p-anisyl thioketone,

$$CH_3O-\langle\bigcirc\rangle-\overset{\overset{S}{\|}}{C}-\langle\bigcirc\rangle-OCH_3$$

which is claimed to be a good scavenger of carbon radicals (32), was added to the thermolysis system, good yields of the following adduct were obtained:

An—S—C—Ph with H above, Ph below; An—S—C—Ph with H below; central C connecting the two S groups; O attached to lower S.

Trapping experiments using well known 1,3-dipolarophiles were unsuccessful and the authors concluded that the reaction takes place by a two step mechanism involving a biradical intermediate:

Ph· —CH—CH(Ph)—·S→O biradical structure

4) Sulphur Atom Reactions with Olefins

General Features

The reaction of ground state triplet sulphur atoms, $S(^3P)$
with olefins has been studied extensively (33,34). The source of the
sulphur atoms is photolysis of carbonyl sulphide in the presence
of high pressures of carbon dioxide, which readily deactivates ^1D
sulphur atoms to the ground state, or mercury photosensitization of
COS. It has been shown that the only reaction of the ^3P sulphur atoms
with an olefin is to produce the corresponding episulphide in a highly
stereospecific fashion. In the case of the reaction with cis-
dideuterioethylene the product episulphide contains at least 75% cis
isomer (35) and for the case of cis-butene-2, the reaction is 90%
stereospecific:

$$S(^3P) + \underset{H}{\overset{R}{\diagdown}}C = C\overset{R}{\underset{H}{\diagup}} \rightarrow \underset{H}{\overset{R}{\diagdown}}C\underset{S}{\diagup\diagdown}C\overset{R}{\underset{H}{\diagup}} \qquad [4]$$
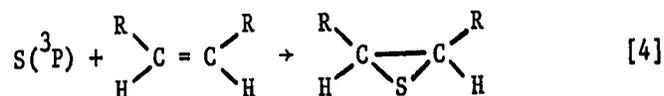
It was found that reaction [4] is so rapid that a low olefin
to COS ratio of 1/10 or smaller is sufficient to scavenge the sulphur
atoms. Recent determinations (36, 37) of the absolute rate constant
for the reaction with ethylene, using the technique of kinetic
spectroscopy, confirm this finding. Fair et al. (36) determined the
rate constant to be 7.2×10^{11} cc/mole sec at $25°C$, and more recently
Davis et al. (37) measured the Arrhenius parameters as

$$k_{S+C_2H_4} = 4.29 \times 10^{12} \times \exp(-1580/RT) \text{ cc/mole sec.}$$

A striking feature of the sulphur-olefin addition reaction becomes apparent upon comparison of the relative Arrhenius parameters for the reaction of a series of substituted olefins, Table I-I. The activation energies for the reaction decrease with increased alkyl substitution, clearly demonstrating the electrophilic nature of the sulphur atom. Furthermore, from a knowledge of the absolute Arrhenius parameters for the ethylene reaction, one arrives at a negative activation energy of 1.5 kcal/mole for reaction with tetramethylethylene.

This unique temperature dependence has also been found to occur in reactions of other Group VIa atoms, namely $Te(^3P)$, $Se(^3P)$ (34a) and $O(^3P)$ (38), and it is a surprising result, since there appears to be no precedent for the occurrence of a negative activation energy for an addition reaction in the second order region.

As an explanation for this behavior, it was proposed that the reactants approach on a potential surface intersecting a second one near its minimum. The repulsive portion of this surface intersects an attractive potential surface.

$S + C_2H_4$
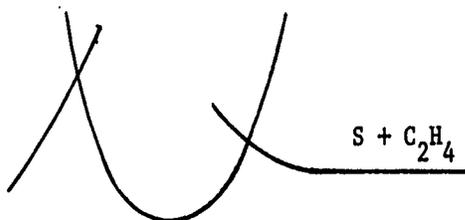
The rate of reaction is then governed by a) the energy difference between the separated reactants and the points of curve crossing and b) the probability of crossing between the surfaces. A positive experimental activation energy will, therefore, result when the point of the second

TABLE I-I

Relative Rate Constants and Arrhenius Parameters

for $S(^3P)$ Addition to Olefins [a]

Compound	$k/k(C_2H_4)$	$E_a(C_2H_4)-E_a$	$A/A(C_2H_4)$
$CH_2 = CH_2$	1.0	0	1.0
$CH_3CH = CH_2$	6.8	1.14	1.0
cis-$CH_3CH = CHCH_3$	18	2.09	0.53
trans-$CH_3CH = CHCH_3$	23	2.01	0.65
$CH_3CH_2CH = CH_2$	11	1.72	0.75
$(CH_3)_2C = CH_2$	54	2.36	0.97
$(CH_3)_2C = CH(CH_3)$	88	3.01	0.51
$(CH_3)_2C = C(CH_3)_2$	131	3.36	0.50
$CH_2 = CH-CH = CH_2$	77	2.04	2.4
$CH_3CH_2C(CH_3) = CH_2$	63	2.83	0.78

a) ref. 33

intersection lies above the small barrier of separated reactants. An increase in temperature would therefore enhance curve crossing. A negative activation energy will be measured when the crossing point lies below the separated reactants since higher temperatures will favor redissociation.

In the case of the reaction of ground state oxygen atoms, a negative activation energy is also found for the reaction with tetramethylethylene (38). In this case the value is only -0.6 kcal/mole and the authors claim the result is due to a negative temperature dependence in the Arrhenius pre-exponential factor becoming manifest due to a very small positive activation energy. This explanation is not favored for the reactions of the other group VIa atoms, since it is felt unlikely that the effect would make the activation as negative as -1.5 kcal/mole.

Further insight into the sulphur atom addition reaction was sought by measuring the kinetic isotope effect. Reaction of $S(^3P)$ with deuterated ethylene demonstrated the existence of an inverse secondary isotope effect (39):

	k_D/k_H
C_2D_4	1.14
CD_2CH_2	1.07
cis-CDHCDH	1.04

As will be seen in a following section, calculated kinetic isotope effects depend upon the model of the activated complex. For the specific case of the sulphur atom addition to ethylene, two models were chosen. In one model, reaction is visualized as a suprafacial,

least motion approach of the sulphur atom yielding a symmetrical

episulphide molecule, and in the other an asymmetrical approach at an

angle of 100° to the C-C bond resulting in a ring-opened biradical.

Unfortunately, the calculation was not particularly sensitive

to either of the two models and it was possible to reproduce the

observed inverse kinetic isotope effect for all three molecules, C_2D_4,

CH_2CD_2 and cis-CHDCHD, using either model.

An interesting feature of the calculations, however, was that

they revealed an insight into the nature and origin of the secondary

isotope effect in the asymmetrical model. Calculations showed that

the effect is due to a newly created vibration, namely the asymmetric

CH_2 twist mode of the episulphide, not present in the ethylene molecule.

Theoretical Studies

A theoretical study of the interaction of sulphur atoms and

ethylene was carried out within the framework of the Extended Hückel

MO formalism by Hoffmann and coworkers (40). For the $S(^1D) + C_2H_4$

reaction, potential surface calculations revealed two minima

corresponding to the vinyl mercaptan formation (insertion in a C-H bond)

and episulphide formation. The latter minimum was due to a least-motion

symmetry allowed addition across the double bond. Similar calculations

for the $S(^3P) + C_2H_4$ system demonstrated the presence of only one

minimum corresponding to episulphide formation. The stereospecificity

of the reaction was attributed to a correlation with an excited state

of episulphide (40, 41) which retains C-C bonding but is unstable to

C-S bonding. In the ring opened intermediate, the CCS angle is 100°

with the terminal methylene group plane perpendicular to the CCS plane.

The barrier to rotation of the terminal methylene was calculated to be 5 kcal/mole.

The results of recent systematic, non-empirical and semi-empirical molecular orbital studies (42) on the sulphur atom-ethylene system and its reaction products, are in general agreement with the EHMO investigations described above. As found in the latter calculations, the reaction of $S(^1D)$ with ethylene is shown to be an energetically feasible process, leading to the formation of ground state episulphide. This is illustrated in a correlation diagram shown in Fig. I-1. However, the $S(^3P)$ addition reaction yielding the lowest vertical triplet excited state of the episulphide is endothermic, requiring an appreciable activation energy, contrary to experimental results. It therefore appears that this process is not as simple as implied by the earlier qualitative explanations of the reaction (40, 41). This discrepancy is resolved if the lowest triplet state of the episulphide in a ring distorted geometry is considerably more stable than the symmetric species. This would correspond to non-vertical triplet excitation.

Further insight into the potential surface of the $S(^3P) + C_2H_4$ addition reaction was obtained from more detailed ab initio SCF calculations (43). The results of this work are in general agreement with the previous studies. Singlet and triplet states of the adduct were investigated and indeed a ring distorted structure with a CCS angle of $100°$ is found to represent a stable configuration. For the case of the lowest triplet state, this stable configuration lies at an energy about 40 kcal/mole above the ground state episulphide. An energy
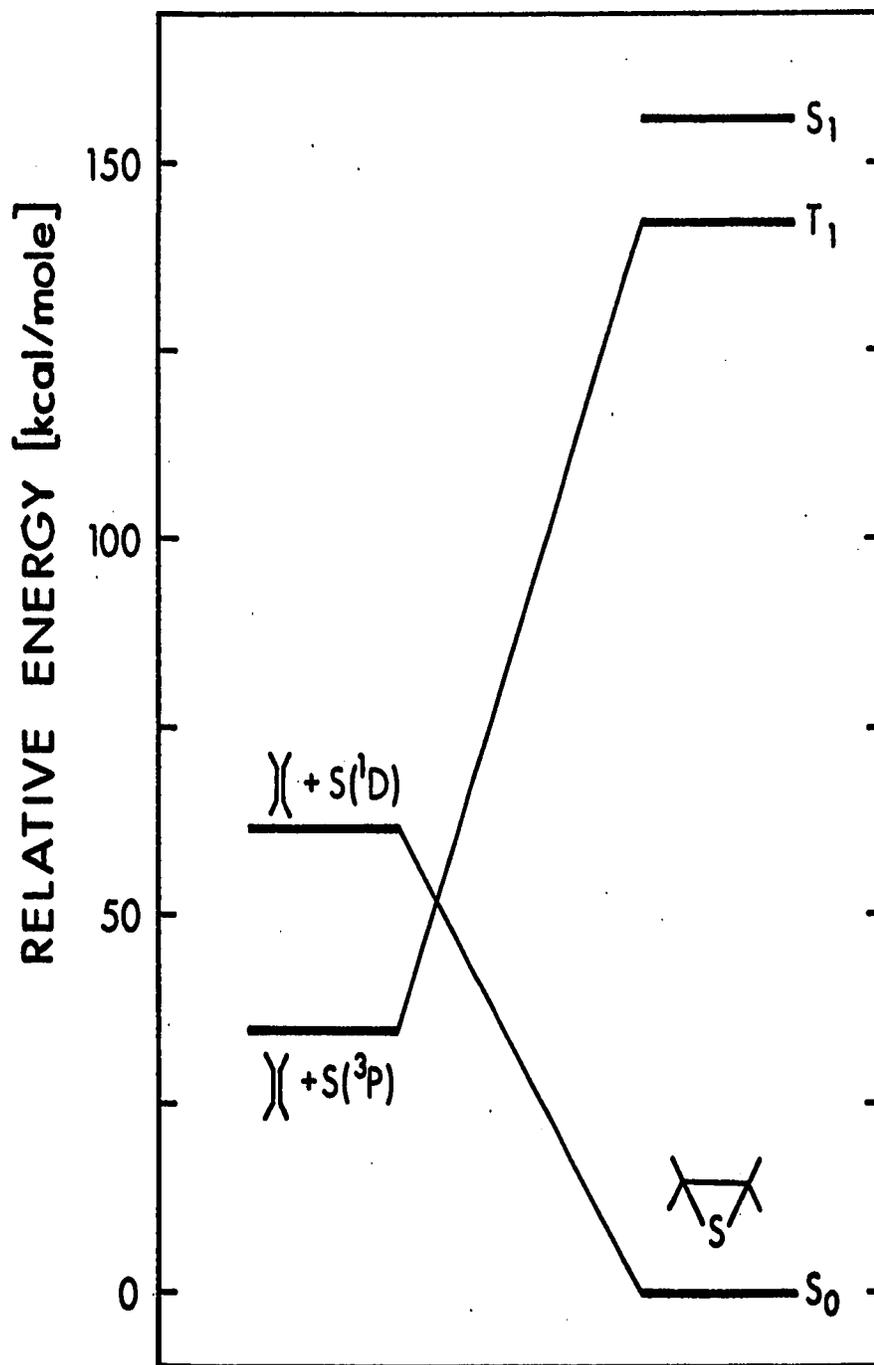
Figure I-1. Correlation diagram for sulphur addition to ethylene

profile of the excited states as a function of ring geometry is shown in Fig. I-2. It is seen that an initial symmetric approach to the ethylene molecule leads to the immediate formation of a ring opened structure. These results, therefore, resolve the discrepancy mentioned above, by which the calculated energy for reaction yielding the vertical triplet was much greater than the experimental activation energy. The fate of the triplet episulphide is then probably collision-induced intersystem crossing to the ground state.

The primary product of the $S^3(P) + C_2H_4$ reaction can be viewed as a non-vertical triplet excited state of ethylene episulphide having approximately 20 kcal/mole excess vibrational energy. ($\Delta H - E(\text{Triplet}) \simeq 20$ kcal/mole). The experimental results (35) show that the reaction is greater than 75% stereospecific. In order for the vibrationally hot product to maintain its stereochemical information content in the course of reaction, torsional rotation of the terminal methylene in the triplet intermediate must have a considerable energy barrier. In a calculation of the total energy as a function of the angle of CC rotation, at a CCS angle of 100°, it is indeed found that there exists an energy barrier to rotation of 23 kcal/mole in the lowest triplet excited state (43). This barrier is greater than that necessary to account for the experimental results, and the stereospecificity of triplet sulphur atom addition is thus attributed to a relatively strong binding interaction between sulphur and the terminal methylene carbon.

The results of photolysis of ethylene episulphide (44) also bear relevance to the studies of sulphur atom interaction with olefins. The chief product is ethylene, which is proposed to arise (a) from
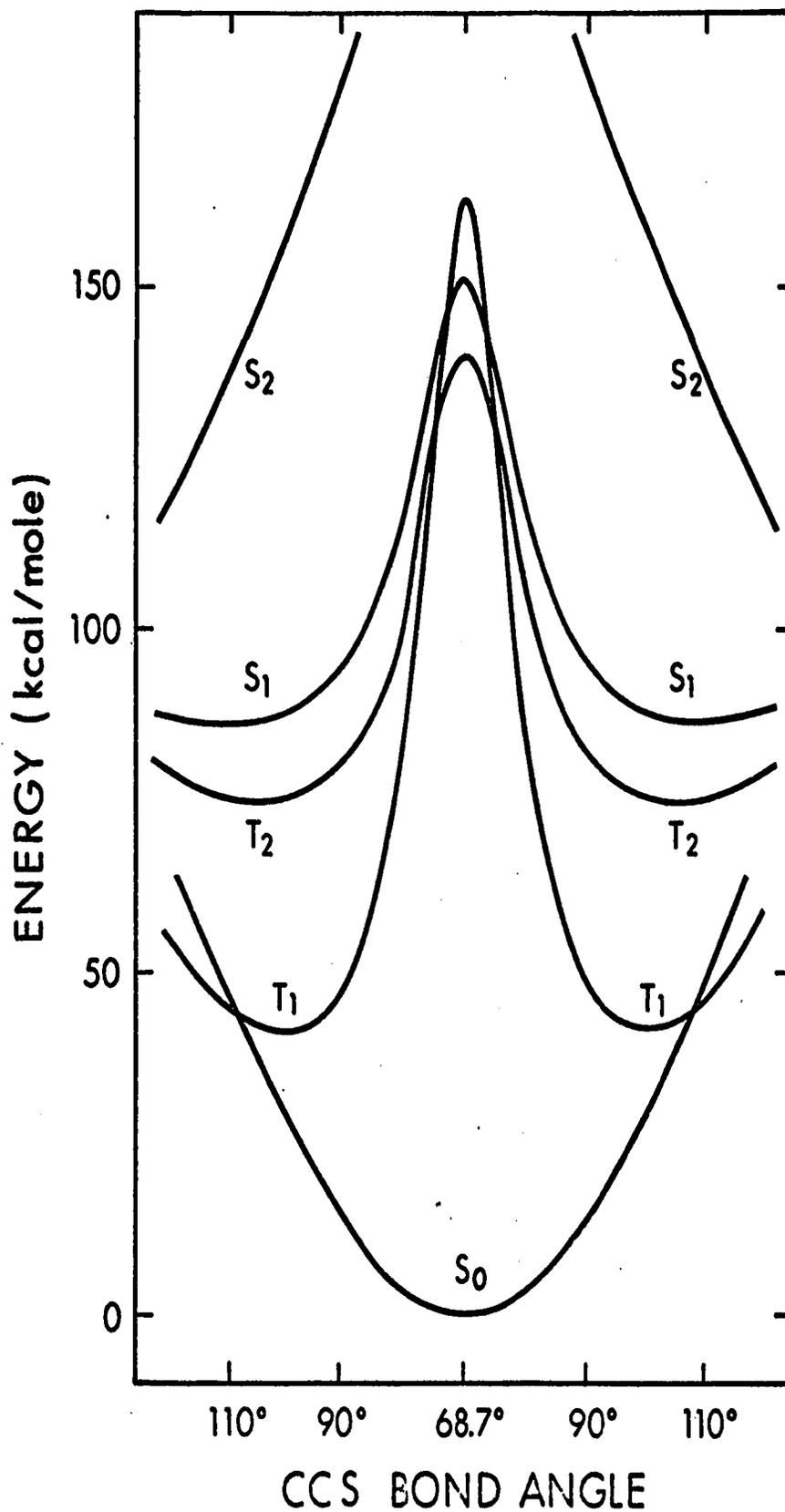
Figure I-2. Variation of total energy with CCS angle;

S = singlet, T = triplet

decomposition of triplet episulphide and (b) by reaction of triplet

episulphide with ground state substrate forming C_2H_4 and S_2. The

interesting result in the context of the S atom addition work, is

that photolysis of ethylene episulphide in the presence of a large excess

of C_2H_4 yields small amounts of thiacyclopentane. It was proposed

that this product resulted from an addition reaction of

thiodimethylene ($\cdot CH_2CH_2S\cdot$) with ethylene, providing chemical proof

for the existence of the biradical.

5) Biradicals

The preceding discussion has shown that the chemistry of

small cyclic molecules is intimately related to the physical and

chemical properties of biradicals and it would therefore seem appropriate

to review some properties of biradicals.

Usually a chemical species with two unpaired electrons is

called a biradical in contrast to those with one unpaired electron,

namely monoradicals, which are necessarily always in a doublet state.

Since monoradicals have an odd number of electrons, valence saturation

cannot take place by an intramolecular process. A biradical has an

even number of electrons, just as a valence saturated molecule does,

but two of the electrons are unpaired. Consequently, it is possible

for a biradical species to become valence saturated by an intramolecular

process. Depending on the molecule, the unpaired electrons can be in

very close proximity on one atom, as $:CH_2$, $:O$, $:S$ or the electrons can

be on different atoms separated by long distance. The consequence of

this fact is not trivial. When electrons are sufficiently close to

each other that they can interact, they occur either in a paramagnetic

triplet state when the electron spins are parallel, or a diamagnetic

singlet state for the case of two anti-parallel spins. When the electrons

are sufficiently far apart that there is no interaction, they behave as

single free electrons; such a case is presented by bisgalvinoxyl:
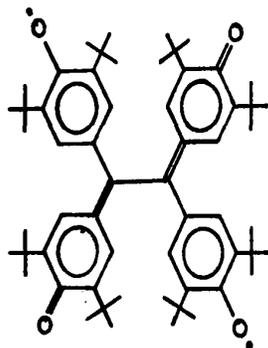
The above species gives an ESR spectrum characteristic of two

doublet states, typical of monoradicals, rather than one characteristic

triplet state (19, 45). By forcing the radical centers closer to

each other, the electronic characteristics of the molecule change. Thus,

for the case of
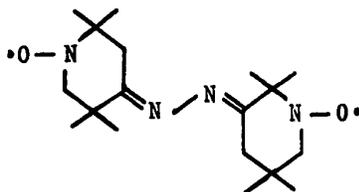
it is found that the ESR spectrum is that of a well defined triplet

state indicating that the odd electron interaction is already consid-

erable (19, 46). An interesting case is presented by the following

molecule:
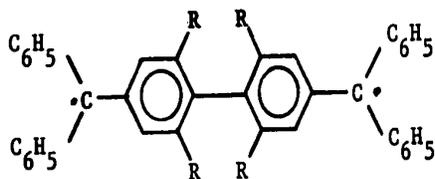
which has been considered to be at the borderline between the case where the system can be described by two doublet states (i.e. two non-interacting electrons) and where electron interaction is sufficient for distinction between two distinct singlet and triplet states (19, 47).

Recognizing that biradicals with strongly interacting electrons exist in either singlet or triplet states, it becomes apparent that such biradicals can be indistinguishable from excited states, depending on the difference in the triplet and singlet state energies. Freeman (48) suggests that if the energy difference between the singlet and triplet states is less than the energy of relative motion of the two ends of the biradical, then the species can be considered a biradical rather than an excited molecule. Recognizing that biradicals, under the appropriate conditions, are also identical with excited states, it is no longer meaningful to define them as species possessing two unpaired electrons. This would restrict biradicals only to triplet species or those containing two doublets. It is on this basis that Freeman suggests the better definition, "a biradical is an atom or molecule that reacts as though it has two monoradical functions". Recently, Salem and Rowland (19) reported results of an extensive theoretical investigation of biradicals, in which they are described as having two odd electrons in degenerate or nearly degenerate molecular orbitals. The study shows that the form of the two-electron wave function depends entirely on the symmetry of the biradical.

6) Unimolecular Reactions

Due to the fundamental importance of understanding reactions in thermal systems, theories have been developed which describe the microscopic processes involved during the course of reaction. Of the different classes of reactions, i.e. unimolecular, bimolecular and termolecular reactions, unimolecular reactions are understood best. Since the understanding of most thermal decompositions is closely tied to unimolecular theory, a brief survey of the theory will be given here.

In principle, unimolecular reactions are the simplest kind of reaction since they involve the isomerization or decomposition of only a single isolated molecule:

$$A \rightarrow Products$$

$$and \quad -\frac{d[A]}{dt} = k[A]. \tag{5}$$

The earliest theory describing this behavior was due to Perrin (49). He argued that since the specific rate of such a reaction is independent of pressure, the pressure of the gas could be reduced indefinitely without affecting the first order rate constant. Collisions would therefore not be activating the molecules for reaction and they must be absorbing radiation from the walls.

The error in Perrin's explanation is that the order of reaction does not remain unity at sufficiently low pressures but becomes second order. Lindemann (50) and Christiansen (51) later recognized the difficulty and proposed a three step mechanism involving collisional activation and deactivation of the substrate:

$$A + M \rightarrow A^* + M \qquad\qquad [6]$$

$$A^* + M \rightarrow A + M \qquad\qquad [7]$$

$$A^* \rightarrow \text{Products} \qquad\qquad [8]$$

where A^* is a substrate molecule sufficiently energized that it can react, and M is any bath molecule. The rate expression for the Lindemann scheme is

$$\text{Rate} = \frac{k_6 k_8 [A][M]}{k_7 [M] + k_8} . \qquad\qquad [9]$$

Thus when $k_7[M] \gg k_8$

$$k_{uni} = \frac{k_6 k_8}{k_7}$$

and the reaction is first order.

Hinshelwood (52) later proposed that k_6 is dependent on the energy of the reacting molecules and made the assumption that the critical energy required for reaction to occur in one particular part of the molecule could be drawn, in part, from the vibrational degrees of freedom. Shortly after Hinshelwood's proposal, Rice and Ramsperger (53), and independently, Kassel (54) suggested that k_8 also was dependent upon the total internal energy of the molecule. The reaction is considered to occur when a critical amount of energy, E_o, becomes concentrated in one particular part of the molecule. The total amount of energy E acquired by collisions is assumed to be distributed throughout the molecule extremely rapidly, so that for any molecule with $E > E_o$ there is a finite statistical probability that an energy E_o will be located in the relevant part of the molecule. It is then assumed that the rate constant for reaction to products is proportional to this

probability. The difference between the two treatments rests in the assumption concerning the part of the molecule into which the critical energy E_o must be localized. In the treatment of Rice and Ramsperger, it was taken to be one square term in the energy expression, whereas Kassel assumed it to be one oscillator. By either treatment, the resulting expression has the same form. Relabelling k_8 as k_E to denote the energy dependence, the following expression is derived,

$$k_E \propto \left[\frac{E - E_o}{E}\right]^{s-1}$$

where E is total energy, E_o is critical energy for reactions and s is the number of oscillators.

Kassel (54) later sought further improvement using the same assumptions but a quantized form for the oscillators. The resulting expression for k_E was again the same as in the non-quantized theory.

Although the theory of Rice, Ramsperger and Kassel (RRK) achieved a certain degree of success, it has been found that best agreement between theory and experiment is only obtained with values of s less than the total number of degrees of freedom of the molecule. The theory also does not predict a value for preexponential factor A, but it can be associated with the A-factor in the Arrhenius expression for the rate constant at high pressure.

After the development of transition state theory, Marcus (55) applied its basic concepts in conjunction with the methods of quantum statistics, to derive an expression for the energy dependence of k_E. The fundamental assumptions, namely those regarding the free flow of energy within the molecule, remained the same as in the RRK theory,

only that rotations could also become active in the flow of energy among the internal modes.

The quantum-statistical-mechanical treatment mentioned above is applied not only to derive an expression for k_E, but also for k_6. Applying the Absolute Rate Theory, the reaction of the energized molecule A^* to products is now divided into two steps,

$$A^* \rightarrow A^{\dagger} \rightarrow \text{Products}$$
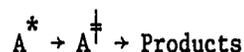
where $A^{\dagger}$ is the activated complex. The distinction between A^* and $A^{\dagger}$ is that the former molecule is one which is sufficiently energized to react but is still a substrate molecule and the activated complex $A^{\dagger}$ is a species which is intermediate between reactant A^* and products. It can be characterized by having a configuration on the top of the energy barrier between reactant and products.

According to the Marcus formalism the energy dependent rate constant is of the following form:

$$k_E = \frac{L^{\dagger}}{h} \frac{\Sigma P(E^{\dagger})}{N(E^*)} \qquad [10]$$

where

$L^{\dagger}$ is a statistical factor governed by the number of ways a certain reaction can occur

h is Planck's constant

$P(E^{\dagger})$ is the total number of vibrational-rotational quantum states of $A^{\dagger}$ with an energy $E^{\dagger}$ above E_o

$N(E^*)$ is the density of vibrational states of the substrates at an energy E^*.

At this point, it should be recalled that the unimolecular rate constant k_{uni} varies with pressure, being essentially invariant at high pressures (the first order region) but falling off to decreasing values with lower pressures (second order region). For most larger organic molecules the fall-off region usually appears at extremely low pressures that are experimentally not readily accessible.

The high pressure rate constant is essentially the product of k_E and the Boltzman factor:

$$k_\infty = \int_{E_0}^\infty k_E \, B(E)dE$$

$$k_\infty = \text{constant} \int_{E_0}^\infty \frac{\Sigma P(E^\ddagger)}{N(E^*)} \frac{N(E^*)}{Q^*} e^{-E_0/kT} dE.$$

This expression reduces to the quantities $\Sigma P(E^\ddagger)/Q^*$, which is simply the ratio of the partition functions for the activated complex and energized molecules, and the Boltzman factor. The ratio, predicted by Absolute Rate Theory, is relatively insensitive to the structural features of the reactant. It is due to this fact that it is virtually impossible to perform an experiment with a large molecule in a thermal system that will provide information about the microscopic processes involved in the reaction.

A number of investigations have been carried out comparing the RRK and RRKM formulations with the main focus of attention centered on the classical empirical Kassel fit parameter s. Placzek, Rabinovitch, Whitten and Tschuikow-Roux (56) showed that this parameter is a complex function of temperature, the critical energy E_0 and the vibrational pattern of the molecule and activated complex. Within the framework

of the RRKM theory, s can be expressed in terms of the average energy

of the reacting species produced by thermal collisional activation:

$s = E_{vib}(T)/RT$. Tschuikow-Roux (57) extended the investigation of the

comparison somewhat further and concluded that the parameter s is

strictly an empirical fit parameter and that the widely held inter-

pretation of s as a measure of the number of effective oscillators is

a misnomer.

In an effort to revive the less complicated RRK theory, Golden,

Solly and Benson (58) proposed a definition of the s parameter as

$s = C_{vib}/R$, where C_{vib} is the vibrational heat capacity. It was claimed

that an application of this definition of s led to good agreement with

RRKM theory when determining the pressure region for fall-off. Recently,

Skinner and Rabinovitch (59) published results of a further analysis

of the characteristics of the parameter s. They found that in general,

not one, but two Kassel s parameters are necessary for a correct

description of fall-off behavior; one for a correct fitting of the

pressure region and the other for a correct description of the shape

of the curve. It was found that $s = C_{vib}/R$ may be used to find the

approximate pressure region for fall-off, provided $s > E_o/3RT$.

However, under virtually all conditions, the numerical values for k_E

given by RRK theory are unrealistic and the authors conclude that no

unique value of the RRK s parameter satisfactorily describes all

aspects of rate behavior.

Some time after the emergence of the RRK theory, but before

the Marcus formalism, N.B. Slater proposed an elegant theory of

unimolecular reactions (60). This theory adopts the basic Hinshelwood-

Lindemann mechanism of collisional energization, but differs quite

markedly in approach from the above statistical theories in that

it is an attempt to relate unimolecular reaction kinetics with molecular

vibrations. The molecule is visualized as a collection of harmonic

oscillators of specific phases and amplitudes. Reaction occurs when a

reaction coordinate (collection of bond distances or angles) reaches

a critical extension. An important assumption made in this theory, is

that there is no exchange of energy among oscillators between collisions

of the molecule with the bath gas. The expression for the rate

constant k_E is then derived in a form identical to the RRK expression,

$$k_E = A \left[\frac{E - E_0}{E} \right]^{s-1}$$

where A is now correlated with a vibrational frequency.

The elegance of the Slater theory lies in the concept that

reaction occurs when a collection of bonds reaches a critical extension.

One recalls that the previously described theories all required that

the energy E_0 find its way into one particular bond. The most serious

objection to the Slater treatment, however, is in the assumption

concerning energy transfer between the modes of the molecule. Most of

the evidence disproving this assumption has come from studies of chemical

activation. Butler and Kistiakowksy (61) showed that vibrationally hot

methylcyclopropane formed by methylene addition to propylene or

insertion into a C-H bond of cyclopropane, decompose to yield mixtures

of various butenes and that the composition of the butene mixture was

independent of the original site and energy of excitation:

$$CH_2 + CH_3CH = CH_2$$

$$CH_2\colon\, + \triangle \longrightarrow \overset{*}{\triangle} \nearrow^{M}\ \text{stabilization}$$

$$\overset{\bullet}{CH_3}\, + \triangle \qquad\qquad\qquad \searrow\ \begin{array}{l}\text{isomerization to}\\ \text{butenes}\end{array}$$
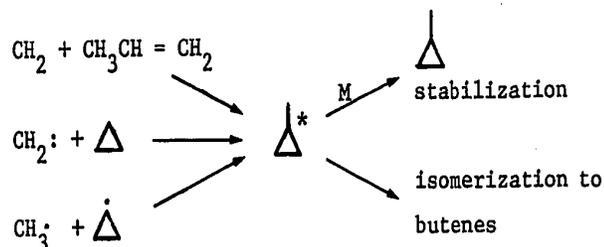
Jakubowski et al. (62) later showed that hot methylcyclopropane,

formed by recombination of methyl and cyclopropyl radical, also

isomerized to yield the same butene mixture. Recent work on the

decomposition of a series of straight chained 2-alkyl radicals by

Rabinovitch and coworkers (63), using carbon chains up to C_{16},

showed that the rate constant for decomposition of the chemically

·activated radical decreased directly with the chain length:

$$CH_3\overset{\bullet}{C}H(CH_2)_n\overset{*}{CH_3} \rightarrow CH_3CH = CH_2 + \overset{\bullet}{C}H_2(CH_2)_{n-2}CH_3$$

$$\overset{M}{\rightarrow} CH_3\overset{\bullet}{C}H(CH_2)_nCH_3\ .$$
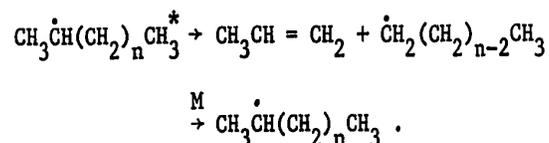
Since the initial energy and the mode of decomposition were identical

for all radicals and the rate constant decreased by several orders of

magnitude for chain lengths of C_5 to C_{16}, it is concluded that the

energy is distributed over the entire molecule prior to

decomposition or deactivation. Studies at very high pressures showed

that randomization of the energy occurs on a time scale of about

10^{-13} sec.

Thus, experimental evidence appears to prove that Slater's

assumption concerning restricted intramolecular energy flow is

invalid, rendering the theory obsolete. Slater has considered a

modified theory, in which free flow of energy is allowed for (64),

but its detailed application to experimental results appears to be difficult.

7) The Secondary Kinetic Isotope Effect

The measurement of rate constants and correlation of Arrhenius parameters with molecular structure are widely used procedures in the investigation of the dynamics of organic reaction systems. Often substituents on the reactant are varied in such studies (e.g. methyl to phenyl), but even if the mechanism remains unaltered, the method suffers from the distinct disadvantage that the potential surface changes upon substitution. A quantitative understanding of substituent effects requires a knowledge of the changes in the potential surface, and although such calculations have met with success in simple systems, an exact treatment for polyatomics remains impossible.

The measurement and analysis of kinetic isotope effects provide a distinct advantage over the above method in gaining insight into the dynamics of a given reaction. Within the limits set by the Born-Oppenheimer approximation, the potential surface (i.e. the electronic energy) is independent of isotopic substitution. Hence, isotope effects result from the motion of the nuclei on the same potential surface. In the context of the precision of the calculations involved, the Born-Oppenheimer approximation may be taken as exact.

Kinetic isotope effects, in chemical kinetics, can experimentally be determined by measuring the ratio of the rate constants of isotopically substituted and non-substituted reactants. Isotope effects are classified into two groups; a) primary effects, in which a bond to the isotopically substituted atom is formed or broken in the course of reaction, and b) secondary effects in which bonds to the substituted atom are not formed or broken.

Halevi (65) modified the definition of the latter by making

a distinction between;

i) secondary isotope effects of the first kind, where the bond to

the isotopic atom undergoes a spatial change, and

ii) secondary isotope effects of the second kind where it does not.

As an example consider:

$$
\begin{array}{c}
\overset{\displaystyle T}{\underset{\displaystyle CD_3}{H-C-{}^{37}Cl}} \rightarrow \overset{\displaystyle T}{\underset{\displaystyle CD_3}{H-C^+}} + {}^{37}Cl^-
\end{array}
$$

$$
\begin{array}{c}
\overset{\displaystyle H}{\underset{\displaystyle CH_3}{H-C-{}^{35}Cl}} \rightarrow \overset{\displaystyle H}{\underset{\displaystyle CH_3}{H-C^+}} + {}^{35}Cl^-
\end{array}
$$
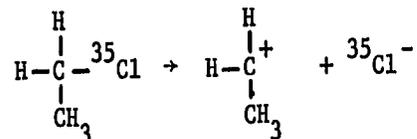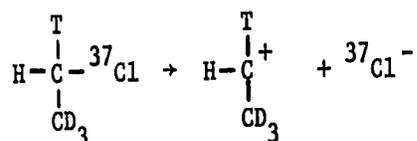
$$
\frac{k^{37}Cl}{k^{35}Cl} = \text{primary effect}
$$

$$
\frac{k_H}{k_T} = \text{secondary effect of the first kind}
$$

$$
\frac{k_H}{k_D} = \text{secondary effect of the second kind.}
$$

The structure $\overset{\displaystyle T}{\underset{\displaystyle CD_3}{H-C-{}^{37}Cl}}$ represents substitution by T^{37}, Cl, or D

respectively. In the context of the present investigation, discussion

will be limited to secondary kinetic isotope effects and a few

illustrative examples.

The theoretical treatment of kinetic isotope effects is

generally carried out within the framework of Absolute Rate Theory (66).

In this theory, the following expression can be derived for the rate

constant of a given reaction:

$$k = \kappa \frac{kT}{h} \frac{Q^{\ddagger}}{Q} e^{-E_a/RT}$$

where κ = transmission coefficient

$Q^{\ddagger}$ = partition function of the activated complex

Q = partition function of the reactant

k = Boltzman constant

h = Planck's constant

and the other terms have their usual significance. Since the partition function Q can be expressed as the product of the translational, rotational and vibrational partition functions, the ratio of the rate constants of reaction for isotopically substituted and non-substituted molecules can also be expressed as:

$$\frac{k_{\ell}}{k_h} = \left[\frac{\left(\frac{I_{A_h} I_{B_h} I_{C_h}}{I_{A_{\ell}} I_{B_{\ell}} I_{C_{\ell}}} \right)^{1/2} \left(\frac{M_h}{M_{\ell}} \right)^{3/2}}{\left(\frac{I_{A_h}^{\ddagger} I_{B_h}^{\ddagger} I_{C_h}^{\ddagger}}{I_{A_{\ell}}^{\ddagger} I_{B_{\ell}}^{\ddagger} I_{C_{\ell}}^{\ddagger}} \right)^{1/2} \left(\frac{M_h^{\ddagger}}{M_{\ell}^{\ddagger}} \right)^{3/2}} \right] \times \left[\frac{\prod\limits_{1}^{3N-6} \left[\frac{1 - \exp\left(-U_{\ell_i}\right)}{1 - \exp\left(-U_{h_i}\right)} \right]}{\prod\limits_{1}^{3N-7} \left[\frac{1 - \exp\left(-U_{\ell_i}^{\ddagger}\right)}{1 - \exp\left(-U_{h_i}^{\ddagger}\right)} \right]} \right] \times \quad [11]$$

$$\left[\frac{\exp\left[\prod\limits_{1}^{3N-6} \left(U_{\ell_i} - U_{h_i}\right)/2 \right]}{\exp\left[\prod\limits_{1}^{3N-7} \left(U_{\ell_i}^{\ddagger} - U_{h_i}^{\ddagger}\right)/2 \right]} \right]$$

The dagger signifies the transition state, and ℓ and h refer to the light and heavy molecules respectively. The I's are the principal moments of intertia, M's the molecular masses, $U_i = hc\omega_i/kT$ and ω_i is a normal vibrational frequency.

Equation [11] is usually abbreviated as a product of three factors:

$$\frac{k_\ell}{k_h} = (MMI) \times (EXC) \times (ZPE) \qquad [12]$$

MMI represents the contributions from the translational and rotational energies, EXC the contributions from the vibrational energies and ZPE the contributions of the zero point energies. The ratio of the transmission coefficients is assumed to be unity.

The question arises as to which changes in the variables of equation [11] result in normal or inverse isotope effects. From detailed model calculations, Wolfsberg and Stern (67) found that a general decrease in the force constants in going from reactant to transition state leads to a normal isotope effect, k (light)/k (heavy) > 1, and an increase in force constants leads to an inverse effect, k (light)/k (heavy) < 1.

The evaluation of equation [11] requires a complete knowledge of the vibrational frequencies of the reactant and transition state. Those of the reactant are obtained from the known data in the literature, or if they are not known, from similar groupings on related molecules. Since the transition state is a hypothetical species, its frequencies must be obtained from a complete set of assumed force constants, atomic masses and geometry. Naturally, it is possible to alter the force field of the transition state in many ways and still obtain the same calculated effect. However, it is probable that some models could be discarded as unrealistic. In other words, while numerical agreement between experiment and a calculated isotope effect

does not necessarily constitute proof for the validity of the chosen model, one which yields sharp disagreement with experiment can in all probability be excluded. Therefore, studies of isotope effects can provide an insight into the structural transitions in the course of reaction.

The studies of Seltzer and coworkers (68) provide an example as one of many studies (69) where exact calculations were compared with experimental results in order to determe the nature of the transition state. The reaction studied was the thermolysis of a series of azo compounds,

$$CH_3\underset{\underset{C_6H_6}{|}}{CH}-N = N-\underset{\underset{C_6H_6}{|}}{CH}CH_3 \qquad CH_3\underset{\underset{C_6H_6}{|}}{CH}-N = N-CH(CH_3)_2$$

$$CH_3\underset{\underset{C_6H_6}{|}}{CH}-N = N-CH_3$$
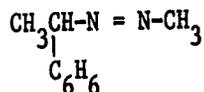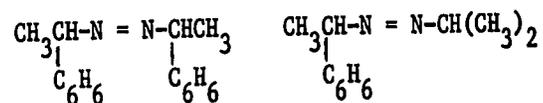
and the force fields chosen were those known of analogous groupings. The calculated effects were in remarkably good agreement with experiment when the transition state was changed from symmetric to unsymmetric with increasing dissymmetry in the molecule.

Streitweiser et al. (70) proposed a simplified form of equation [11], based on the following assumptions:

a) deuterium substitution only changes significantly
    those frequencies which are associated with the bond
    to the substituted hydrogen.

b) the C-H and C-D stretching and bending modes have sufficiently high frequency that only the zero point energy difference need be considered,

c) $\omega_{C-D}/\omega_{C-H} = 1/1.35$, and

d) $m_D^{\ddagger}/m_H^{\ddagger} = 1$.

The resulting equation is

$$\frac{k_H}{k_D} \cong \exp \frac{0.187}{T} \sum_i (\omega_{H_i} - \omega_{H_i}^{\ddagger}) \qquad [12]$$

where ω_{H_i} and $\omega_{H_i}^{\ddagger}$ are the frequencies in cm^{-1} of the C-H bending and stretching modes in the unsubstituted reactant and transition state respectively. On the basis of this equation, the secondary isotope effect is interpreted as being due mainly to the difference in the zero point energies between light and heavy reactant molecules and the transition states.

This equation was used in the interpretation of the secondary effect observed in the acetolysis of cyclopentyltosylate-1-d. It was concluded that the main cause of the secondary isotope effect is the frequency decrease in one of the out of plane C-H vibrations during transition from an sp^3 to sp^2 configuration. This postulate was later generalized to a number of addition reactions involving olefins (71), in which a change of hybridization from sp^2 to sp^3 occurs in either one or two carbon atoms. However, recent studies on sulphur addition to olefins, mentioned earlier, and model calculations (72) indicate that the main single contribution to the isotope effect in these addition reactions is not due to the rehybridization of the carbon atom, but rather to the creation of new normal modes in the transition state.

As these results suggest, there is considerable danger in oversimplifying the treatment of isotope effects.

It would perhaps be appropriate to review some conclusions that have been gained about isotope effect calculations. It is found that, except at extremes of the temperature scale, all terms in equation [11] may contribute significantly to the effect and that its temperature dependence can be quite complicated. The most important conclusion is that isotope effects are essentially determined by changes in the force constants describing the motions at the sites of isotopic substitution in the reactant and transition state. Inasmuch as force constant changes can be correlated with geometric changes, in many cases it may be possible to relate transition state geometries with isotope effects. It has also been found that, for calculations on large molecular systems, it is possible to omit from the calculations those portions of the molecule which are far away from the site of isotopic substitution, without significantly affecting the final result.

8) The Present Investigation

The chemistry of three-membered ring compounds such as cyclopropanes and epoxides has become a subject of fundamental interest. It is the aim of the present investigation to extend our meager knowledge of episulphide chemistry, and the results of this study can then be compared with the chemistry of cyclopropanes, epoxides and episulphoxides. The thermal isomerization of cyclopropane in particular is well documented and it is of great interest to know to what extent this pattern is repeated in the decomposition of episulphides.

The pyrolysis of episulphides is also fundamental to the understanding of the sulphur atom reactions with olefins, in particular the reactions of ground state triplet atoms. Since these reactions result in episulphide formation, it is hoped that a study of the corresponding thermal decomposition will lead to further insight into the nature of the interaction of the electrophilic sulphur atom and olefins.

In order to obtain further information on the decomposition reaction and the structure of the transition state, the secondary deuterium isotope effect is measured for decomposition of ethylene episulphide-d_4.

In the course of this work it became evident that the addition of olefins has a marked effect on the decomposition. Hence, the effect of various added olefins on the reaction was studied in the hope that this would yield further information on episulphide chemistry.

A preliminary account of episulphide pyrolysis has been published (107).

CHAPTER II

EXPERIMENTAL

1) **High Vacuum System**

A conventional static high-vacuum system, constructed of Pyrex tubing and evacuated to 10^{-6} torr, was used throughout the course of the present investigation. The evacuation of the system was achieved by means of two two-stage mercury diffusion pumps backed by Welch duoseal Model 1405 mechanical pumps. The vacuum system was kept grease free by using Delmar mercury float valves and Hoke helium tested teflon seated valves throughout. The sole exception was the valve leading to the reaction vessel which was a stainless steel high temperature helium tested Hoke valve. The vacuum system, illustrated in Fig.II-1, consisted of two distillation trains (one for purification of substrates and one for separation of products), a pyrolytic furnace and assembly, a gas storage system, a Toepler pump, gas burette and a photolysis cell in an aluminum block furnace. Pressures of gases in the system below one torr were monitored by the use of six Pirani gauge tubes (Consolidated Vacuum Corporation Catalogue No. GP-001) powered by a Pirani gauge which was calibrated by means of a McLeod gauge.

2) **The Pyrolytic Furnace Assembly**

The furnace assembly consisted of a Pyrex cell suspended in an aluminium block furnace as depicted in Fig. II-2. The cell was suspended from a high temperature Hoke valve which in turn was fastened to the furnace block.
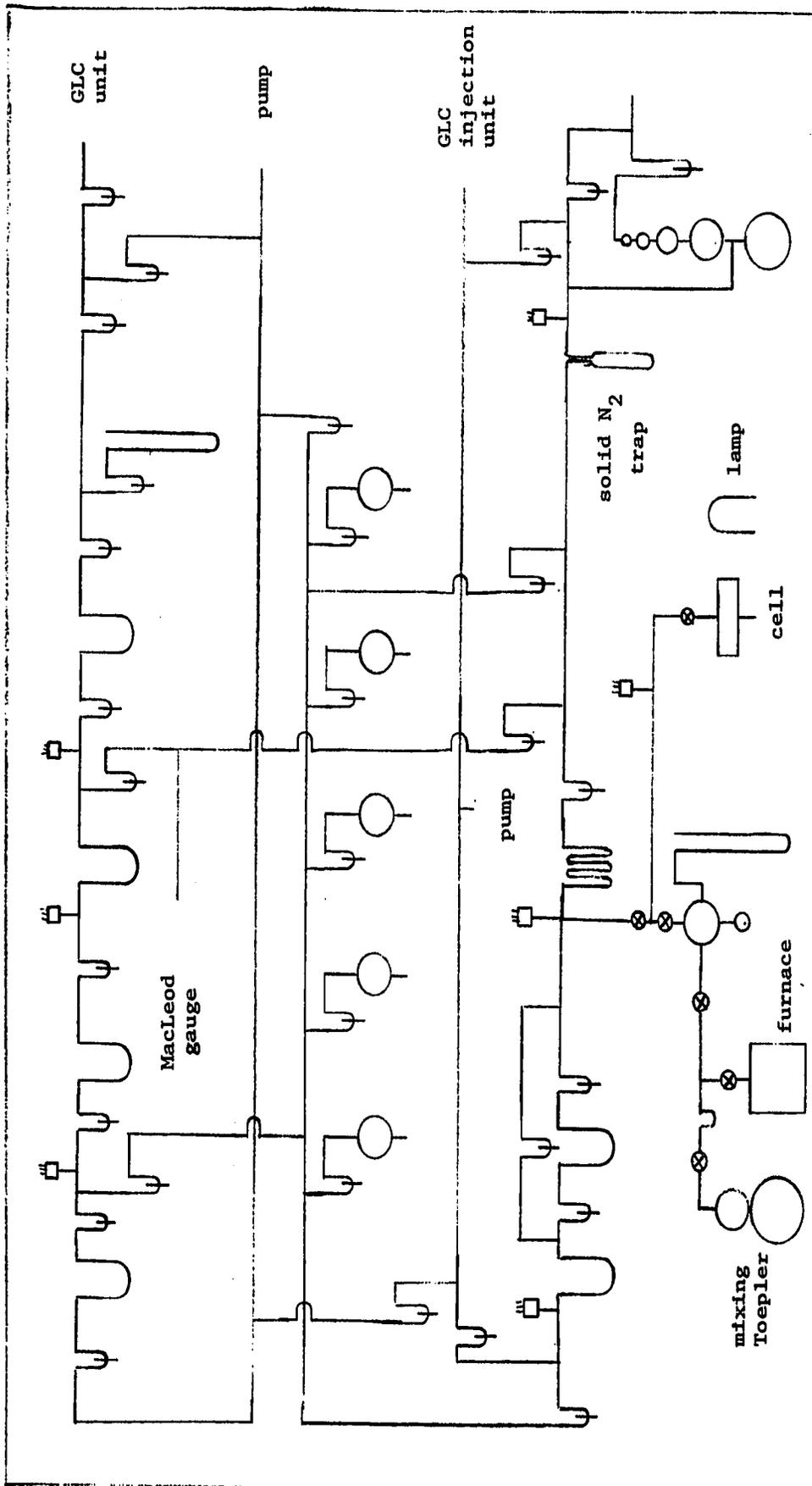
Figure II-1. Diagram of the Vacuum System
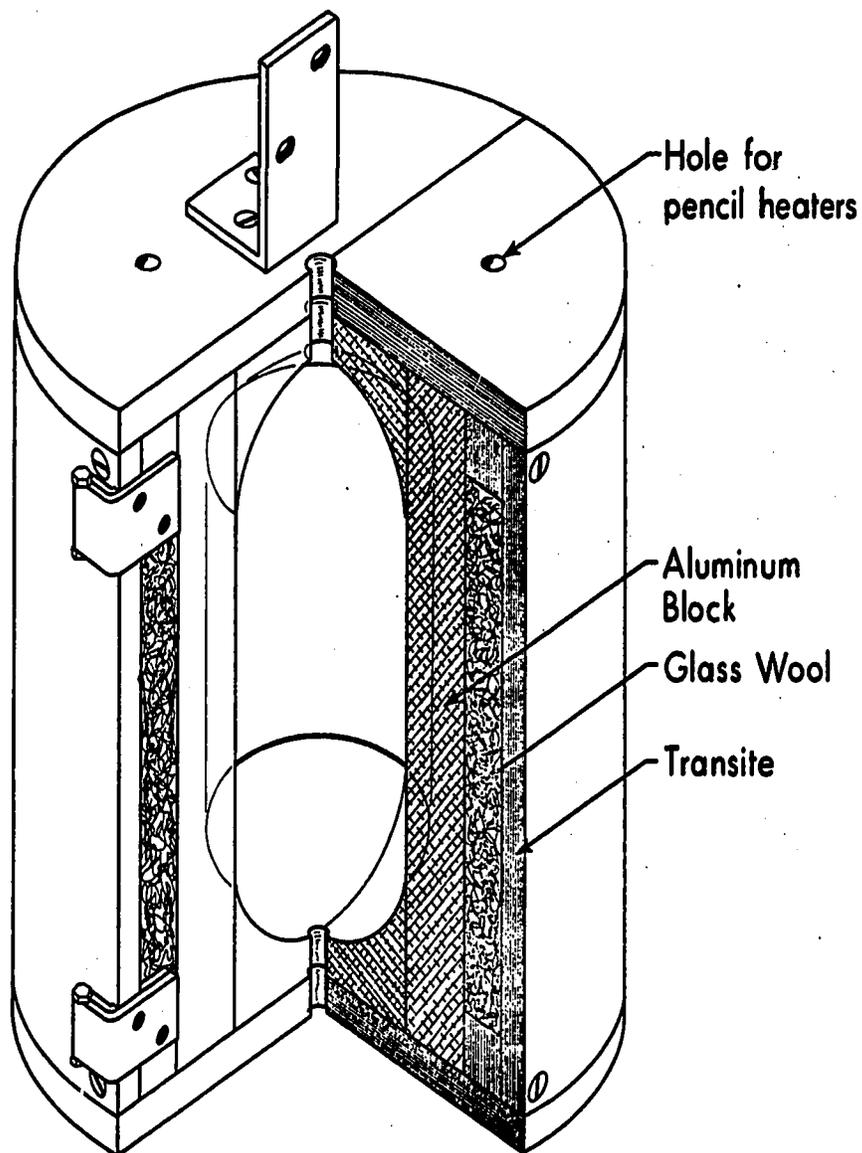
Figure II-2. Sectional view of the furnace used for pyrolysis studies

The cylindrically shaped furnace consisted of two halves connected by hinges allowing closing about the reaction vessel. The aluminium block was surrounded by a layer of glass wool and transite in order to maintain temperature uniformity. The heating of the furnace was achieved by means of eight 300 watt pencil heaters arranged in parallel to ensure uniform heating. The pencil heaters were powered and regulated by means of an API 2 mode electronic regulator. An iron-constantan thermocouple from the regulator was inserted into the block with the junction barely touching one of the pencil heaters. By keeping the regulatory thermocouple in such close proximity to the pencil heater, the time lag between power output and sensing of the resulting temperature change was kept to a minimum. Indeed, no perceptible change in temperature of the cell with time was observed. In order to eliminate the effect of any potential fluctuations due to miscellaneous voltages of metal junctions within the vacuum system, the regulatory thermocouple was surrounded by a small sleeve of glass tubing. The temperature difference across the aluminum block furnace was found to be less than $0.1^{\circ}C$.

Before use, the reaction vessel itself was treated with aqua regia and then with a hot 1:1 mixture of concentrated nitric and sulphuric acids. The cell was then rinsed with distilled water and dried in a vacuum oven at $100^{\circ}C$. Packed cells with surface volume ratios up to 16 cm^{-1} were prepared by filling Pyrex cells, of volumes of about 350 cm^3, with pieces of Pyrex tubing each 2 cm long with inner and outer diameters of 4 mm and 6 mm. The ends of the tubes were fire polished.

3) The Photolytic System

The photolytic assembly consisted of a cylindrical quartz cell 10 cm long and with a 5 cm diameter. The cell was connected to the vacuum system by means of a helium tested Hoke valve which in turn was connected to the cell by a graded seal. The cell was surrounded by a hollowed out cylindrical aluminum block furnace which was heated by four 300 watt pencil heaters. The two open ends of the furnace were covered with quartz plates to prevent heat loss due to air currents, and the aluminum block was surrounded by a thick layer of glass wool as insulating material. The temperature was controlled by adjusting the voltage to the heater through a powerstat. A small drop of mercury in the cold finger of the cell ensured ample mercury vapor for the mercury photosensitization experiments. A low pressure mercury resonance lamp was used as source of radiation with the effective radiation being the 2537 Å resonance line. The lamp was always operated one hour before irradiation was carried out.

4) The Analytical System

The principal analytical method employed was gas-liquid chromatography. The arrangement of the GLC unit is illustrated in Fig. II-3.

The gas chromatograph consisted of a component unit comprising of a Gow-Mac hot wire detector Model TR III operated at $120^\circ C$ powered by a Gow-Mac power supply Model 9999. The filament current was kept constant at 250 ma. The signals produced by the detector were fed into a Sargent Model 72180-2 recorder. The carrier gas used throughout all experiments was Helium which was dried by passage through a column of
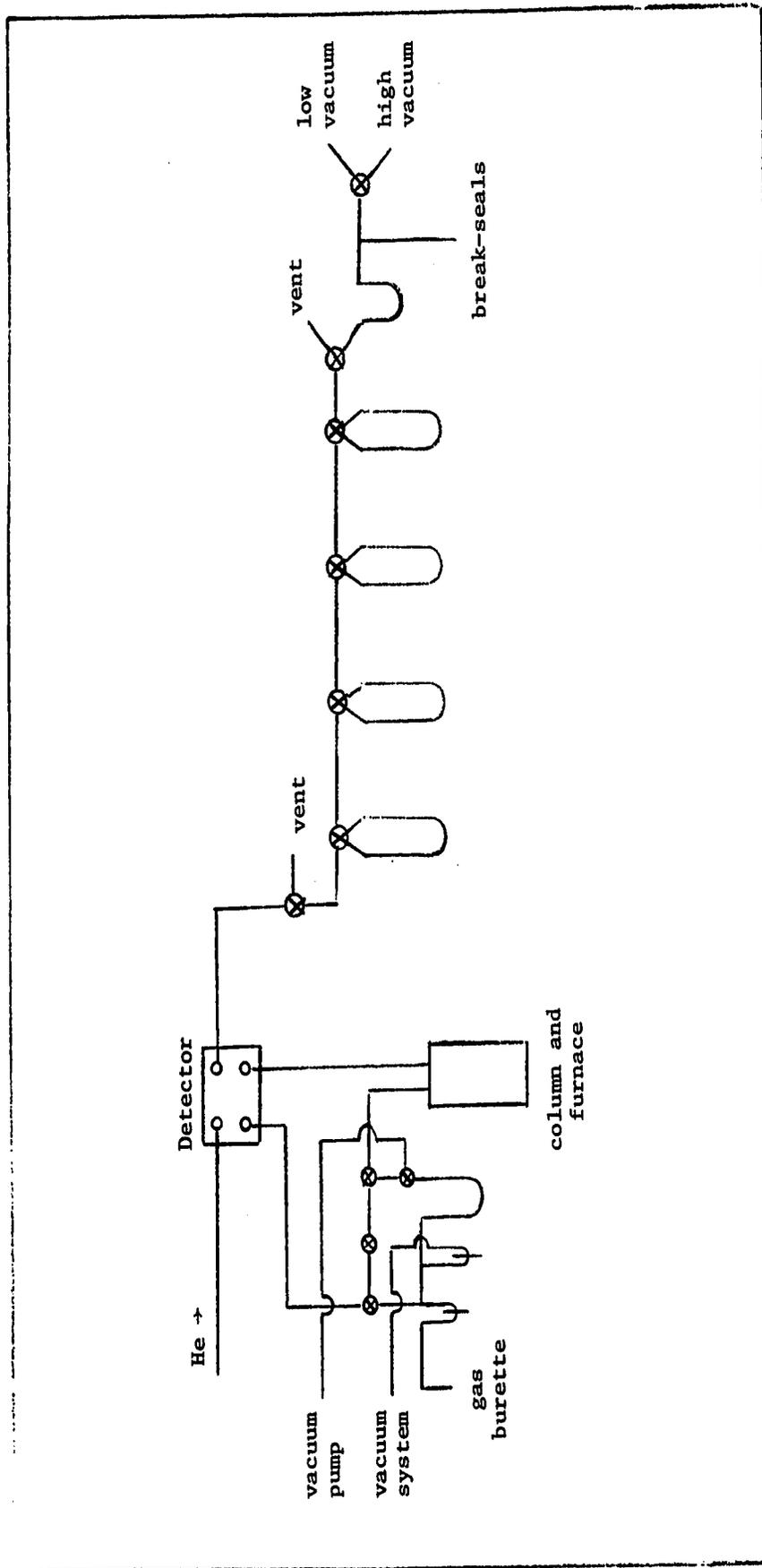
Figure II-3. The GLC unit

Molecular Sieves 13X. The flow rate of the carrier gas was determined

by means of a bubble flow meter. The response factors were calibrated

for all gases. After passage through the column and detector, individual

products could be trapped by a series of spiral traps at -196°C or vented

to a fume cupboard.

Column packings, lengths, operating conditions and retention

times are given in Table II-I.

5) Operating Procedure

All experiments were carried out in the gas phase and

reproducibility of the results was obtained after one run had been carried

out in the reaction vessel.

The reactants were measured out with a mercury manometer while

they occupied the calibrated volume A in Fig. II-1. The gas was then

transferred to the dump trap adjacent to the reaction cell. The gas was

allowed to vaporize and then expanded into the reaction vessel. When

reaction pressures higher than the vapor pressure of the episulphide

were required, the dump trap and tubing connecting the cell were heated

slightly with an air blower. The possibility of this preheating causing

some decomposition was investigated and shown to be negligible. The

remaining gas in the dump trap and tubing was then quantitatively

determined in volume A. Thus, from a knowledge of the difference of

gas pressures, the volume and temperature of the reaction vessel, it was

possible to calculate the pressures of reactants in the reaction cell.

For experiments involving mixtures of gases, the reactants were

individually measured in volume A and transferred to the dump trap.

The mixture of gases was expanded into a large adjacent Toepler of three

TABLE II-I

Materials Used

Material	Source	Purification
Ethylene	Phillips	Degassed at −196°C
Propylene	Phillips	Degassed at −196°C
Butene-1	Phillips	Degassed at −196°C
1,3-Butadiene	Phillips	Degassed at −196°C
cis-Butene	Phillips	Degassed at −196°C
trans-Butene	Phillips	Degassed at −196°C
Trimethylethylene	Matheson, Coleman and Bell	Distilled at −78°C
Pentene-1	Merck, Sharpe and Dohme	Degassed at −196°C
C_2D_4	Farchan Res. Lab.	Distilled at −78°C
Butyne-2	Matheson	Passed through a soda lime trap at −78°C and P_2O_5 column at ambient temperature, degassed at −196°C, distilled at −186°C
NO		

TABLE II-I

Materials Used (cont'd)

Material	Source	Purification
CO_2	Airco	Assayed Reagent
O_2	Airco	Assayed Reagent
Ethylene Episulphide	Prepared (72)	Degassed at $-130^\circ C$, distilled at $-78^\circ C$
	Aldrich	Degassed at $-130^\circ C$, distilled at $-78^\circ C$
Propylene Episulphide	Prepared (72)	Degassed at $-130^\circ C$, distilled at $-78^\circ C$
	Aldrich	Degassed at $-130^\circ C$, distilled at $-78^\circ C$
cis- and trans-Butene Episulphide	Prepared (72, 75, 76)	Degassed at $-107^\circ C$, distilled at $-78^\circ C$
Carbonyl Sulphide	Matheson	Bubbled through sat. solutions of NaOH and $Pb(OAc)_2$, dried, distilled at $-130^\circ C$
Propane	Phillips	Degassed at $-196^\circ C$
Neopentane	Phillips	Degassed at $-196^\circ C$
CO	Airco	Assayed Reagent

liter volume. Total mixing of the gases was ensured by successive
raising and lowering of the mercury level in the Toepler about 25 times
previous to expansion of the gases into the reaction vessel. The reaction
was stopped by freezing the reaction mixture directly into a trap at
-196°C. Distillation of the products at the appropriate temperatures
was followed by measurements in the gas burette and on the GLC.

The procedure in the mercury photosensitization experiments
was slightly different. The reactants were individually measured in the
volume A, transferred to the dump trap and moved back to the original
measuring volume where the gas was allowed to mix overnight. It was found
that the episulphide did not decompose by leaving it for this period of
time. The gas mixture was then expanded into photolytic cell.

6) Materials

The materials used, their source and method of purification
are listed in Table II-II.

7) Further Analysis

a) Samples which were separated and collected on the gas
chromatograph were analyzed mass spectrometrically on Associated
Electronics Industries Model MS2 and MS12 instruments. On both of these
instruments it was possible to carry out gas chromatographic analysis
with simultaneous mass spectrometry of each peak as it eluted.

b) In studies involving analyses of mixtures of deuterated
and non-deuterated ethylene, the measurements were done on an Associated
Electronics MS 10 mass spectrometer.

TABLE II-II

GLC Operating Conditions and Retention Times

Compound	Column	Column Temp [°C]	Retention Time [min]
Ethylene	I	25	3.2
	II	0	4.2
	II	25	2.0
Propylene	I	25	8.0
	II	0	6.2
Butene-1	II	0	10.2
trans-Butene	II	0	11.5
cis-Butene	II	0	12.7
1,3-Butadiene	II	0	15.0
Carbonyl Sulphide	I	25	5.8
Carbon Dioxide	VI	25	3.5
Trimethylethylene	III	70	3

TABLE II-II (cont'd)

GLC Operating Conditions and Retention Time

Compound	Column	Column Temp [°C]	Retention Time [min]
Ethylene Episulphide	III	70	7.1
Propylene Episulphide	III	70	12.1
trans-Butene Episulphide	III	70	17
cis-Butene Episulphide	III	70	22
Trimethylethylene Episulphide	III	70	23
Pentene-1	IV	48	4.5
NO	I	15	1.6
CO	V	25	3.2

I   9ft medium activity silicagel, 60 ml/min
II   24ft glutaronitrile/propylene carbonate 70:30 weight percent on Chromosorb WAW, 50 ml/min
III 10ft 20% TCP on Chromosorb WAW, 120 ml/min
IV   9ft 20% TCP on Chromosorb W, 60 ml/min
V   8ft 5 A Linde molecular sieve, 30 ml/min
VI   8ft Porapak Q, 50 ml/min

CHAPTER III

KINETIC FEATURES AND MECHANISM OF THE

PYROLYSIS OF EPISULPHIDES

A. Results

1) Products

The pyrolysis of episulphides was studied in the following
temperature ranges:

$$\text{ethylene episulphide} \quad 180 - 250^{\circ}\text{C}$$

$$\text{propylene episulphide} \quad 170 - 220^{\circ}\text{C}$$

$$\text{butene-2 episulphide} \quad 150 - 200^{\circ}\text{C}$$

Within these ranges the only products found were the corresponding
olefins and polymeric sulphur. In the case of ethylene episulphide
other modes of reaction occur at temperatures higher than 250°C,
resulting in isomerization to vinyl mercaptan followed by decomposition
to acetylene and hydrogen sulphide. For low conversions, which were
usually less than 5%, plots of appearance of product versus time
demonstrated a linear relationship as shown in Figs. III-1 to III-3
Curvature of the plots became apparent only when the reaction was
carried out to high conversions as illustrated in Fig. III-4. These
findings considerably simplified the determination of the initial
rates of product formation, since the rates could be measured by a
single product analysis.

TABLE III-I

Variation of the C_2H_4 Yield with Time for

Ethylene Episulphide Pyrolysis[a]

C_2H_4 [μmoles]	Time [min]
189.4°C; 160 torr	
9.62	55
7.59	45
5.16	30
11.13	65[b]
210.4°C; 167 torr	
7.48	15
10.02	20
15.31	30[c]
4.54	10

a) cell volume 238.4 cc, $S/V = 11 \text{ cm}^{-1}$

b) 0.8% conversion

c) 1.2% conversion
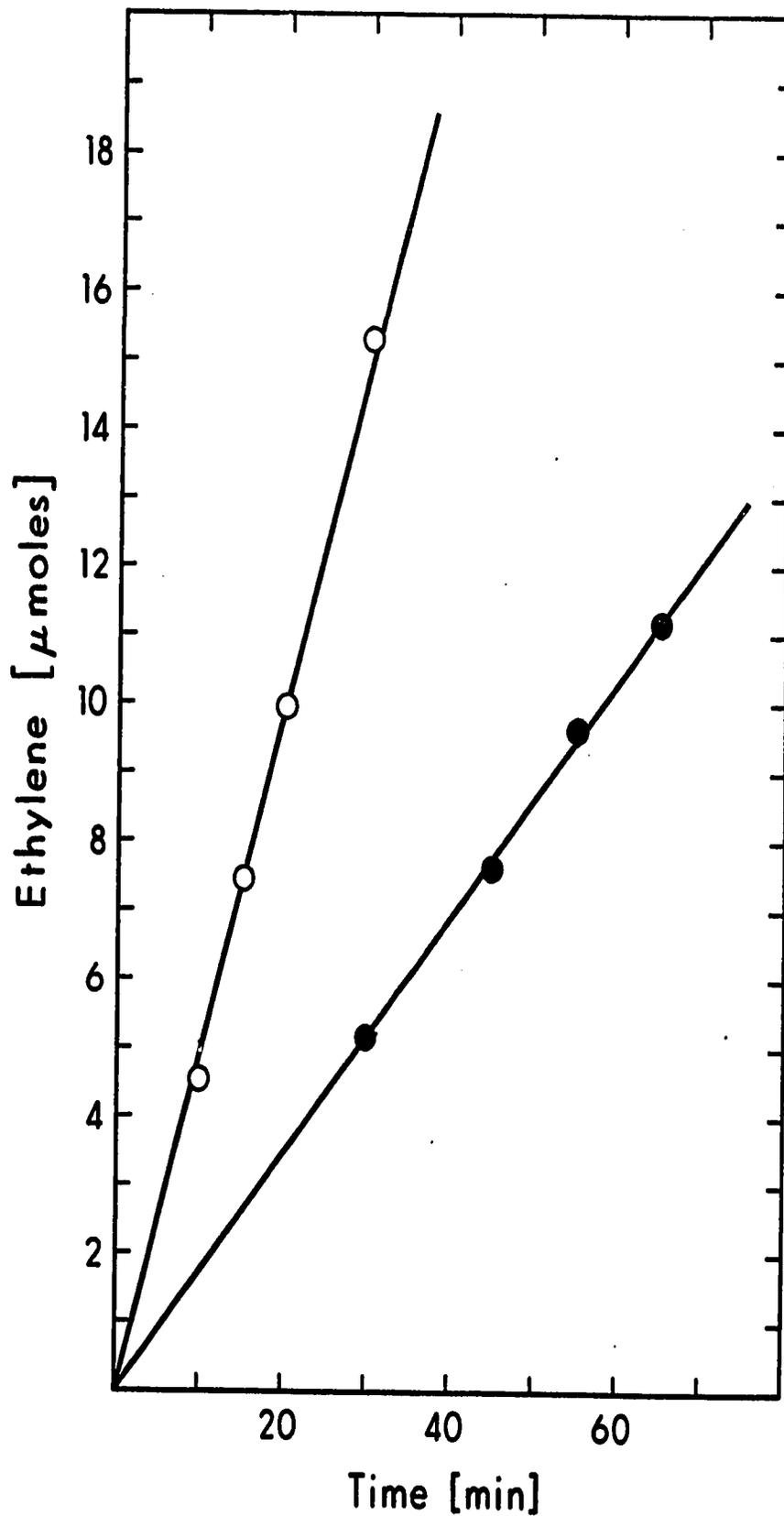
Figure III-1. Ethylene yield vs time in C_2H_4S pyrolysis;
(o) $210.4^{\circ}C$, (•) $189.4^{\circ}C$

TABLE III-II

Variation of the Propylene Yield with Time

for Propylene Episulphide Pyrolysis at $187^{\circ}C$ [a]

C_3H_6 [µmoles]	Time [min]
270 torr	
16.81	8
33.25	16
40.92	20[b]
24.47	12
178 torr	
25.84	20
18.51	15
32.13	25[c]
13.80	12

a) cell volume 406.4 cc, S/V = 0.9 cm^{-1}

b) 1.1% conversion

c) 1.3% conversion
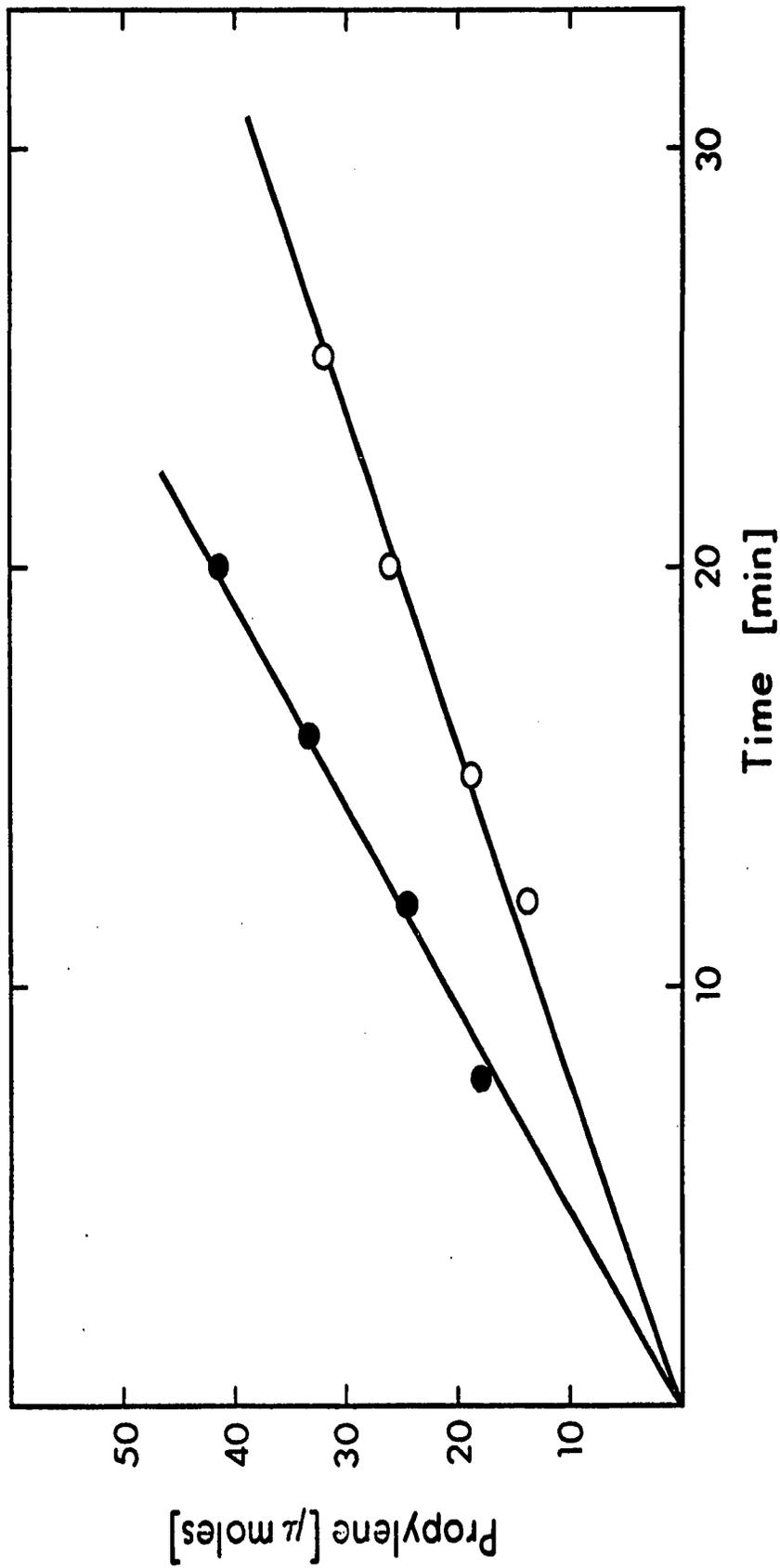
Figure III-2. Propylene yield vs time for C_3H_6S pyrolysis at 187°C; (●) 270 torr, (○) 178 torr

59

TABLE III-III

Variation of the trans-Butene Yield with Time

for Pyrolysis of trans-Butene Episulphide [a]

trans-C_4H_8 [μmoles]	Time [min]
194°C	
99.36	30
58.52	20
122.48	40[b]
31.04	10
188°C	
15.68	10
24.64	15
31.03	20
37.19	25[c]

a) at ca. 50 torr

b) 14% conversion

c) 4.8% conversion
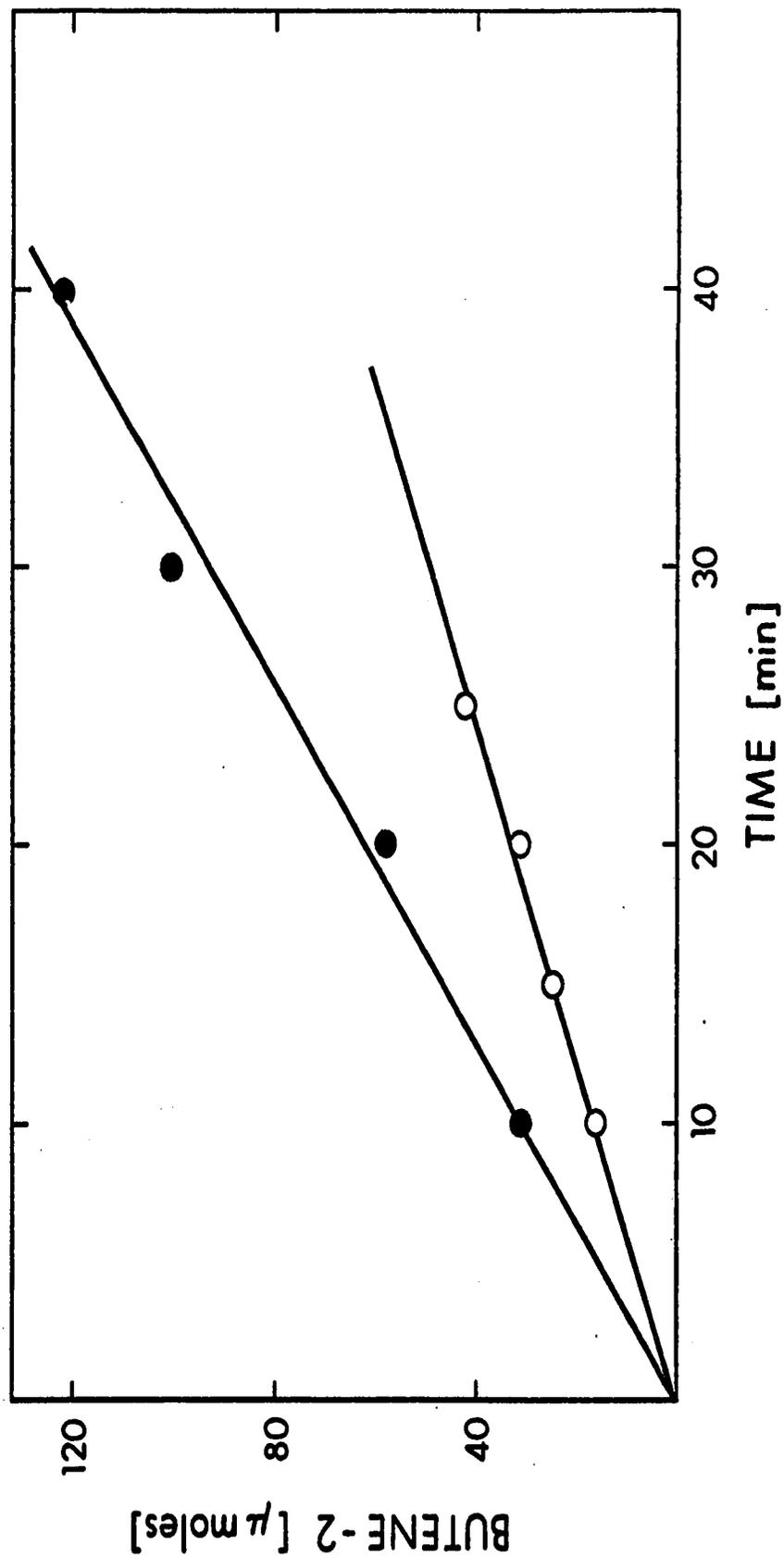
Figure III-3. Trans-butene yield vs time for trans-C_4H_8 pyrolysis at 50 torr;
($\bullet$) 194°C, (o) 188°C

TABLE III-IV

Variation of the C_2H_4 Yield with Time

at High Conversions [a]

C_2H_4 [μmoles]	Time [min]
10.0	7.5
22.6	15
58.0	35
155.3	100
201.9	180
240.1	360
296.2	564[b]

a) at 232°C and 172 torr, cell volume 101.9 cc, S/V = 9.2 cm^{-1}

b) corresponds to 53% conversion
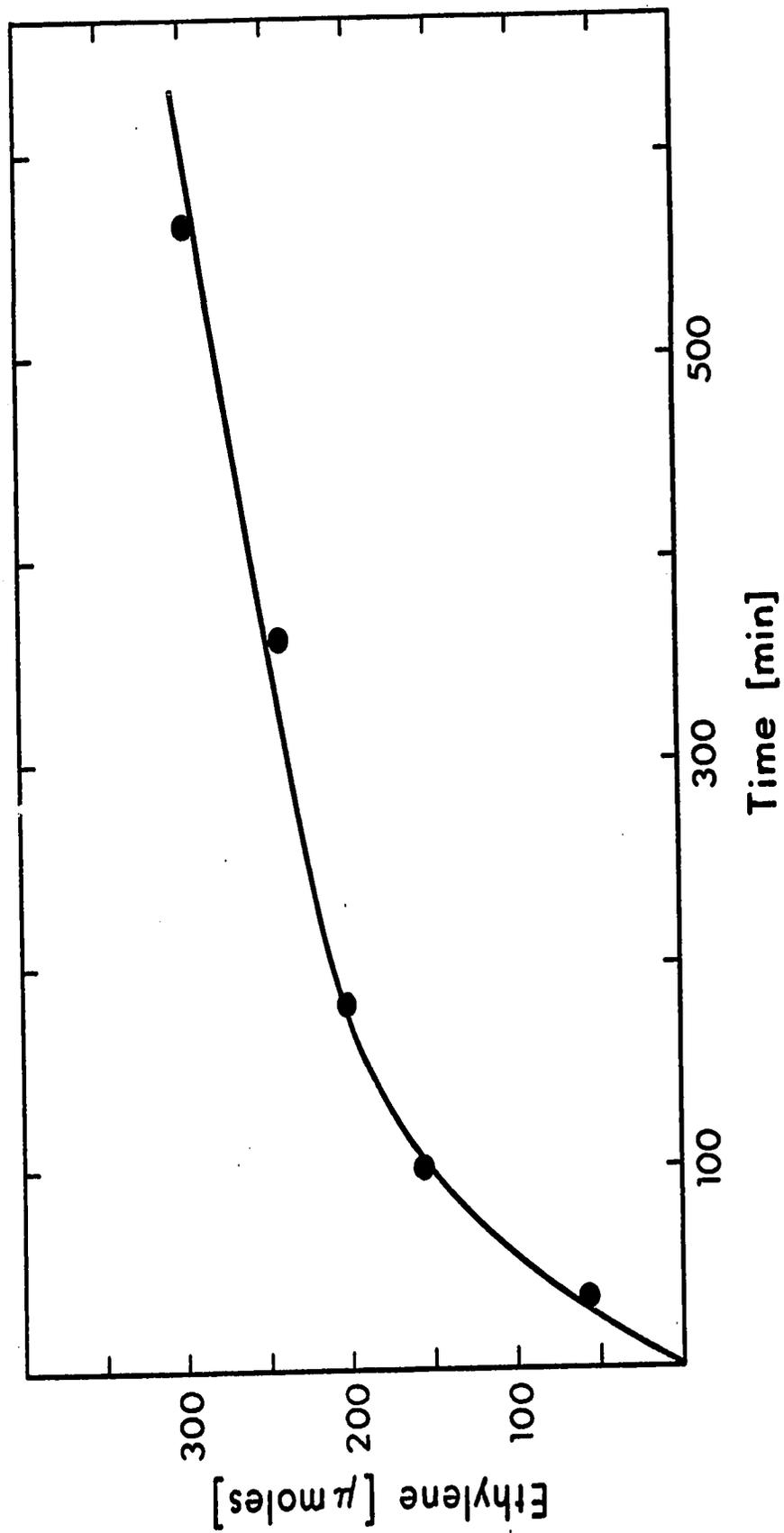
Figure III-4. Ethylene yield at high conversion for ethylene episulphide pyrolysis

2) Effect of Surface

The kinetics of gas phase thermal reactions are often complicated by the contribution of heterogeneous reactions. Since surface reactions are particularly prevalent in new, unused reaction vessels, the walls of the vessel are usually conditioned by repeatedly pyrolyzing substrate until the experimental results become reproducible. With episulphides, reproducibility was obtained after one run had been carried out in the vessel. However, even when the reaction vessel has been conditioned in this way, some of the reaction can still be occurring on the walls. A simple way to assess the magnitude of this heterogeneous component is to examine the effect of the variation in the surface to volume ratio on the rate of reaction.

We can consider the absolute rate of the reaction in a particular vessel to be the sum of the homogeneous rate, R_{hom}, and heterogeneous rate, R_{het}, $R = R_{hom} + R_{het}$. Since the two rates R_{hom} and R_{het} are each directly proportional to the volume and surface of the vessel respectively,

$$R_{hom} = c_{hom}V \quad \text{and} \quad R_{het} = c_{het}S,$$

the total rate becomes $R = c_{hom}V + c_{het}S.$

When the decomposition is carried out at the same temperature and pressure in two vessels of very different surface/volume ratios, the above equations allow one to determine the ratio c_{het}/c_{hom} and consequently the relative proportions of the homogeneous and heterogeneous processes.

The ratio of the rates in the packed and unpacked vessels is given by

$$\frac{R_p}{R_u} = \frac{c_{hom}V_p + c_{het}S_p}{c_{hom}V_u + c_{het}S_u}$$

where p and u respectively, denote the vessels of high and low surface/volume ratios. If the following substitutions are made,

$$r_p = \frac{S_p}{V_p}; \qquad r_u = \frac{S_u}{V_u}; \qquad \alpha = \frac{R_p}{R_u} \cdot \frac{V_u}{V_p}$$

suitable rearrangement yields the expression for c_{het}/c_{hom}:

$$\frac{c_{het}}{c_{hom}} = \frac{\alpha - 1}{r_p - \alpha r_u}.$$

From a knowledge of this ratio, one readily obtains the fraction of the total rate which occurs by homogeneous reaction in a given reaction vessel:

$$\frac{R_{hom}}{R} = \frac{1}{1 + \dfrac{c_{het}}{c_{hom}} \cdot \dfrac{S}{V}}.$$

The results of a series of studies of the episulphide pyrolysis under different conditions, in vessels of surface/volume ratios varying from 0.9 to 16 are presented in Tables III-V and III-VI.

Inspection of the ratios c_{het}/c_{hom} for the three episulphides investigated, reveals a decreasing trend in the relative importance of surface decomposition with increasing molecular weight. Two other notable trends also become apparent. As the temperature of the reaction vessel is increased, the extent of heterogeneous reaction diminishes, and at a fixed temperature, the same effect is observed as the

TABLE III-V

Effect of Surface Reaction in the Decomposition

of Ethylene Episulphide

Temperature [$^\circ$C]	Pressure [torr]	$\dfrac{c_{heterogeneous}}{c_{homogeneous}}$ [cm]
253	183	0.0016
232	335	0.021
232	176	0.050
232	68	0.060
232	57	0.069
210	293	0.041
210	165	0.098
210	58	0.169
189	330	0.170
189	159	0.418
189	47	1.27

TABLE III-VI

Effect of Surface Reaction in the Decomposition

of Propylene and trans-Butene Episulphide

Temperature [$^\circ$C]	Pressure [torr]	$\dfrac{c_{heterogeneous}}{c_{homogeneous}}$ [cm]
Propylene Episulphide		
202	142	0
202	58	0.028
173	170	0.011
173	137	0.015
trans-Butene Episulphide		
189	34	0

substrate pressure is increased. Thus, by choosing suitable reaction
conditions, it is possible to minimize the fraction of reaction
occurring on the surface of the vessel. As an example, taking the
case of ethylene episulphide at $210^{o}C$ and 165 torr, the contribution
of the homogeneous reaction in unpacked vessels (for which
$S/V \simeq 0.9$ cm^{-1}) is found to be at least 92%. Thus by limiting work
to suitably high pressures and temperatures the importance of the
surface reaction becomes negligible.

The data for the reactions of propylene and butene episulphide,
shown in Table III-VI, demonstrate that the heterogeneous decomposition
mode is sufficiently small to be neglected.

Although the possibility of a surface component in
decomposition reactions is usually revealed by the method of varying
surface/volume ratios, a heterogeneous reaction could escape detection
if a radical-chain mechanism were involved, which is both surface-
initiated and surface-terminated (102). Consequently, studies were
also undertaken in reaction vessels having surfaces of different
nature. Pyrex and quartz vessels are suitable for studies of this
kind since Pyrex has a much more basic surface than quartz does. The
cells used in this experiment were both unpacked and had surface/volume
ratios of 0.9 cm^{-1}. Ethylene episulphide was used as the substrate
molecule in these experiments the results of which are presented in
Table III-VII. The conditions were chosen such that the c_{het}/c_{hom} ratios
described above, were very small. The absolute rates of the reactions
in the two reaction vessels agree within experimental accuracy,
from which it is concluded that the reaction is entirely homogeneous

TABLE III-VII

A Comparison of Rates of Decomposition in

Pyrex and Quartz Reaction Vessels

Temp [$^\circ$C]	$P(C_2H_4S)$ [torr]	Rate[a] (Pyrex) $\times 10^2$ [μm/cc min]	Rate[b] (Quartz) $\times 10^2$ [μm/cc min]
210.4	206.5	1.502	1.599
210.4	275.8	2.221	2.412
252.0	157.5	2.553	2.716

a) cell volume 354.5cc, S/V = 0.9 cm^{-1}

b) cell volume 246.1cc, S/V = 0.9 cm^{-1}

under the conditions of suitably high temperatures and pressures.

3) <u>Determination of Order of Product Formation</u>

In order to obtain some insight into the kinetic features of the episulphide decomposition, experiments were carried out to determine the order of formation of the olefinic product.

The order of product formation can be calculated using the relationship

$$R = k[S]^n$$

where R, k, S, and n are the initial rate of product formation, specific rate constant, substrate concentration and order, respectively. The slope of logarithmic plots of rate and substrate pressure yield the order of reaction. The results of the rate data given in Tables III-VIII to III-XIII are presented in the form of log-log plots in Figs. III-5 to III-12, and the orders as determined by least means square analysis are given in Table III-XIV. Except for the case of propylene episulphide decomposition at 187°C, which shows slight curvature, all the plots were found to be linear. Since there is a considerable heterogeneous component at 190°C for ethylene episulphide pyrolysis, an appropriate correction can be made. A corrected plot is shown in Fig. III-13, from which the order is determined as 1.90.

In the case of the ethylene episulphide, the order decreases from 2.0 to 1.0 with increasing temperature. The results of the studies in the case of propylene and <u>trans</u>-butene episulphide yield an order of unity.

TABLE III-VIII

Variation of the C_2H_4 Yield with Ethylene Episulphide

Pressure at 189°C and 232°C

$P(C_2H_4S)$ [torr]	C_2H_4 [μmoles]	Time [min]	% Conversion
189°C [a]			
178.9	2.81	40	.14
396.3	11.39	40	.25
277.3	9.45	60	.30
465.7	13.20	35	.25
165.2	4.96	70	.26
162.4	3.22	70	0.23
232°C [a]			
166.3	44.95	20	2.39
202.8	61.57	20	2.69
269.6	40.60	10	1.34
428.3	81.99	10	1.70
80.1	17.45	20	1.95
203.7	28.17	10	1.23
58.5	14.24	25	2.16
437.2	76.70	10	1.55

a) cell volume 354.5 cc, S/V = 0.9 cm^{-1}
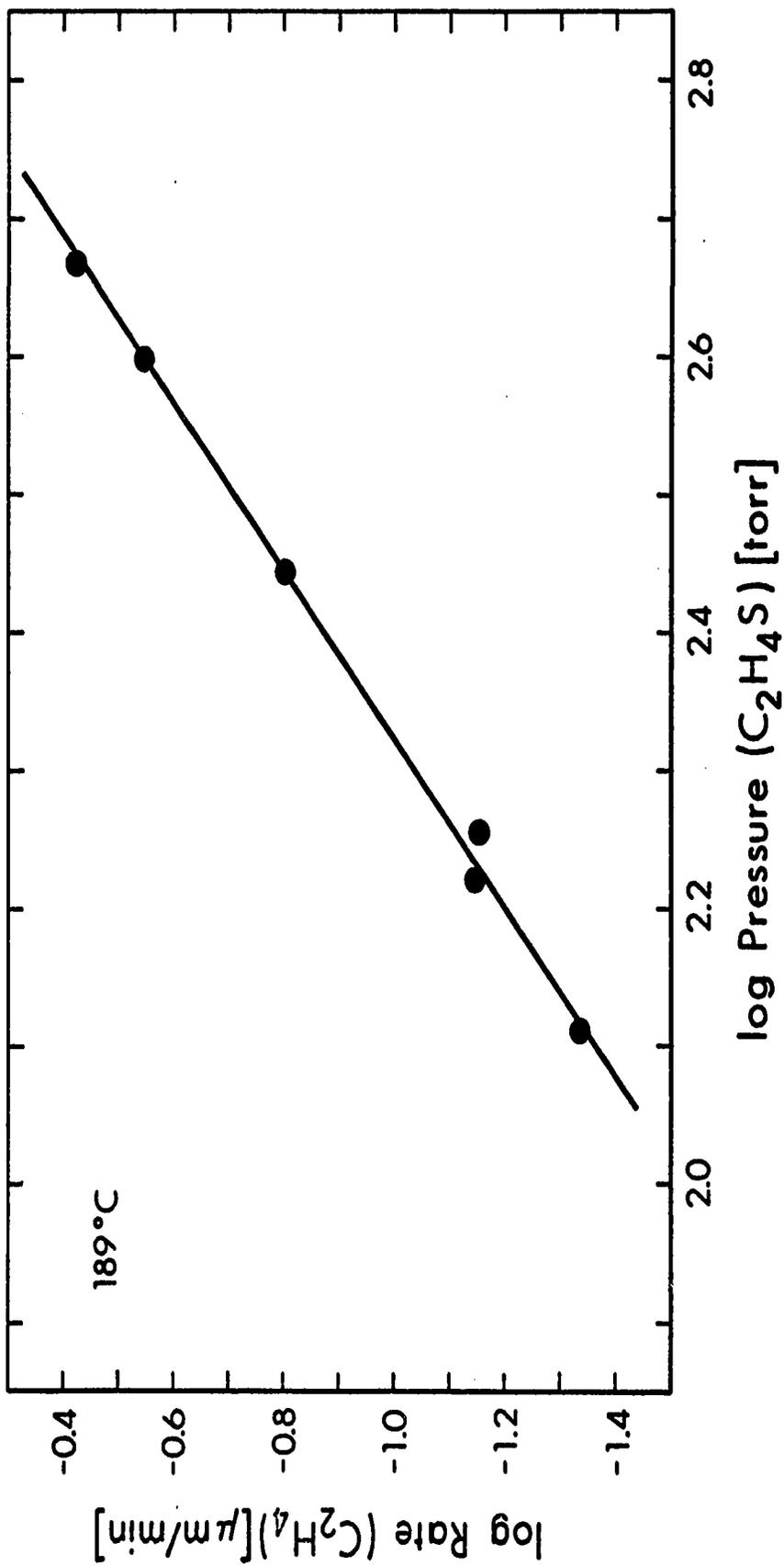
Figure III-5.   Order plot for ethylene episulphide pyrolysis

TABLE III-IX

Variation of the C_2H_4 Yield with Ethylene

Episulphide Pressure at $210^{\circ}C$ [a]

$P(C_2H_4S)$ [torr]	C_2H_4 [μmoles]	% Conversion
177.5	17.74	0.85
172.9	16.95	0.84
288.3	37.83	1.10
207.5	22.67	0.80
249.8	30.95	1.05
345.3	50.05	1.80
388.3	59.34	1.30
481.2	80.62	1.50
164.7	14.80	0.82
121.5	10.00	0.70
502.6	87.32	1.49
101.6	7.09	0.66
85.7	6.21	0.62
98.9	7.71	0.70
78.3	5.41	0.58
60.7	3.69	0.40
46.2	2.62	0.49

a) all runs 40 min, cell volume 354.5 cc, $S/V = 0.9$ cm^{-1}
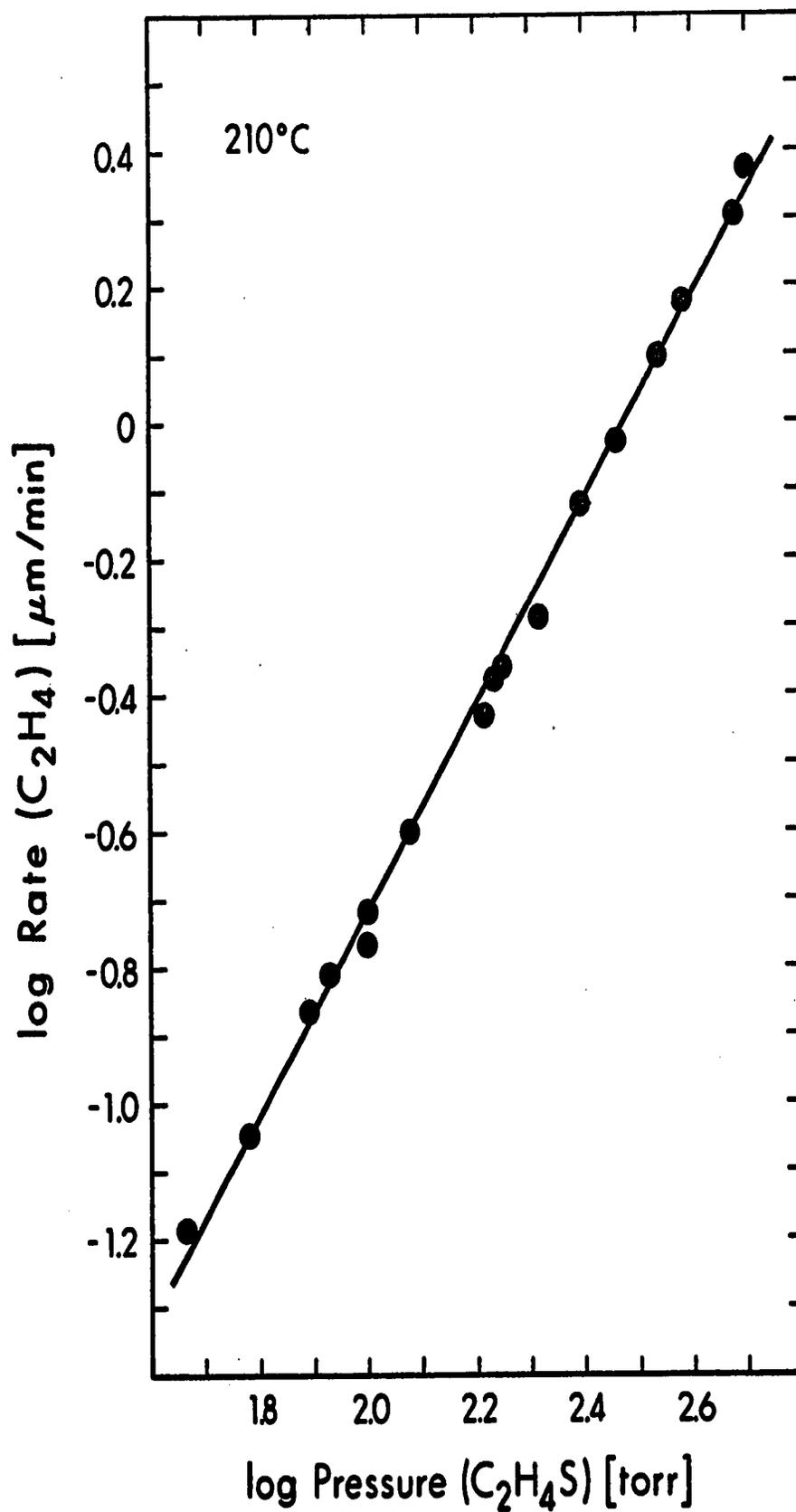
Figure III-6.   Order plot for ethylene episulphide pyrolysis
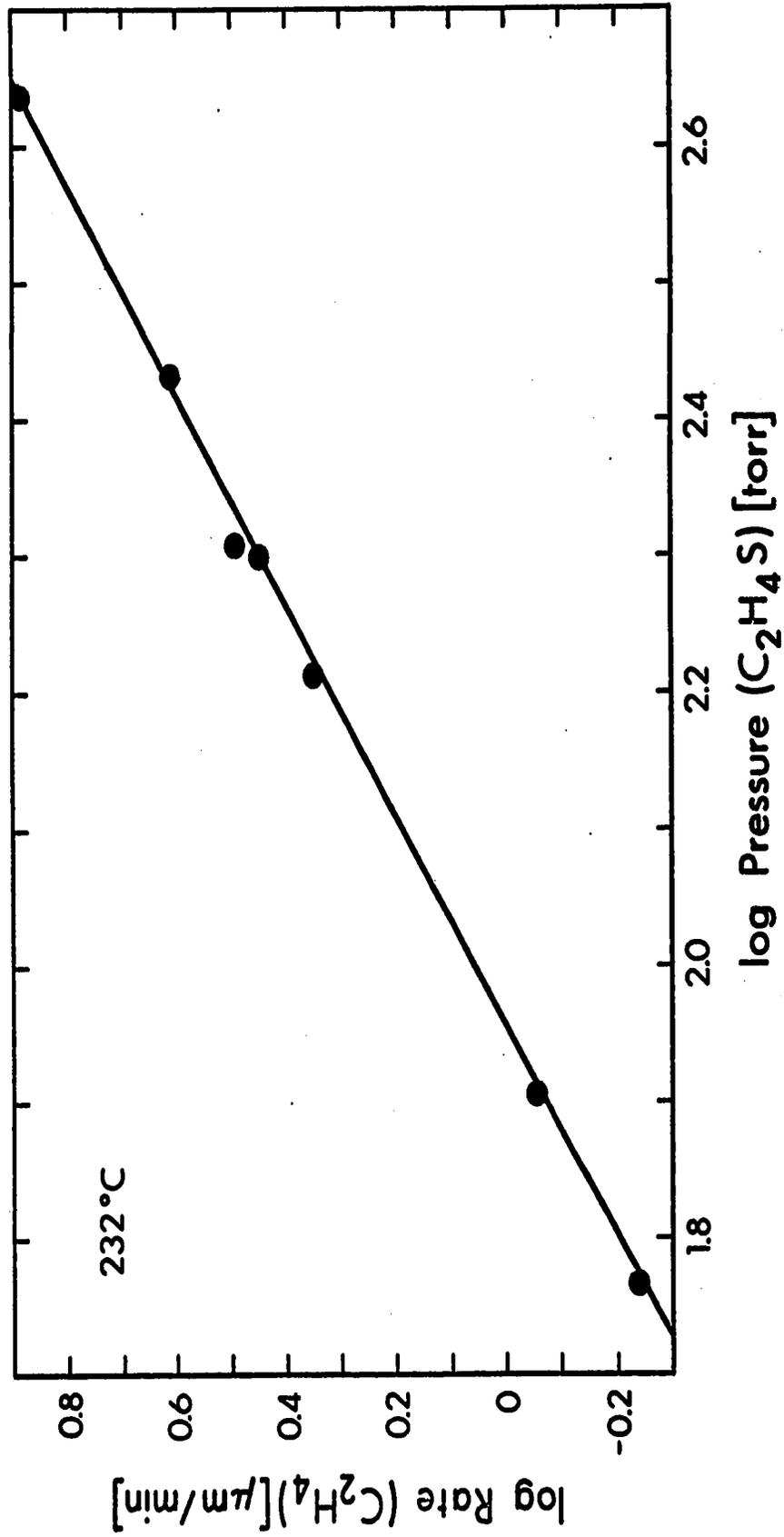
Figure III-7. Order plot for ethylene episulphide pyrolysis

TABLE III-X

Variation of the C_2H_4 Yield with Ethylene

Episulphide Pressure at $253^\circ C$ [a]

$P(C_2H_4S)$ [torr]	C_2H_4 [μmoles]	Time [min]	% Conversion
56.9	31.57	12	5.1
162.7	46.60	5	2.7
258.4	91.60	5	3.3
434.2	147.33	4	3.1
471.4	233.33	6	4.6

a) cell volume 354.5 cc, S/V = 0.9 cm^{-1}
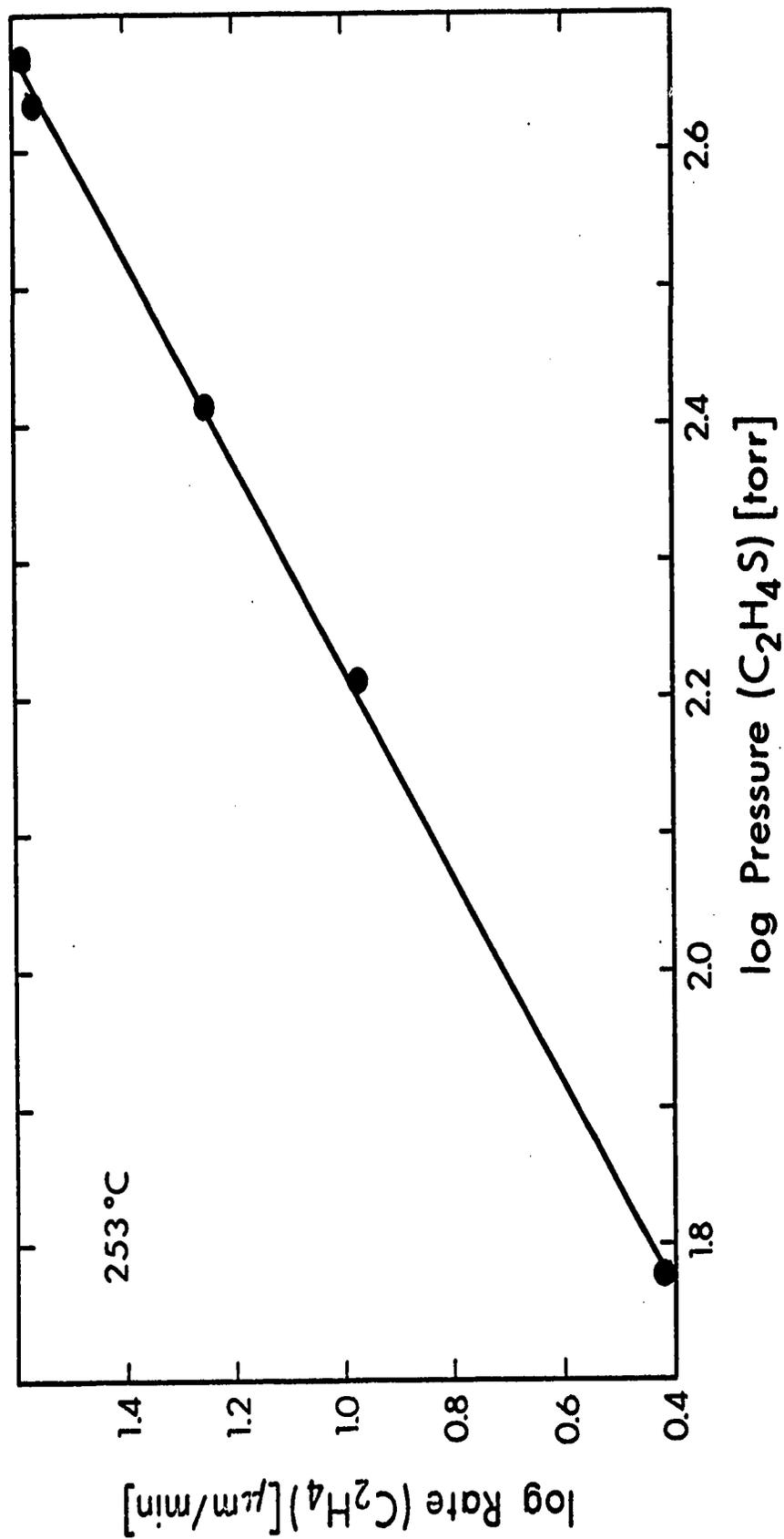
Figure III-8. Order plot for ethylene episulphide pyrolysis

TABLE III-XI

Variation of the C_3H_6 Yield with Propylene

Episulphide Pressure at $202^{\circ}C$ [a]

$P(C_3H_6S)$ [torr]	C_3H_6 [µmoles]	Time [min]	% Conversion
55.7	41.45	30	5.5
66.3	27.92	17	3.1
73.0	59.27	30	5.0
122.3	49.48	15	2.9
202.6	92.85	15	3.2
306.7	153.3	15	3.6

a) cell volume 406.4 cc, $S/V = 0.9$ cm^{-1}
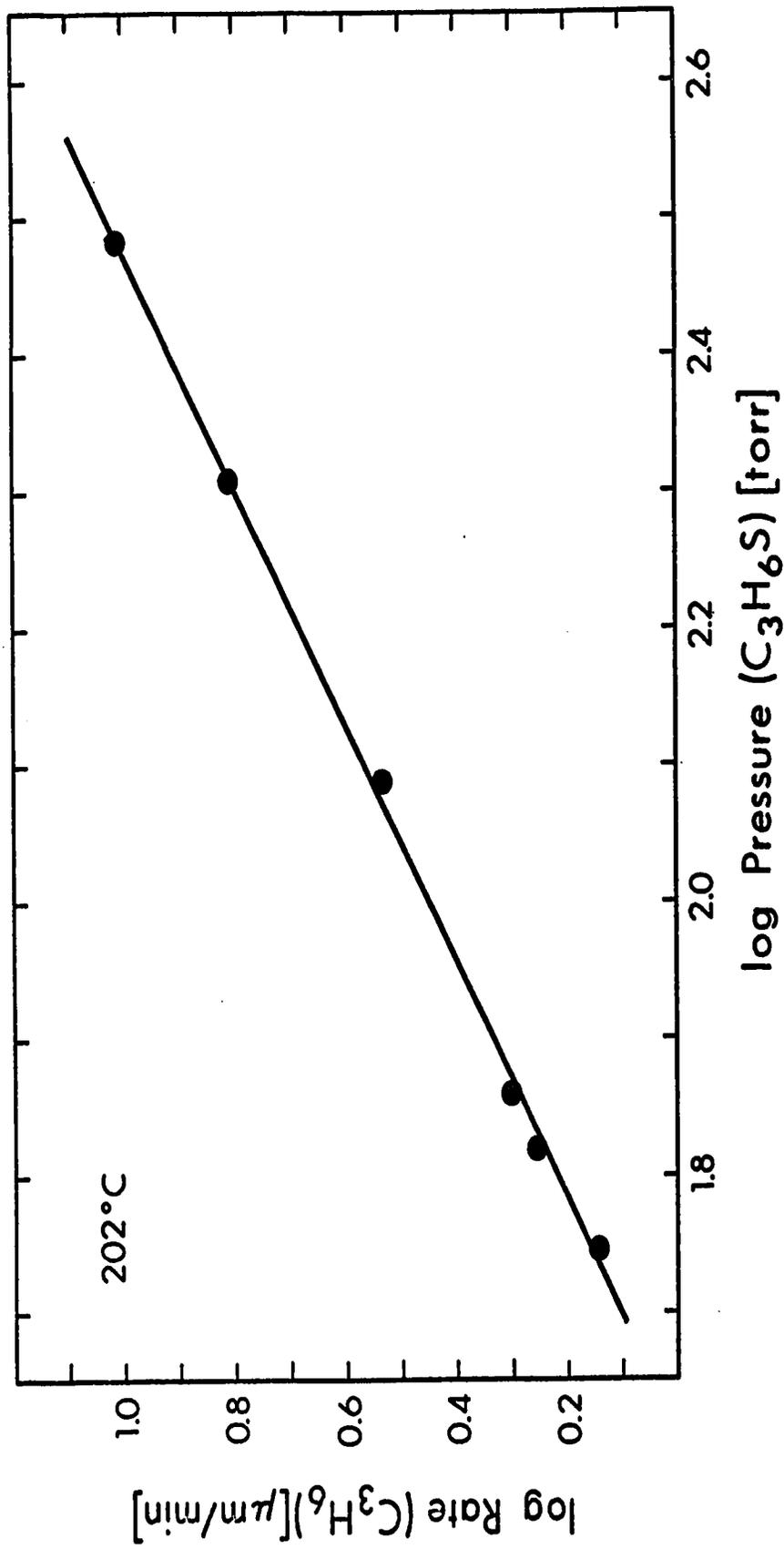
Figure III-9. Order plot for propylene episulphide pyrolysis

TABLE III-XII

Variation of the C_3H_6 Yield with

Propylene Episulphide Pressure at $187^\circ C$ [a]

C_3H_6 [μmoles]	Time [min]	C_3H_6 [μmoles]	Time [min]
52.9 torr		178.4 torr	
5.72	20	13.80	12
8.33	30	18.51	15
12.61	40	25.84	20
16.12	50[b]	32.13	25
		42.83	30[e]
64.4 torr		270.7 torr	
11.25	30	16.81	8
16.48	40	24.47	12
21.67	50	33.32	16
25.58	60[c]	40.95	20[f]
100.0 torr			
13.20	20		
21.22	30		
28.17	40		
39.81	50[d]		

a) cell volume 412.2 cc, $S/V = 0.9 \ cm^{-1}$ d) 2.5% conversion

b) 2.1% conversion   e) 1.6% conversion

c) 2.8% conversion   f) 1.0% conversion
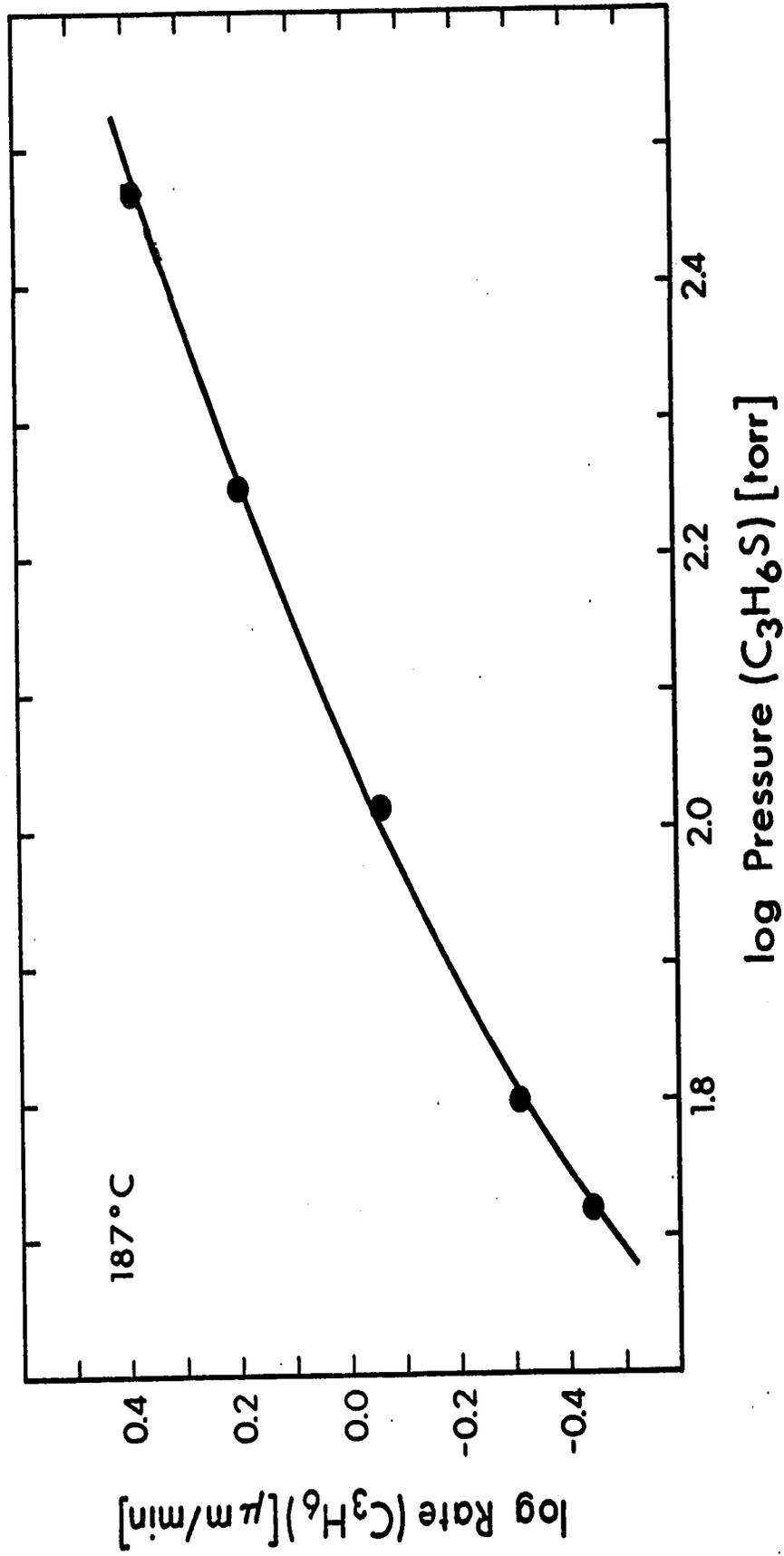
Figure III-10. Order plot for propylene episulphide pyrolysis

TABLE III-XIII

Variation of the trans-Butene Yield with

trans-Butene Episulphide Pressure [a]

P(trans-C_4H_8S) [torr]	trans-C_4H_8 [μmoles]	Time [min]
188°C [a]		
43.6	31.35	30
58.9	28.50	20
91.9	21.91	10
251.9	59.70	10
148.8	38.07	10
172°C [a]		
56.8	12.30	40
112.6	25.78	40
79.7	18.07	40
221.4	54.5	40
164.0	40.29	40

a) all runs 40 min, cell volume 364.7 cc, S/V = 0.9 cm^{-1}
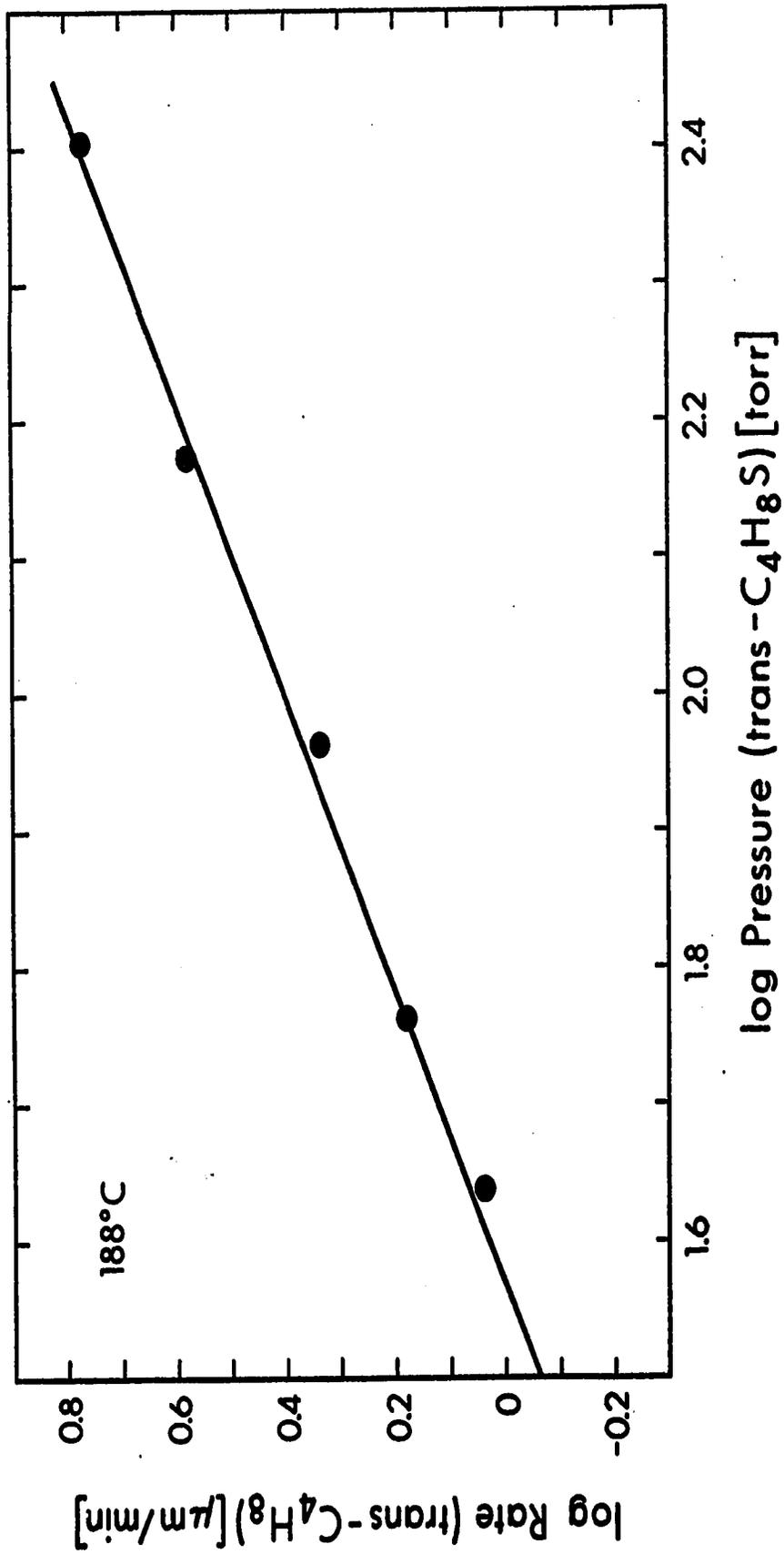
Figure III-11. Order plot for <u>trans</u>-butene episulphide pyrolysis
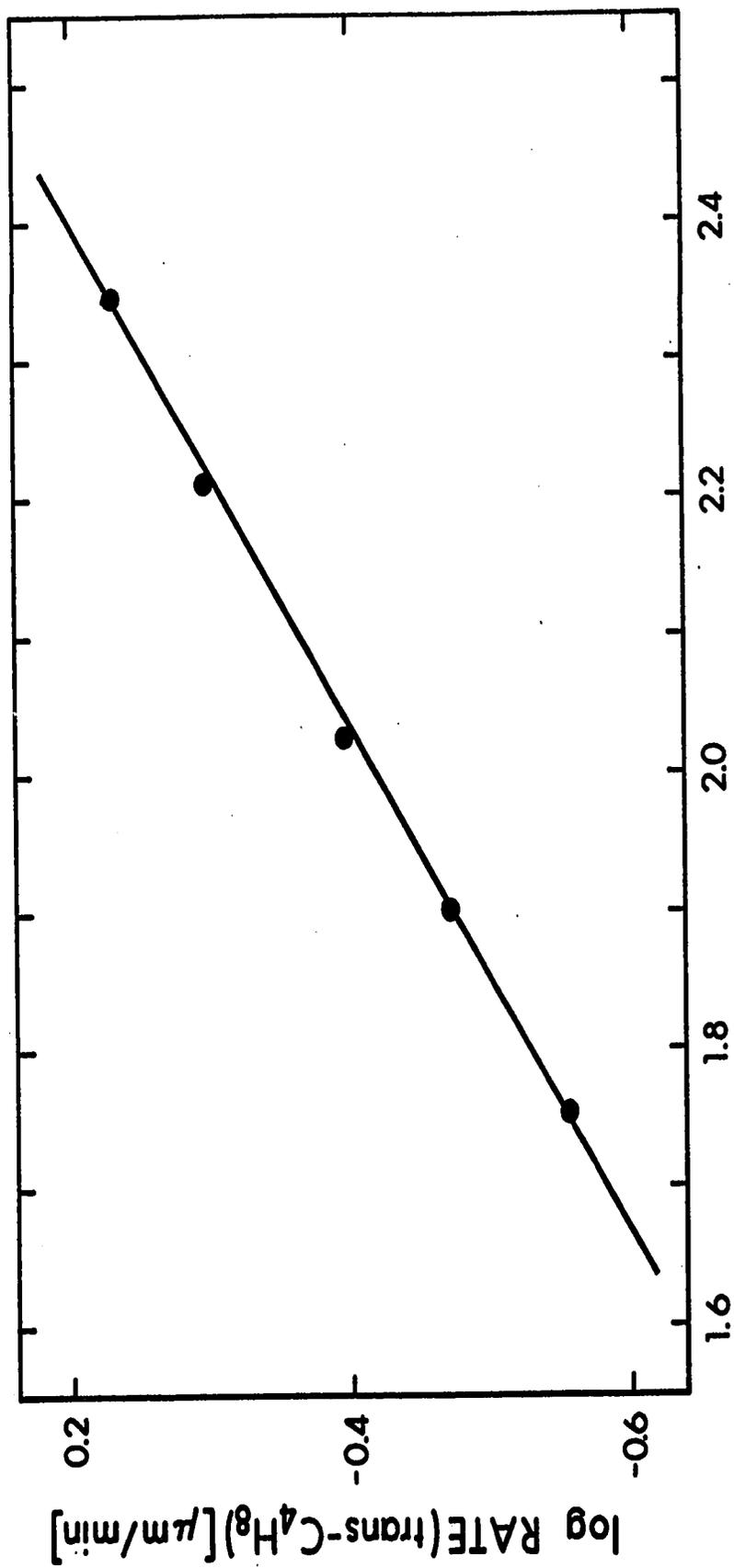
Figure III-12. Order plot for _trans_-butene episulphide pyrolysis at 172°C
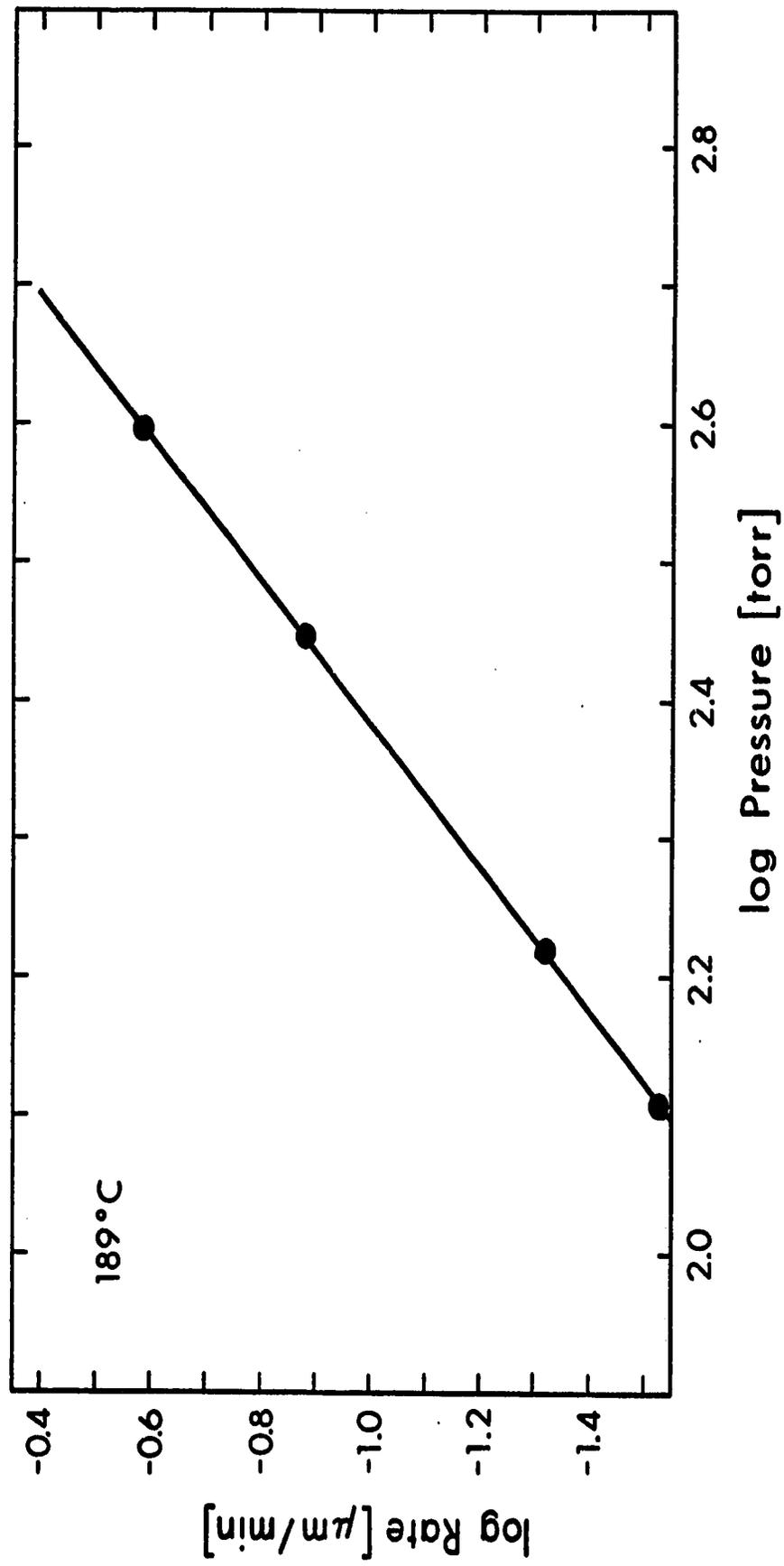
Figure III-13. Order plot for ethylene episulphide at 189°C corrected for surface reaction

TABLE III-XIV

Orders of Reaction

Temperature [$^\circ$C]	Order
Ethylene Episulphide	
189	1.63[a]
210	1.49
232	1.31
252	1.29
Propylene Episulphide	
202	1.14
187	0.90
trans-Butene Episulphide	
188	0.96
172	1.10

a) not corrected for surface effect

4) Effect of Inert Gases

The results of the order studies indicate the possibility that the decomposition occurs via a unimolecular mechanism. For unimolecular kinetics, the order of reaction increases from unity at high pressures to two at very low pressures, becoming non-integral at intermediate pressures. In this low pressure region, inert gases can exert an accelerating effect on the rate of reaction.

The effect of inert gases on the rate of episulphide decomposition was investigated with ethylene episulphide in the fall-off region and propylene episulphide in the high pressure region. Ethylene episulphide decomposition was carried out using CO_2, neopentane and propane as inert gases. The results of the ethylene episulphide/CO_2 system at various substrate pressures are presented in Table III-XVI and the data of the pyrolysis of ethylene episulphide in the presence of neopentane and propane, tabulated in Table III-XV, are illustrated in Fig. III-14. The results show a definite increase in the rate of decomposition upon the addition of inert gas. In the case of the addition of propane, an increase in the rate of 23% is found at an episulphide pressure of 57 torr and propane pressure of 305 torr. The results presented in Table III-XVI show that the percentage increase in the rate at low C_2H_4S pressures is greater than that observed at high substrate pressures.

For the case of propylene episulphide pyrolysis, low pressures of substrate were used with neopentane as the inert gas. From the results of these experiments, shown in Table III-VII, it

TABLE III-XV

Pyrolysis of Ethylene Episulphide in the Presence

of Neopentane and Propane at $231^{\circ}C$ [a]

P(EES) [torr]	P(C_5H_2) [torr]	P(C_3H_8) [torr]	C_2H_4 [μm]	Time [min]
59.3	-	-	4.58	10
58.1	-	-	10.25	20
56.3	-	-	10.92	21.5
57.3	77.5	-	5.75	10
57.7	79.6	-	10.98	20 [b]
59.2	-	309.9	6.04	10
57.9	-	301.3	12.45	20 [c]

a) cell volume 238.7 cc, S/V = 16 cm^{-1}

b) corresponds to a 8.1% rate increase

c) corresponds to a 22.8% rate increase
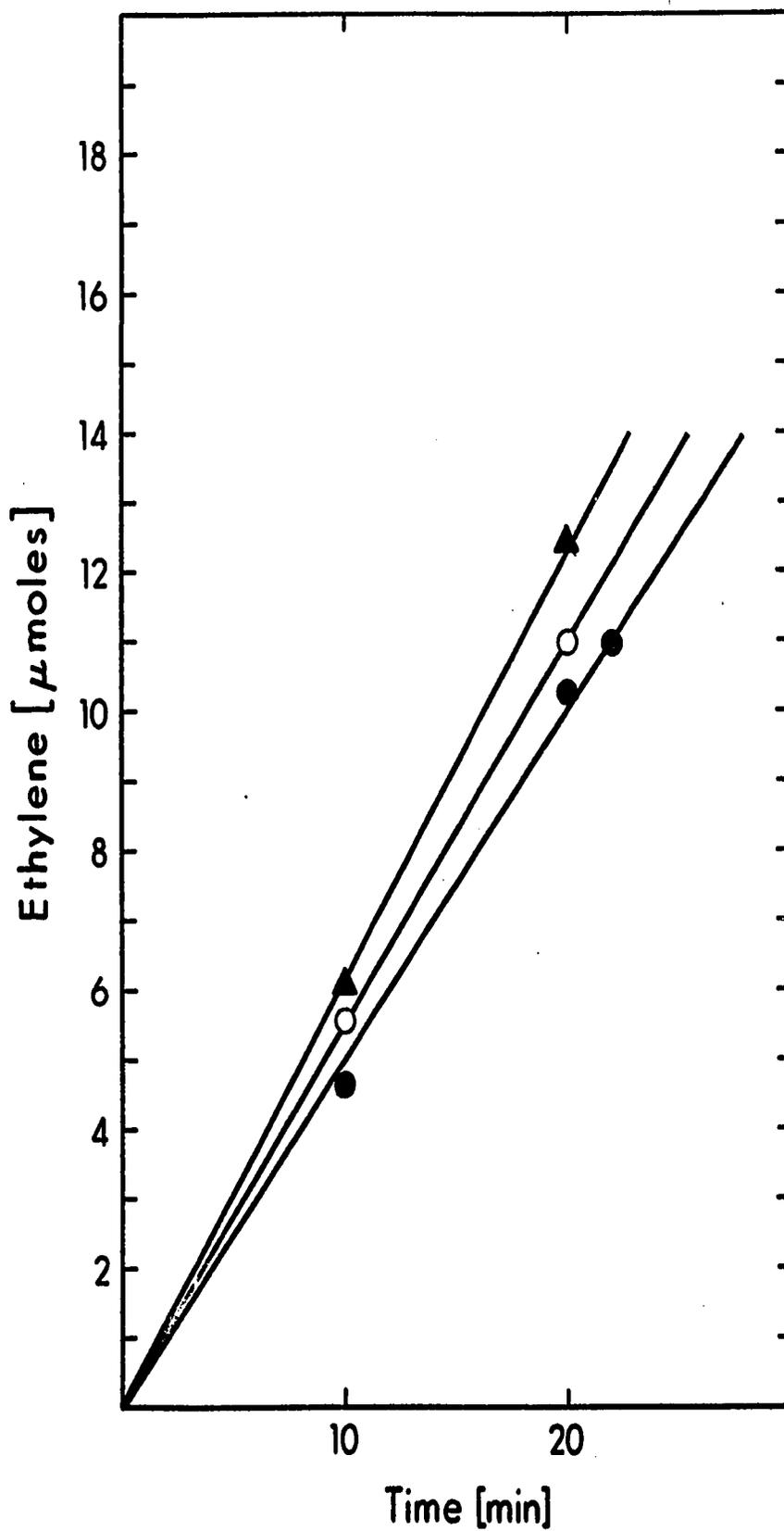
Figure III-14 Pyrolysis of C_2H_4S (●); with added neopentane (o)
and propane (▲)

TABLE III-XVI

Pyrolysis of Ethylene Episulphide

in the Presence of CO_2[a]

$P(C_2H_4S)$ [torr]	$P(CO_2)$ [torr]	Rate [μmoles/min]
192.7	-	0.507
192.7	265.7	0.542[b]
33.8	-	0.050
39.7	392.8	0.070[c]

a) temperature 207.6°C, cell volume 359.5 cc, S/V = 0.9 cm^{-1}
b) 7% rate increase   c) 40% rate increase.

TABLE III-XVII

Pyrolysis of Propylene Episulphide in the

Presence of Neopentane at 204.3°C [a]

$P(C_3H_6S)$ [torr]	$P(C_5H_{12})$ [torr]	Rate [μmole/min]
58	-	0.96
57	173	0.98[b]
49	-	0.79
49	147	0.84[c]

a) cell volume 238.7 cc, S/V = 16 cm^{-1} b) 2% rate increase
c) 6% rate increase

appears that inert gas has essentially no effect on the rate of decomposition.

5) The Effect of Nitric Oxide

Nitric oxide is a molecule well known for its behavior as a radical scavenger. In order to investigate the possibility of the intervention of free radicals in the reaction, the pyrolysis of trans-butene-2 episulphide was carried out in the presence of NO. The results shown in Table III-XIX and Fig. III-15 demonstrate that there is no effect even at an 8-fold excess of NO.

6) The Effect of Oxygen

The effect of oxygen on the pyrolysis of episulphides was also investigated. The results presented in Table III-XVIII indicate that as the O_2/episulphide ratio is increased, the trans-butene yield increases. Analysis of the reaction mixture showed that SO_2 is a product of the reaction, suggesting the occurrence of extensive oxidation reactions.

7) Arrhenius Parameters

The activation energies and pre-exponential factors associated with the olefin forming reaction were determined at constant substrate concentrations using the logarithmic form of the Arrhenius equation,

$$\log k = \log A - \frac{E_a}{2.3RT}$$

where k is the first order rate constant and the other terms have the usual significance.

TABLE III-XVIII

Pyrolysis of trans-Butene Episulphide in

the Presence of Oxygen at 191.3°C

P(trans-C$_4$H$_8$S) [torr]	P(O$_2$) [torr]	trans-Butene [a] [μmoles]
39.8	-	22.9
38.8	5.88	33.1
39.7	26.0	32.5
39.3	73.8	33.4
39.1	338.1	54.3

a) all runs 20 min, cell volume 325.2 cc, S/V = 11 cm^{-1}

TABLE III-XIX

Pyrolysis of trans-Butene Episulphide in

the Presence of Nitric Oxide at 191.3°C

P(trans-C$_4$H$_8$S) [torr]	P(NO) [torr]	trans-Butene [a] [μmoles]
38.5	-	23.7
37.7	39.0	22.9
37.6	67.7	23.0
39.7	323.0	25.1

a) all runs 20 min, cell volume 325.2 cc, S/V = 11 cm^{-1}
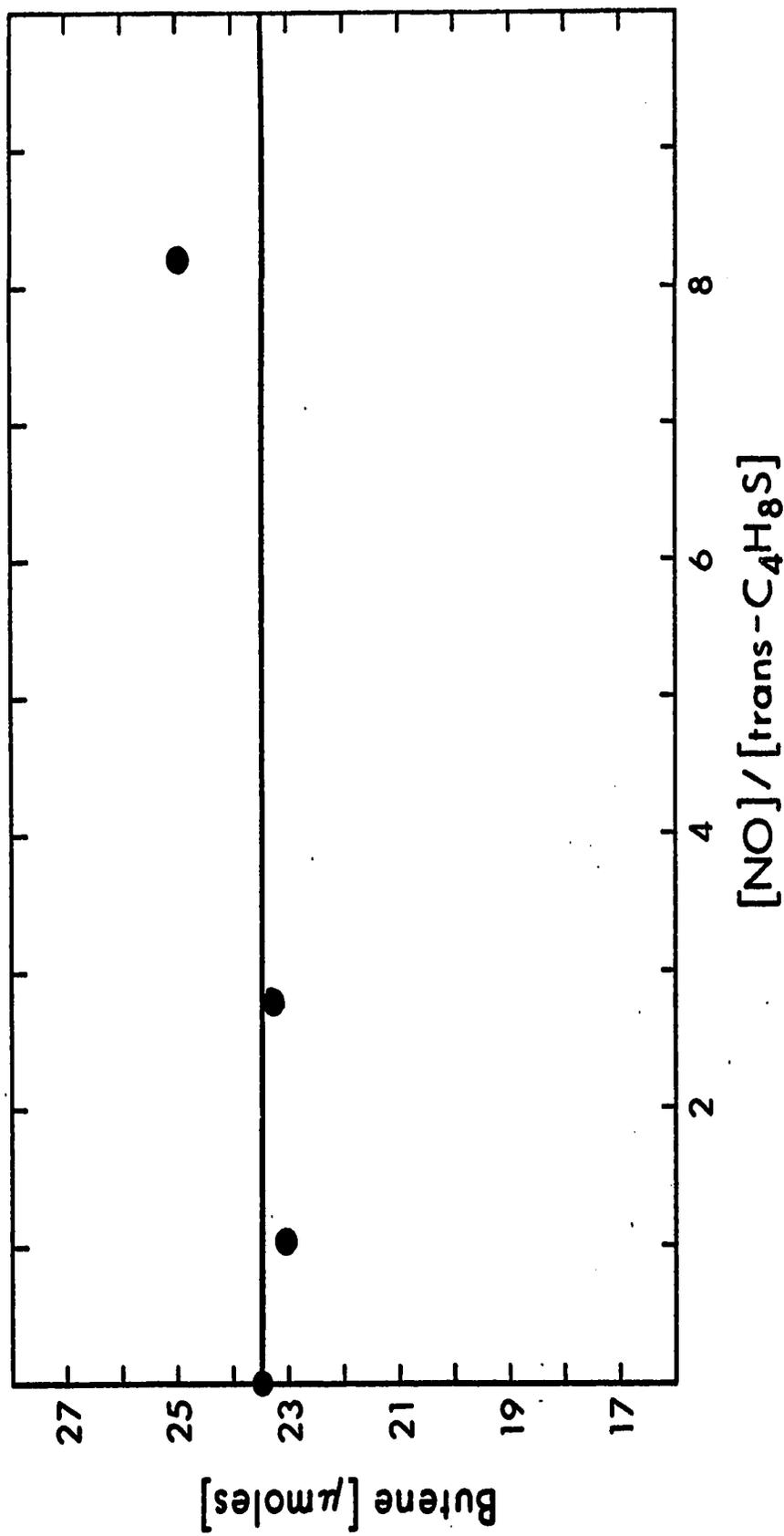
Figure III-15. Pyrolysis of <u>trans-butene</u> in the presence of NO

From the following equation,

$$\ln \frac{a}{a - x} = kt$$

where a, x, and t are the initial substrate concentration, product

yield and reaction time respectively, the first order rate constant,

k, could be obtained from the slopes of plots of ln a/a-x versus t.

The data from which the rate constants were obtained are listed in

Tables III-XX to III-XXII. Some representative time plots obtained

from this data are shown in Figs. III-16, III-17, III-18.

The Arrhenius plots for decomposition of ethylene, propylene

and trans-butene episulphide are shown in Figs. III-19 to III-21 and

the corresponding Arrhenius parameters obtained by least mean square

analyses are presented in Table III-XXIII.

The experimental activation energies can be contrasted to

those computed for the hypothetical, unimolecular sulphur atom

extrusion reaction,

$$\text{episulphide} \rightarrow \text{olefin} + S(^3P) \qquad [1]$$
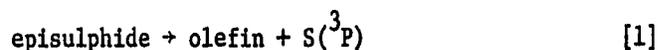
The activation energy is equal to the sum of the enthalpy

change and the activation energy of the reverse reaction, the addition

of ground state sulphur atom to the olefin [-1]. The enthalpy changes

can be obtained from available heats of formation and the activation

energies are known from the literature. The data are compiled in

Table III-XXV. It is seen that the experimental activation energies

are all about 20 kcal/mole lower than the computed values, which

strongly militates against the involvement of a simple unimolecular

process such as [1].

Since decomposition reactions occurring by chain reactions can feature apparent activation energies lower than the energy required for chain initiation (103), it was then necessary to determine the possibility of a chain reaction occurring in the pyrolysis of episulphides. This was accomplished by examining the effect of added olefin.

8) Decomposition in the Presence of Olefin

Since the only products in the episulphide decompositions are olefin and polymeric sulphur, the only possible chain carrier for the reaction must be an elemental sulphur species S, S_2, up to S_7. The chain initiating step would then be the sulphur atom extrusion reaction [1]. Sulphur atoms are known to react with episulphides by the abstraction reaction (33),

$$\text{episulphide} + S(^3P) \rightarrow \text{olefin} + S_2. \qquad [2]$$
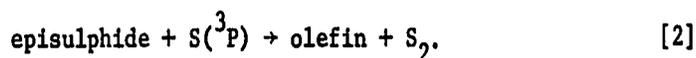
The rate constants for these reactions are in the order of 10^{13} cc/mole sec at room temperature and consequently the reaction goes to completion at a few torr pressure of the episulphide even at room temperature. The chain carrier would then have to be a polymeric sulphur species S_2 to S_7. The reactivity of the S_2 molecule, probably formed in its ground $^3\Sigma_g^-$ state, with respect to episulphides is not known. There is no information available either on the higher polymeric sulphur species S_3 - S_7 which must be present in the systems as transients.

TABLE III-XX

Variation of the Ethylene Yield with Time and Temperature

in the Ethylene Episulphide Pyrolysis[a]

$[C_2H_4S] \times 10^5$ [m/cc]	C_2H_4 [µmoles]	Time [min]
211.3°C		
1.177	14.76	30
1.130	20.07	40
1.134	9.24	20
	log k = -5.034	
195.4°C		
1.126	8.87	60
1.082	10.36	75
1.144	6.48	45
	log k = -5.611	
217.7°C		
1.175	18.57	20
1.092	12.12	15
1.144	21.30	25
	log k = -5.072	
225°C		
1.099	33.00	15
1.060	40.90	20
1.079	54.59	25[b]
	log k = -4.466	

a) cell volume 406,4 cc, S/V = 0.9 cm^{-1}

b) corresponds to the highest conversion, 1.3%
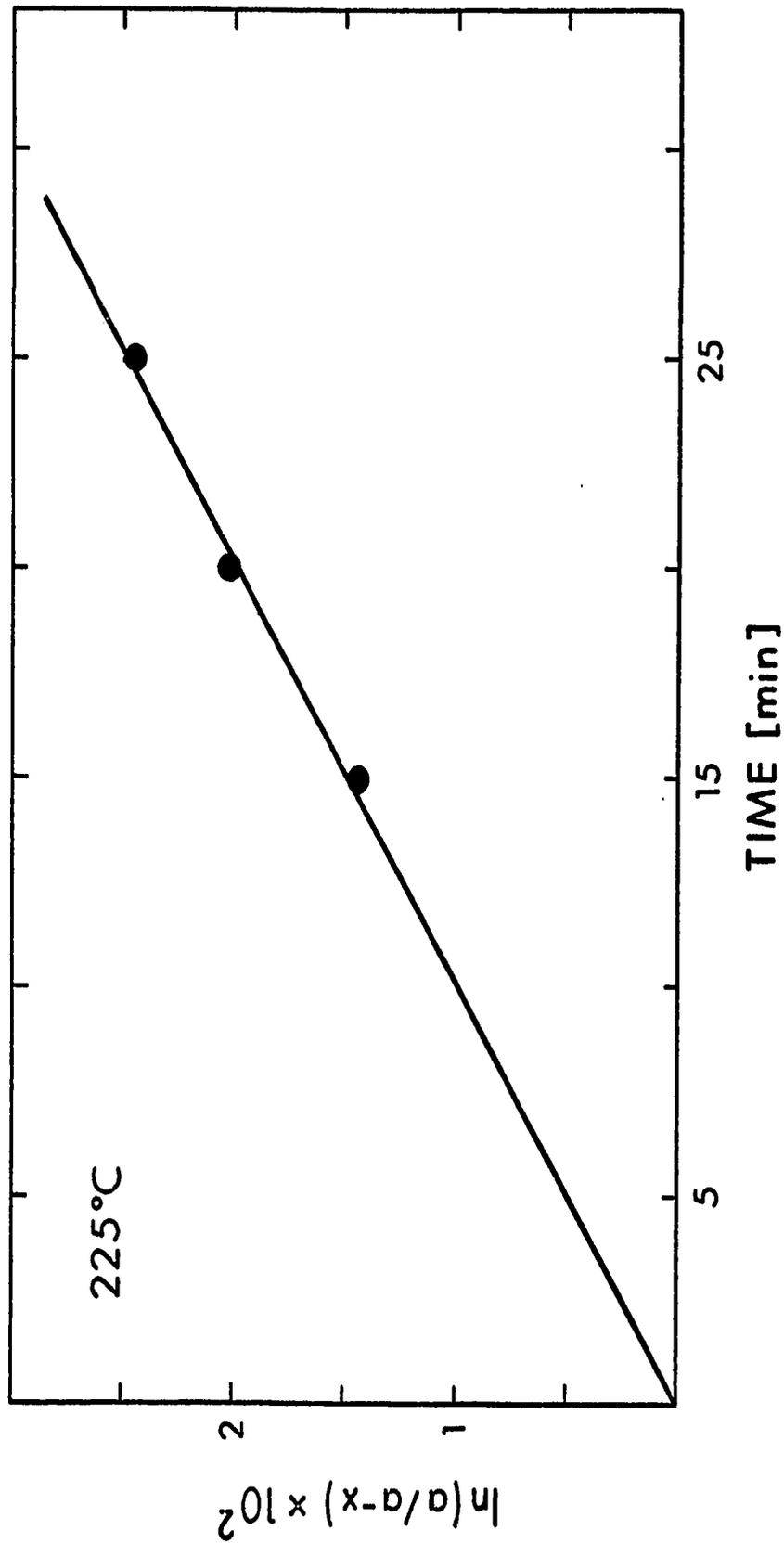
Figure III-16. First order plot for C_2H_4S decomposition

TABLE III-XXI

Variation of the Propylene Yield with Time and

Temperature in the Propylene Episulphide Pyrolysis

$[C_3H_6S] \times 10^6$ [m/cc]	C_3H_6 [μmoles]	Time [min]
	$172°C$ [a]	
3.84	8.42	45
3.94	10.88	50
4.02	13.21	65
4.03	4.51	25
3.97	6.54	35
3.99	12.33	75
4.03	11.26	50
4.06	11.60	55
4.02	15.57	70
4.05	4.00	20
4.03	8.32	40
	$\log k = -5.370$	

a) cell volume 406.4 cc, $S/V = 0.9 \ cm^{-1}$

TABLE III-XXI   (cont'd)

Variation of the Propylene Yield with Time and

Temperature in the Propylene Episulphide Pyrolysis

$[C_3H_6S] \times 10^6$ [m/cc]	C_3H_6 [μmoles]	Time [min]
187°C [b]		
3.29	11.91	20
3.58	38.32	50
3.77	39.81	50
3.58	21.22	30
3.48	28.17	40
3.58	13.20	20
log k = -4.789		
202°C [c]		
3.97	63.40	20
3.92	36.27	12
4.26	51.01	16
log k = -4.212		

b) cell volume 412.1 cc, S/V = 0.9 cm^{-1}

c) corresponds to the highest conversion, 3.9%
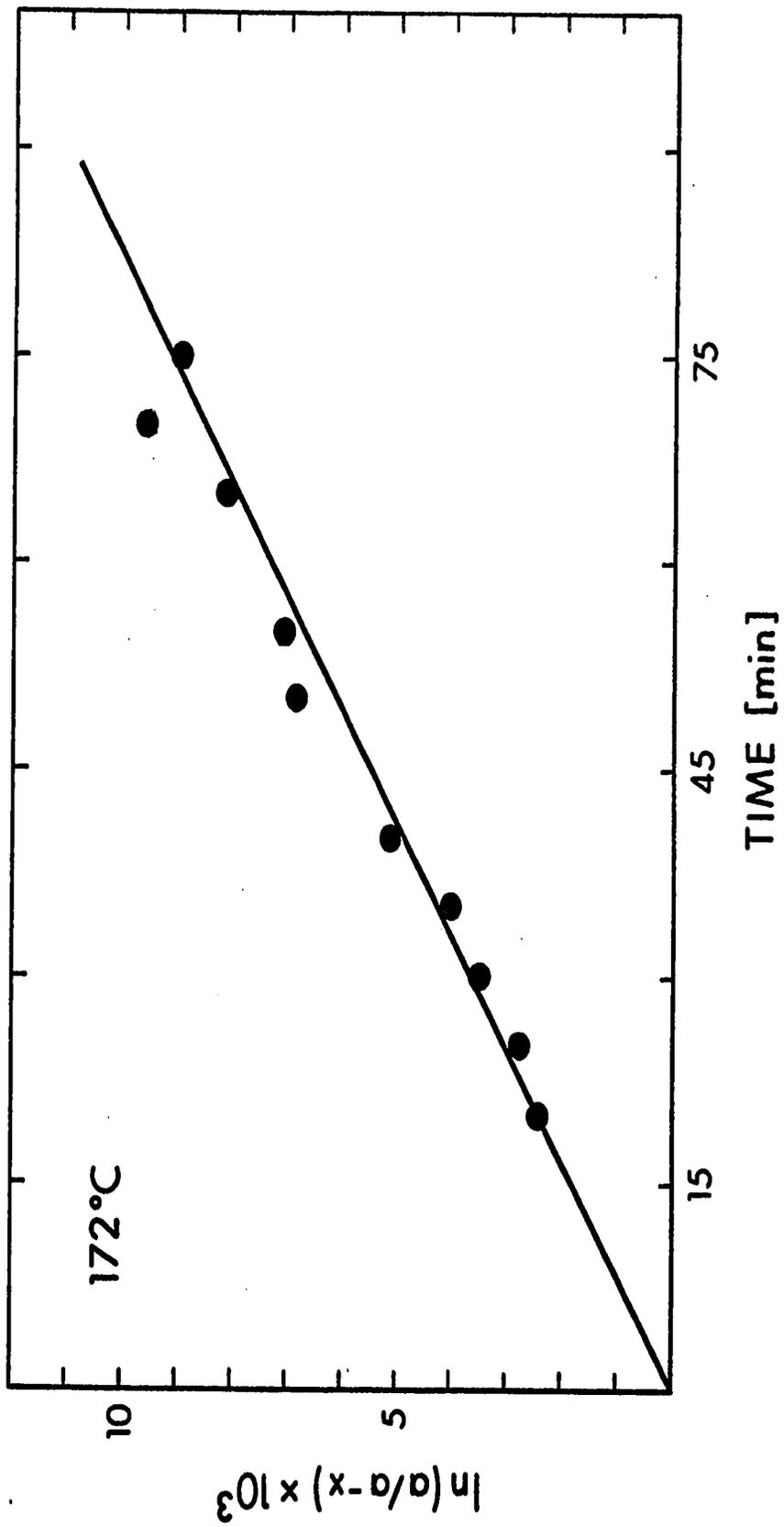
Figure III-17. First order plot for C_3H_6S decomposition

TABLE III-XXII

Variation of the trans-Butene Yield with Time and

Temperature in the trans-Butene Episulphide Pyrolysis [a]

[trans-C_4H_8S] × 10^6 [m/cc]	trans-C_4H_8 [μmoles]	Time [min]
	194°C	
1.64	99.36	30
1.59	58.52	20
1.63	122.48	40
1.60	31.04	10
	log k = -3.912	
	173°C	
1.60	23.07	60
1.59	10.27	30
1.64	34.42	80
1.65	42.37	100
	log k = -4.699	

a) cell volume 461.6 cc, S/V = 0.9 cm^{-1}

TABLE III-XXII (cont'd)

Variation of the trans-Butene Yield with Time and

Temperature in the trans-Butene Episulphide Pyrolysis

[trans-C_4H_8S] × 10^6 [m/cc]	trans-C_4H_8S [μmoles]	Time [min]
	219.0°C	
1.60	88.37	5[b]
1.69	50.72	2.5
1.62	77.59	3.5
1.70	67.21	3
	log k = -3.118	
	187.4°C	
1.71	15.68	10
1.66	24.64	15
1.69	31.03	20
1.64	37.19	25
	log k = -4.161	

b) highest conversion, 30%

TABLE III-XXII (cont'd)

Variation of the trans-Butene Yield with Time and

Temperature in the trans-Butene Episulphide Pyrolysis

[trans-C_4H_8S] × 10^6 [m/cc]	trans-C_4H_8 [μmoles]	Time [min]
	182°C	
1.60	53.36	60
1.60	39.50	40
1.62	41.72	50
1.63	66.93	75
1.65	23.20	25
	log k = -4.389	
	203.0°C	
1.69	149.4	20
1.69	200.5	30
1.67	66.16	10
1.63	93.41	15
1.60	149.37	25
	log k = -3.560	
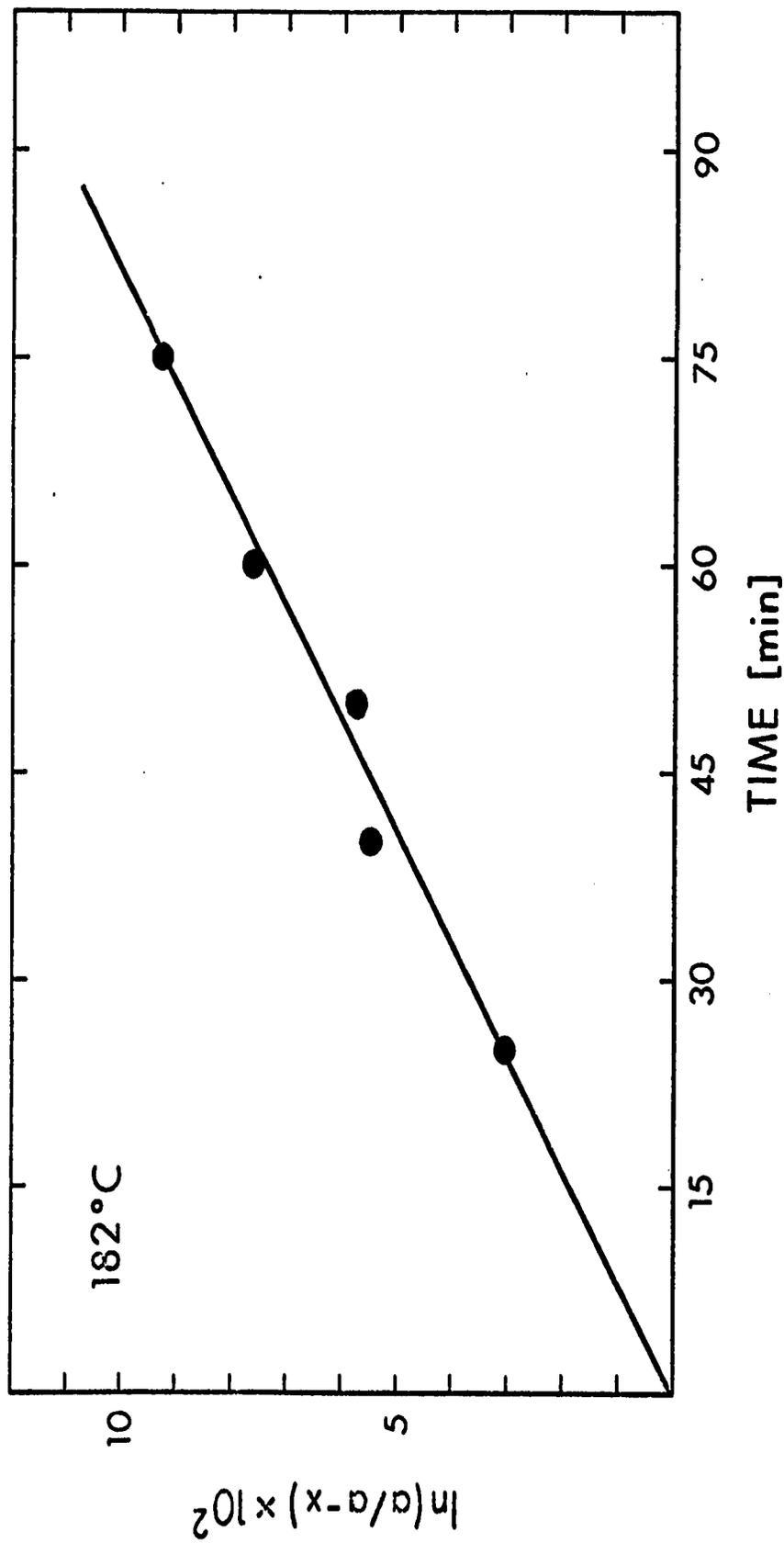
Figure III-18. First order plot for trans-C_4H_8S decomposition
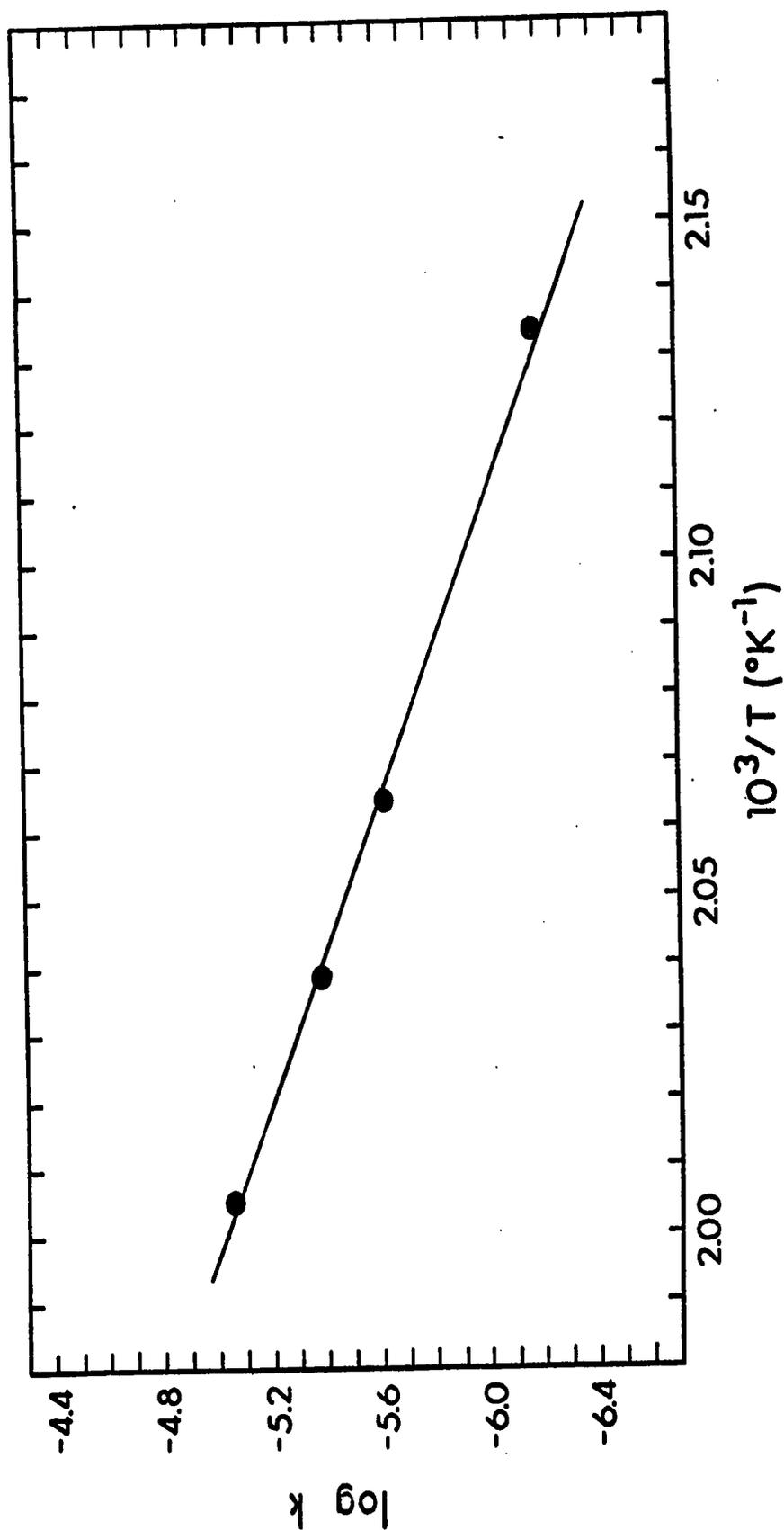
Figure III-19.   Arrhenius plot for ethylene episulphide pyrolysis
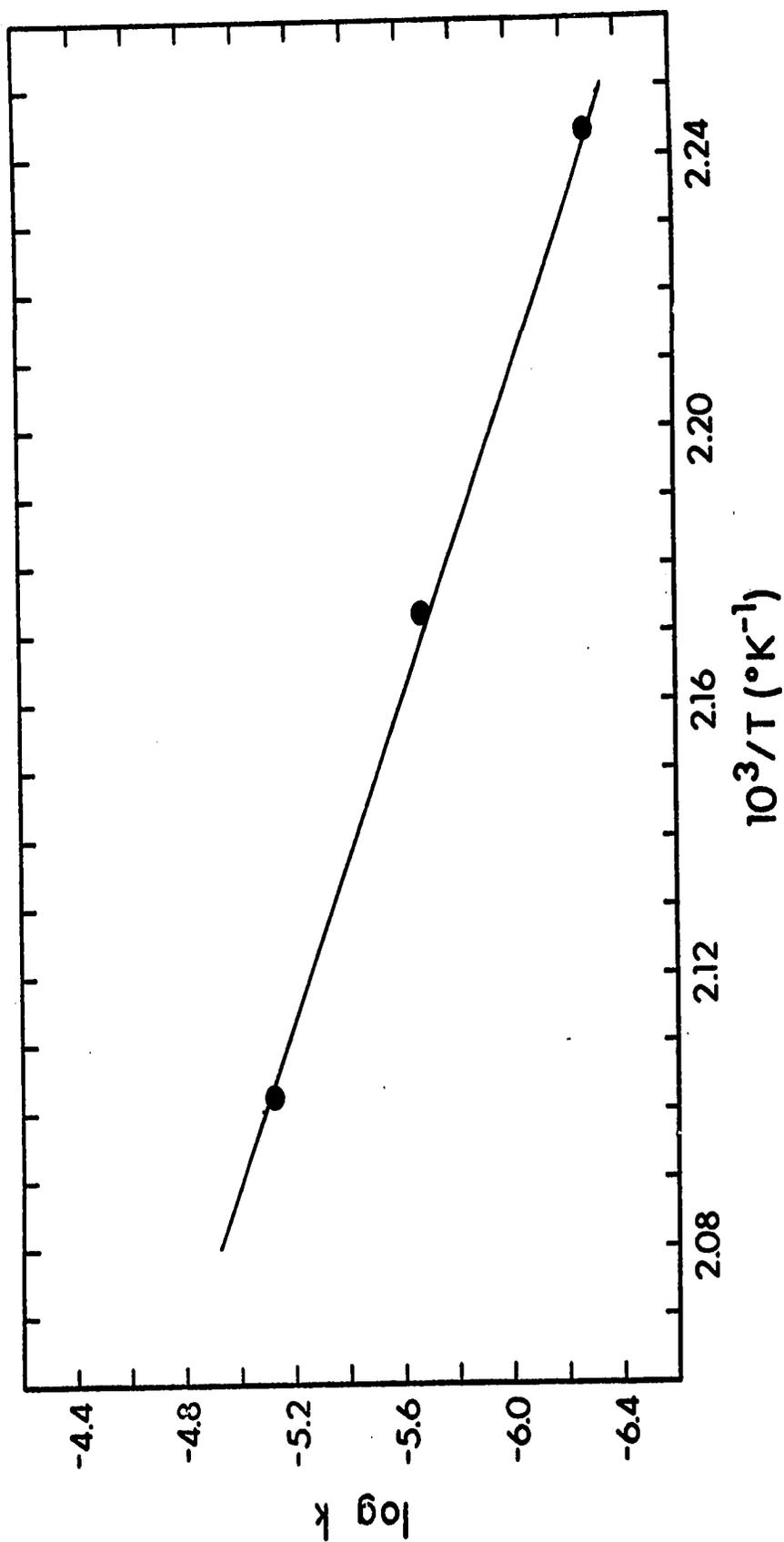
Figure III-20.   Arrhenius plot for propylene episulphide pyrolysis
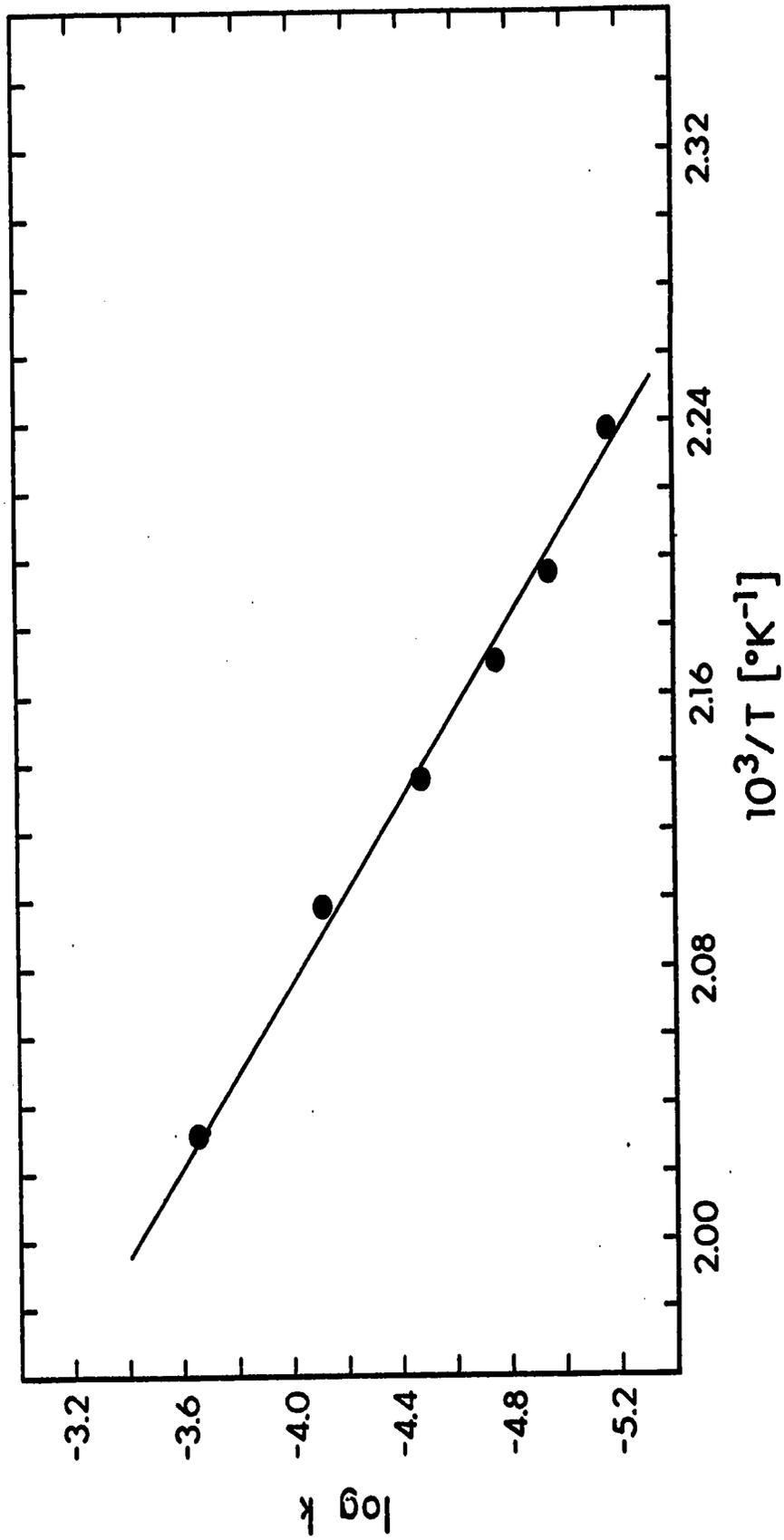
Figure III-21. Arrhenius plot for <u>trans</u>-butene episulphide pyrolysis

TABLE III-XXIII

Arrhenius Parameters in the Thermal Decomposition

of Ethylene, Propylene and trans-Butene Episulphide

	E_a [kcal/mole]	log A [sec^{-1}]
C_2H_4S	40.2 $\pm$ 1.0	12.52 $\pm$ 0.56
C_3H_6S	38.5 $\pm$ 0.7	12.57 $\pm$ 0.35
trans-C_4H_8S	35.4 $\pm$ 0.7	12.08 $\pm$ 0.35

TABLE III-XXIV

Pyrolysis of C_2H_4S in the Presence of an Excess

of cis-Butene at 225.0°C [a]

P(C_2H_4S) [torr]	P(cis-C_4H_8) [torr]	C_2H_4 [μmoles]	cis-C_4H_8S [μmoles]
110.2	-	36.2	-
114.0	480.6	12.9	<1.0

a) all runs 45 min, cell volume 365.8 cc, S/V = 0.9 cm^{-1}

TABLE III-XXV

Thermochemical Calculation of the Energy Barrier

for the Sulphur Extrusion Reaction[a]

	ΔH (formation)[a] kcal/mole	reverse reaction	E_a^c
C_2H_4S	19.8	$S + C_2H_4 \rightarrow C_2H_4S$	1.5
C_3H_6S	11.0	$S + C_3H_6 \rightarrow C_3H_6S$	.4
trans-C_4H_8S	0.9	$S + $ trans-$C_4H_8 \rightarrow$ trans-C_4H_8S	0
C_2H_4	12.5		
C_3H_6	4.9		
trans-C_4H_8	-2.7		
S	66		

$$C_2H_4S \rightarrow C_2H_4 + S \qquad E = 60.3 \text{ kcal/mole}$$

$$C_3H_6S \rightarrow C_3H_6 + S \qquad E = 60.2 \text{ kcal/mole}$$

$$\text{trans-}C_4H_8S \rightarrow \text{trans-}C_4H_8 + S \qquad E = 62.3 \text{ kcal/mole}$$
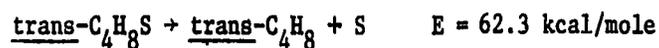
a) the energy barrier is ΔH (reaction) $+ E_a$ (reverse)

b) Ref. 80 and Ref. 86

c) Ref. 50c

Now the sulphur atoms if present in the system should be scavengable by added olefins to yield the appropriate episulphide, with the simultaneous suppression of the rate of product formation.

The reactivity of ground state sulphur atoms with cis-butene is known to be about the same as that with ethylene episulphide (33):

$$S(^3P) + \underline{cis}\text{-}C_4H_8 \rightarrow \underline{cis}\text{-}C_4H_8S \tag{3}$$

$$S(^3P) + C_2H_4S \rightarrow C_2H_4 + S_2 \tag{4}$$
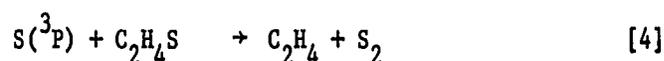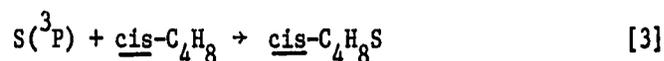
$$\frac{k_4}{k_3} = 1.2 \text{ at } 25^\circ C$$

Should sulphur atoms be formed in the initiation step, then decomposition in the presence of a four-fold excess of cis-butene over episulphide should result in a reduction of the C_2H_4 yield to a value slightly greater than one-half the yield in the pure episulphide pyrolysis, with the simultaneous formation of cis-butene episulphide. The results of such experiments are presented in Table III-XXIV. While it is seen that some cis-butene episulphide is formed, its yield is much less than that of C_2H_4. Most striking is that the reduction in the C_2H_4 yield is not to a half but to one-third of the value obtained in the absence of olefin. The reduction of the rate is also temperature dependent, as will be shown in a more detailed study of the decomposition of episulphides in the presence of olefins, Chapter V.

9) <u>The Mercury Photosensitization of COS in the Presence of C_2H_4S</u>

In order to assess the importance of the invervention of the S_2 - S_7 sulphur species in the decomposition of episulphides, these species must be produced in a kinetically controllable way in the presence of episulphides. Since there is no simple method of producing S_2 directly in the thermal system under consideration, an indirect method was applied. Mercury photosensitization of COS leads to the production of CO and ground state triplet sulphur atoms (34b). If these sulphur atoms in turn can abstract another sulphur atom from some molecule, one obtains an indirect source of S_2. Let us consider the following scheme:

$$Hg + h\nu(\lambda = 2537\text{Å}) \rightarrow Hg^* \qquad I_a$$

$$Hg^* + COS \rightarrow CO + S + Hg \qquad [5]$$

$$Hg^* + C_2H_4S \rightarrow C_2H_4 + S + Hg \qquad [6]$$

$$S + COS \rightarrow CO + S_2 \qquad [7]$$

$$S + C_2H_4S \rightarrow C_2H_4 + S_2 \qquad [8]$$

$$S_2 + C_2H_4S \rightarrow C_2H_4 + S_3 \qquad [9]$$
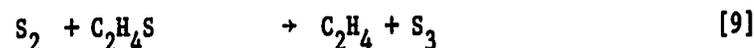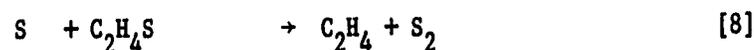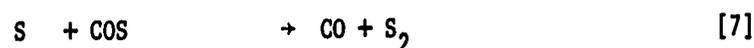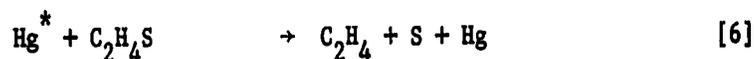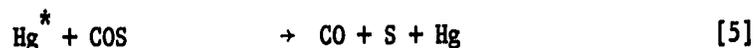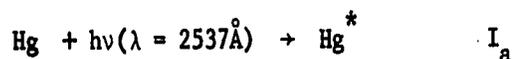
where $Hg^* = Hg(^3P_1)$ and $S = S(^3P)$.

The value of k_5 has been established as being very close to the collision frequency, 2×10^{14} cc/mole sec at 25°C (113). Since the rate constant for reaction of $Hg(^3P_1)$ with ethylmercaptan has been determined as about 2×10^{14} cc/mole sec as well (105), it is to be expected that k_6 and k_5 will be approximately equal. Therefore, if the reaction is carried out with a large excess of COS over C_2H_4S,

sensitization of carbonyl sulphide will predominate.

The Arrhenius parameters for k_7 have been determined by Jakubowski et al. (77), and k_7 is estimated as being about 10^{11}cc/mole sec. k_8 has a value of 3×10^{13} cc/mole sec at $25^{\circ}C$ (52) and will only be slightly larger at $212^{\circ}C$ since its activation energy is probably very close to zero. Hence, since $k_8/k_7 \simeq 300$, sulphur atom reaction via [8] will predominate. Thus, each sulphur atom produced by reaction [5] will react with C_2H_4S by [8] producing ethylene and S_2, and the net ethylene yield should then be equal to the CO produced by step [5], provided S_2 does not react with ethylene episulphide. The results of these experiments, carried out at $194^{\circ}C$ and $212^{\circ}C$ are presented in Table III-XXVI, and illustrated in Figs. III-22 and III-23.

The data clearly indicate that the reaction of S_2 or higher species with C_2H_4S is inefficient. Although the ethylene yield becomes larger than the yield of CO at the higher C_2H_4S pressures, this can be attributed to the fact that some sensitization of the episulphide occurs. It is possible to estimate the extent of sensitization of C_2H_4S.

Applying a steady state kinetic treatment to the previous reaction scheme, the rate of formation of CO is given by

$$R(CO) = I_a \left[\frac{k_5(COS)}{k_5(COS) + k_6(C_2H_4S)} + \frac{k_7(COS)}{k_7(COS) + k_8(C_2H_4S)} \right] \quad [10]$$

Since $k_7 \ll k_8$ and $k_5 \simeq k_6$, as was shown above, the second term in equation [10] can be neglected and

TABLE III-XXVI

Variation of the C_2H_4 and CO Yields in the

Hg-COS-C_2H_4S System[a]

P(C_2H_4S) [torr]	CO [μmoles]	C_2H_4 [μmoles]
194°C[b]		
0	5.16	0
8.1	3.34	2.51
14.7	3.11	2.96
23.4	3.04	3.34
32.6	2.98	3.04
40.4	2.84	3.48
212°C[c]		
0	5.17	0
4.4	3.58	2.39
11.9	3.33	2.92
20.1	3.23	3.43
27.2	3.15	3.90
33.4	3.02	4.22
43.2	2.96	5.28
50.0	2.88	5.48

a) all runs 7 min, cell volume 135 cc

b) P(COS) = 434.9 torr

c) P(COS) = 414.5 torr
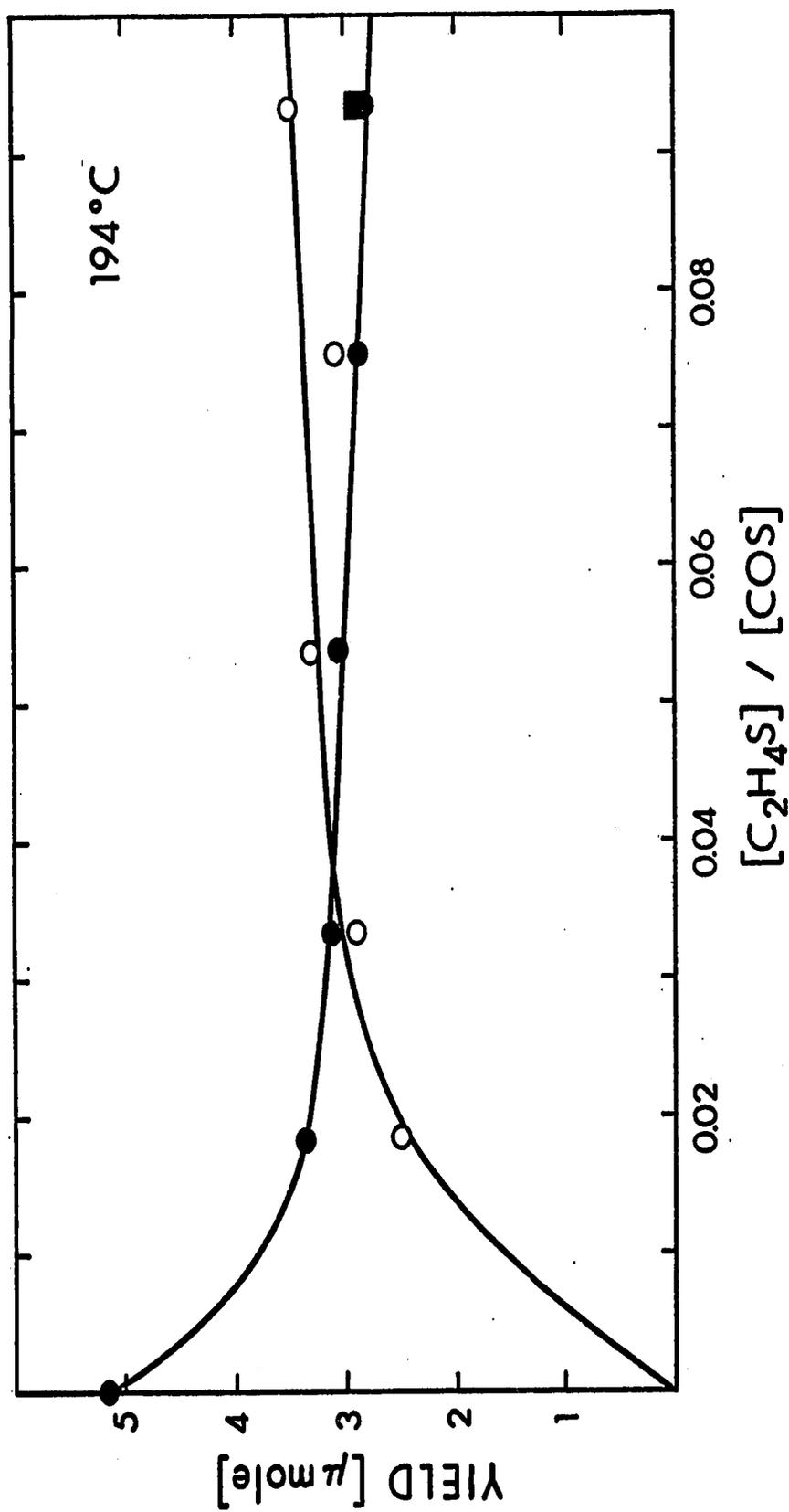
Figure III-22. Yields of CO (●) and C_2H_4 (○) and corrected C_2H_4 (■) in the $Hg/COS/C_2H_4S$ system.
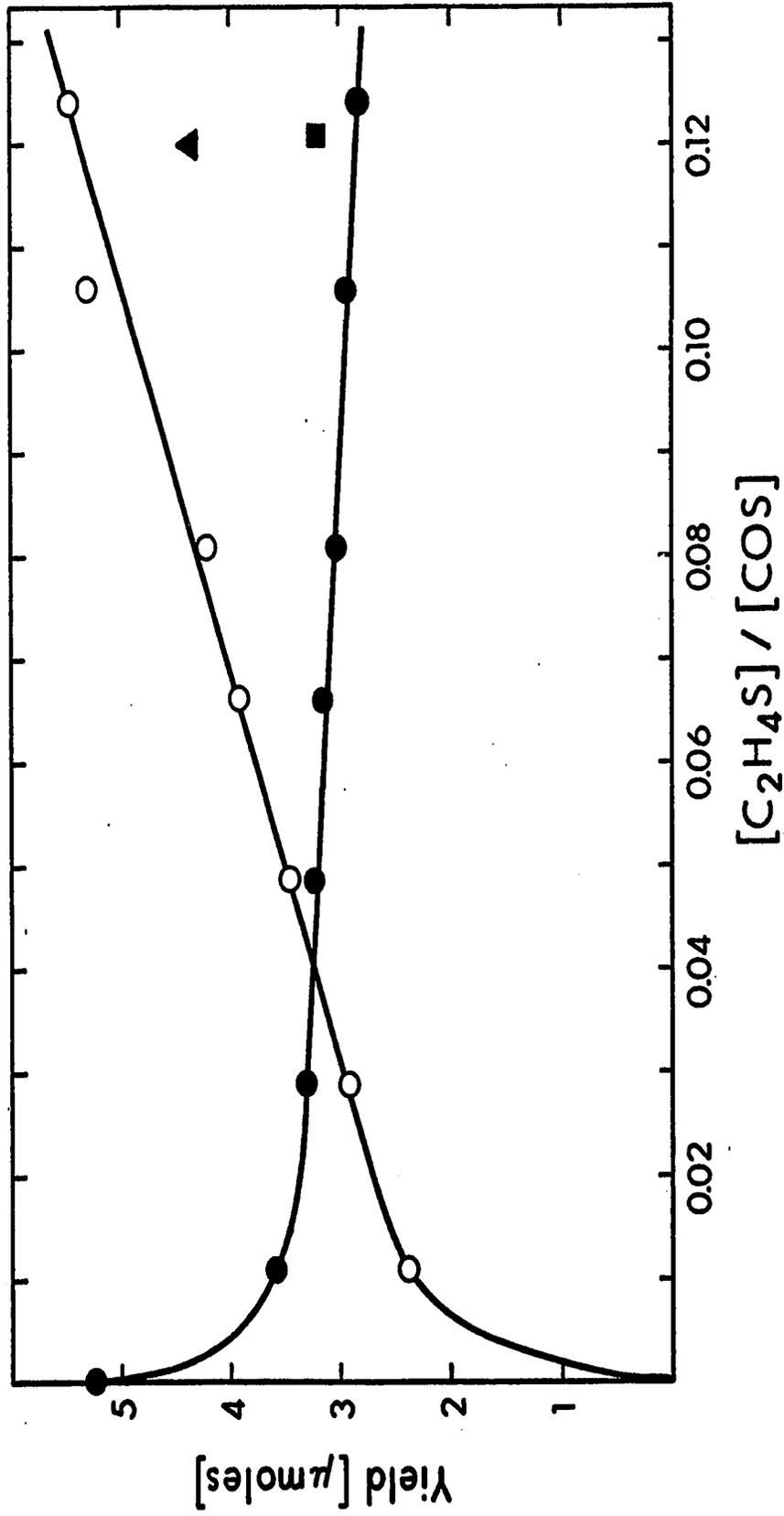
Figure III-23. Yields of CO (●) and C_2H_4 (○) in the $Hg/COS/C_2H_4S$; (▲) C_2H_4 corrected for sensitization and (■) for sensitization and pyrolysis.

$$R(CO) = \frac{I_a k_5 (COS)}{k_5 (COS) + k_6 (C_2H_4S)} \quad .$$

Rearrangement of this expression yields

$$\frac{1}{R(CO)} = \frac{1}{I_a} + \frac{k_6}{I_a k_5} \cdot \frac{(C_2H_4S)}{(COS)} \quad . \qquad [11]$$

Equation [11] predicts a linear relationship between

$1/R(CO)$ and the ratio $(C_2H_4S)/(COS)$ from which the ratio of the rate

constants k_6/k_5 can be obtained. The predicted linear relationship is

indeed found as shown in Fig. III-24, and from a ratio of the slope

and intercept, k_6/k_5 is calculated to be 1.78.

Using this value for k_6/k_5, a correction to the ethylene

yields arising from photosensitization of C_2H_4S can be made. In the

case of the experiments carried out at $194^\circ C$, depicted in Fig. III-22, it

is seen that the CO and corrected C_2H_4 yields are equal. This is not

the case for the results obtained at $212^\circ C$, however, where the

corrected yield is slightly higher than the CO yield. The residual

C_2H_4 yield after correction for sensitization can be attributed to

thermal decomposition of the episulphide which would become important

at this temperature. Indeed, a blank run of 39 torr ethylene episulphide

resulted in about 0.4 μmoles C_2H_4. However, as was shown by the results

presented in Table III-XVI, CO_2 has an accelerating effect on the

decomposition at low episulphide pressures, and since COS should have

about the same effect as CO_2, an additional correction to the C_2H_4

yield must be made. This second correction is also shown in

Fig. III-23. The CO and C_2H_4 yields are seen to be essentially equal

indicating that reaction [9] is not important.
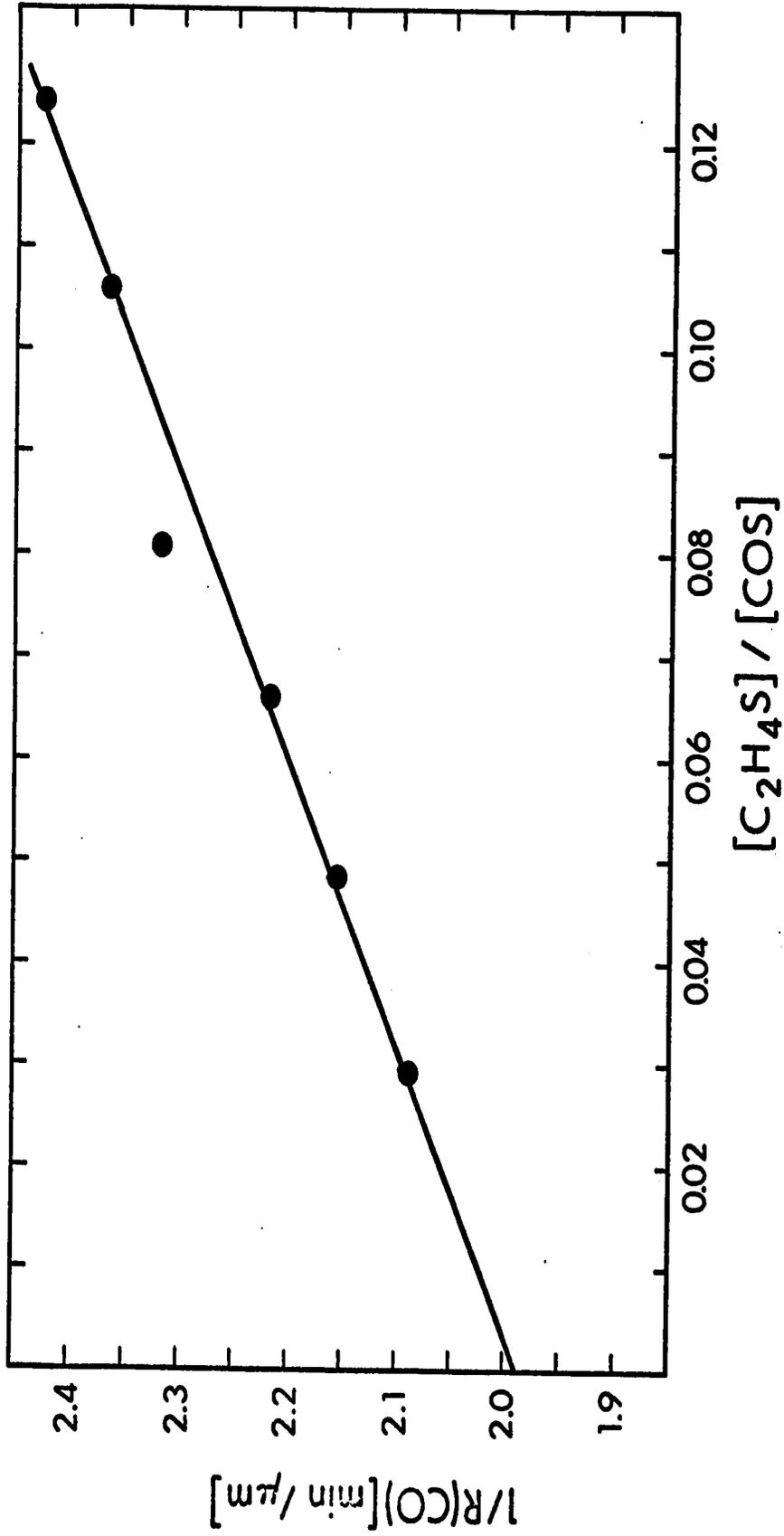
Figure III-24. Stern-Volmer plot for the Hg/COS/C_2H_4S system

10) <u>The Stereospecificity of the Pyrolysis of Butene-2 Episulphides</u>

Due to the difficulty in obtaining pure <u>cis</u>-or <u>trans</u>-dideuterioethylene episulphide, the <u>cis</u> and <u>trans</u> isomers of butene-2 episulphide were used to investigate the stereospecificity of the episulphide pyrolysis. The results, presented in Table III-XXVII, demonstrate the high degree of stereoselectivity in the overall reaction.

B. Discussion

Thermal activation of the substrate molecules occurs by successive collisional activation and deactivation steps, until the molecule is sufficiently energized that it can react. A complete description of such a process would necessarily involve the explicit evaluation of the probabilities of each activation step between two vibrational levels. Since the analysis of such ladder-climbing processes is very difficult, it is commonly assumed that the molecules are directly activated to an energized state by strong collisions in which relatively large energies are transferred (greater than RT). The collisions are assumed to be so violent, that the initial state before the reaction in no way governs the state of the molecule after reaction, and that one therefore need not consider the dynamics of the collision. The activation-deactivation process is then simply written as

$$A + M \rightleftharpoons A^* + M$$
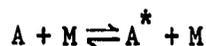
where A^* is an energized substrate molecule and M a bath molecule.

TABLE III-XXVII

Stereochemical Investigation of cis-and

trans-Butene Episulphide Pyrolysis[a]

Pressure (torr)	C_4H_8S before pyrolysis		C_4H_8S after pyrolysis		Butene-2	
	% cis	% trans	% cis	% trans	% cis	% trans
cis-Butene Episulphide[b]						
37.64	99.3	0.7	98.9	1.1	90	10
trans-Butene Episulphide[c]						
48.42	0.2	99.8	0	100	3.8	96.2

a) at a temperature of 154°C.

b) P = 37.6 torr; reaction time 24 hrs; 14.5% conversion; product yield 94.7 µmoles.

c) P = 48.4 torr; reaction time 24 hrs; 4.7% conversion; product yield 40.2 µmoles.

In the study of thermal decomposition reactions it is important

to investigate the possibility of chain reactions occurring after

the substrate molecule has been sufficiently energized that it can react.

As mentioned earlier, a manifestation of extensive chain

reactions is that the apparent activation energy can be considerably

lower than the activation energy of the initiation step. The Arrhenius

parameters listed in Table III-XXIII show that the decomposition proceeds

with a low energy barrier of about 40 kcal/mole. In comparison, the

activation energies for the isomerization of cyclopropane and

decomposition of ethylene oxide are 65 and 57 kcals/mole respectively.

The enthalpy change of the reaction forming olefin and atomic sulphur

is about 60 kcal/mole. However, the possibility of a sulphur chain

reaction which could lower the apparent activation energy can be

discounted. The only fate of the sulphur atoms would be an abstractive

attack upon the substrate episulphide to yield olefin and S_2. Sulphur

atoms, however, do not appear to be present in the reaction system.

The results of the mercury photosensitization experiments presented

in Table III-XXVI demonstrate that S_2 molecules do not readily react

with the episulphide to produce olefin and S_3 even at elevated

temperatures.

For analogous reactions in a homologous series, Evans and

Polanyi (111), and Semenov (112) proposed a simple empirical linear

relationship between the exothermicities and enthalpies of reactions.

Although there is no such quantitative correlation between the

exothermicities of different bimolecular reactions and the magnitude of

their respective energy barriers, one usually associates a

qualitative correspondence between the two quantities. The reaction of S_2 with ethylene episulphide is slightly exothermic:

$$S_2 + C_2H_4S \rightarrow C_2H_4 + S_3 \qquad \Delta H = -6.3 \text{ kcal/mole} \qquad [12]$$
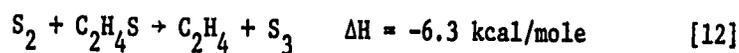
Other similar reactions in which the sulphur atom is abstracted from episulphides have been studied quantitatively (77) and can be used as a comparison to reaction [12]. Both methyl and methyl-thiyl radicals react with episulphides via S-abstraction:

$$CH_3 + C_2H_4S \rightarrow CH_3S + C_2H_4 \qquad \Delta H = -12.4 \text{ kcal/mole} \qquad [13]$$

$$CH_3S + C_2H_4S \rightarrow CH_3S_2 + C_2H_4 \qquad \Delta H = -12.6 \text{ kcal/mole} \qquad [14]$$

The two reactions have nearly equal exothermicities and similar rate constants:

$$k_{13} = 10^{10.85} \exp(-6700/RT) \text{ cc/m sec}$$

$$k_{14} \simeq 10^{11.5} \exp(-8800/RT) \text{ cc/m sec}.$$

The activation energies for the two reactions are comparable, with the methylthiyl radical having a slightly higher barrier. The heavier methylthiyl radical probably resembles the S_2 species more closely since both have non-bonding p orbitals or unfilled d orbitals. On the basis of the reactions of these species, therefore, it is reasonable to assume that reaction [12] will also have a considerable energy barrier and that the most probable fate of the S_2 molecules is polymerization. The analogous reaction of S_3

$$S_3 + C_2H_4S \rightarrow C_2H_4 + S_4 \qquad \Delta H = 0.3 \text{ kcal/mole}$$
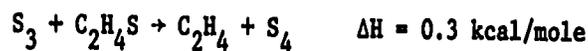
is slightly endothermic, and the activation energy for this reaction would probably exceed that of [12]. Thus, this reaction would also

seem unlikely to be occurring in the reaction system under investigation.

The polymeric sulphur species which result from decomposition of episulphides should not decompose to form reactive sulphur atoms (79) at the temperatures of this study. Since the behavior of sulphur compounds is very much the same as that of oxygen containing species, it is reasonable to assume that the pre-exponential factor for decomposition of S_2 to atoms is the same as the corresponding reaction of O_2 (104), namely $10^{14.2}$ sec^{-1}. The bond energy for S_2 is about 104 kcal/mole. With Arrhenius parameters of this magnitude, the decomposition of S_2 can be neglected as a complicating feature in the episulphide system.

In systems where molecular sulphur is produced it is also of interest to determine which of the various elemental forms predominates under the given conditions. The composition of sulphur species S_2 to S_8 in the saturated vapor has been reported (79) and the results demonstrate the tendency of sulphur to polymerize to S_8. In the temperature range of the present investigation, the composition of sulphur vapor is approximately 68%, 17% and 1% for S_8, S_7, S_6 and S_5 respectively. The fraction of S_2, S_3 and S_4 is found to be considerably less than 0.1%. Therefore all the sulphur formed in the pyrolysis of episulphides polymerizes.

Clearly, the above arguments rule out the possibility of a chain reaction with sulphur species as chain carrier. The possibility of monoradicals occurring as chain carriers can be discounted on the basis of the reaction products. This is also borne out experimentally

by studies using NO as an added gas. As is shown in Fig. III-15, there is no change in the rate of reaction.

As was stated previously, the energy barrier to the removal of a sulphur atom from an episulphide to form the olefin product is close to 60 kcal/mole, which is approximately 20 kcal/mole higher than the experimental activation energy. Having shown that these low activation energies for decomposition are not attributable to a chain mechanism being operative, it is evident that the reaction proceeds via a path of low activation energy leading to the formation of an intermediate species which, in turn, decomposes to product. The reaction of this intermediate episulphide molecule ($ES^{\dagger}$), having an energy content of 40 kcal/mole corresponding to the activation energy, to give ethylene via

$$C_2H_4S^{\dagger} + C_2H_4S \rightarrow 2C_2H_4 + S_2 \qquad \Delta H = -24.0 \text{ kcal/mole}$$
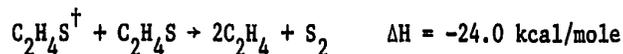
is exothermic.

Let us now consider the processes which lead to the formation of the reaction intermediate ($ES^{\dagger}$). The order studies and the effect of inert gases suggest that the initial stages of episulphide decomposition are consistent with a Lindemann mechanism of thermal activation. In the case of ethylene episulphide the orders are found to lie between 1 and 2 in the pressure region from 40 to 500 torr, indicating that the reaction is in the fall-off region at these pressures. In the case of the heavier trans-butene episulphide the order for product formation is unity in the pressure region 40-250 torr and at both 178° and 188°C, indicating that the reaction is in the high pressure region. Propylene episulphide, however, demonstrates an intermediate behavior: at 202°C the order is

unity over the pressure range 50-300 torr but at $187^{\circ}C$ the order is

unity above 100 torr and increases at lower pressures, to about 1.4 at

50 torr. The fall-off regions of the corresponding cyclic carbon

compounds, cyclopropane, dimethylcyclopropane and methylcyclopropane,

lie in the same pressure regions (2, 114, 115). It should be noted

however, that while a decrease in order with temperature is predicted

by Kassel theory (54), the inverse behavior is found here. This is

not entirely unexpected, since episulphide decomposition is not a simple

unimolecular reaction.

The fall-off behavior described above is in general agreement

with the characteristics of unimolecular kinetics. It is well known that

the fall-off region, that is the pressure range in which the reaction

changes from first to second order, shifts to lower substrate pressures

as the complexity of the reacting molecule increases (78). The uni-

molecular decomposition of N_2H_4 reaches its high pressure region at about

10 atm. The decomposition of ethylchloride on the other hand, is in its

high pressure region above 1 atmosphere, where N_2H_4 approaches its low

pressure region.

A Lindemann mechanism for the formation of an intermediate in

the decomposition of episulphides is lent further support by the effect

of inert gases on the rates of decomposition. If indeed episulphide

decomposition is in a pressure region intermediate between the first

and second order domains, then at low pressures, where activating

collisions are rate determining, inert diluent gases should enhance

the rate of decomposition. At higher pressures, however, where

collisional activation no longer is the rate determining step and

an equilibrium between non-energized and energized molecules begins

to occur, added inert gas would not be expected to increase the rate

of reaction. In the case of propylene episulphide, which was studied

essentially in its high pressure region, inert gas should have

basically no effect. These trends are indeed found to occur, as was

shown in Tables III-XV to III-XVII and Fig. III-14.

Recognizing that the formation of the intermediate, $ES^{\dagger}$,

follows unimolecular kinetics, we can formulate the following kinetic

scheme:

$$ES + ES \rightarrow ES^{*} + ES \qquad [15]$$

$$ES^{*} + ES \rightarrow ES + ES \qquad [16]$$

$$ES^{*} \rightarrow ES^{\dagger} \qquad [17]$$

$$ES^{\dagger} + ES \rightarrow ES + ES \qquad [18]$$

$$ES^{\dagger} + ES \rightarrow 2 \text{ Olefin} + S_{2} \qquad [19]$$
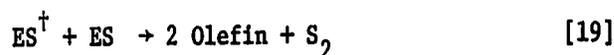
Collisional activation results in the formation of an

energized molecule, ES^{*}, which either undergoes collisional

deactivation by [16] or is transformed by [17] to the intermediate

which can react to products by [19] or revert to substrate by [18].

Having established the kinetic mechanism by which reaction

occurs, it becomes necessary to characterize the intermediate ES[t].

Recognizing that rupture of both carbon-sulphur bonds does not occur

simultaneously since S atoms are not formed, there remains the

possibility of just one C - S bond breaking to yield a thiodimethylene

biradical which can be identified with ES[t]. Such a reaction is

analogous to C - C bond cleavage to form trimethylene in the

thermolysis of cyclopropane. In order to determine the possibility of

this reaction, a knowledge of the heat of formation of the biradical is

necessary. Let us consider the case of ethylene episulphide. In this

case the reaction is

$$\overset{\triangledown}{_S} \rightarrow \cdot CH_2CH_2S \cdot. \qquad [20]$$
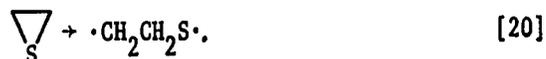
$\Delta H_f(\cdot CH_2CH_2S \cdot)$ can be estimated using the same method as Benson (6)

applied for trimethylene. The enthalpy of formation is obtained by

removing a hydrogen atom from both ends of the parent saturated

molecule, which is ethylmercaptan in this case, assuming that the

radical ends are independent of each other.

$$CH_3CH_2SH \rightarrow \cdot CH_2CH_2S \cdot + 2H \qquad \Delta H = D(S-H) + D(CH_2-H)$$

From the heats of formation $\Delta H_f(CH_3CH_2SH) = -11$ kcal/mole,

$\Delta H_f(H) = 52$ kcal/mole and the bond energies $D(S-H) = 88$ kcal/mole and

$D(CH_2-H) = 99$ kcal/mole, the heat of formation of the thiodimethylene

biradical is calculated to be 72 kcal/mole. Since the heat of

formation of ethylene episulphide is about 20 kcal/mole, ΔH for

reaction [20] is 52 kcal/mole. Application of the same technique for

the case of propylene and <u>trans</u>-butene episulphides, using propane-1-

thiol and butane-2-thiol as reference compounds, one finds,

$$\triangle\!\!\!\!/_S \rightarrow CH_3\overset{\bullet}{C}HCH_2S\cdot \qquad \Delta H = 51 \text{ kcal/mole}$$

$$\wedge\!\!\!\!/_S \rightarrow CH_3\overset{\bullet}{C}H\underset{\underset{\bullet S}{|}}{C}HCH_3 \qquad \Delta H = 54 \text{ kcal/mole} .$$
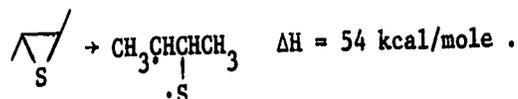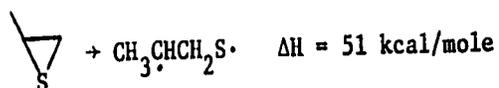
The thermochemical calculations are given in Appendix A.

The results of these calculations suggest that the intermediate $ES^{\dagger}$ cannot be an open biradical as is thought to occur in the pyrolysis of cyclopropane or ethylene oxide, since the enthalpy of reaction forming the biradicals is greater than the activation energy for decomposition of all three episulphides. This result is not surprising, however, since if a loose biradical species were the intermediate, one would expect the decomposition of the cis- and trans-butene episulphides to be considerably less stereospecific than is actually found. The energy barrier to isomerization then would not exceed that of the rotational barrier in methyl substituted hydrocarbons, which is about 5 kcal/mole. Such an energy barrier is inconsistent with the experimental results.

Some insight into the nature of the intermediate occurring in episulphide pyrolysis can be found in the preliminary results obtained when olefins are added to the reaction system. While this reaction will be discussed in more detail in a later chapter, it is instructive to mention some features of it here. The decomposition is found to be quenched strongly by olefins. When the reaction is carried out using ethylene episulphide in a 4-fold excess of butene-2 at $225^{\circ}C$, the ethylene yield is reduced to one-third of the yield in the pure system

and the only new sulphur-containing product is butene-2 episulphide,

in a yield much less than the amount of decomposition that is quenched.

If the reaction were adiabatic, then the effect of the added gas would

not be rate suppressing. These results, then, strongly suggest that

the pathway for decomposition of episulphides is via an electronically

excited state of the substrate, as postulated in the decomposition of

cyclopropane (19). In contrast to the reaction of cyclopropane, the

reaction of episulphides is shown to be highly stereospecific suggesting

a strong binding interaction in the ring relaxed intermediate.

This conclusion is consistent with the kinetic features of

the reaction and is supported by the recent theoretical investigations

of the sulphur-olefin system discussed in Chapter I. Briefly

recapitulating, qualitative Extended Hückel MO calculations (40) on the

ethylene episulphide molecule showed that the excited molecule can

exist in a stable configuration with an expanded ring geometry in which

the CCS angle is about 100°. More recent detailed ab initio SCF MO

calculations on the molecule reveal that energies of the low lying

triplet and singlet excited states are strongly dependent upon the

geometry of the molecule (43). As was shown in Fig. I-2, the excited

states have a ring distorted equilibrium configuration, in which the

CCS angle is about 100° and the terminal methylene is perpendicular to

the CCS plane. The lowest lying triplet state has its minimum at an

energy of approximately 40 kcal/mole. Since such molecular orbital

calculations can only be performed with a limited basis set of orbital

functions, the energy values are always somewhat higher than the

experimental value. Hence, it is probable that the true minimum has an

energy slightly less than 40 kcal/mole. Nevertheless, these results

clearly support the experimentally indicated existence of a low lying excited state.

An additional feature of the theoretical work is that it indicates a strong binding interaction between the terminal CH_2 group and the sulphur end. This interaction is revealed by the large calculated barrier to rotation of 23 kcal/mole about the C-C bond in the lowest triplet excited state (43). This finding is also in accord with the results of the pyrolysis of cis- and trans-butene-2 episulphides which showed decomposition to occur with a high degree of stereo-specificity.

Having established that the decomposition of episulphides proceeds via the intermediacy of a molecule in its lowest non-vertical triplet excited state, it would perhaps be pertinent to compare the activation energies for decomposition in the series ethylene, propylene and trans-butene episulphide. The results, which were presented earlier in Table III-XXIII, show a trend of decreasing activation energy with increased substitution. Recalling the thermochemical estimates presented earlier, no such trend was apparent for the removal of sulphur atom from the episulphide. The lower activation energy in the case of the heavier episulphides must be due to an inductive effect of the methyl groups.

Returning to the kinetic scheme presented earlier, the species $ES^†$ can now be identified with the episulphide molecule in the equilibrium configuration of its lowest triplet excited state. Reaction [17] now also takes on added significance as it involves intersystem

crossing of the singlet ground state molecule to the triplet state,

and reaction [18] is interpreted as collisionally induced intersystem

crossing of triplet to the singlet ground state. Since it is reasonable

to expect that this reaction might also occur spontaneously, the

following step

$$ES^\dagger \rightarrow ES^* \qquad\qquad [21]$$

must be included in the kinetic scheme presented earlier. ES^* is the

vibrationally energized molecule which can also revert to an

unenergized state by loss of vibrational energy. The observed variation

of order with temperature, mentioned earlier, would be explained by a

temperature dependence of this reaction. Since the molecule $ES^\dagger$ is in

an excited state, emission might occur

$$ES^\dagger \rightarrow ES + h\nu .$$

This is unlikely, however, since the Franck-Condon factors governing the

transition would be small. Because S_2, as does O_2, exists as a triplet

in its ground state, reaction [19] is not only energetically favorable

but also spin allowed on the basis of the Wigner spin conservation

rule. The rate expression for olefin formation can now be written as

$$R = \frac{2k_{15}k_{17}k_{19}[ES]^2}{k_{16}k_{19}[ES] + k_{16}k_{18}[ES] + k_{18}k_{17} + k_{17}k_{19} + k_{19}k_{21}}$$

Presumably, step [21] involving an intersystem crossing of

triplet state episulphide to the ground state has a small energy

barrier and is less favorable than collisionally induced intersystem

crossing, since a considerable geometry change is involved (116).

Hence, reaction [18] predominates over reaction [21]. The [ES] terms,

therefore, cancel out in the second product term of the equation, and

the equation takes on the form of the unimolecular expression

multiplied by a constant, $k_{19}/(k_{18} + k_{19})$. The episulphide reaction,

therefore, is not a unimolecular one in a strict sense, but can be

called pseudo-unimolecular. Since the production of the intermediate,

the triplet episulphide, follows unimolecular behavior, it is interesting

to discuss the previous conclusions in such a context.

Of the unimolecular reactions that have been investigated and

described in the literature, the vast majority presumably occur by spin

allowed reactions in the singlet ground state and only a small portion

have been shown to proceed by spin forbidden intersystem crossing to

the triplet state. Of the latter group of reactions, the main examples

are the dissociation of small molecules such as N_2O (82), CO_2 (83)

and CS_2 (84).

The obvious feature of spin forbidden unimolecular reactions

is that the pre-exponential factors are always less than those for spin

allowed reactions, which are of the order of $10^{14} - 10^{15}$ sec^{-1}. In

the case of the reaction

$$N_2O(^1\Sigma^+) \rightarrow N_2(^1\Sigma_1^+) + O(^3P)$$
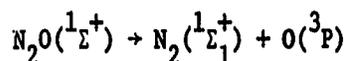
the A-factor was found to be $10^{11.1}$ sec^{-1}. It is sometimes possible to

relate the experimental A-factor to the probabilities of curve crossing,

if one has a knowledge of the nature of the potential surface at the

point of crossing. Unfortunately, this is only possible for small

molecules, of which N_2O has met with most success. In the absence of a

better theory to describe such reactions, one must resort to Absolute

Rate Theory, in which the rate constant can be expressed as

$$k = \kappa \frac{kT}{h} \frac{Q^{\ddagger}}{Q} e^{-E_a/RT} . \qquad [22]$$

The terms in the equation were defined in Chapter I.

As pointed out by Laidler (82), if $\kappa = 1$ and $Q^{\ddagger}/Q$ is close to unity, the pre-exponential factor will be close to 10^{13} sec^{-1}. Since the ratio of the partition functions for most reactions is somewhat higher than unity, the frequency factors are usually about 10^{14} sec^{-1}. The low pre-exponential factors observed in spin forbidden reactions are commonly attributed to small values of the transmission coefficient. Thus, for the case of the pyrolysis of N_2O, the crossing of a repulsive and attractive potential curve gives rise to a curve splitting of a few hundred cal/mole, leading to a transmission coefficient of about 10^{-2}. The analogous situation occurs in the decomposition of CO_2 and CS_2 which have frequency factors of $10^{11.4}$ sec^{-1} and $10^{12.6}$ sec^{-1}, and consequently must have transmission coefficients of about 10^{-2} and 10^{-1}.

Inspection of the pre-exponential factors found for the pyrolysis of episulphides, listed in Table III-XXIII, reveals a behavior much the same as that of the molecules described above. The values all lie below 10^{14} sec^{-1} and can again be attributed to the low transmission coefficients of intersystem crossing.

Pursuing the subject of pre-exponential factors somewhat further, it is instructive to compare those of the episulphide reaction with those of cyclopropane and ethylene oxide. The frequency factor for the isomerization of cyclopropane is $10^{16.1}$ sec^{-1} and for the

decomposition of ethylene oxide, $10^{14.5}$ sec^{-1}. According to

thermodynamic formulation of the Absolute Rate Theory, the unimolecular

rate constant can be expressed as

$$k = \kappa \frac{ekT}{h} \cdot e^{\Delta S^{\ddagger}/R} e^{-E_a/RT}$$

where $\Delta S^{\ddagger}$ is the entropy of activation and the other terms are the same

as in equation [22]. In the case of cyclopropane and ethylene oxide,

κ is assumed to be unity. Hence, the following entropies of activation

can be calculated:

$$\Delta S^{\ddagger}(C_3H_6) = 12.0 \text{ cal/}^o\text{mole}$$

$$\Delta S^{\ddagger}(C_2H_4O) = 5.7 \text{ cal/}^o\text{mole}$$

These values reflect an increase in the degrees of freedom of the

molecule as the ring rupture occurs. This is consistent with the models

reviewed in Chapter I which suggest that these molecules cleave to

produce loose biradicals with very small barriers to rotation of the

terminal methylene groups.

Similar calculations for the pyrolysis of episulphides

yield a negative entropy of activation. Naturally, such a result is

unreasonable since one does not expect the molecule to become more

constrained during reaction. If we keep in mind, however, that the

transmission coefficient might be about 10^{-1} as is the case for CS_2,

then the entropy of activation is estimated to be about 0.5 cal/^{o}mole.

One notes that the A-factors for propylene and ethylene episulphide

are the same at about $10^{12.54}$ sec^{-1} while trans-butene episulphide

exhibits a value of $10^{12.08}$ sec^{-1}. The two values are within the

respective experimental error limits and it is therefore difficult to
ascertain whether the difference is meaningful or not.

The low values for $\Delta S^{\ddagger}$ provide further evidence for the
postulate that episulphide decomposition occurs via a ring relaxed
species in which the terminal ends strongly interact. This fact probably
also provides a reasonable explanation as to why 1,2-hydrogen shifts
occur so readily in the $\cdot CH_2CH_2CH_2 \cdot$ and $\cdot OCH_2CH_2 \cdot$ species and not in the
sulphur analogue. Firstly, the C=S bond energy is not as large as the
C=C and C=O bond energies and there is consequently a smaller
driving force for the isomerization. Then, the strong residual binding
of the ring expanded episulphide is sufficient to prevent valence
saturation to occur by hydrogen shift. In the case of cyclopropane
and ethylene oxide in particular, the interaction is too small,
resulting in valence saturation by a 1,2-hydrogen shift. Naturally,
this can also occur by ring closure and this is indeed found to occur
as shown by the studies of cis- and trans-cyclopropane-d$_2$ and cis- and
trans-2,3-butene-2 oxide (27,25). In the former case, ring closure is faster
than the hydrogen shift and in the latter the opposite effect is
observed. Since there is no geometric isomerization in the episulphides,
one cannot determine the rate of ring reclosure.

It is interesting to note that sulphur atoms have been shown
to exhibit binding interaction over distances greater than a bond length
in molecules other than episulphides. In their studies on the thermal
decomposition of azobis (1-cyano-3-thiacyclohexane) [23] and azobis
(1-cyano-4-thiacyclohexane) [24],

$$\text{[23]}$$

$$\text{[24]}$$

Ohno and Ohnishi (85) found a decrease in the activation parameters

relative to the methylene analogue

$$\text{[25]}$$

Since the thiane ring is free of ring strain (10), the authors argue

that there is transannular participation of the sulphur atom at the β

or γ position in the ring, causing a stabilization of the radical:

The stabilization energy is estimated as approximately 2 kcal/mole.

The entropies of activation support the claim of sulphur atom

participation in the transition state, since $\Delta S^{\ddagger}$ for reactions [23]

and [24] were found to be 8.7 and 8.5 entropy units lower than for

reaction [25].

Presumably the binding interaction in the above radicals is not as strong as that found in the ring expanded episulphides, but this is not unexpected since the sulphur atom in these molecules is valence saturated. In the excited episulphide molecule however, there is radical character in both the sulphur and methylene moieties, which results in stronger interaction.

The thermal decomposition of episulphoxides bears a striking resemblance to that of episulphides, and it is instructive to compare the behavior of these molecules. As was pointed out in Chapter I, episulphoxides decompose via ring relaxation of a carbon-sulphur bond forming the corresponding biradical. This intermediate then undergoes loss of SO, yielding the olefin of the parent episulphoxide. Since this mode of decomposition is analogous to that found in episulphide pyrolyses, it would be interesting to compare the activation parameters for the two reactions. Unfortunately, the Arrhenius parameters for stilbene episulphoxide decomposition were not reported. Nevertheless, from a knowledge of the published first order rate constant, it is possible to estimate the activation energy if we assume a reasonable pre-exponential factor. Choosing $A = 10^{12.5}$ sec^{-1}, as is the case for episulphides, and since $k = 1.1 \times 10^{-5}$ sec^{-1} at 26°C (31), the activation energy is about 24 kcal/mole. (Increasing the assumed A-factor also increases the activation energy: thus for $A = 10^{16}$ sec^{-1}, which presumably would be an upper limit, the activation energy becomes 28 kcal/mole.) Comparison of these values with the enthalpy of reaction,

$$\text{(structure)} \longrightarrow \text{(structure)} \qquad \Delta H = 45.5 \text{ kcal/mole}$$

yields the interesting result, $E_a \ll \Delta H$. (The enthalpies of the substrate and biradical were determined using thermochemical group values as outlined in Appendix B.) This behavior also appears to be reflected in the pyrolysis of ethylene episulphoxide:

$$\begin{array}{c} CH_2 \!-\! CH_2 \\ \diagdown S \diagup \\ \downarrow \\ 0 \end{array} \longrightarrow C_2H_4 + SO \;.$$

The reaction is claimed to be first order and have an activation energy of 35 kcal/mole. Unfortunately, the exact mechanism by which reaction occurs was not reported. However, assuming that decomposition proceeds via a biradical,

$$\begin{array}{c} CH_2 \!-\! CH_2 \\ \diagdown S \diagup \\ \downarrow \\ 0 \end{array} \longrightarrow \begin{array}{c} \cdot CH_2 \!-\! CH_2 \\ \cdot S \\ \downarrow \\ 0 \end{array} \qquad \Delta H = 60 \text{ kcal/mole}$$

we again find that the enthalpy of reaction is considerably greater than the activation energy, as is the case for stilbene episulphoxide and episulphides. It should be noted that butene episulphoxide also has been shown to decompose via a ring opened intermediate (29, 30). Thus, it appears that episulphoxides like episulphides react via the intermediacy of an excited state of the molecule. The molecule in the excited state then decomposes by loss of sulphur monoxide in an exothermic process. Due to its thermodynamic instability, the fate of

the sulphur monoxide is presumably disproportionation to give elemental sulphur and sulphur dioxide (28). Naturally, the nature of the electronic excited state in episulphoxides is different from that of episulphides due to the presence of the electronegative oxygen atom. This might have the consequence of reducing the extent of bonding interaction between the radical centers, allowing some rotation about the C-C bond.

An obvious test for the intermediacy of a species in a low lying triplet state is the addition of a well known triplet quencher such as oxygen to the reaction system. Oxygen exists as a triplet in the ground state, $O_2(^3\Sigma_g^-)$ and has a low lying excited singlet state $(^1\Delta_g)$ at about 23 kcal/mole above the ground state (86). In order to investigate the possibility of triplet quenching, O_2 was added to the trans-butene episulphide system. A slight increase in the rate of reaction was found, and SO_2 was discovered as a reaction product. This can be attributed to the high reactivity of O_2 with episulphides:

$$\text{trans-}C_4H_8S + O_2 \rightarrow \text{trans-}C_4H_8 + SO_2 \qquad \Delta H = -75.5 \text{ kcal/mole.}$$
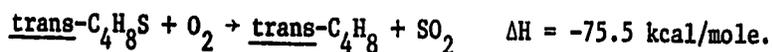
The reaction of triplet episulphide with O_2 is probably even more favorable since it would not only be more exothermic but also spin allowed. Unfortunately, therefore, O_2 cannot reliably be used as a test for the existence of the triplet episulphide.

CHAPTER IV

THE SECONDARY DEUTERIUM KINETIC ISOTOPE EFFECT

IN THE PYROLYSIS OF ETHYLENE EPISULPHIDE

A. Results and Discussion

The secondary deuterium isotope effect in the thermal

decomposition of ethylene episulphide and ethylene episulphide-d_4 was

determined by the co-pyrolysis of the two compounds at equal pressures.

The ethylenes were separated from the reaction mixture and then

analyzed by mass spectrometry. The relative amounts of C_2H_4 and

C_2D_4 were determined from calibrated mass spectra and the isotope

effect was obtained from the equation:

$$\frac{k_H}{k_D} = \frac{R(C_2H_4)}{R(C_2D_4)} \frac{P(C_2D_4S)}{P(C_2H_4S)}$$

In the calibration of the mass spectra, a number of known samples of

C_2H_4 and C_2D_4 in amounts corresponding to the expected decomposition

yields were measured quantitatively. About three to five recordings

of each sample were made and finally the peak heights calibrated to

the quantity of ethylene for both light and heavy molecules. In the

case of C_2D_4, the peak height ratio 32/28 was also determined, and was

found to be 0.594.

From the experimental ratio 32/28 for pure C_2D_4, the

contribution to the 28 peak by C_2D_4 can be subtracted, and thus from

the relative response factors for C_2H_4 and C_2D_4,

$rf(C_2H_4)/rf(C_2D_4) = 1.073$, the ratio of C_2H_4/C_2D_4 could be calculated. The response of the machine was periodically checked using mixtures of known composition.

The episulphide pressures were kept essentially equal to 115 torr. The results of a number of experiments done at different temperatures are given in Table IV-I.

The results presented show a normal secondary isotope effect for the thermolysis of ethylene episulphide with a magnitude of 1.16 at $190^\circ C$ and 1.20 at $230^\circ C$. This result is not unexpected since it is well known that most decomposition reactions demonstrate normal secondary isotope effects.

In an effort to derive some information on the mechanistic details of the decomposition, let us begin by examining equation [I-11] which was presented in Chapter I. As it was pointed out, a direct isotope effect of $k_H/k_D = 1.2$ requires a lowering of the vibrational frequencies, and therefore, a general loosening of the episulphide during passage from reactant to transition state. Undoubtedly, this process will be brought about by a change in the bonds to the sulphur atom and can conceivably occur in one of two ways;

i) by a perpendicular symmetric motion away from the C-C bond, in which the bonding characteristics of the S atom to both carbon atoms are the same, or

ii) by an asymmetric motion away from only one carbon atom yielding a ring distorted structure, described in the previous chapter.

TABLE IV-I

Isotope Effects as a Function of Temperature[a]

T^o[C]	C_2H_4/C_2D_4	C_2D_4S/C_2H_4S	k_H/k_D
189.0	1.171	1.013	1.189
189.1	1.147	1.017	1.164
189.1	1.089	0.984	1.106
191.0	1.143	0.989	1.130
189.6	1.195	0.992	1.185
		average k_H/k_D = 1.16 $\pm$ 0.04	
230.2	1.182	0.987	1.169
230.6	1.230	0.983	1.209
232.4	1.171	1.034	1.211
232.4	1.153	1.034	1.193
232.4	1.223	1.011	1.238
		average k_H/k_D = 1.20 $\pm$ 0.03	

a) total pressure about 230 torr, cell volume 373.4 cc

Since the decomposition kinetics implicate the involvement of the lowest triplet excited state as the reactive intermediate and this has been shown to possess a ring distorted equilibrium conformation, the distorted ring model is chosen as the transition state (Fig. IV-1).

As was pointed out earlier, the secondary isotope effect is due to changes in the force constants on going from reactant to the transition state. Since frequencies are directly related to force constants, we can equally well discuss the effect in terms of changes in the frequencies of the normal modes.

On the basis of theoretical calculations (43) of the ring distorted episulphide, we adopted a C^1C^2S angle of 100° and the rotational barrier for the C^1H_2 group of 23.6 kcal/mole. Since the bond between C^1 and S should become slightly weaker as the distance between the atoms increases and because of the gradual transition of the C^1H_2 sp^3 configuration towards sp^2, the out of plane angle of the C^1H_2 group is decreased somewhat from that of the episulphide. We shall assume that the C^2H_2 group remains largely unchanged.

Evaluation of the factor MMI in equation [1],

$$\frac{k_H}{k_D} = (MMI) \times (EXC) \times (ZPE), \qquad [1]$$

yields a value very close to unity, 1.008. This result is due to the fact that the structure of the activated complex does not differ significantly from that of the stable reactant. Consequently, the isotope effect must predominantly be due to changes in the
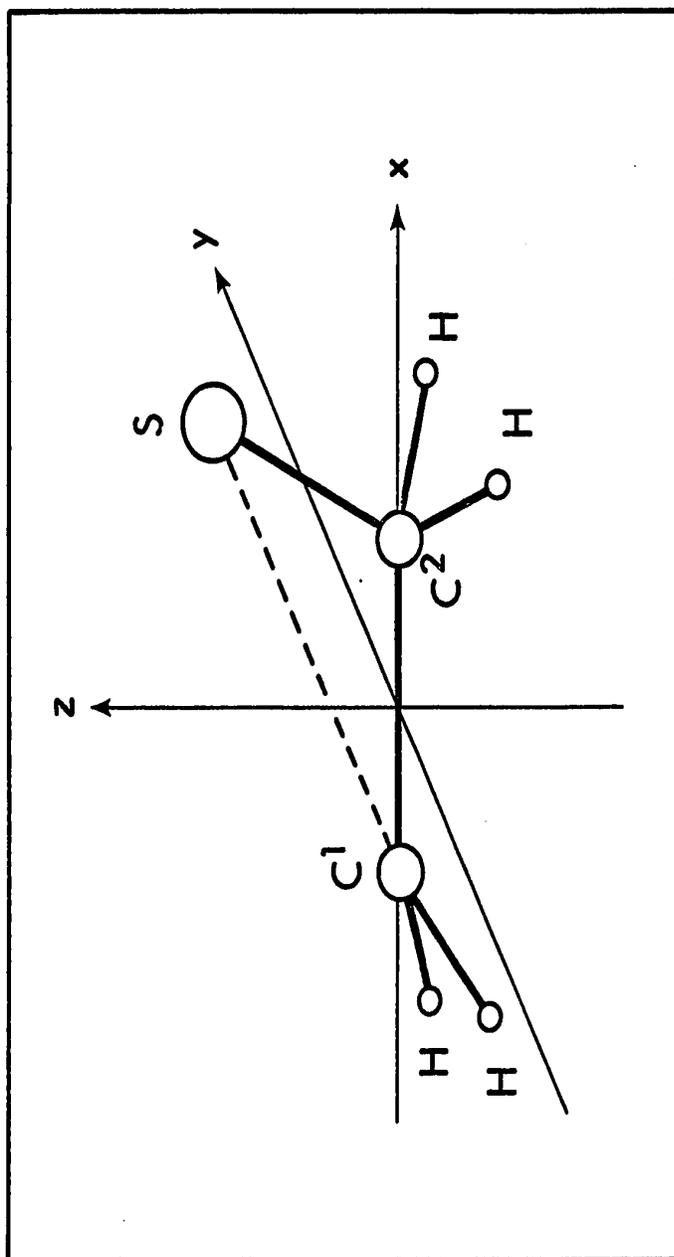
Figure IV-1. Model of the activated complex for C_2H_4S decomposition

vibrational frequencies during transition leading to the activated complex.

In the analysis of the vibrational contribution, the C^1S stretching motion which is not significantly sensitive to deuterium substitution was taken as the reaction coordinate. It was furthermore assumed that the C-H stretching modes remain essentially unchanged in the activated complex and do not contribute to the isotope effect. The normal vibrational frequencies of the activated complex were assigned by comparison to related frequencies in stable molecules (117).

For a normal isotope effect, $k_H/k_D > 1$, some of the force constants (frequencies) in the activated complex must be lower than those in the reactant. Due to the slight weakening of the C^1-S bond, we can assume a partial rehybridization of the C^1 atom from sp^3. Consequently, the frequencies of the C^1H_2 group can be expected to approach the values of the related frequencies in the ethylene molecule. It was on this basis, then, that the vibrational frequency of the C^1H_2 deformation mode was lowered from 1470 to 1410 cm^{-1}, (1343 cm^{-1} in C_2H_4) and the C^1H_2 wag mode from 1050 to 1000 cm^{-1} (947 cm^{-1} in C_2H_4). The value for the C^1H_2 twist mode was calculated from the height of the rotational barrier and found to be 772 cm^{-1}. The normal frequencies of the C^2H_2 group were assumed to be identical to those of the reactant. The vibrational frequencies of the reactant and activated complex with their contributions to the various factors in equation [1] are presented in Table IV-II. One observes that the changes in the frequencies discussed above reproduce the experimentally determined isotope effect quite well.

TABLE IV-II

Calculated Increments of Individual Vibrational Motions to

the Kinetic Isotope Effect[a]
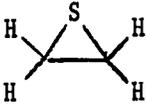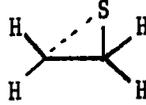
Vibration cm^{-1}			EXC	ZPE	EXC × ZPE
C-C stretch	1120	1120	1.000	1.000	1.000
CH$_2$	1470	1410	0.996	1.051	1.046
deform	1450	1450	1.000	1.000	1.000
CH$_2$	875	875	1.000	1.000	1.000
rock	824	810	0.997	1.005	1.002
CH$_2$	1040	1040	1.000	1.000	1.000
wag	1050	1000	1.005	1.096	1.102
CH$_2$	1100	1100	1.000	1.000	1.000
twist	920	772	0.978	1.067	1.043

$$\frac{k_H}{k_D} = MMI \times \Pi(EXC \times ZPE) = 1.21; \quad \Pi(EXC \times ZPE) = 1.203$$

a) Ref. 117

Let us consider the effects of changes in the configuration about the C^2 atom as well. Any changes required in the C^2H_2 group would probably be such that the structure and corresponding normal frequencies will approach those of a $-CH_2-S-$ group in a mercaptan molecule. Since the frequencies of the CH_2 wag and CH_2 twist modes in ethyl mercaptan are 1269 and 1246 cm^{-1} respectively, a corresponding modification of the activated complex in this direction necessitates an increase in the frequencies of the C^2H_2 group. An increase in the frequencies of the transition state generates an inverse isotope effect ($k_H/k_D < 1$), and reduces the normal effect caused by the frequency changes in the C^1H_2 group. Therefore, in order to reproduce the experimentally obtained value of $k_H/k_D = 1.2$, a further decrease in the frequencies of the C^1H_2 group would be necessary. Such a change would make these frequencies essentially the same as those of the related values in the ethylene molecule. However, such changes in the transition state lead to inconsistencies. If the above changes on the C^2H_2 group are made, we force the C^1H_2 group into the configuration of one-half an ethylene molecule attached to a CH_2-S mercaptyl-like grouping in which case the interaction between C^1 and S should be negligibly small. In fact, the experimental stereochemical results and the theoretical results discussed previously both argue against this. Needless to say, the above frequency changes at C^2H_2 lead to an unrealistic model of the transition state, and it can be concluded that the findings of the present kinetic isotope effect study support a mechanism involving the intermediacy of a ring distorted episulphide species.

It is interesting to compare the isotope effect in ethylene
episulphide pyrolysis with that obtained in the addition of $S(^3P)$ to
ethylene (39). In the latter reaction, the isotope effect k_D/k_H
for C_2H_4 and C_2D_4 was found to be inverse with a value of 1.14.
The experimental value could be reproduced by computation using a model
analogous to the one presented here.

Let us consider the following schematic illustration of the
relative positions of the potential surfaces for ring distortion of
ground state ethylene episulphide (I), the lowest triplet state of the
episulphide (II) and the surface for initial sulphur atom approach to
ethylene (III):
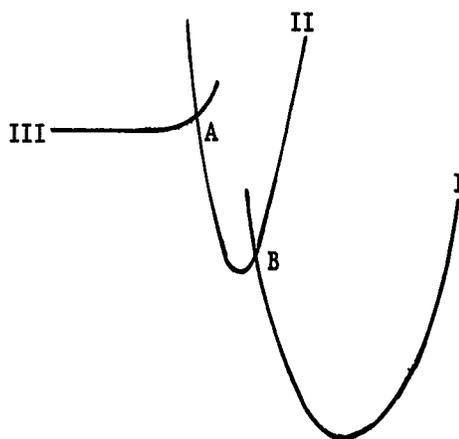
Point A represents the transition state for the
$S(^3P) + C_2H_4$ addition reaction and B the one for episulphide
decomposition and one notes that the two positions both lie close
to the equilibrium configuration of the triplet state. The successful
computations in the estimation of the isotope effects using a similar
transition state for the two reactions, namely the theoretically
derived lowest non-vertical, ring distorted episulphide triplet state,

lend further support to the decomposition mechanism postulated in the present study.

Further comparison of the two reactions reveals that the isotope effect is virtually temperature independent over the temperature range studied. Because of the narrowness of the temperature range employed, however, this fact cannot be exploited in an interpretation of the isotope effect in the present study. The model calculations of Vogel and Stern (73), for example, show that temperature dependencies can be extremely complex, exhibiting minima, maxima and inflections. While a reasonable understanding of a system requires values of k_H/k_D over a fairly large temperature range, it still remains a difficult task.

CHAPTER V

PYROLYSIS OF ETHYLENE EPISULPHIDE

IN THE PRESENCE OF OLEFINS

As mentioned in Chapter III, olefins exhibit the unique

effect of quenching the rate of decomposition of episulphides. In

an effort to shed some light on this aspect of episulphide chemistry,

the effect of a number of different olefins was investigated. In

particular, it was hoped that these results would provide further

insight into the intermediacy of the triplet excited state in the

pyrolysis of episulphides.

A. Results

1) The Pentene-1-Ethylene Episulphide System

The pyrolysis of the episulphide was carried out at a

constant substrate pressure of about 100 torr, with varying pressures

of added pentene-1 in the temperature range 207 to 241°C. Owing to the

formation of an azeotrope, it was not possible to study the reaction

at pentene-1/episulphide ratios greater than about three.

The results of this study are presented in Tables V-I and

II, and the quenching effect of the olefin at different temperatures

is illustrated in Figs. V-1 to 4. The rate of ethylene formation is

seen to decrease first upon addition of the olefin, and then levels

off to constant values. Since the amount of quenching was temperature

dependent, varying from 51% at 207°C to 80% at 241°C, an Arrhenius

plot was made for the reaction in the level-off region. The results

are presented in Tables V-III, and the corresponding Arrhenius plot,

shown in Fig. V-5, yields an apparent A-factor of

$\log A = 5.68 \pm 0.42 \text{ sec}^{-1}$ and an apparent activation energy of

25.4 ± 1.0 kcal/mole.

2) The cis-Butene-2-Ethylene Episulphide System

As in the pentene-1/episulphide system, the episulphide

pressure was kept constant at about 110 torr. Analysis of the reaction

mixture revealed the presence of ethylene, as expected, and also large

quantities of trans-butene-2 and a small quantity of cis-butene

episulphide. The results are presented in Tables V-IV. The cis-butene

episulphide yield was not always determined and was usually small, of

the order of less than 1 µmole at 225°C and at pressures of 110 torr

C_2H_4S and 422 torr cis-butene.

As in the case when pentene-1 was added to the episulphide,

azeotrope formation occurs when a large excess of olefin is used. In

the case of butene-2, it was possible to obtain ratios of olefin to

episulphide up to 4.8 when using an episulphide pressure of 100 torr.

As illustrated by the results shown in Table V-IV and Fig. V-6, the

quenching behavior is similar to that found when pentene-1 was added to

the episulphide. The corresponding plot of the trans-butene yield at

varying cis-butene/ethylene episulphide ratios is shown in Fig. V-7.

Due to the problem of azeotrope formation, the product yields

illustrated at a butene/episulphide ratio of 6.2 were estimated from

an experiment at lower episulphide pressure, assuming first order

kinetics.

In an effort to determine the order of ethylene formation at the level-off region, the reaction was studied at varying episulphide pressures keeping the cis-C_4H_8/C_2H_4S ratio and temperature constant. The results of these experiments are presented in Table V-V and Fig. V-8. From the slope of a plot of log rate vs. log pressure, the order for C_2H_4 formation is found to be 1.0. The order for trans-butene formation was also investigated and found to be 1.2 with respect to episulphide. Since Figs. V-6 and 7 illustrate that the rate of trans-butene and ethylene formation level-off at a large excess of cis-butene, one concludes that rates of formation are independent of cis-butene pressure. On the basis of this result, all rate constants in the episulphide-olefin system were calculated as being first order with respect to episulphide.

In order to gain further understanding of the reaction system, the Arrhenius parameters for the formation of ethylene and trans-butene in the level-off region were determined. A least means square treatment of the Arrhenius plots, shown in Figs. V-9, gives the following apparent A-factors and activation energies:

	log A (sec^{-1})	E_a (kcal/mole)
C_2H_4	5.85 $\pm$ 1.02	26.6 $\pm$ 1.8
trans-C_4H_8	12.46 $\pm$ 1.03	37.9 $\pm$ 2.3

Due to the very small yields of cis-butene episulphide and the concommittant difficulty in obtaining reproducibility, the Arrhenius parameters for this product were not determined. It was also not possible to determine the stereospecificity of the reaction yielding cis-butene episulphide.

TABLE V-I

Variation of the C_2H_4 Yield with Added Pentene-1 in the

Pentene-1/C_2H_4S System

$P(C_2H_4S)$ [torr]	$P(C_5H_{10}\text{-}1)$ [torr]	$\dfrac{P(C_5H_{10}\text{-}1)}{P(C_2H_4S)}$	C_2H_4 [μmoles]
		207.4°C [a]	
97.6	-	0	12.35
98.4	13.7	0.14	8.23
95.8	28.1	0.29	7.00
99.5	50.7	0.51	6.55
96.8	100.7	1.04	6.18
92.6	103.6	1.12	6.16
96.1	210.0	2.18	6.32
95.0	296.0	3.12	6.03
		214.7°C [b]	
100.2	-	0	19.31
99.1	26.7	0.27	9.21
100.6	54.8	0.54	7.46
95.9	100.6	1.05	7.01
100.3	299.4	2.99	6.32

a) all runs 60 min, cell volume 406.4 cc

b) all runs 50 min, cell volume 406.4 cc
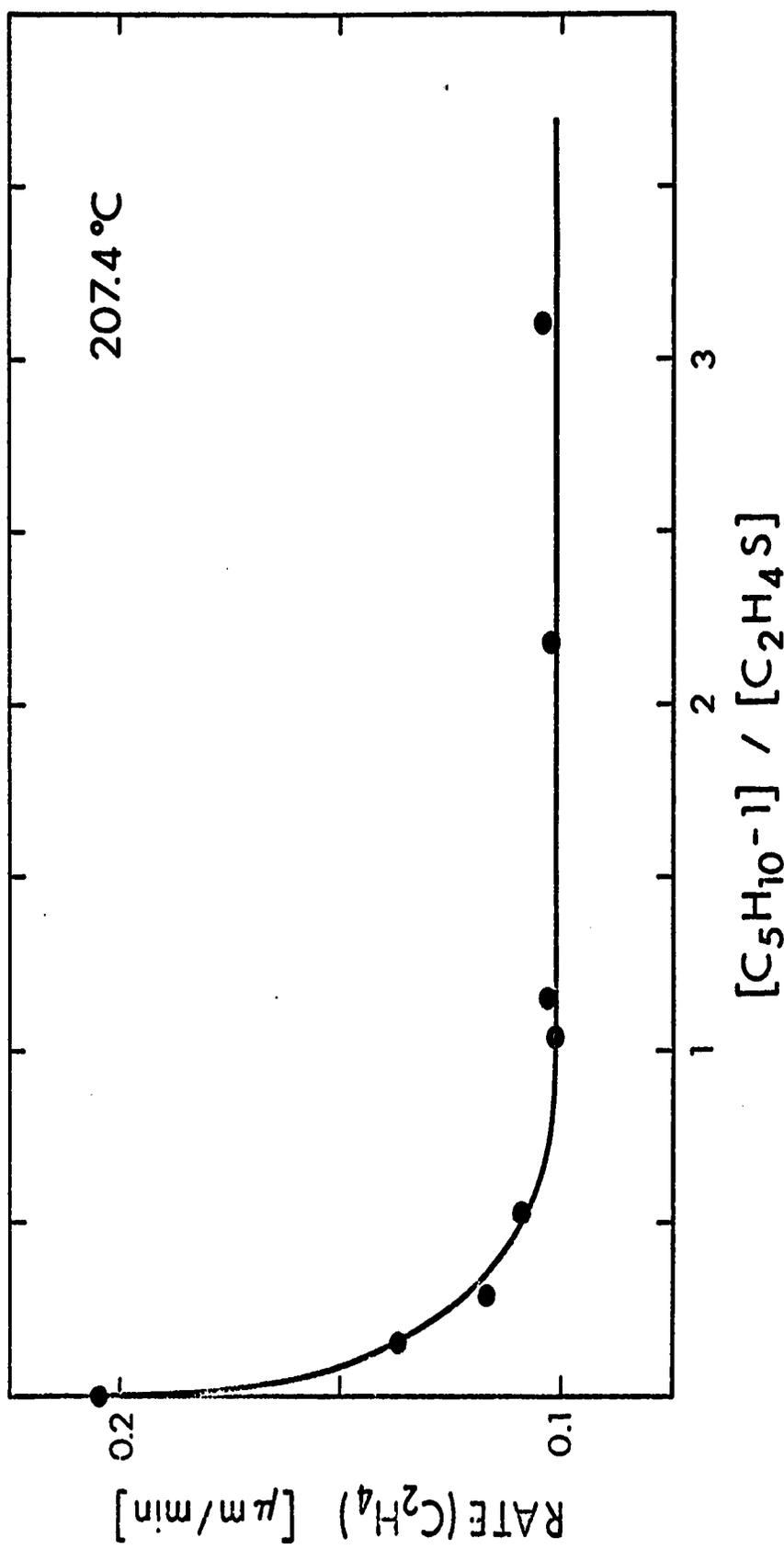
Figure V-1. Effect of added pentene-1 on C_2H_4S pyrolysis
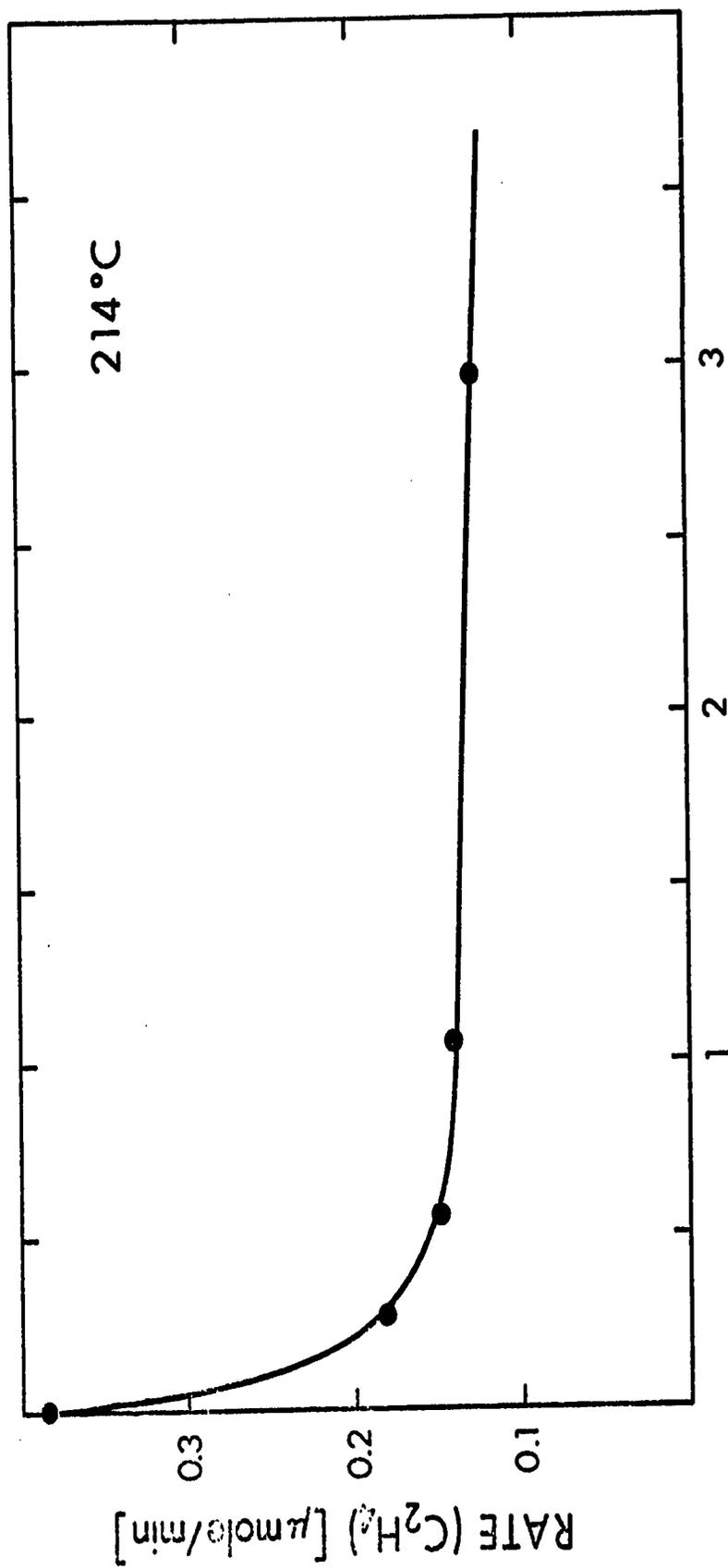
Figure V-2. Effect of added pentene-1 on the decomposition of C_2H_4S

TABLE V-II

Variation of the C_2H_4 Yield with Added Pentene-1 in the

C_5H_{10}-1/C_2H_4 System

$P(C_2H_4S)$ [torr]	$P(C_5H_{10}$-1) [torr]	$\dfrac{P(C_5H_{10}\text{-}1)}{P(C_2H_4S)}$	C_2H_4 [μmoles]
		223.3°C [a]	
92.2	-	0	33.85
96.5	21.3	0.22	22.50
97.7	48.3	0.50	15.57
96.7	96.3	0.99	10.84
98.7	201.9	2.05	10.36
		241.3°C [b]	
102.5	-	0	63.80
103.9	24.7	0.24	47.61
104.8	53.5	0.51	34.04
103.7	100.7	0.97	26.60
107.1	162.4	1.52	14.70
97.6	218.1	2.23	14.70
109.7	284.9	2.60	12.53

a) all runs 40 min, cell volume 406.4 cc

b) all runs 20 min, cell volume 406.4 cc
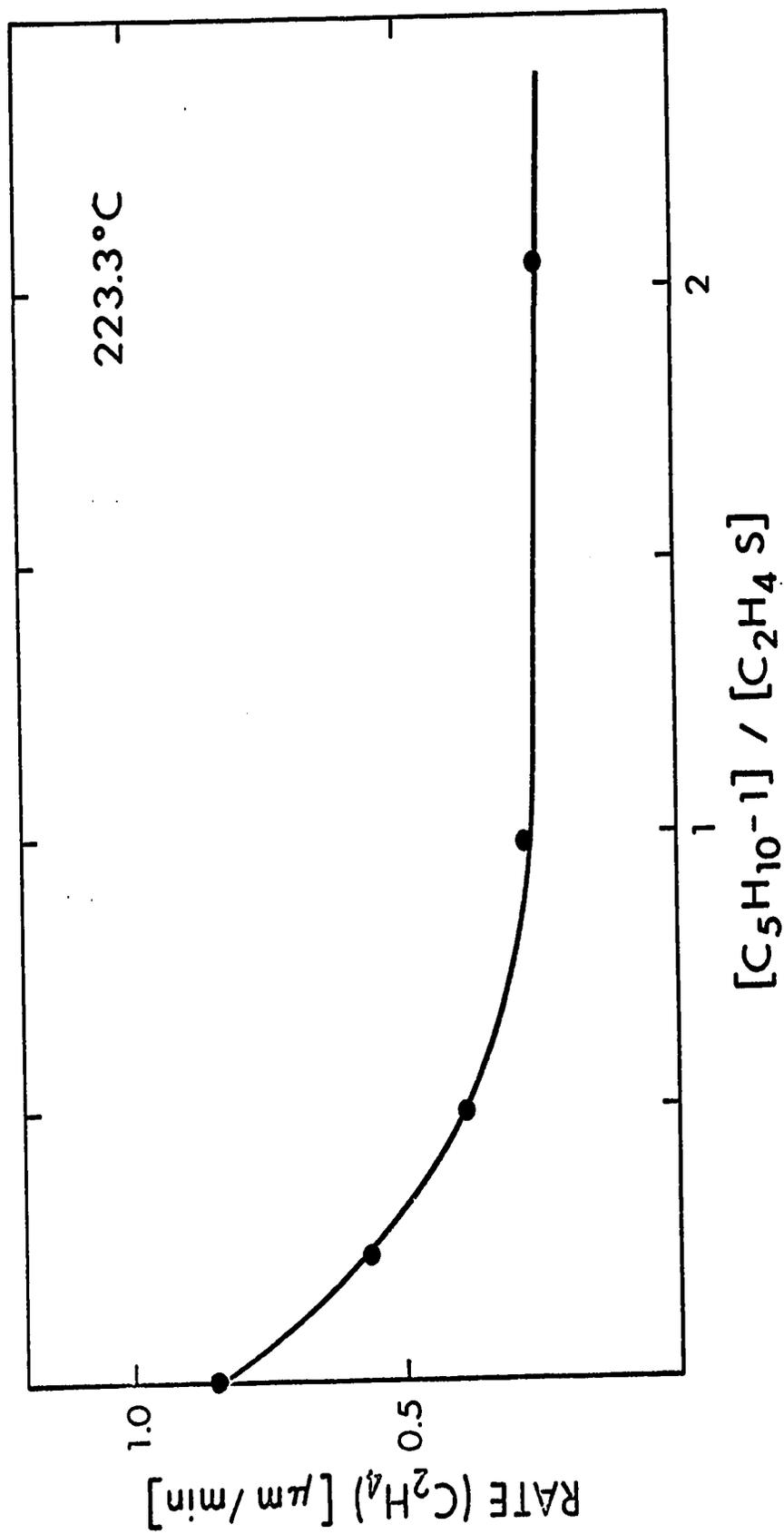
Figure V-3. Effect of added pentene-1 on the decomposition of C_2H_4S
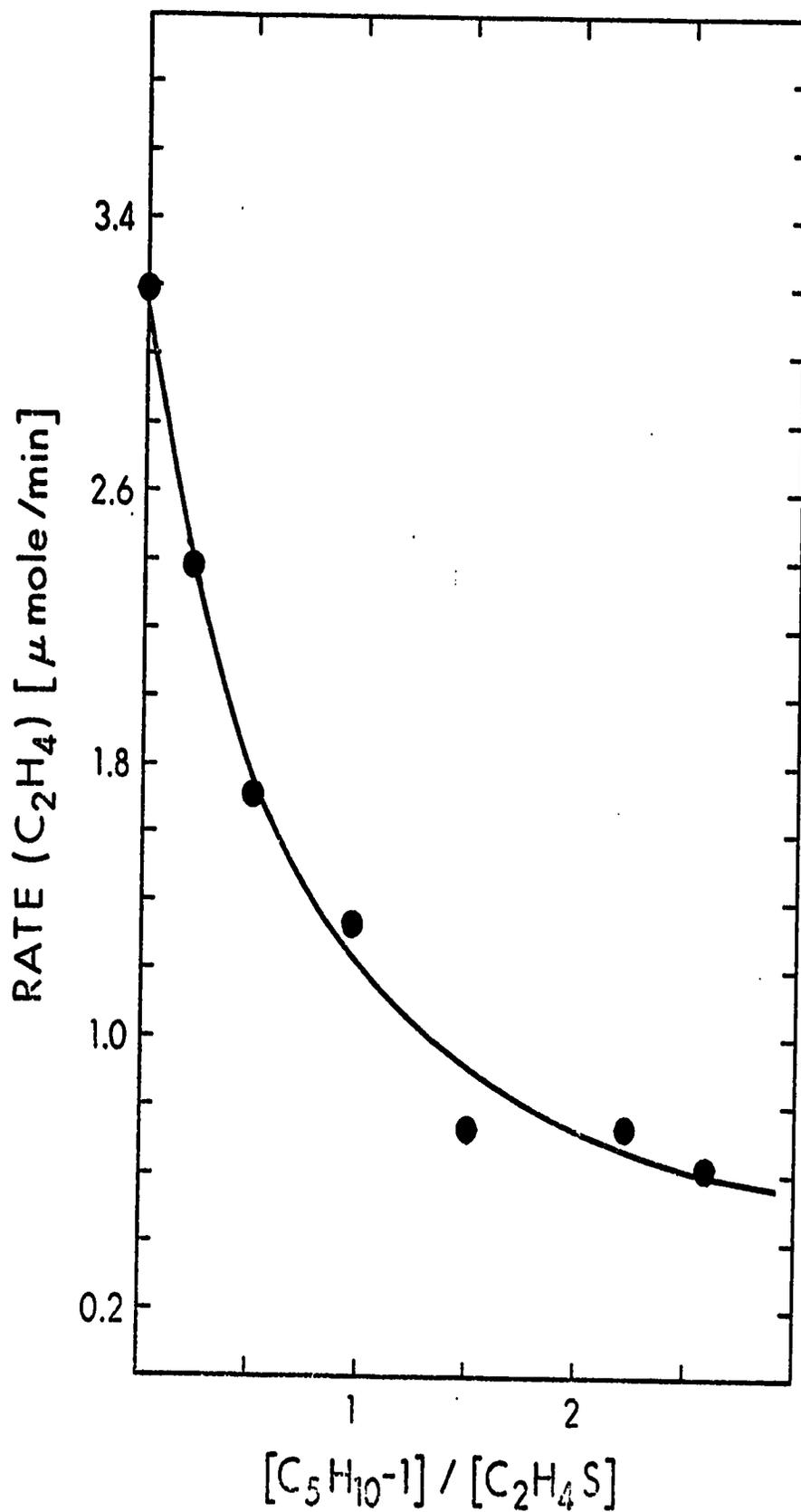
Figure V-4. Effect of added pentene-1 on the decomposition of C_2H_4S at 241°C

TABLE V-III

The Pentene-1-Ethylene Episulphide System. Variation of the C_2H_4 Yield

with Temperature at an Excess of Pentene-1 [a]

T [°C]	C_2H_4 [µmoles]	$\dfrac{[C_5H_{10}\text{-}1]}{[C_2H_4S]}$	Time [min]	log k[b] [sec^{-1}]
241.3	12.53	2.60	20	-5.122
223.3	10.36	2.04	40	-5.471
207.4	6.03	3.12	60	-5.885
214.2	6.32	2.99	50	-5.800

a) $[C_2H_4S] = 3.14 \times 10^{-9}$ M, cell volume = 406.4 cc

b) first order in C_2H_4S
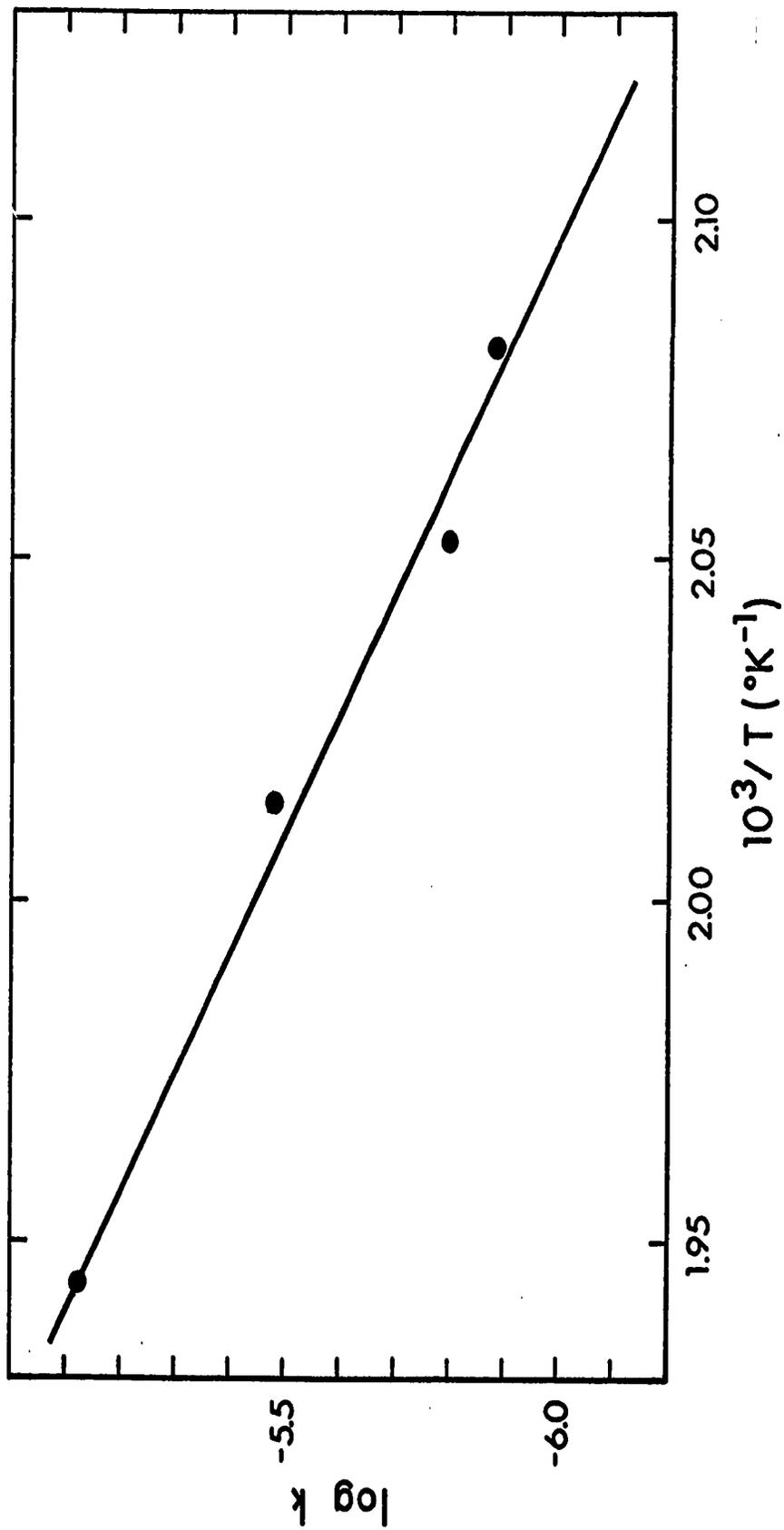
Figure V-5. Arrhenius plot for C_2H_4 formation in the pentene-$1/C_2H_4S$ system

TABLE V-IV

Variation of the C_2H_4 and trans-C_4H_8 Yields with Added

cis-Butene Pressure in the cis-C_4H_8-C_2H_4S System at 225°C [a]

$P(C_2H_4S)$ [torr]	$P(cis-C_4H_8)$ [torr]	$\dfrac{P(cis-C_4H_8)}{P(C_2H_4S)}$	C_2H_4 [μmoles]	trans-C_4H_8 [b] [μmoles]
110.2	0	0	36.2	0
104.5	74.0	0.71	23.8	166.5
106.1	158.9	1.50	20.1	278.6
106.4	323.8	3.04	12.2	281.7
114.0	480.6	4.22	12.9	345.7
108.2	518.1	4.79	7.2	302.0
79.3	493.2	6.22	6.7	204.0

a) all runs 45 min, cell volume 365.8 cc

b) blank runs with cis-butene alone did not yield any trans-butene
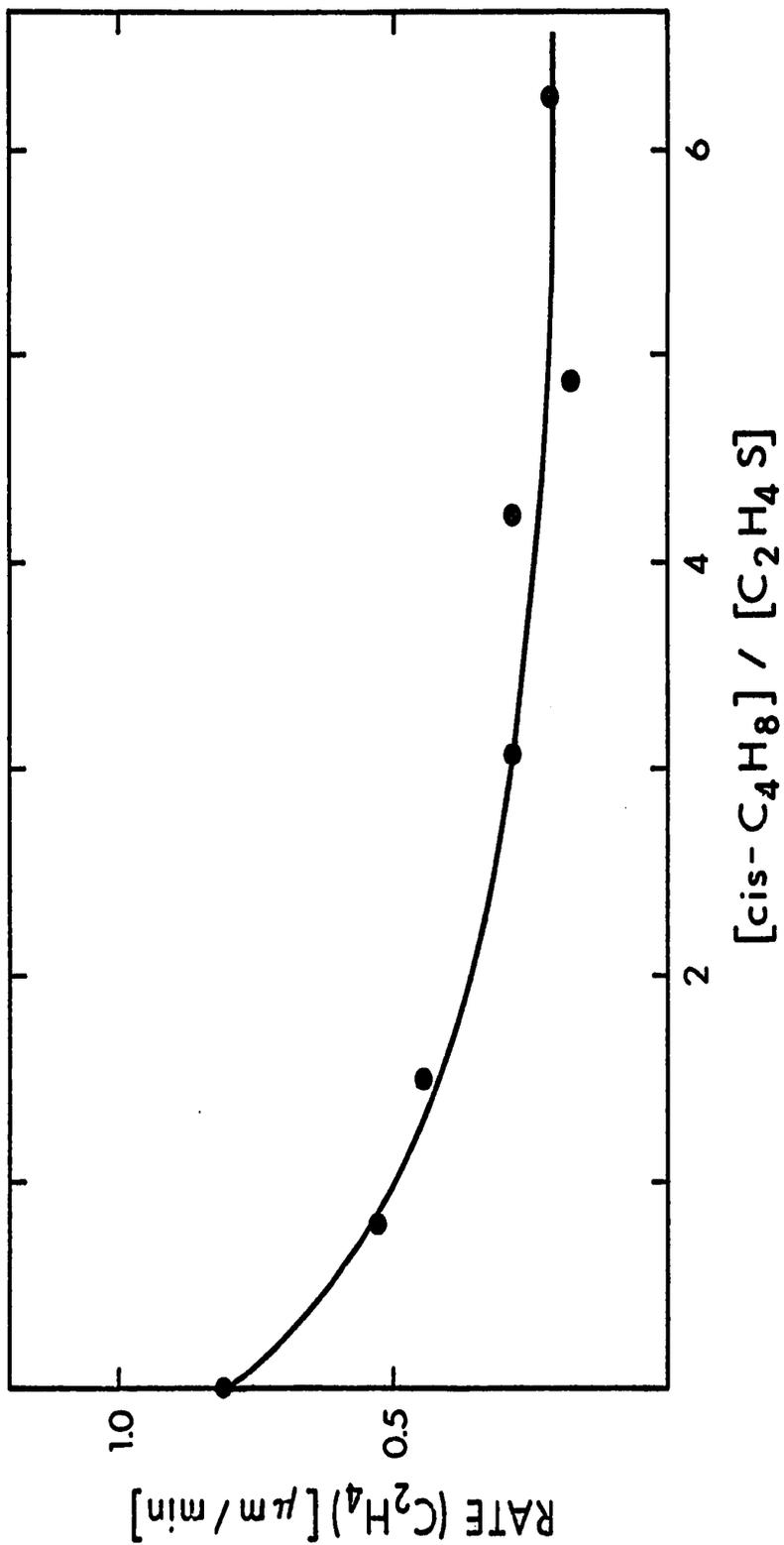
Figure V-6.   Effect of added cis-butene on the C_2H_4S decomposition at $225^\circ C$
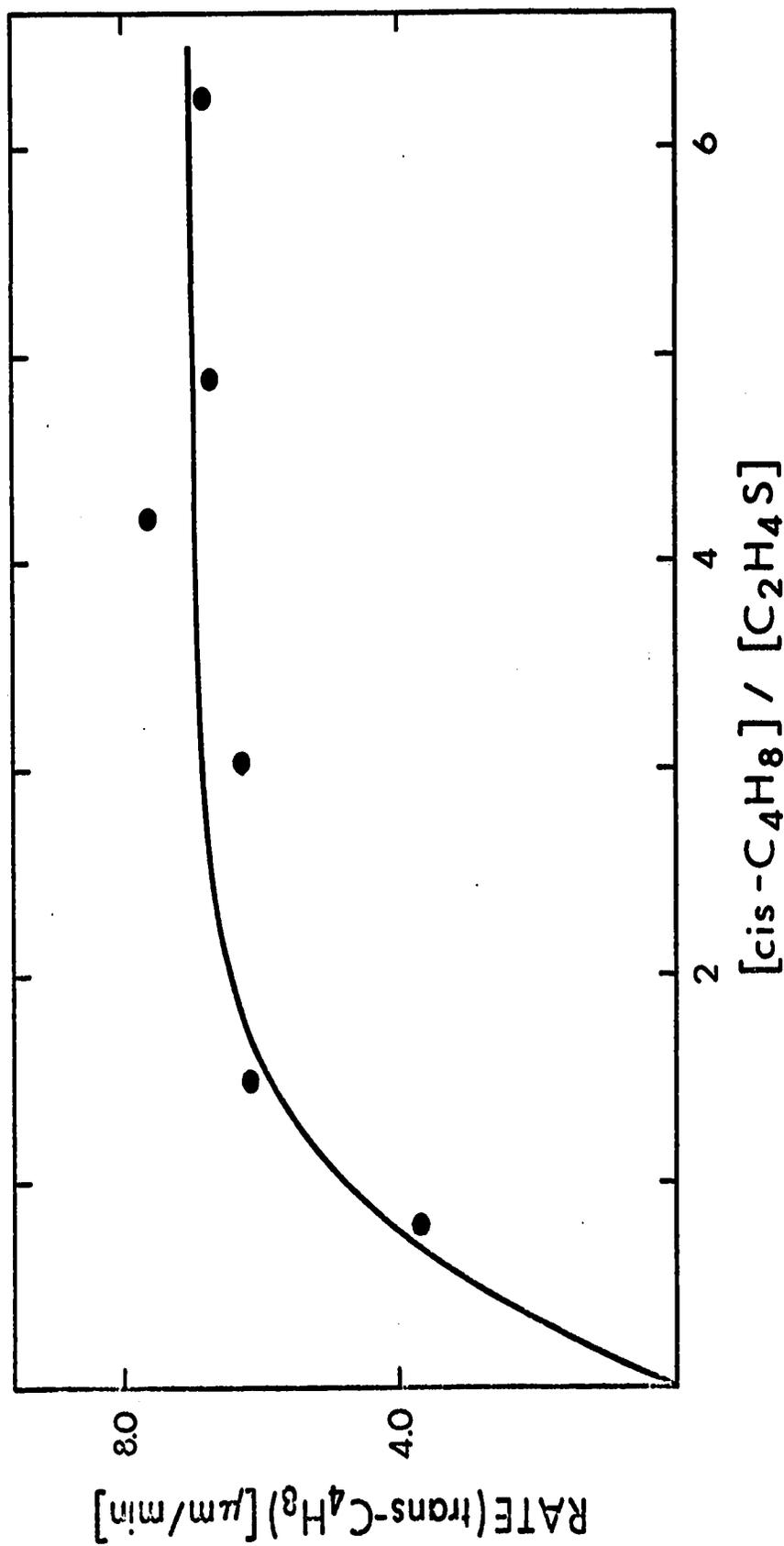
Figure V-7. Rate of *trans*-butene formation with added *cis*-butene in the *cis*-C_4H_8/C_2H_4S system

TABLE V-V

The cis-Butene/Ethylene Episulphide System. Variation of the C_2H_4 and

trans-Butene Yields with Pressure at an Excess cis-Butene [a]

P(C_2H_4) [torr]	P(cis-C_4H_8) [torr]	C_2H_4 [μmoles]	trans-C_4H_8 [μmoles]	log P(C_2H_4)	log Rate (C_2H_4)	log Rate (trans-C_4H_8)
73.5	213.6	8.3	180.4	1.866	−0.734	0.603
106.4	323.8	12.2	281.7	2.027	−0.566	0.796
134.9	417.3	16.9	387.4	2.130	−0.423	0.935

a) all runs 45 min, 225°C
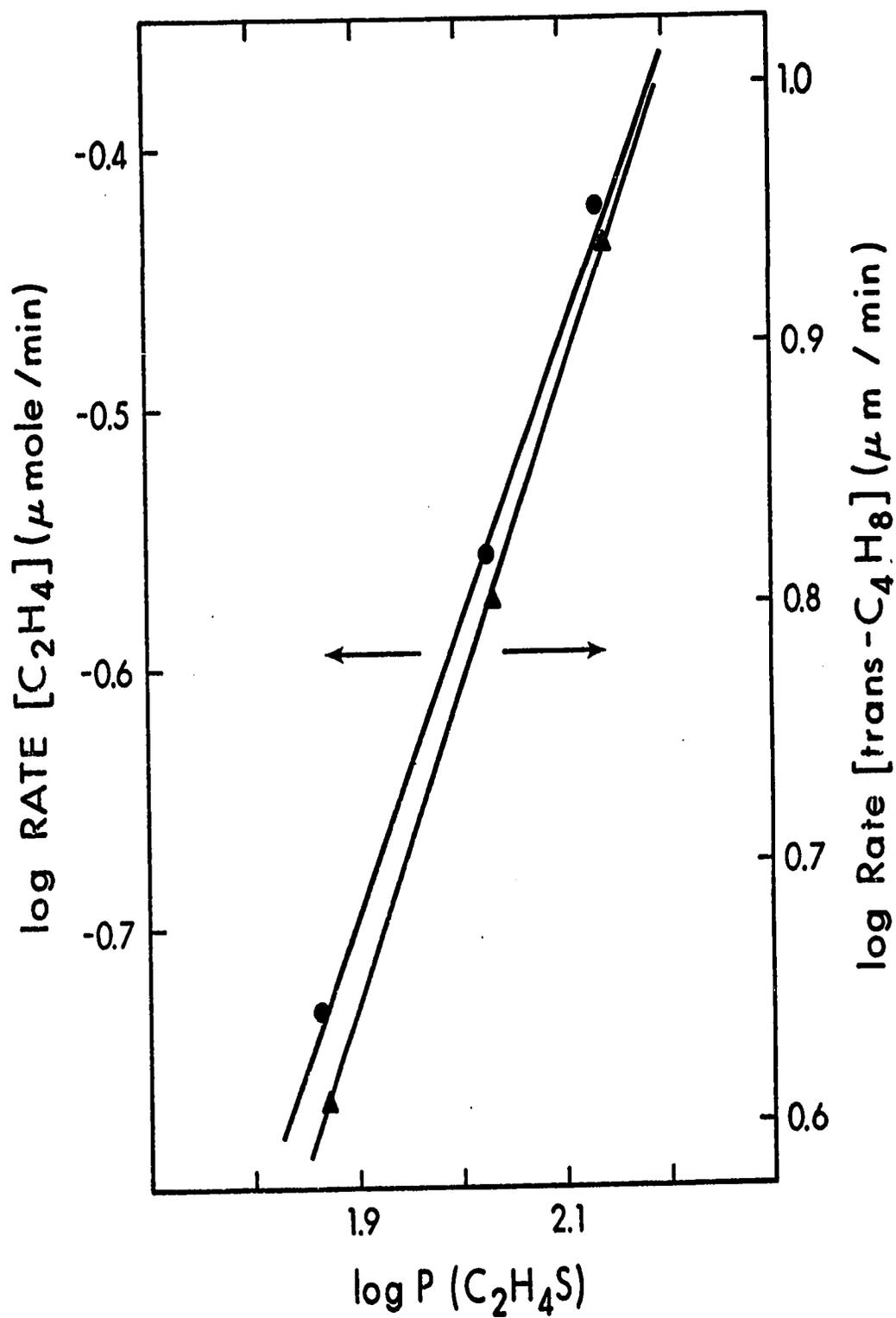
Figure V-8. Order plot for C_2H_4 and _trans_-C_4H_8 formation

TABLE V-VI

The cis-Butene-Ethylene Episulphide System. Variation of the C_2H_4 and trans-C_4H_8 Yields with Temperature at an Excess of cis-Butene [a]

T [°C]	C_2H_4 [µmoles]	trans-C_4H_8 [µmoles]	$\frac{[cis\text{-}C_4H_8]}{[C_2H_4S]}$	Time [min]	log k (C_2H_4)[b] [sec^{-1}]	log k (trans-C_4H_8)[b] [sec^{-1}]
202.7	5.0	45.4	3.49	60	-5.551	-5.011
188.5	4.6	34.0	3.46	90	-5.894	-5.354
213.1	7.5	106.5	3.50	60	-5.182	-4.642
237.2	12.9	367.1	4.27	20	-4.239	-3.699
224.5	12.2	345.7	4.23	45	-4.646	-4.105

a) $[C_2H_4S] = 3.49 \times 10^{-9}$ M, cell volume 365.8 cc

b) first order in C_2H_4S

164
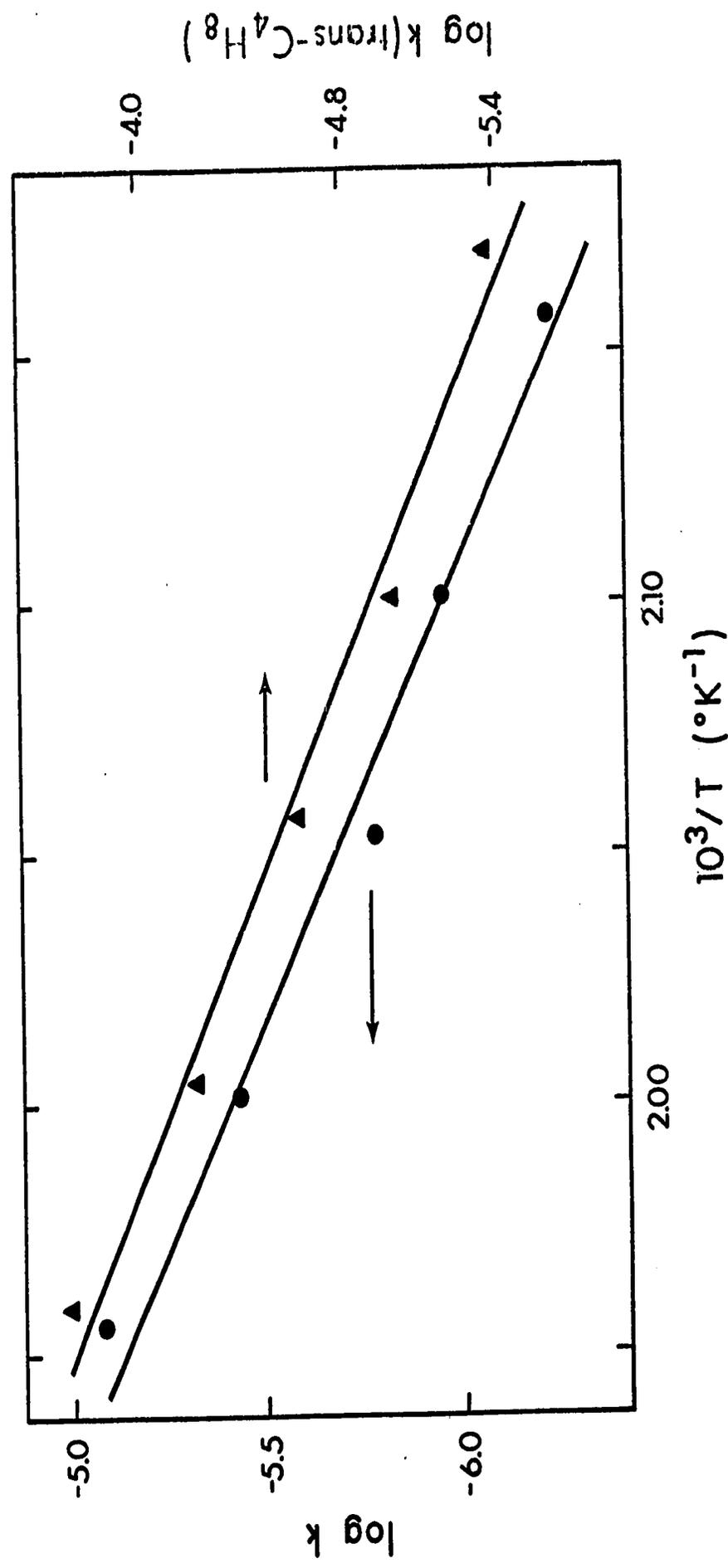
Figure V-9. Arrhenius plot for C_2H_4 (●) and $trans$-C_4H_8 (▲) formation in the cis-C_4H_8/C_2H_4S system

In order to eliminate the possibility of monoradical reactions occurring, NO was added to the reaction mixture. The experiment was carried out at $225^{o}C$ and substrate pressures of $P(C_2H_4S) = 111$ torr, $P(\underline{cis}\text{-}C_4H_8) = 430$ torr and $P(NO) = 18$ torr. The yields of ethylene and trans-butene were 11 and 331 μmoles respectively, the same as obtained without the presence of NO (Table V-IV).

3) The Propylene-Ethylene Episulphide System

As in the previous systems, the reaction was carried out using an episulphide pressure of about 110 torr. The quenching behavior of propylene was not expected to be very different from that of pentene-1 or cis-butene-2, and consequently only the temperature dependence of the ethylene formation in the level-off region was investigated. The results of these experiments are presented in Table V-VII. The apparent Arrhenius parameters for ethylene formation were obtained from the plot in Fig. V-10 and were found to be

$$\log A = 4.81 \pm 0.20 \text{ sec}^{-1} \text{ and } E_a = 23.49 \pm 0.45 \text{ kcal/mole.}$$

4) The Trimethylethylene-Ethylene Episulphide System

Trimethylethylene (TME) was found to form an azeotrope with ethylene episulphide even more readily than pentene-1 or cis-butene at a pressure of C_2H_4S of 100 torr. Therefore, in order to obtain suitably high TME/C_2H_4S ratios it was necessary to use a lower pressure of episulphide of 88 torr. The results of this study are presented in Tables V-VIII and V-IX. An illustration of the quenching effect of TME on episulphide decomposition is shown in Fig. V-11. The reduced portion of decomposition is about 44% as compared to

TABLE V-VII

The Propylene/Ethylene Episulphide System. Variation of the

C_2H_4 Yield with Temperature at an Excess of Propylene [a]

T [°C]	C_2H_4 [μmoles]	$\frac{[C_3H_6]}{[C_2H_4S]}$	Time [min]	log k[b] [sec^{-1}]
223.6	11.04	3.68	45	-5.505
239.9	9.67	4.53	20	-5.203
199.6	4.49	3.42	60	-6.052

a) $[C_2H_4S] = 3.63 \times 10^{-9}$ M, cell volume 365.8 cc

b) first order in C_2H_4S

TABLE V-XIII

Variation of the C_2H_4 Yield with Added Trimethylethylene

in the TME/C_2H_4 System at 201.6°C [a]

P(C_2H_4S) [torr]	P(TME) [torr]	$\frac{P(TME)}{P(C_2H_4S)}$	C_2H_4 [μmoles]
90.0	-	0	5.45
88.0	45.7	0.52	4.04
88.0	134.5	1.53	3.74
89.8	218.4	2.43	3.00
87.4	306.9	3.51	3.21

a) All runs 60 min, cell volume 365.6 ml
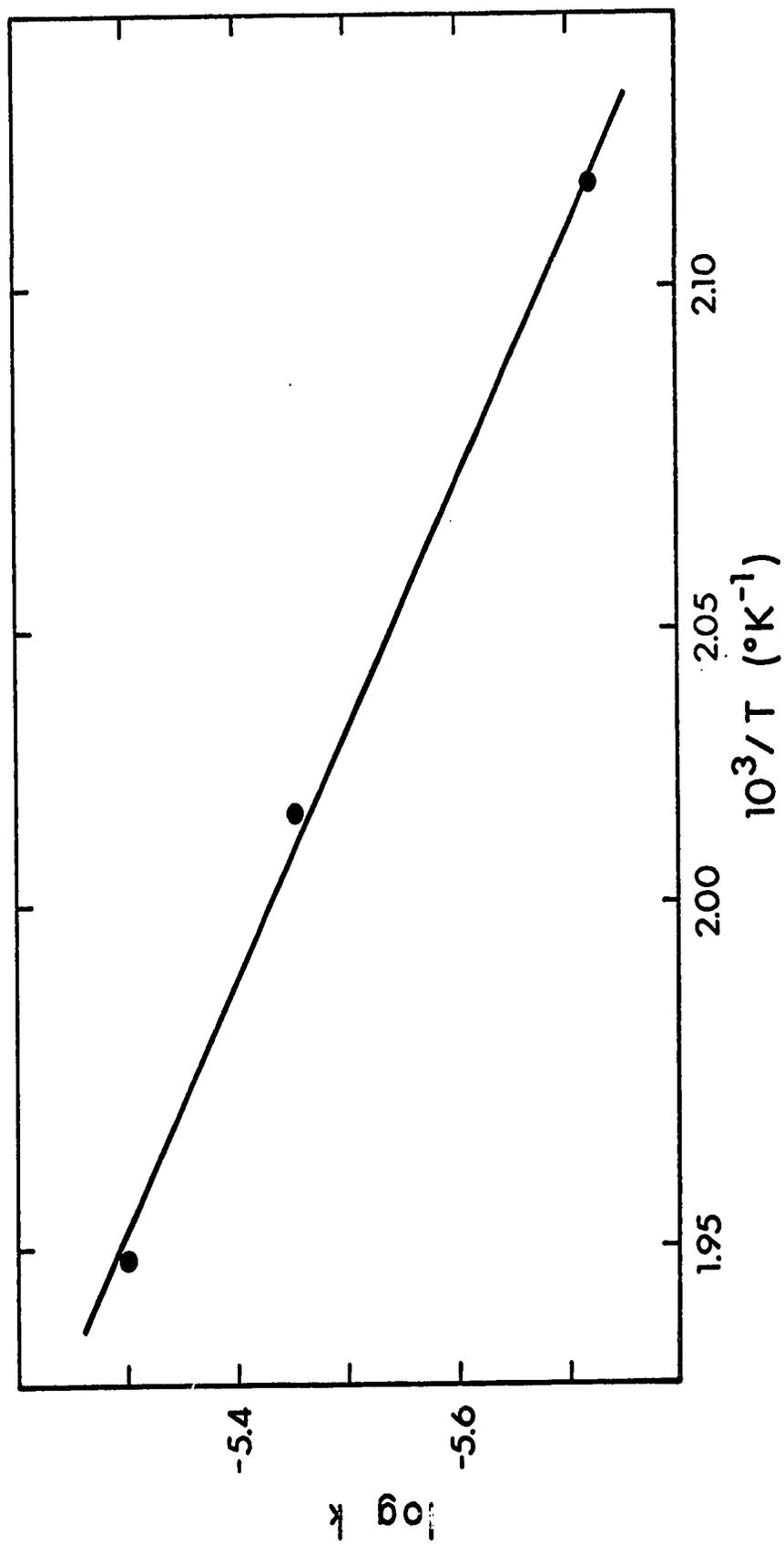
Figure V-10. Arrhenius plot for C_2H_4 formation in the C_3H_6/C_2H_4S system
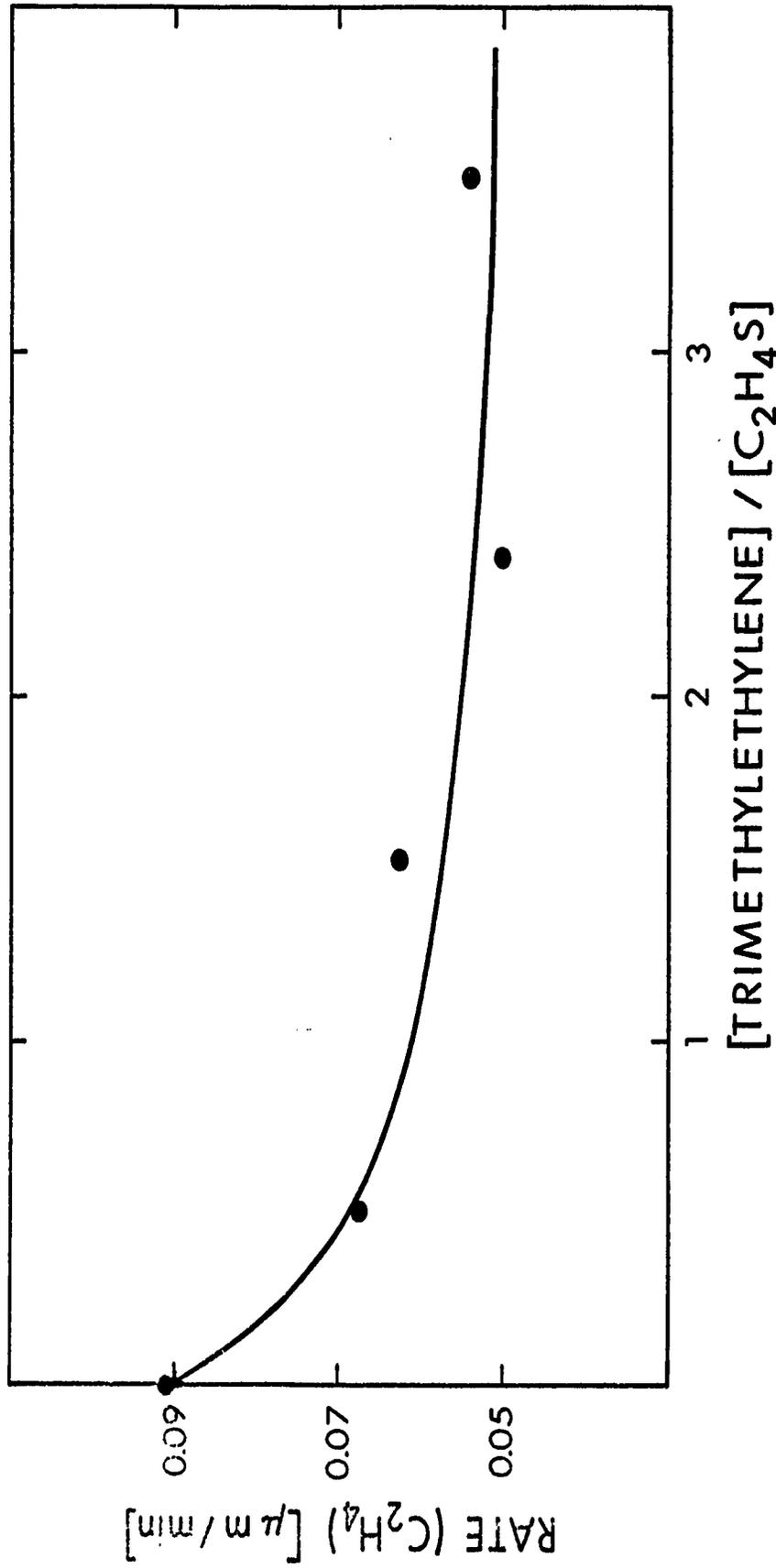
Figure V-11. Effect of added TME on the decomposition of C_2H_4S at $202°C$

TABLE V-IX

The Trimethylethylene-Ethylene Episulphide System. Variation of C_2H_4 and

$C_5H_{10}S$ Yields with Temperature at an Excess of TME [a]

T [°C]	C_2H_4 [μmoles]	$C_5H_{10}S$ [μmoles]	$\dfrac{[C_5H_{10}]}{[C_2H_4S]}$	Time [min]	$\log k\,(C_2H_4)$ [b] [sec^{-1}]
202.2	3.47	0.60	3.86	60.2	-6.052
237.7	18.14	3.82	3.86	20	-4.821
213.8	7.18	1.92	3.67	60	-5.712
227.2	19.36	3.41	3.85	45	-5.153
226.3	20.20	-	3.71	45	-5.136
226.9	20.30	-	3.65	45	-5.133
239.0	22.68	-	3.66	20	-4.722
201.2	3.21	-	3.51	60	-6.086

a) $[C_2H_4S] = 2.85 \times 10^{-9}$ M, cell volume 365.6 cc

b) first order in C_2H_4S
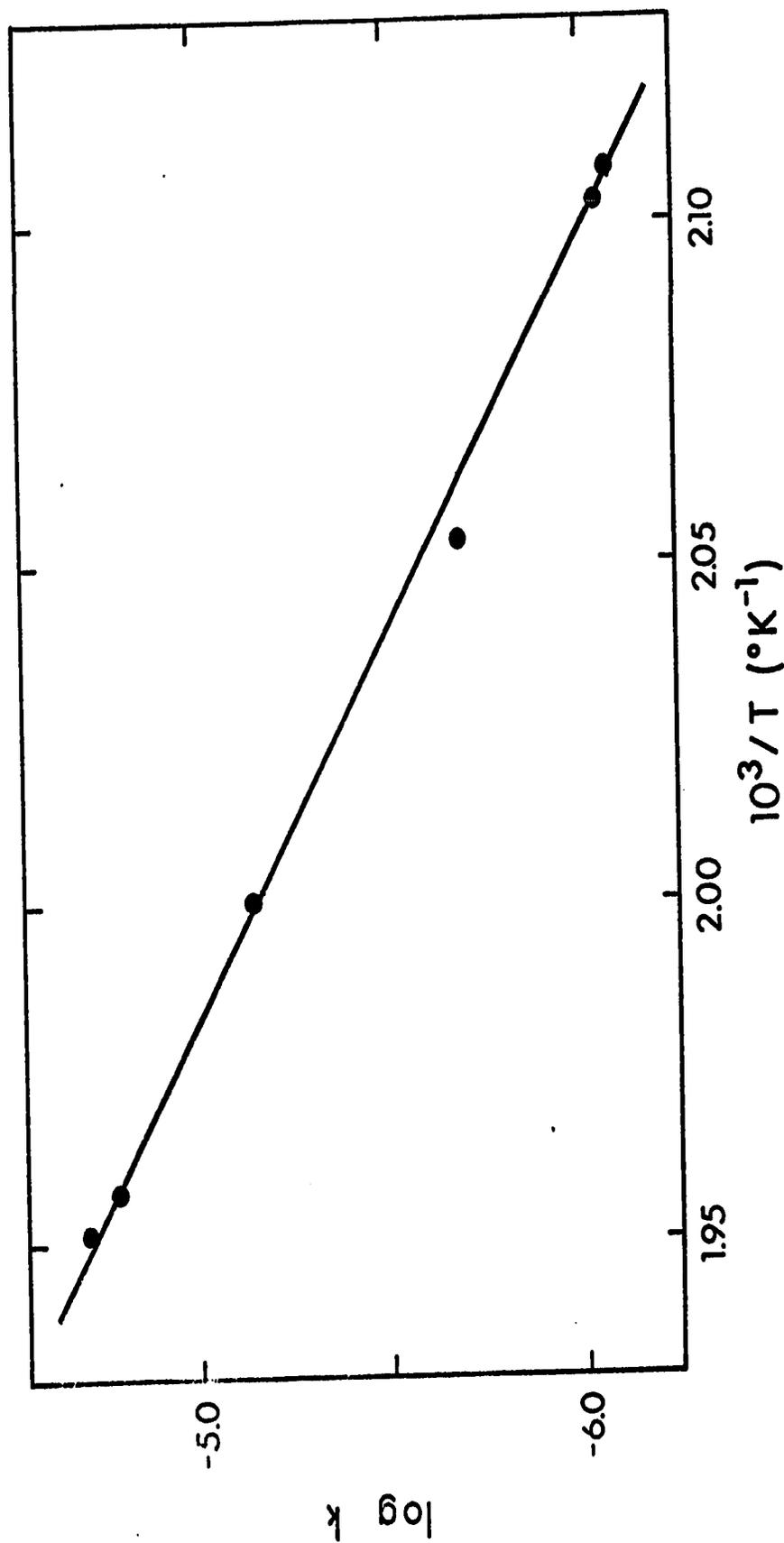
Figure V-12. Arrhenius plot for C_2H_4S decomposition in the TME/C_2H_4S system

about 50% in the case of pentene-1, indicating that TME is less efficient

as a quencher than pentene-1. This result is even more obvious at

higher temperatures. In the case of the pentene-1 system at $241^{\circ}C$, the

reduction in the rate is approximately 80% whereas in the TME system at

$237^{\circ}C$ it is estimated to be about 56%.

The Arrhenius parameters for the formation of C_2H_4 in the

presence of TME were obtained from the plot shown in Fig. V-12, and

were found to be log A = 12.14 $\pm$ 0.28 sec^{-1} and E_a = 39.6 $\pm$ 0.6 kcal/mole.

It is interesting that there was a considerable amount of

the trimethylethylene episulphide formed.

5) The 1,3-Butadiene-Ethylene Episulphide System

The decomposition of ethylene episulphide was carried

out in the presence of 1,3-butadiene, in order to establish the effect

of conjugation. The reaction was carried out at a pressure of

110 torr C_2H_4S and a roughly 4-fold excess of butadiene, again corre-

sponding to the decomposition in the level-off region. The results

of experiments done at different temperatures are given in Table V-X.

From the corresponding Arrhenius plot, shown in Fig. V-13, the

following apparent Arrhenius parameters for C_2H_4 were obtained,

log A = 3.42 $\pm$ 0.34 sec^{-1} and E_a = 20.8 $\pm$ 0.8 kcal/mole. Vinyl-

thiacyclopropane has been shown to be unstable and undergo polymeri-

zation reactions and some decomposition to thiophene (109).

Neither vinylthiacyclopropane nor thiphene were found in this

study.

TABLE V-X

The 1,3 Butadiene-Ethylene Episulphide System. Variation of the C_2H_4 Yield with Temperature at an Excess of 1,3-Butadiene [a]

T [$^{\circ}$C]	C_2H_4 [μmoles]	$\dfrac{[1,3\text{-}C_4H_6]}{[C_2H_4S]}$	Time [min]	log k [b] [sec^{-1}]
198.5	3.22	3.50	60	-6.184
242.4	6.41	4.42	20	-5.357
224.8	7.28	3.47	45	-5.686
225.3	6.64	4.72	45	-5.716

a) $[C_2H_4S] = 3.49 \times 10^{-9}$ M, cell volume 365.8 cc

b) first order in C_2H_4S
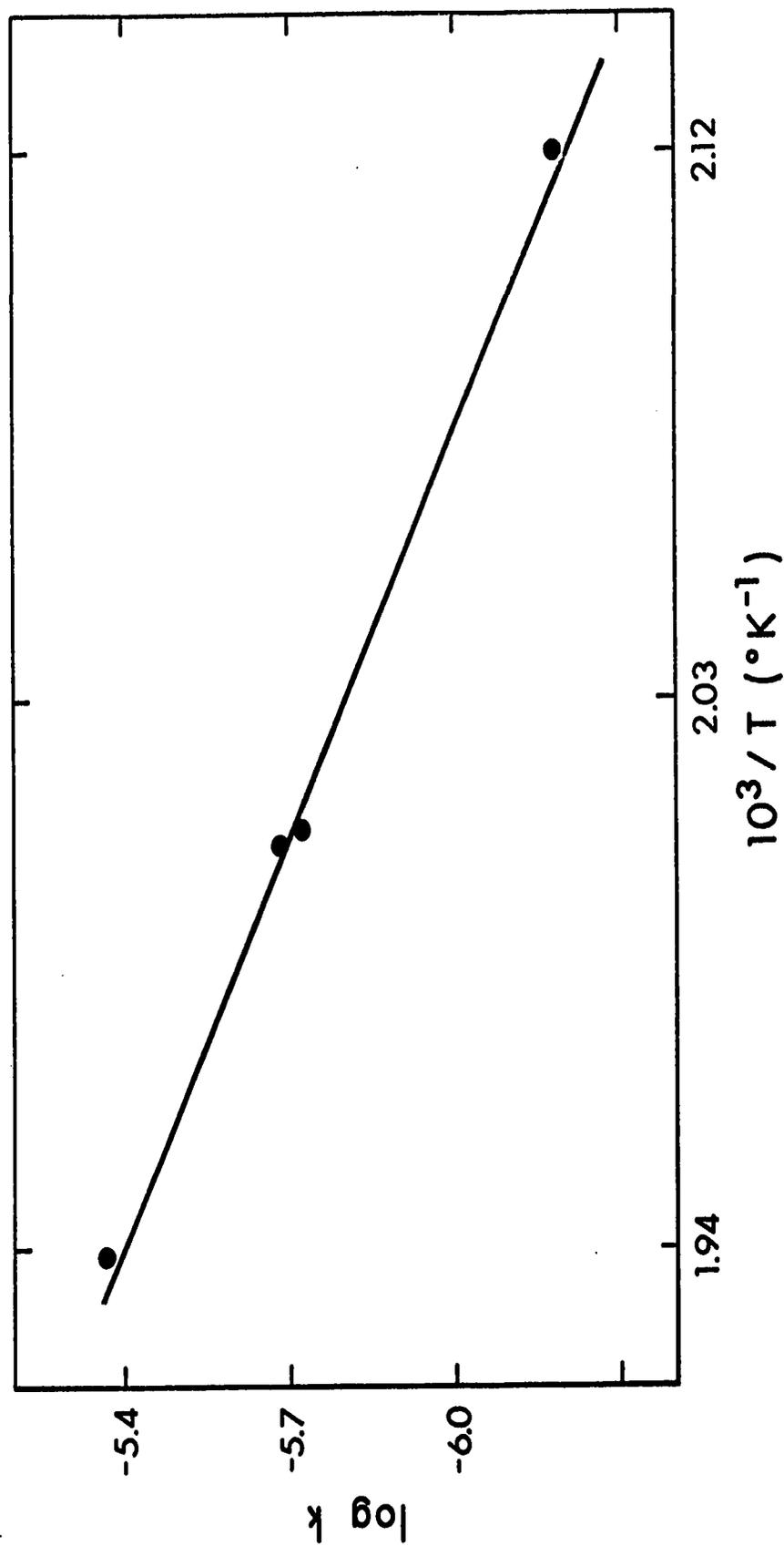
Figure V-13. Arrhenius plot for C_2H_4 formation in the 1,3-C_4H_6/C_2H_4S system

6) The Butyne-2-Ethylene Episulphide System

The effect of an alkyne on the pyrolysis of episulphides was investigated using butyne-2. Again the C_2H_4S pressure was kept at about 100 torr. The quenching effect of added butyne-2 is very much the same as was found with the alkenes as is shown by the results presented in Table V-XI and Fig. V-14. The results of experiments done at different temperatures and C_4H_6/C_2H_4S ratios of 2.7 or greater are given in Table V-XII. An analysis of the corresponding Arrhenius plot yields log A = 5.48 $\pm$ 0.17 sec^{-1} and E_a = 25.7 $\pm$ 0.4 kcal/mole. Since the episulphides of alkynes are extremely unstable (110) no attempt was made to detect them in the reaction mixture.

7) The Pyrolysis of Ethylene Episulphide in the Presence of Mixtures of Olefins

The results of the cis-butene-ethylene episulphide system, presented earlier, show that not only does a retardation in the rate of C_2H_4 formation occur when cis-butene is added to ethylene episulphide, but that a significant amount of isomerization of the cis-butene to trans-butene also takes place.

Since the species causing isomerization might be expected to exhibit different reactivities with various olefins, it was hoped that addition of an alkene to the episulphide-cis-butene system would shed some light on the nature of this process. Experiments were carried out with added propylene, butene-1, trimethylethylene and 1,3-butadiene. In each case the cis-butene pressure was kept at a level at which the rate of isomerization was independent of cis-butene pressure. Inspection of the data, presented in Table V-XIII,

TABLE V-XI

Variation of the C_2H_4 Yield with Added Butyne-2

in the CH_3CCCH_3/C_2H_4S System [a]

$P(C_2H_4S)$ [torr]	$P(C_4H_6)$ [torr]	$\dfrac{P(C_4H_6)}{P(C_2H_4S)}$	C_2H_4 [µmoles]
100.2	–	0	36.20
98.2	90.6	0.97	18.69
101.2	264.0	2.70	5.99
100.0	375.8	3.76	5.56

a) all runs 40 min, cell volume 360.0 cc, $225^{\circ}C$

TABLE V-XII

The Butyne-2/Ethylene Episulphide System. Variation of the

C_2H_4 with Temperature at an Excess of Butyne-2 [a]

T [$^{\circ}$C]	C_2H_4 [µmoles]	$\dfrac{[C_4H_6-2]}{[C_2H_4S]}$	Time [min]	log k [b] [sec^{-1}]
226.5	5.56	3.76	45	-5.747
203.2	2.14	2.70	60	-6.290
215.4	3.91	2.60	60	-6.021
191.3	1.90	2.62	105	-6.607

a) $[C_2H_4S] = 3.14 \times 10^{-9}$ M, cell volume 359.3 cc

b) first order in C_2H_4S
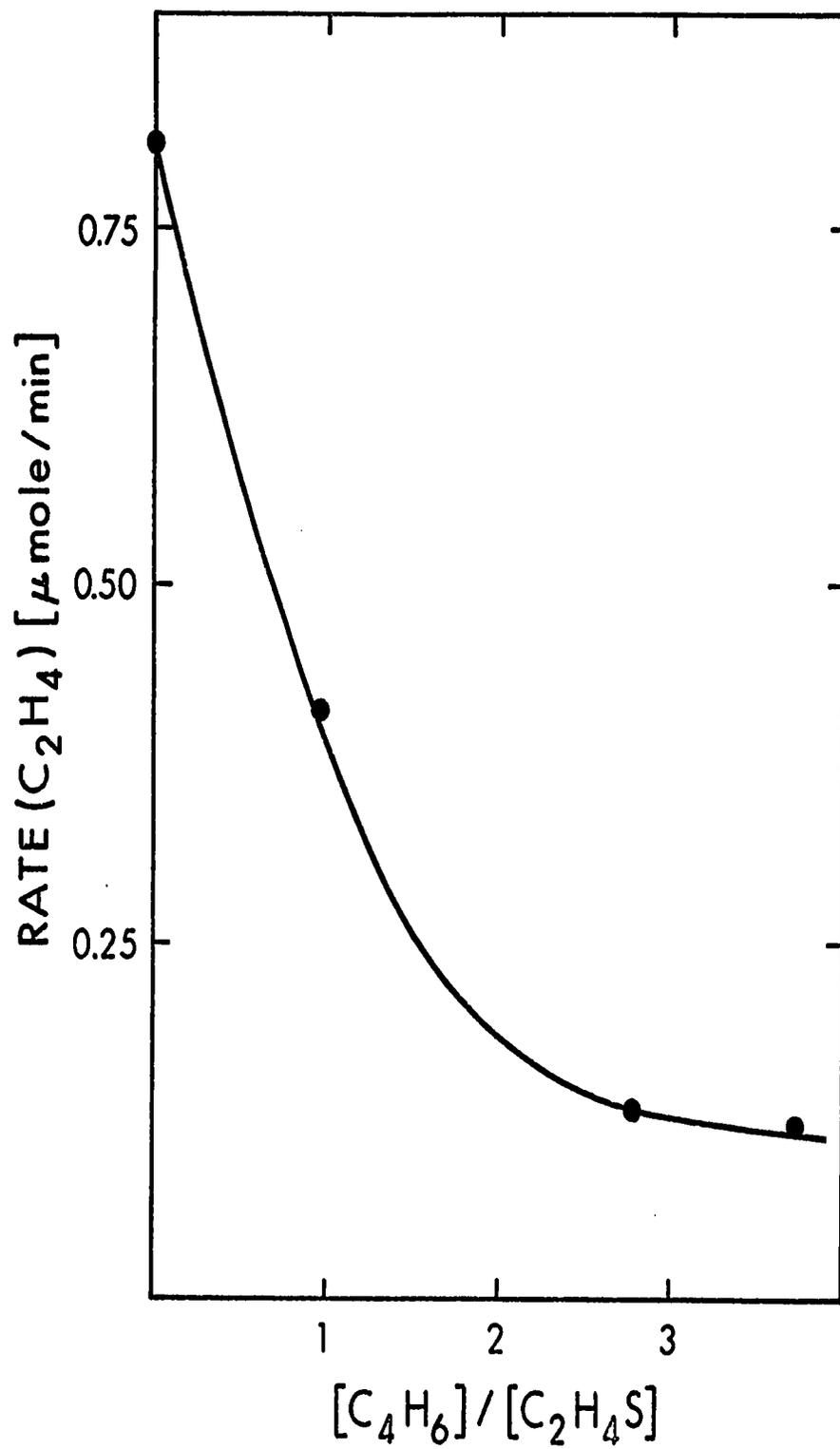
Figure V-14. Effect of added Butyne-2 on C_2H_4S decomposition
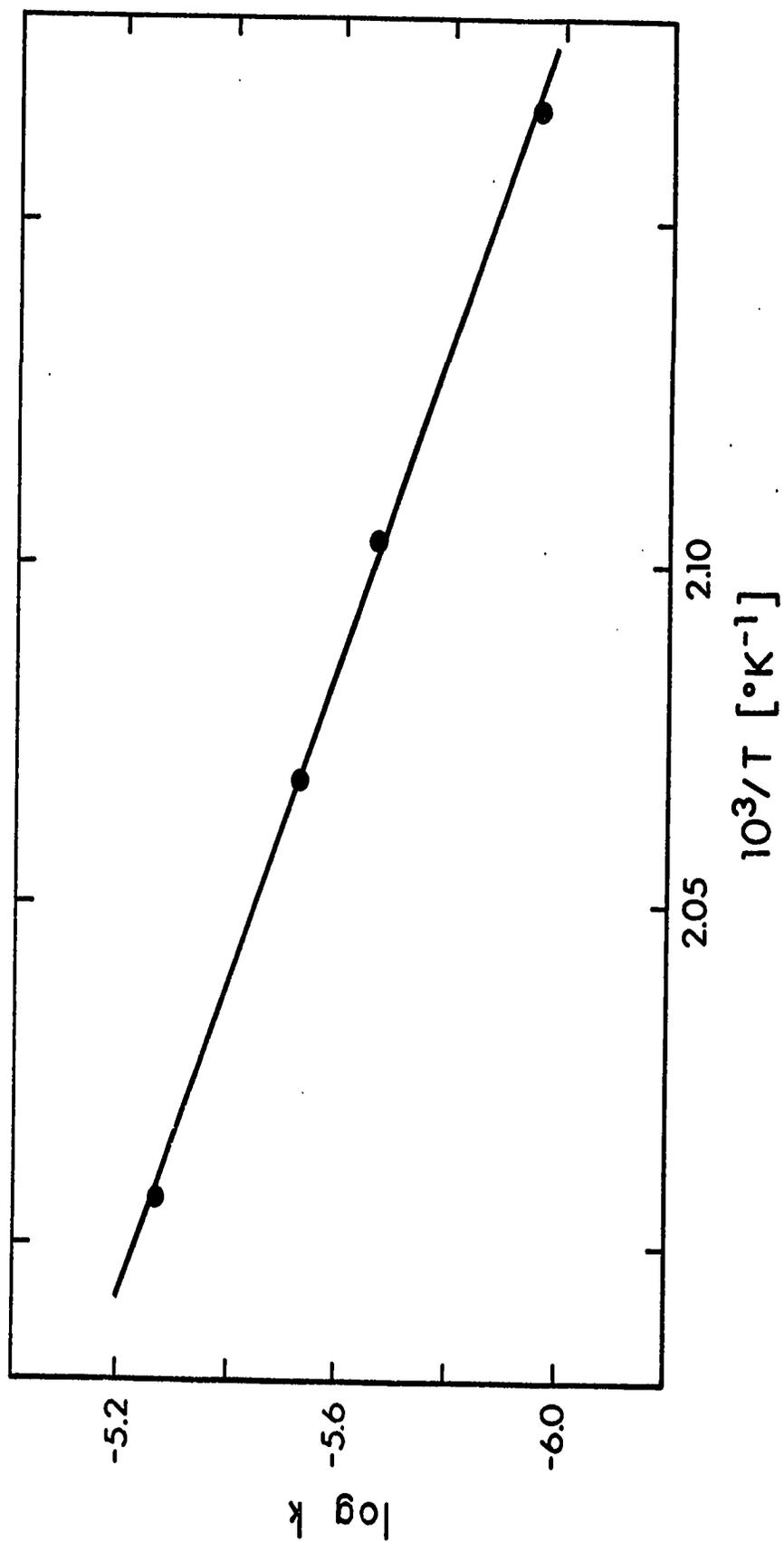
Figure V-15. Arrhenius plot for C_2H_4 formation in the butyne-2/C_2H_4S system

reveals that the isomerization of cis-butene-2 is not only affected

by the presence of a second olefin, but that the extent depends

strongly upon its nature as well. 1,3-Butadiene clearly shows the

greatest efficiency in suppressing the rate of isomerization, propylene

and butene-1 appear to be about equally effective and trimethyl-

ethylene shows no effect under these conditions. The extent of

isomerization with added TME appears higher than the simple

$C_2H_4S/cis-C_4H_8$ system but this is probably due to the experimental

difficulty in obtaining accurately reproducible results.

8) The cis-Butene-Propylene Episulphide System.

An investigation was also made into the olefinic quenching

effect for the case of propylene episulphide decomposition. The added

gas was cis-butene. The cis-butene/propylene episulphide mixtures

also demonstrated the tendency to form azeotropes but at even lower

olefin/episulphide ratios than was the case for ethylene episulphide.

The C_3H_6S pressure used in these experiments was 90 torr. As was the

case in the cis-butene C_2H_4S system, significant quenching occurs, as

well as some isomerization of the butene. Without the presence of

olefin, a 20 minute pyrolysis at $202.5^\circ C$ results in a C_3H_6 yield of

36 μmoles whereas a 3.8-fold excess of cis-butene reduces the yield

to 3 μmoles.

The results of a temperature study carried out at high

cis-butene/propylene episulphide ratios, which correspond to the

level-off region, are presented in Table V-XIV. The corresponding

Arrhenius plots for propylene and trans-butene formation are

illustrated in Fig. V-16. The apparent Arrhenius parameters obtained

TABLE V-XIII

The Effect of Various Olefins on the cis-Butene Isomerization

in the cis-Butene-Ethylene Episulphide System[a]

X	P(cis-C_4H_8) [torr]	P(X) [torr]	C_2H_4 [μmoles]	trans-C_4H_8 [μmoles]
—	480.6	0	12.9	345.7
C_3H_6	208.2	208.5	15.2	87.6
C_4H_8-1	326.8	113.5	11.8	176.5
TME	332.4	112.7	17.8	383.6
1,3-C_4H_6	218.0	229.7	8.0	0
1,3-C_4H_6	436.3	31.5	9.4	86.5

a) all runs 45 min, P(C_2H_4S) ≈ 110 torr, 225°C cell volume 359.5 cc

TABLE V-XIV

The cis-Butene/Propylene Episulphide System. Variation of the C_3H_6

and trans-C_4H_8 Yields with Temperature at an Excess of cis-Butene[a]

T [°C]	C_3H_6 [μmoles]	trans-C_4H_8 [μmoles]	$\dfrac{[cis-C_4H_8]}{[C_3H_6S]}$	Time [min]	log k (C_3H_6) [sec^{-1}]	log k (trans-C_4H_8) [sec^{-1}]
225.0	8.4	32.2	4.43	25	-5.276	-4.687
210.2	2.2	4.0	3.92	11	-5.526	-5.266
202.5	3.0	4.2	3.76	20	-5.663	-5.517
188.2	3.6	4.0	3.84	50	-5.954	-5.908

a) P(C_3H_6S) = 90.0, cell volume 365.8 cc
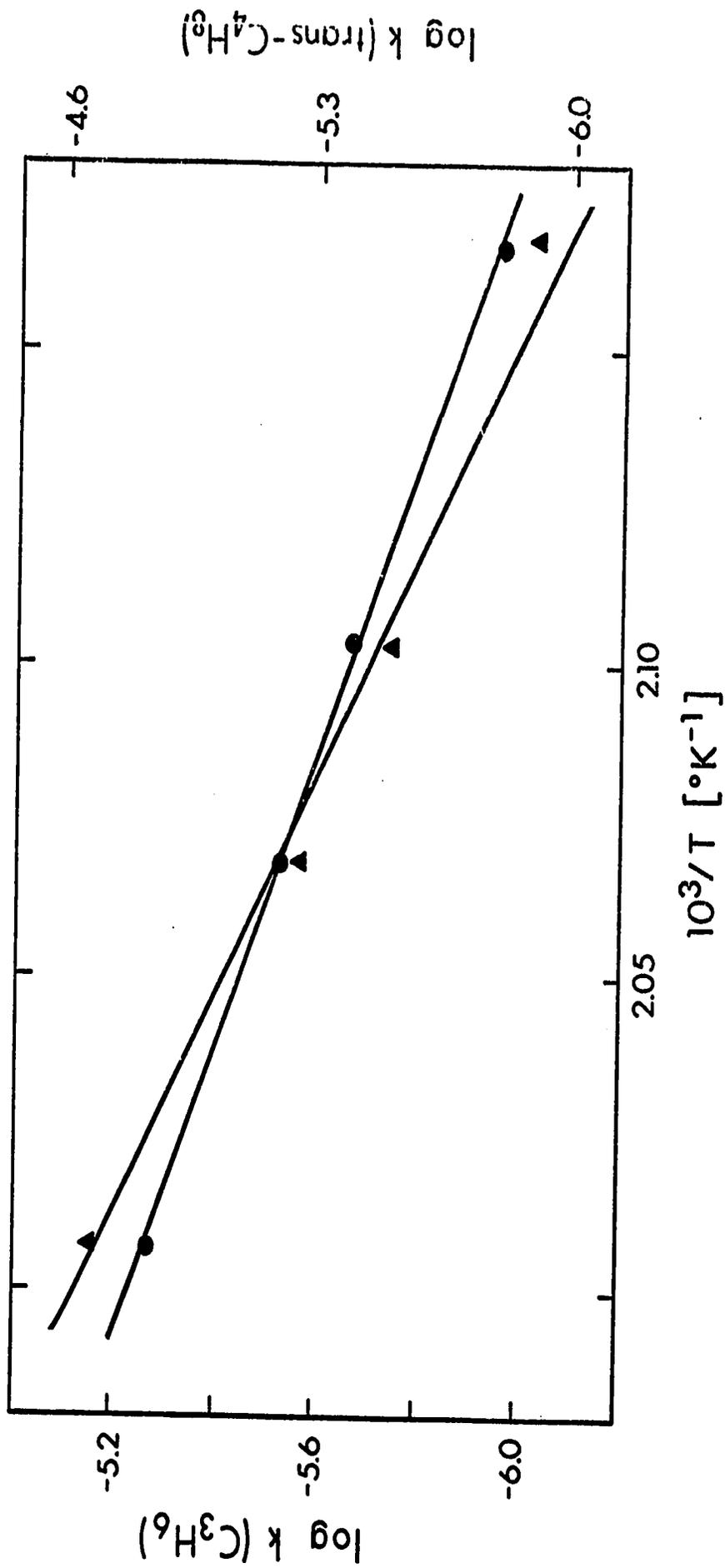
Figure V-16. Arrhenius plots for C_3H_6 and $\underline{trans}$-C_4H_8 formation in the $\underline{cis}$-C_4H_8/C_3H_6S system

TABLE V-XV

Arrhenius Parameters for Product Formation

in Various C_2H_4S/Olefin Systems [a]

Olefin	log A $[sec^{-1}]$	E_a [kcal/mole]
	Ethylene Formation	
——	12.57	40.2
C_5H_{10}-1	5.68 ± 0.42	25.4 ± 1.0
cis-C_4H_8	5.86 ± 1.02	25.7 ± 2.3
C_3H_6	4.81 ± 0.20	23.5 ± 0.5
1,3-C_4H_6	3.42 ± 0.34	20.8 ± 0.8
C_4H_6-2	5.48 ± 0.17	25.7 ± 0.4
TME	12.14 ± 0.28	39.6 ± 0.64
	trans-Butene Formation	
cis-C_4H_8	12.46 ± 1.03	37.9 ± 2.3

a) obtained with the presence of an excess of olefin.

from these plots are

	log A $[\text{sec}^{-1}]$	E_a [kcal/mole]
C_3H_6	3.29 ± 0.15	19.5 ± 0.3
trans-C_4H_8	10.67 ± 0.94	35.1 ± 2.1

B. Discussion

The results just presented demonstrate that addition of olefins has a marked suppressing effect on the rate of episulphide decomposition, indicating that the olefin intercepts some intermediate which is a precursor in the formation of decomposition products. The resulting rate profiles exhibit unique features in that there is a rapid initial decrease in rate in the presence of a small olefin concentration, and this is followed by a levelling-off in the decomposition rate at high pressures of olefin. In addition, a strong temperature dependence is found in the extent of quenching in the level-off region. The results of the pentene-1-ethylene episulphide system show that the amount of quenching ranges from about 51% at $207^{\circ}C$ to 80% at $241^{\circ}C$. On the basis of the mechanism for the episulphide decomposition presented in Chapter III, the reactive intermediate should be the episulphide in a triplet excited state.

If the olefin-excited episulphide interaction competes with the pathway for decomposition, then a constant increase in the olefin pressure should ultimately reduce the rate of episulphide decomposition to zero. However, experimentally it is found that a levelling-off in the rate occurs. An immediate explanation for this behavior would be

that episulphides decompose via two pathways, and that while the one major route is inhibited by added olefin, the other less important one is unaffected. This explanation can be discounted on the following grounds. Inspection of the apparent Arrhenius parameters presented in Table V-XV shows that the activation energies, in the region where the level-off occurs, are not the same for all olefin systems, but vary from 20.8 kcal/mole in the 1,3-butadiene system to 39.6 kcal/mole in the TME system. The A-factors demonstrate analogous behavior suggesting that reaction is dependent on the nature of the olefin present. It should also be noted that if episulphides decompose by two reaction paths, one of which has an activation energy of about 25 kcal/mole then the Arrhenius plots for pure episulphide might be expected to show some curvature at lower temperatures. This was not found to occur, however.

The following mechanism will be shown to be consistent with the experimental data. Since the cis-butene-ethylene episulphide system exhibits the key features of the olefin-episulphide system, cis-butene (c-B) and ethylene episulphide (EES) will be used as examples of added olefin and substrate episulphide:

$$EES + M \rightarrow EES^* + M \qquad [1]$$

$$EES^* + M \rightarrow EES + M \qquad [2]$$

$$EES^* \rightarrow EES^\dagger \qquad [3]$$

$$EES^\dagger + EES \rightarrow EES + EES \qquad [4]$$

$$EES^\dagger + EES \rightarrow 2C_2H_4 + S_2 \qquad [5]$$

$$EES^\dagger + c\text{-}B \rightarrow C_2H_4 + c\text{-}BES \qquad [6]$$

$$EES^\dagger + c\text{-}B \rightarrow t\text{-}B + EES^\dagger \qquad [7]$$

$$EES^\dagger + c\text{-}B \rightarrow c\text{-}B + EES \qquad [8]$$

$$EES^\dagger + c\text{-}B \rightarrow t\text{-}B + EES \qquad [9]$$
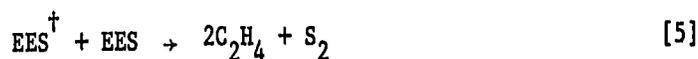
where c-BES, and t-B represent cis-butene episulphide and trans-butene
respectively. M represents any bath molecule. The first five steps
are those proposed for the simple episulphide decomposition
(Chapter III). Reactions [8] and [9] are the steps in which the triplet
episulphide is quenched. A distinction between [8] and [9] is made,
since the olefin is expected to revert to either configuration from
the $EES^\dagger$ - c-B complex. Reaction [7] is introduced on the basis of
results obtained in other photochemical studies and will be discussed
later.

Applying steady state assumptions, the rate equations for
ethylene and trans-butene formation are derived as:

$$R(C_2H_4) = \frac{k_1 k_3 [EES][M]}{k_2[M] + k_3} \cdot \frac{2k_5[EES] + k_6[c\text{-}B]}{(k_4 + k_5)[EES] + (k_8 + k_9)[c\text{-}B]} \qquad [10]$$

$$R(t\text{-}B) = \frac{k_1 k_3 [EES][M]}{k_2[M] + k_3} \cdot \frac{(k_7 + k_9)[c\text{-}B]}{(k_4 + k_5)[EES] + (k_8 + k_9)[c\text{-}B]} \qquad [11]$$

Division of equation [11] by [10] yields

$$\frac{R(C_2H_4)}{R(t\text{-}B)} = \frac{2k_5}{k_7 + k_9} \frac{[EES]}{[c\text{-}B]} + \frac{k_6}{k_7 + k_9} \qquad [12]$$

which provides a convenient test for the mechanism since a linear
relationship is predicted between $R(C_2H_4)/R(t\text{-}B)$ and $[EES]/[c\text{-}B]$. As
is shown by Fig. V-17 a straight line is indeed found for the data

TABLE V-XVI

Realtive Rates as a Function of Relative Concentrations

for the $\underline{cis}$-C_4H_8/C_2H_4S System[a]

$\dfrac{[C_2H_4S]}{[\underline{cis}\text{-}C_4H_8]}$	$\dfrac{R(C_2H_4)}{R(\underline{trans}\text{-}C_4H_8)}$
3	.329
2	.214
1.5	.156
1	.103
.75	.078
.6	.064
.5	.054
.4	.048

a) at 225°C; values calculated from the curves in Figures V-6 and 7
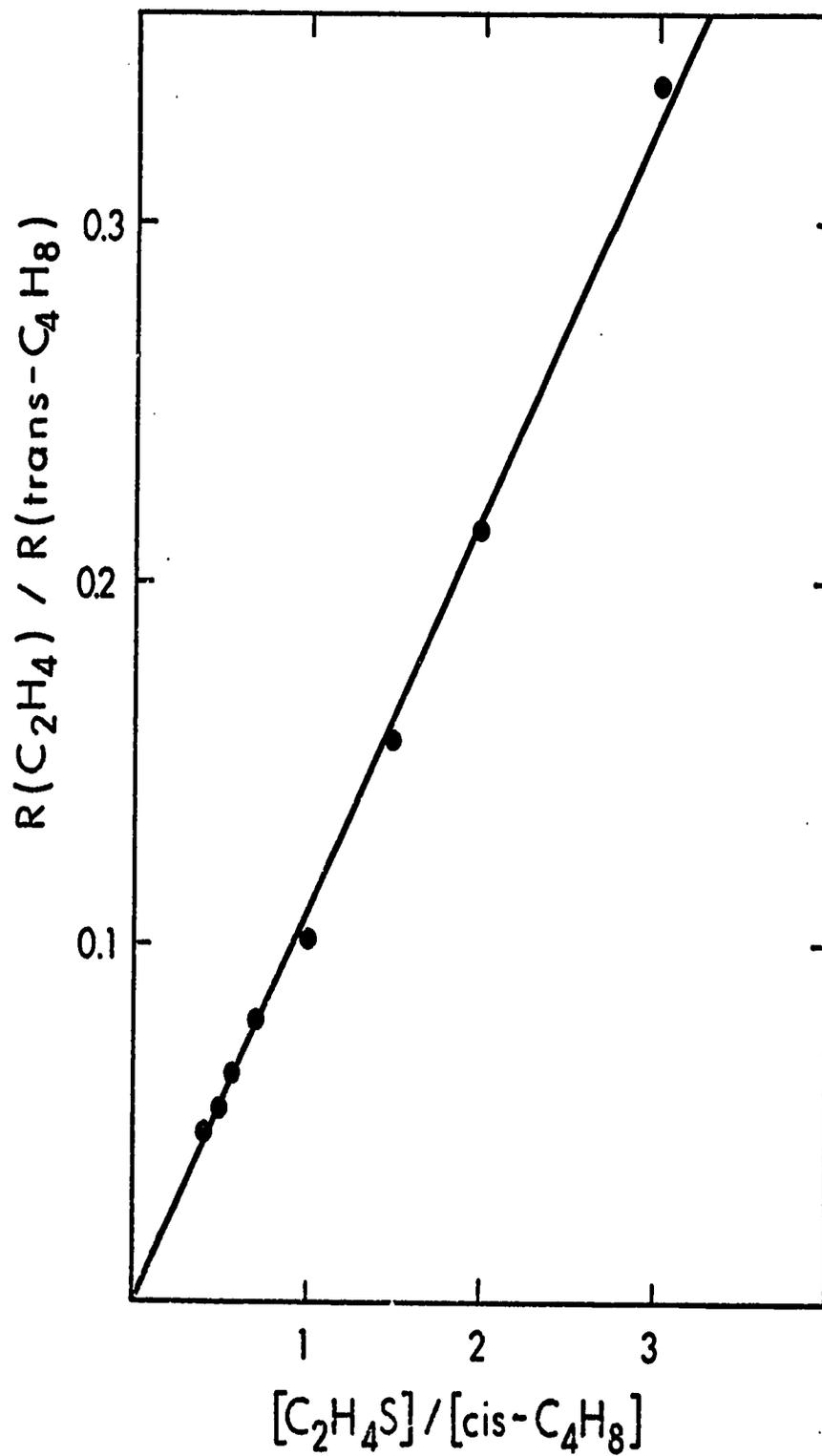
Figure V-17. Plot of R(C$_2$H$_4$)/R(trans-C$_4$H$_8$) versus [C$_2$H$_4$S]/[cis-C$_4$H$_8$]

at 225°C and from the slope $k_5/(k_7+k_9)$ is 0.06. Unfortunately, the intercept is such a small number that, within experimental error, it cannot be distinguished from zero.

From equations [10] and [11], the orders for C_2H_4 and trans-C_4H_8 formation in the level-off region should be about the same as for decomposition of the pure episulphide. They were found to be 1.0 and 1.2, which agrees well with 1.3 within the precision of the log-log plots.

Equation [10] has a form which is consistent with the experimental results. If $k_8 + k_9$ is relatively large, then as butene is added there will be a decrease in the rate of reaction. At some point, the new C_2H_4 producing reaction, [6], will gain in importance, there will no longer be a continuous drop in the rate of decomposition, and the rate will begin to level-off upon further olefin addition.

From the results presented in Table V-XV it is seen that the apparent Arrhenius parameters in the level-off region of the cis-C_4H_8/C_2H_4S system are considerably smaller than those obtained for pure episulphide pyrolysis; log A = 5.86 (sec^{-1}) and E_a = 25.7 kcal/mole versus 12.57 (sec^{-1}) and 40.2 kcal/mole respectively. Inspection of the rate equation for ethylene formation [10] reveals that the decrease in activation energy is due to the new term in the denominator, namely $k_8 + k_9$, having an activation energy which is larger than that of k_6. Since the decrease in net activation energy is about 12 kcal/mole, steps [8] and [9] must have an activation energy this much larger than [6]. For the pyrolysis of propylene episulphide in the presence of cis-butene the difference is

estimated to be about 18 kcal/mole. The observed decrease of the A-factors in these systems must be due to an analogous effect.

Recent studies of the photolysis of ethylene episulphide at 2537Å in the presence of cis-butene, also demonstrate the occurrence of extensive cis-trans isomerization of butene-2 (106). The quantum yield for the isomerization at room temperature is as high as 30 with an estimated chain length for the reaction of about 60. It was also found that the extent of isomerization decreased at higher temperatures. Similar results were obtained in studies of the sulphur atom addition to cis-butene (88, 106). Again, extensive cis-trans isomerization was discovered. While Schmidt and Lee (88) proposed a scheme involving labile S-atom addition to olefin, this mechanism has recently been questioned by the results of flash photolysis of similar systems studied by kinetic spectroscopy (108), since no pressure dependence was found for the rate of sulphur atom disappearance. Comparison of the results presented in this work with results of the photolysis system suggests that a similar chain reaction occurs in the thermal cis-butene-ethylene episulphide system. It is on these grounds that reaction [7] is introduced into the mechanism. Unfortunately, it is not possible to obtain even a relative value for k_7, but an upper limit for a chain length can be estimated. Consider the rate expression for decomposition in the pure episulphide system:

$$R(C_2H_4) = \frac{k_1 k_3 [EES]^2}{k_2[EES] + k_3} \cdot \frac{k_5}{k_4 + k_5} \qquad [13]$$

If the ratio $k_5/(k_4+k_5)$ is unity then the rate of ethylene formation without added cis-butene gives a measure of the amount

of triplet episulphide formed. Since the trans-butene yield in the

level-off region at 225°C is nearly ten times as great as the ethylene

yield at [c-B] = 0, the chain length would be about twenty. This must be

an upper limit, however, since some isomerization also occurs via

reaction [9]. In addition, the rate of ethylene formation in pure

episulphide is an underestimate for the production of EES[†] since some

deactivation by ground state episulphide via reaction [4] probably

also occurs (44). The shorter chain length for isomerization at

higher temperatures is due to a larger activation energy for reactions

[8] and [9] than for [7], as is found in the photolytic system (106).

Since k_7 is not very much greater than k_9 and since

(k_8+k_9)[c-B] must be larger than (k_4+k_5)[EES], by the above

arguments, the ratio

$$\frac{(k_7+k_9)[c-B]}{(k_4+k_5)[EES] + (k_8+k_9)[c-B]}$$

in equation [11] would have a net activation energy approaching zero.

The apparent activation energy measured for cis-trans isomerization

should therefore, by equation [11], be that associated with the

following equation:

$$R(t-B) = \frac{k_1 k_3 (ES)(M)}{k_2(M) + k_3} \qquad [14]$$

This expression, however, is precisely that which is derived for the

rate of formation of the triplet episulphide intermediate. The

activation energy for trans-butene formation is 2.3 kcal/mole lower

than that observed in the decomposition of pure episulphide and since

the rate expression for the latter reaction is

$$R(C_2H_4) = \frac{k_1 k_3 (ES)(M)}{k_2(M) + k_3} \cdot \frac{k_5}{k_4 + k_5}$$

this result suggests that $k_5/k_4+k_5)$ has an apparent energy barrier amounting to 2.3 kcal/mole. Hence, k_4 must be comparable to or larger than k_5 since the ratio would otherwise be unity. It should be noted, that the experimental error in the net activation energy for isomerization is comparable to the difference in the activation energies, but the same phenomenon was observed when propylene episulphide was pyrolyzed in the presence of cis-butene. In this case the activation energy was 3.4 kcal/mole lower than that found for pure C_3H_6S, again indicating that deactivation by ground state episulphide also occurs.

Returning now to the results obtained from equation [12], some conclusions can be drawn about the sulphur abstraction reaction, [6]. Within the framework of the mechanism postulated here, the yield of cis-butene episulphide should be comparable to the ethylene yield at large olefin/C_2H_4S ratios. While this was not found experimentally, the discrepancy can be accounted for as follows. From the plot in Fig. V-17, $k_5/(k_7+k_9)$ was calculated to be 0.06. Unfortunately, $k_6/(k_7+k_9)$ could not be determined, but this ratio should be comparable in magnitude to the relative rates of C_2H_4 and trans-butene formation at large cis-butene concentrations. Hence, $k_6/(k_7+k_9) \simeq 0.02$, and k_5/k_6 is estimated to be about 3. This provides an explanation for the low butene episulphide yields mentioned earlier. In addition, a blank run, in which trans-butene episulphide in an amount corresponding to the expected C_2H_4 yield was added to the reaction mixture, revealed that a considerable amount of the butene episulphide was lost by decomposition.

In a consideration of reaction [8] and [9], it is necessary to investigate the possibility of interaction of triplet episulphide with the triplet state of the olefins. It is well established that the energies of the first triplet and ground states of olefins change with a twisting motion about the double bond. In the case of the first triplet state, the energy decreases reaching a minimum at a twist angle of 90° while the exact opposite behavior is found for the singlet ground state. The activation energy for thermal cis-trans isomerization of about 65 kcal/mole is usually considered to correspond to this maximum. The minimum for the triplet state has not definitively been established, but a number of studies suggest that the value lies below 60 kcal/mole. Spectroscopic studies give a value of 57 kcal/mole (89), consistent with a low value of 58 kcal/mole obtained on theoretical grounds (90,91). As was shown earlier, the activation energy for the quenching reactions [8] and [9] is at least 12 kcal/mole, which might suggest that the nature of the triplet episulphide-olefin interaction is a triplet-triplet energy transfer since the total energy is close to 57 kcal/mole namely, 40+12 = 52 kcal/mole for the case of ethylene episulphide and 38+19 = 57 kcal/mole for propylene episulphide. It is seen, however, that the Arrhenius parameters for decomposition of ethylene episulphide in the presence of butyne-2 are approximately the same as for the alkenes. Unfortunately, the energy of the triplet state of butyne-2 is not well established, so that the possibility of triplet-triplet interaction remains open.

Before continuing, a brief summary of the results and discussion presented so far, would perhaps be warranted. Olefins are experimentally found to have a large quenching effect on episulphide decomposition, but at high pressures there remains a small but

measurable ethylene producing reaction. The reduction in the rate of

decomposition is attributed to quenching of the excited triplet

episulphide by the olefin and the residual decomposition in the level-

off region arises from a new process involving the added olefin.

The net temperature dependence of the residual decomposition rate is

different from that of the pure episulphide, exhibiting a lower

activation energy and A-factor. This change in Arrhenius parameters

is due primarily to the temperature dependence of the quenching

reaction, which must have an energy barrier of at least 12 kcal/mole.

Unfortunately, the Arrhenius parameters for this process can only

be measured relative to the product forming steps in the decomposition.

Such a quenching effect seems to be a novel feature in a thermal

system, although it has recently been reported in a photochemical study.

In their investigation into the photochemistry of 2,3-pentanedione,

Jackson and Yarwood (87) also found a temperature dependent quenching

process of the triplet state when acrolein, crotonaldehyde and

methylvinylketone were added to the system. The Arrhenius

parameters were log A $\cong$ 13 (cc/mole sec) and E_a $\cong$ 12 kcal/mole

for all systems. The effect could not be assigned to triplet-triplet

quenching and was attributed to chemical interaction. In the thermal

system reported here, the quenching step is much the same, only that

it has added significance in that it can also give rise to cis-trans

butene isomerization.

The cis-trans isomerization of butenes has been shown to be

catalyzed by a number of reagents including O_2 (92), NO (93, 94),

I (95, 96), S (88), HS (97), NO_2 (98, 99) and RS (100, 101).

Activation energies have been measured for the NO, NO_2 and I catalyzed isomerizations and were found to be 26.2, 12.1 and 9.4 kcal/mole respectively, and it should be pointed out that no additional products were found. Theories have been advanced which propose that paramagnetic substances can catalyze isomerization by inducing a polarizing effect on the π electron structure of the double bond (94) or by providing a non homogeneous magnetic field which allows mixing of different electronic states with the appropriate enhancing of the singlet-triplet transition probability.

Tamamushi and Akiyama (92) studied the isomerization of maleic acid in solution in the presence of a number of paramagnetic molecules and believed the reaction was catalyzed by the above effect. A later effort to correlate the isomerizing ability of molecules with their magnetic suspectibility was unsuccessful, but apparently the system was complicated by other factors and the results were therefore inconclusive. While considerable effort has gone into the examination of paramagnetically catalyzed isomerization of olefins, the theory has yet to be conclusively proven.

Treating cis-trans isomerizations in terms of a radical catalyzed reaction has met with considerably more success than the above mentioned theories. In this case the reaction is envisaged as a radical attack on the double bond, followed by rotation about the C-C bond in the radical adduct. This isomerized radical adduct then decomposes to isomerized olefin and original radical:
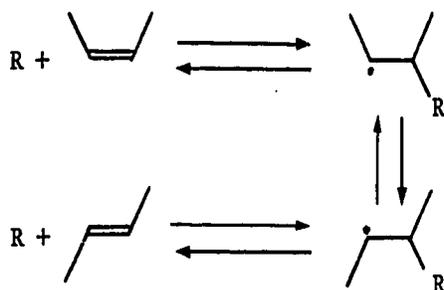
Benson, Egger and Golden (96) applied thermochemical calculations in such a study of the iodine atom catalyzed isomerization of cis- and trans-butene and extended the treatment to the NO reaction as well. From estimates of the thermodynamic properties of the reactants and intermediates, they were able to assign values to the individual rate constants in the scheme. More recently, Sprung, Akimoto and Pitts (98) analyzed the results of the NO_2 catalyzed isomerization of cis-butene on a similar basis.

Triplet excited ethylene episulphide is a paramagnetic species and in the context of the theories regarding paramagnetically catalyzed isomerization, would be expected to cause isomerization. On the other hand, the molecule can conceivably behave as a radical-like species, since the excited state is essentially indistinguishable from a biradical. Being a triplet, the species would be expected to have a fairly long lifetime with the result that its chemistry will differ from that of trimethylene which is a singlet in thermal systems. Although it would be interesting to carry out thermochemical calculations in the manner done by Benson et al.(96), and Sprung et al. (98), unfortunately it is impossible to obtain meaningful results from such a calculation, since the present study only yields relative

values for the Arrhenius parameters for [6] and [8] and [9]. Since

the C-S bond strength is greater than the $D(\pi)$ bond strength, (given by

Benson (10)) it can be shown that the rate determining step is the

formation of the radical/butene adduct but the activation energy

for this reaction cannot be calculated.

Let us now consider triplet episulphide-olefin interaction

in a qualitative manner. As was seen from Table V-XV, the Arrhenius

parameters for the decomposition of ethylene episulphide in the

presence of various olefins depend upon the nature of the olefin .

and therefore the intermediate, triplet episulphide, must have

differing reactivity with the various olefins. This effect can also

be seen from the results of Table V-XIII which shows that the

various alkenes exhibit differing efficiencies in reducing the amount

of isomerization of _cis_-butene when mixtures of a _cis_-butene and a

second olefin are used. On the basis of the results presented there,

the efficiencies of intercepting the triplet ethylene episulphide by

the olefins relative to _cis_-butene can be estimated:

$$\frac{(k_7 + k_9)_{\text{olefin}}}{(k_7 + k_9)_{\text{cis-butene}}}$$

propylene	3.0
butene-1	2.7
1,3-butadiene	41.6
TME	< 1 .

CHAPTER VI

SUMMARY AND CONCLUSIONS

The results presented in the preceeding chapters provide

a reasonable and self-consistent picture of the thermal chemistry of

episulphides. The reaction is shown to be a homogeneous, pseudo-

unimolecular process, in which the lowest-lying triplet state is an

intermediate. The order of reaction and the fact that inert gases,

such as carbon dioxide, accelerate the rate of reaction indicate that

the rate determining step is the unimolecular thermal activation

of the substrate. The fall-off regions for the three episulphides are

estimated to lie below 1000 torr, 300 torr and 50 torr for ethylene,

propylene and trans-butene episulphide, respectively.

The Arrhenius parameters for decomposition are unusually

low in comparison to those found in cyclopropane and epoxide decomposi-

tion. It is also found that the enthalpy change for the hypothetical

unimolecular sulphur extrusion reaction is greater than the experi-

mental activation energy. It is concluded that this is due to

reaction occurring via intersystem crossing to a low lying non-vertical

triplet excited state of the episulphide. The energy of this state is

about 40 kcal/mole above the ground state. From molecular orbital

calculations, the triplet excited episulphide is postulated to have a

ring distorted equilibrium conformation with a CCS angle of 100° (43).

Decomposition of cis- and trans-butene episulphides is highly stereo-

specific indicating that the carbon-sulphur interaction is still

significant in the extended bond. The low A-factors are due to two

effects;

a) intersystem crossing during the reaction of the ground state

episulphide to the triplet state with the concommittantly small

transmission coefficient and

b) only very slight loosening of the molecule in the transition state.

It is shown that these conclusions are consistent with

recent findings on other cyclic sulphur containing molecules.

A kinetic study of the secondary isotope effect was also

undertaken. From the co-pyrolysis of C_2H_4S and C_2D_4S the measured

value of k_H/k_D was 1.20 at $230^\circ C$. A detailed calculation of the

effect, using the frequencies of the C_2H_4S molecule and assigned

frequencies in the activated complex, showed that the experimental

value was indeed reproduced when a model for the activated complex was

chosen in which there was considerable relaxation of the ring. The

calculations lent further support to the postulate that there is

considerable interaction in the extended C-S bond.

The pyrolysis of episulphide in the presence of olefins

showed that olefins inhibit the decomposition reaction. On the basis

of the kinetic data, the effect is assigned to quenching of the

excited episulphide by the olefin. It is also found that the triplet

episulphide catalyzes the cis-trans isomerization of cis-butene. When

a large excess of olefin is added to the episulphide the quenching

effect is found to level-off, and this is attributed to a new process

of episulphide decomposition, namely, abstraction of the sulphur

atom from triplet episulphide by the olefin. Unfortunately, the

limitations of the thermal system do not allow a complete

characterization of this particular reaction.

The results of this study provide a useful extension of the thermal chemistry observed in the structurally analogous cyclopropanes and epoxides. These molecules also decompose via ring relaxation but reaction appears to proceed on a singlet surface, whereas, episulphides decompose via a triplet surface. The longer lifetime of triplet episulphide allow efficient quenching by olefins. Whereas valence saturation of the biradical in the cyclopropanes and epoxides can occur by isomerization to form C=C and C=O double bonds, this process is absent in episulphides. This is due to the weaker C=S bond strength and the strong residual C-S interaction in the biradical.

Future studies in which the episulphide molecule is selectively energized to specific energies by chemical activation should yield considerable insight into episulphide chemistry. In addition, the possibility of molecules other than simple olefins affecting the decomposition reaction might yield further information about the reactivity of triplet episulphides.

BIBLIOGRAPHY

1. T.S. Chambers and G.B. Kistiakowsky, J. Am. Chem. Soc., 56, 399 (1934).

2. H.O. Pritchard, R.G. Sowden and A.F. Trotman-Dickenson, Proc. Roy. Soc. (London), A217, 563 (1953).

3. B.S. Rabinovitch, E.W. Schlag and K.B. Wiberg, J. Chem. Phys., 28, 504 (1958).

4. F.T. Smith, J. Chem. Phys., 29, 235 (1958).

5. M.C. Lin and K. Laidler, Trans. Farad. Soc., 64, 927 (1968).

6. S.W. Benson, J. Chem. Phys., 34, 521 (1961).

7. M.C. Flowers and H.M. Frey, J. Chem. Soc., 2758 (1960).

8. R.J. Crawford and T.R. Lynch, Can. J. Chem., 46, 1457 (1968);

    J.A. Berson and J.M. Balquist, J. Am. Chem. Soc., 90, 7343 (1968);

    W.L. Carter and R.G. Bergman, ibid., 90, 7344 (1968);

    R.G. Bergman and W.L. Carter, ibid., 91, 7411 (1969).

9. C.A. Wellington, J. Phys. Chem., 66, 1671 (1962);

    M.C. Flowers and H.M. Frey, J. Chem. Soc., 3547 (1961).

10. S.W. Benson, Thermochemical Kinetics, Wiley, New York, 1968.

11. H.E. O'Neal and S.W. Benson, J. Phys. Chem., 72, 1866 (1968).

12. L.B. Sims and P.E. Yankwich, J. Phys. Chem., 71, 3459 (1967).

13. R.J. Crawford and A. Mishra, J. Am. Chem. Soc., 87, 3768 (1965); ibid., 88, 3963 (1966).

14. R. Hoffmann, J. Am. Chem. Soc., 90, 1475 (1968).

15. D.H. White, P.B. Condit and R.G. Bergman, J. Am. Chem. Soc., 94, 7931 (1972).

16. P.J. Hay, W.J. Hunt and W.A. Goddard III, J. Am. Chem. Soc.,
    94, 638 (1972).

17. J.A. Horsley, Y. Jean, C. Moser, L. Salem, R.M. Stevens and
    J.S. Wright, J. Am. Chem. Soc., 94, 279 (1972).

18. L. Salem, Bull. Soc. Chim. Fr., 3161 (1970).

19. L. Salem and C. Rowland, Angew. Chemie, internat. Ed., 11,
    92 (1972).

20. M.L. Neufeld and A.T. Blades, Can. J. Chem., 41, 2956 (1963);
    and references therein.

21. W.H. Heckert and E. Mack Jr., J. Am. Chem. Soc., 51, 2706 (1929).

22. K.H. Mueller and W.P. Walters, J. Am. Chem. Soc., 76, 330 (1954).

23. S.W. Benson, J. Chem. Phys., 40, 105 (1963).

24. D.W. Setser, J. Phys. Chem., 70, 826 (1966).

25. M.C. Flowers and R.M. Parker, J. Chem. Soc. (B), 253 (1971).

26. M.C. Flowers and R.M. Parker, Int. J. Chem. Kin., 3, 443 (1971).

27. M.C. Flowers and H.M. Frey, Proc. Roy. Soc. A, 257, 122, 424 (1960).

28. G.E. Hartzell and J.N. Paige, J. Am. Chem. Soc., 88, 2616 (1966).

29. G.E. Hartzell and J.N. Paige, J. Am. Chem. Soc., 89, 459 (1967).

30. J.E. Baldwin, G. Hoefle and S.E. Choi, J. Am. Chem. Soc., 39,
    2810 (1971).

31. K. Kondo, M. Matsumoto and A. Negishi, Tetrahedron. Lett.,
    2131 (1972).

32. G. Tsuchihashi, M. Yamamuchi and A. Ohno, Bull. Chem. Soc. Jap.,
    43, 968 (1970).

33. O.P. Strausz, W.B. O'Callaghan, E.M. Lown and H.E. Gunning,
    J. Am. Chem. Soc., 93, 559 (1971).

34. a) J. Connor, A. van Roodselaar, R.W. Fair and O.P. Strausz,

    J. Am. Chem. Soc., $\underline{93}$, 561 (1971); b) K.S. Sidhu, I.G. Csizmadia,

    O.P. Strausz and H.E. Gunning, J. Am. Chem. Soc., $\underline{88}$, 2412 (1966);

    c) H.E. Gunning and O.P. Strausz, Advan. Photochem., $\underline{4}$, 143

    (1966).

35. A.W. Jackson and O.P. Strausz, Private Communication.

36. R.J. Donovan, D. Hussain, R.W. Fair, O.P. Strausz and H.E. Gunning,

    Trans. Farad. Soc., $\underline{66}$, 1635 (1970).

37. D.D. Davis, R.B. Klemm, W. Braun and M. Pilling, Int. J. Chem.

    Kin., $\underline{4}$, 383 (1972).

38. R. Atkinson and R.J. Cvetanovic, J. Chem. Phys., $\underline{56}$, 432 (1972).

39. O.P. Strausz, I. Safarik, W.B. O'Callaghan and H.E. Gunning,

    J. Am. Chem. Soc., $\underline{94}$, 1828 (1972).

40. R. Hoffmann, C.C. Wan and V. Neagu, Mol. Phys., $\underline{19}$, 113 (1970).

41. E. Leppin and K. Gollnick, Tetrahedron Lett., 3819 (1969).

42. O.P. Strausz, R.K. Gosavi, A.S. Denes and I.G. Csizmadia,

    Theoret. Chim. Acta, $\underline{26}$, 367 (1972).

43. O.P. Strausz, H.E. Gunning, A.S. Denes and I.G. Csizmadia,

    J. Am. Chem. Soc., $\underline{94}$, 8317 (1972).

44. K.S. Sidhu, Ph.D. Thesis, Univ. of Alberta, Edmonton, Alta.,

    1965.

45. E.A. Chandross, J. Am. Chem. Soc., $\underline{86}$, 1263 (1964).

46. R.M. Dupeyere, H. Lemaire and A. Rassat, J. Am. Chem. Soc.,

    $\underline{87}$, 3771 (1965).

47. W.J. van der Hart and L.J. Oosterhoff, Mol. Phys., $\underline{18}$, 281 (1970);

    and references therein.

48. G.R. Freeman, Can. J. Chem., 44, 245 (1966).

49. J. Perrin, Am. Phys., 11, 1 (1919).

50. F.A. Lindemann, Trans. Farad. Soc., 17, 598 (1922).

51. J.A. Christiansen, Z. Physik. Chemie, 103, 99 (1922).

52. C.N. Hinshelwood, Proc. Roy. Soc. A, 113, 230 (1927).

53. O.K. Rice and H.C. Ramsperger, J. Am. Chem. Soc., 49, 1617 (1927).

54. L.S. Kassel, J. Phys. Chem., 32, 225, 1065 (1928); Kinetics of Homogeneous Gas Reactions, Chemical Catalog Co., New York, (1932).

55. R.A. Marcus and O.K. Rice, J. Phys. and Colloid Chem., 55, 894 (1951); R.A. Marcus, J. Chem. Phys., 20, 359 (1952).

56. D.W. Placzek, B.S. Rabinovitch, G.Z. Whitten and E. Tschuikow-Roux, J. Chem. Phys., 43, 4071 (1965).

57. E. Tschuikow-Roux, J. Phys. Chem., 73, 3891 (1969).

58. D.M. Golden, R.K. Solly and S.W. Benson, J. Phys. Chem., 75, 1333 (1971).

59. G.B. Skinner and B.S. Rabinovitch, J. Phys. Chem., 76, 2418 (1972).

60. N.B. Slater, Proc. Camb. Phil. Soc., 35, 56 (1939); Theory of Unimolecular Reactions, Methuen, London 1959.

61. J.N. Butler and G.B. Kistiakowsky, J. Am. Chem. Soc., 82, 759 (1960).

62. E. Jakubowski, H.S. Sandhu and O.P. Strausz, J. Am. Chem. Soc., 93, 2610 (1971).

63. I. Oref, D. Schuetzle and B.S. Rabinovitch, J. Chem. Phys., 54, 575 (1971); E.H. Hardwidge, Ph.D. Thesis, Univ. of Washington, Seattle, 1972.

64. N.B. Slater, Chem. Soc. (London) Spec. Publ., 16, 29 (1962).

65. E.A. Halevi, Prog. Phys. Org. Chem., 1, 109 (1963).

66. S. Glasstone, K. Laidler, and H. Eyring, The Theory of Rate Processes, McGraw-Hill, New York, 1941.

67. M. Wolfsberg and M.J. Stern, Pure Appl. Chem., 8, 325 (1964).

68. S. Seltzer and S.G. Mylonakis, J. Am. Chem. Soc., 89, 6584 (1967), S. Seltzer, ibid., 83, 2625 (1961); ibid., 85, 14 (1963); S. Seltzer and F.T. Dunne, ibid., 87, 2628 (1965).

69. S.E. Scheppele, Chem. Rev., 72, 511 (1972); W.A. Van Hook in "Isotope Effects in Chemical Reactions", ACS Monograph 167, C.J. Collins and N.S. Bowman, Ed., Van Nostrand-Reinhold, New York, 1970, Chpt. 1.

70. A. Streitweiser, Jr., R.H. Jagow, R.C. Fabey, and S. Suzuki, J. Am. Chem. Soc., 80, 2326, (1958).

71. a) S. Seltzer, J. Am. Chem. Soc., 83, 1861 (1961);

    b) M. Feld, A.P. Stefani, and M. Swarc, J. Am. Chem. Soc., 84, 4451 (1962).

72. I. Safarik and O.P. Strausz, J. Phys. Chem., 76, 3613 (1972).

73. P.C. Vogel and M.J. Stern, J. Chem. Phys., 54, 779 (1971).

74. S. Searles and E.F. Lutz, J. Am. Chem. Soc., 80, 3168 (1958).

75. F.G. Bordwell and H.M. Anderson, J. Am. Chem. Soc., 75, 4959 (1953).

76. W.H. Carrothers and J. van Natta, J. Am. Chem. Soc., 52, 314 (1930).

77. E. Jakubowski, M.G. Ahmed, E.M. Lown, H.S. Sandhu, R.K. Gosavi, and O.P. Strausz, J. Am. Chem. Soc., 26, 94, 4094 (1972).

78. J. Troe, Ber. Bunsenges. physik. Chem., 72, 908 (1968).

79. J. Berkowitz, "The Molecular Composition of Sulphur",

    in Elemental Sulphur, B. Meyer, ed., Interscience, New York, 1965.

80. H. Mackle, Tetrahedron, 19, 1159 (1963).

81. H. Mackle and P.A.G. O'Hare, Tetrahedron, 19, 961 (1963).

82. a) K.J. Laidler, Chemical Kinetics, McGraw-Hill Book Co.,

    New York, 1965; b) H.A. Olschweski, J. Troe, and H.Gg. Wagner,

    Ber. Bunsenges. physik. Chem., 70, 450 (1966).

83. H.A. Olschweski, J. Troe, and H.Gg. Wagner, Ber. Bunsenges.

    physik. Chem., 70, 1060 (1966).

84. F. Rosenkranz and H.Gg. Wagner, Z.f.physik. Chem. N.F., 61,

    302 (1968).

85. A. Ohno and Y. Ohnishi, Tetrahedron Lett., 339 (1972).

86. J.G. Calvert and J.N. Pitts, Jr., Photochemistry, John Wiley

    and Sons, New York, 1966.

87. A.W. Jackson and A.J. Yarwood, J. Am. Chem. Soc., 93, 2801 (1971).

88. M.W. Schmidt and E.K.C. Lee, J. Chem. Phys., 51, 2024 (1969).

89. A.J. Mercer and R.S. Mulliken, Chem. Rev., 69, 639 (1969).

90. N.C. Baird, Chem. Comm., 199 (1970).

91. A.J. Lorquet, J. Phys. Chem., 74, 895 (1970).

92. B. Tamamushi and H. Akiyama, Z. Elektrochem., 43, 156 (1937),

    ibid., 45, 72 (1939).

93. B.S. Rabinovitch and F.S. Looney, J. Chem. Phys., 23,

    2439 (1955).

94. R.B. Cundall, Prog. Reaction Kinetics, 2, 165 (1964).

95. M.H. Back and R.J. Cvetanovic, Can. J. Chem., 41, 1396 (1963).

96. S.W. Benson, K.W. Egger, and D.M. Golden, J. Am. Chem. Soc.,

    87, 468 (1965).

97. K. Sugimoto, W. Ando, and S. Oae, Bull. Chem. Soc. Jap., $\underline{38}$,

224 (1965).

98. J.L. Sprung, H. Akimoto, and J.N. Pitts, Jr., J. Am. Chem. Soc.,

$\underline{93}$, 4358 (1971).

99. I.I. Ermakova, B.A. Dolgoplosk, and E.N. Kropachea,

Dokl. Akad. Nauk SSSR, $\underline{141}$, 1363 (1961).

100. G.J. Collin and P.M. Perrin, Can. J. Chem., $\underline{50}$, 2400 (1972).

101. D.M. Graham, R.L. Mieville, and C. Sivertz, Can. J. Chem., $\underline{42}$,

2239 (1964).

102. P.J. Robinson and K.A. Holbrook, Unimolecular Reactions,

Wiley-Interscience, London, 1972.

103. A.A. Frost and R.G. Pearson, Kinetics and Mechanism, 2. ed.,

John Wiley and Sons, New York, 1961.

104. J. Troe and H.Gg. Wagner, Ber. Bunsenges. physik. Chem., $\underline{71}$,

937 (1967), and references therein.

105. B. de B. Darwent, J. Chem. Phys., $\underline{18}$, 1532 (1950).

106. A.W. Jackson and O.P. Strausz, private communication.

107. E.M. Lown, H.S. Sandhu, H.E. Gunning, and O.P. Strausz,

J. Am. Chem. Soc., $\underline{90}$, 7164 (1968).

108. A. van Roodselaar and O.P. Strausz, private communication.

109. E.M. Lown, Ph.D. Thesis, Univ. of Alberta, Edmonton, Alberta,

1968.

110. O.P. Strausz, J. Font, E.L. Dedio, P. Kebarle, and H.E. Gunning,

J. Am. Chem. Soc., $\underline{89}$, 4805 (1967).

111. M.G. Evans and M Polanyi, Trans. Farad. Soc., $\underline{34}$, 11 (1938).

112. N.N. Semmenov, Some Problems in Chemical Kinetics and

Reactivity, Vol. I, Princeton University Press, Princeton, N.Y.

(1958).

113. A.J. Yarwood, O.P. Strausz, and H.E. Gunning, J. Chem. Phys., $\underline{41}$, 1705 (1965.

114. M.C. Flowers and H.M. Frey, Proc. Roy. Soc., $\underline{A257}$, 122 (1960); ibid., $\underline{A260}$, 424 (1961).

115. J.P. Chesick, J. Am. Chem. Soc., $\underline{82}$, 3277 (1960).

116. J. Jortner, R.K. Rice and R.M. Hochstrasser, Adv. in Photochem., $\underline{7}$, 149 (1970).

117. I. Safarik, private communication.

APPENDIX A

Thermochemical Calculations on Episulphide Biradicals

The enthalpies of formation of the biradicals are esti-mated from the known enthalpies of the corresponding thiols and the bond energies at the radical site. The thermochemical values used are:

$D(S-H)$ = 88 kcal/mole

$D(C-H)$ in C_2H_6 = 99 kcal/mole

$i-C_3H_6$ = 94 kcal/mole

$sec-C_4H_{10}$ = 94 kcal/mole
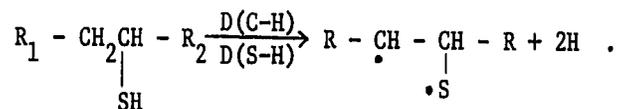
$\Delta H_f(CH_3CH_2SH)$ = -11 kcal/mole

$\Delta H_f(CH_3CH_2CH_2SH)$ = -16 kcal/mole

$\Delta H_f(CH_3CH_2CH(SH)CH_3$ = -23 kcal/mole

$\Delta H_f(H)$ = 52 kcal/mole

The enthalpy of formation of the biradical can then be obtained by the method used by Benson (6) for trimethylene:

$$R_1 - CH_2CH - R_2 \xrightarrow[D(S-H)]{D(C-H)} R - \underset{\bullet}{CH} - \underset{\bullet S}{CH} - R + 2H \quad . $$
$$\qquad\qquad\quad SH$$

The values for the respective biradicals calculated this way are as follows:

ΔH_f (kcal/mole)

$$\begin{array}{c} \underset{|}{\overset{|}{C}H} - \underset{|}{\overset{|}{C}H_2} \\ \bullet S \end{array}$$ 72

$$\begin{array}{c} CH_3\underset{\bullet}{CH} - \underset{|}{\overset{|}{C}H_2} \\ \bullet S \end{array}$$ 62

$$\begin{array}{c} CH_3\underset{\bullet}{CH} - \underset{|}{CH} - CH_3 \\ \bullet S \end{array}$$ 55

The enthalpy of formation of the episulphides of ethylene, propylene and trans-butene are 19.93, 10.99 and 0.89 kcal/mole respectively, so that the enthalpies of reaction forming the above biradicals are correspondingly 52, 51 and 54 kcal/mole.

APPENDIX B

Thermochemical Calculations on Episulphoxides

The application of the thermodynamic group additivities, as developed by Benson and coworkers, provides a facile and reliable method for the determination enthalpies and entropies of organic molecules. Since the enthalpies of formation of <u>trans</u>-stilbene episulphoxide and its corresponding biradical, obtained by ring opening, are not known, this technique was applied. With the exception of one group, $[C-(C_B)(C)(H)(SO)]$, all the necessary groups have been tabulated (10). An estimate for this unknown group can be obtained from
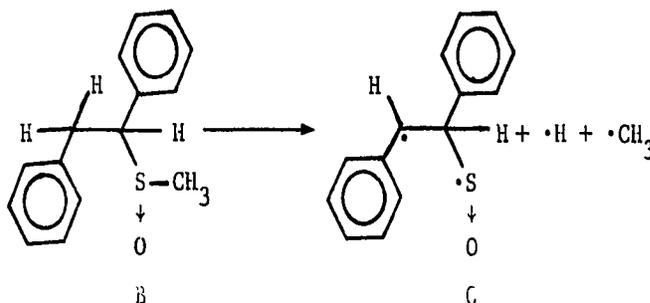
$$[C-(C_B)(C)(H)(SO)] = [C-(C_B)(C)_2(H)] + [C-(C)_3(SO)-C-(C)_4]$$
$$= -4.53 \text{ kcal/mole.}$$

The enthalpy of formation of <u>trans</u>-stilbene-episulphoxide [A] can then be written as

$$\Delta H_f^o(A) = 10[C_B-(H)] + 2[C_B-(C)] + 2[C-(C_B)(C)(H)(SO)] + [SO-(C)_2]$$
$$+ \text{ ring strain}$$
$$= 40.5 \text{ kcal/mole.}$$

The ring strain is taken to be the same as that of episulphides.

The enthalpy of formation of corresponding biradical can be obtained by considering the following reaction:

From a knowledge of the benzilic C-H bond strength, the SO-CH$_3$ bond strength, and the enthalpy of formation of B, we can estimate the enthalpy of formation of the biradical. The heat of formation of B is

$$\Delta H_f^o = 10[C_B-(H)] - 2[C_B-(C)] + [C-(C)(C_B)(H)_2] + [C-(C)(C_B)(H)(SO)]$$
$$+ [SO-(C)_2] + [C-(SO)(H)_3]$$

$$= 10.1 \text{ kcal/mole}$$

D(C-H) for benzilic hydrogens is 83 kcal/mole (10) and we can assume D(CH$_3$-SO) is the same as D(CH$_3$-CO) which is 79 kcal/mole. The enthalpy of formation of the biradical [C] is therefore
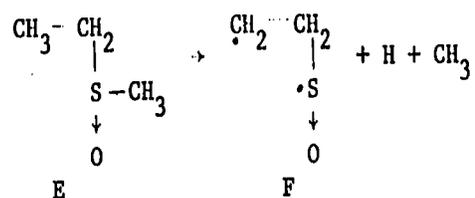
$$\Delta H_f^o(C) = D(C-H) + D(CH_3-SO) - \Delta H_f^o(H) - \Delta H_f^o(CH_3) + \Delta H_f^o(B)$$

$$= 86 \text{ kcal/mole}$$

The enthalpy for the formation of the biradical from trans-stilbene episulphoxide is therefore 86-40.5 = 45.5 kcal/mole.

An analogous scheme can also be used to calculate the enthalpy of ethylene episulphoxide and its biradical. Using the group values, the enthalpy of formation of ethylene episulphoxide (D) is

$$\Delta H_f(D) = 2[C-(C)(H)_2(SO)] + [SO-(C)_2] + \text{ring strain}$$

$$= -10.1 \text{ kcal/mole.}$$

Applying the same process as above, ΔH_f^o for the biradical can be obtained from

$$\underset{E}{\begin{array}{c} CH_3 - CH_2 \\ \qquad\quad | 2 \\ S - CH_3 \\ \downarrow \\ O \end{array}} \rightarrow \underset{F}{\begin{array}{c} CH_2 \cdots CH_2 \\ \bullet 2 \qquad | 2 \\ \bullet S \\ \downarrow \\ O \end{array}} + H + CH_3$$

The heat of formation of E is

$$\Delta H_f^O(E) = [C-(C)(H)_3] + [C-(C)(H)_2(SO)] + [SO-(C)_2]$$
$$+ [C-(SO)(H)_3]$$

$$= -42.3 \text{ kcal/mole}$$

D(C-H) for ethane is 99 kcal/mole and again D(SO-CH$_3$) $\simeq$ 79 kcal/mole, thus the heat of formation of the biradical is

$$\Delta H_f^O(F) = D(C-H) + D(SO-CH_3) - \Delta H_f^O(H)$$
$$- \Delta H_f^O(CH_3) + \Delta H_f^O(E)$$

$$= 50 \text{ kcal/mole}$$

The heat of reaction forming the biradical is then equal to about

$$50 + 10 = 60 \text{ kcal/mole}.$$