

THE THERMAL DECOMPOSITION OF ETHYL CYCLOBUTANE:  
A LOW PRESSURE UNIMOLECULAR REACTION  
STUDY

by

DORAYI MOHAMMED AMINU

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## VITA

NAME OF AUTHOR: Dorayi Mohammed Aminu

PLACE OF BIRTH: Kano City, Kano State, Nigeria

DATE OF BIRTH: November 16, 1942

## UNDERGRADUATE AND GRADUATE SCHOOLS ATTENDED:

Ahmadu Bello University  
University of Oregon

## DEGREES AWARDED:

Bachelor of Science (Honors), 1968, Ahmadu Bello University  
Master of Science, 1970, University of Oregon

## AREAS OF SPECIAL INTEREST:

Physical Chemistry  
Science Education in Developing Countries

## PROFESSIONAL EXPERIENCE:

Chemistry and Science Teacher, Government Girls College,  
Kano, Nigeria, 1965

Chemistry and Mathematics Teacher, Government College,  
Kano, Nigeria, 1968

Teaching Assistant, Department of Chemistry, University of  
Oregon, Eugene, 1968-1969

Research Assistant, Department of Chemistry, University of  
Oregon, Eugene, 1969-1971

Teaching Assistant, Department of Chemistry, University of  
Oregon, Eugene, 1971-1973

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## DEDICATION

To all the African mothers whose children have left home and went to Eastern and Western Europe, North and South America, Russia and China in search of knowledge and truth on behalf of all the African Peoples.

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## CHAPTER ONE

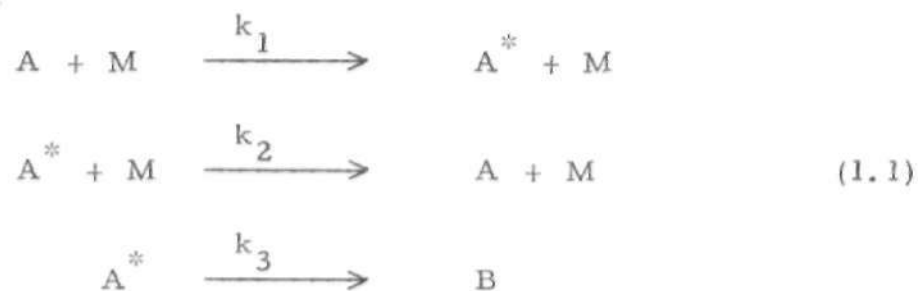
## INTRODUCTION

Resumé of Unimolecular Reaction TheoriesFundamental Concept of Unimolecular Reactions

Perrin (1919) was the first person to attempt to provide a satisfactory microscopic theory for unimolecular reaction in the gas phase. He suggested that infra-red radiation must be absorbed by the reactants in the activation step of such reactions. This theory was however short lived because experimental justification could not be found. The present view of unimolecular reactions rate theory grew out of a suggestion made by Lindemann (1922). He proposed that activated molecules were produced by binary collisions but that there was a time lag, during which a small fraction of the activated molecules underwent unimolecular decomposition. Most of the activated molecules, however, would be deactivated by collision before decomposition occurred.

The scheme derived from Lindemann's proposal can be written

as



Here A is the reactant, A<sup>\*</sup> is an energized reactant molecule, i.e., one with enough energy to react and M is another molecule of reactant, a molecule of the product of the reaction or a molecule of some added inert gas. The rate is given by

$$d(\text{B})/dt = k_3(\text{A}^*) \quad (1.2)$$

The steady-state method can be used to solve for the steady-state concentration of A<sup>\*</sup>. In the usual way

$$d(\text{A}^*)/dt = k_1(\text{A})(\text{M}) - k_2(\text{A}^*)(\text{M}) - k_3(\text{A}^*) = 0 \quad (1.3)$$

hence  $(\text{A}^*) = k_1(\text{A})(\text{M})/(k_2(\text{M}) + k_3)$

Substituting for (A<sup>\*</sup>) in Equation (1.2), the rate is simply

$$\begin{aligned}
 d(\text{B})/dt &= k_1 k_3 (\text{A})(\text{M}) / (k_2(\text{M}) + k_3) \\
 &= k_{\text{uni}}(\text{A}) = k_{\text{exp}}(\text{A})
 \end{aligned} \quad (1.4)$$

where  $k_{\text{exp}}$  is the experimental rate constant for the first order process.

It is apparent that  $k_{\text{exp}}$  will depend on the concentration of  $M$  which is proportional to the total pressure. There are two limiting cases that lead to particularly simple forms of  $k_{\text{exp}}$ . At high pressures, if  $k_2(M) \gg k_3$ , we find that the experimental rate constant is

$$k_1 k_3 / k_2 = k_{\infty}$$

The quantity  $k_{\infty}$  is independent of pressure, so that the reaction is indeed first order. In this case, the rate of reaction of energized molecules is so slow compared with the rate of energy removal in the second step that an equilibrium fraction of

$$(A^*) / (A) = k_1 / k_2$$

is maintained. Thus the observed rate constant is merely the product of the rate constant for spontaneous decomposition and the fraction of molecules that are energized. At low pressures  $k_2(M) \ll k_3$  and we find that the experimental rate constant is

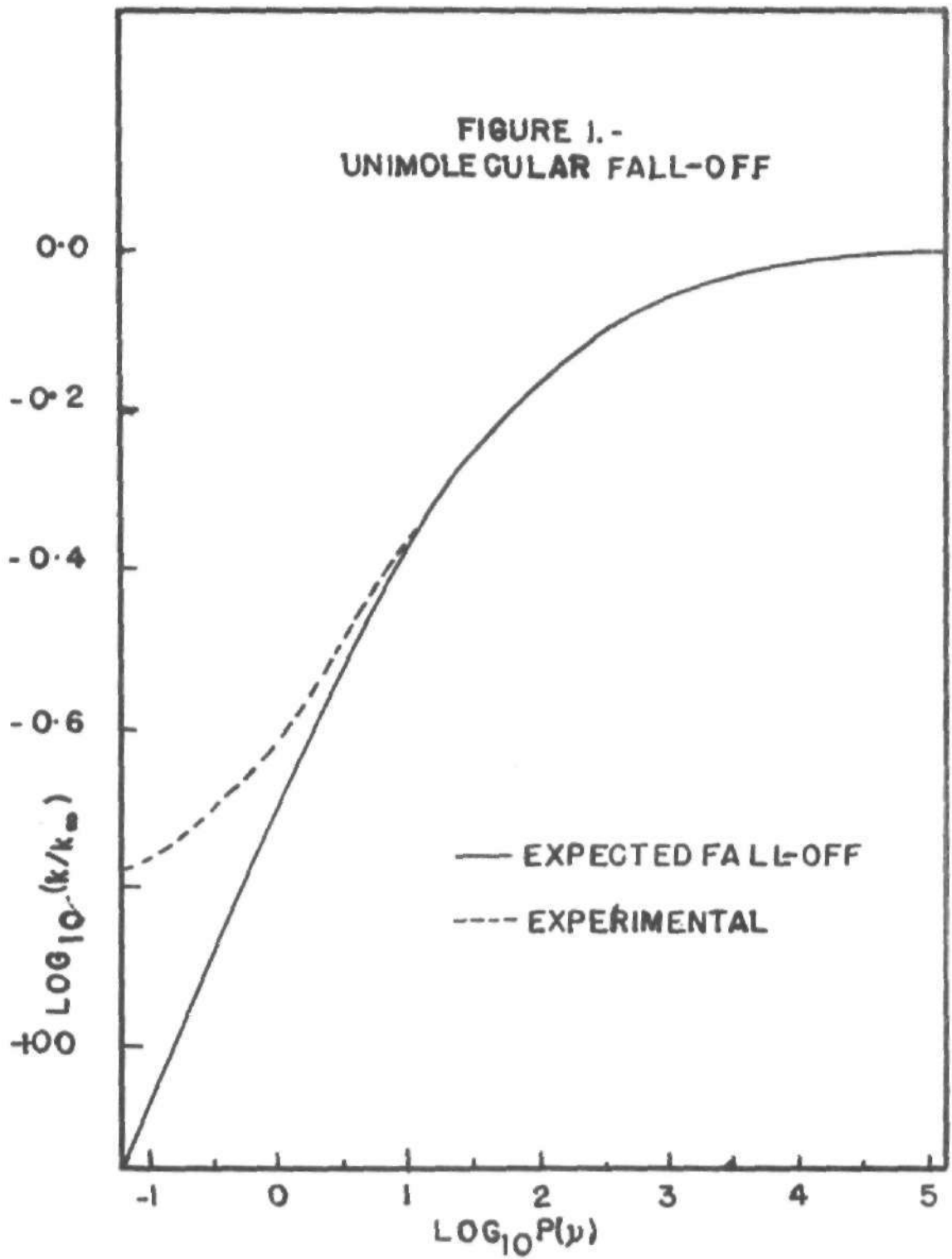
$$k_o = (k_{\text{uni}})_{p=0} = k_2(M) \quad (1.5)$$

In this limiting pressure region, the rate-determining step has become the production of energized molecules by collisions. We expect to find that  $k_{\text{uni}}$  is proportional to the total pressure. The

products of the reaction are generally not as effective as the reactant in transferring energy during a collision. In these cases one molecule of the reactant generally reacts to give two or more smaller molecules of the products, which means that if the product molecules are half as efficient as the reactant molecules in transferring energy during collision, the rate expression is predicted to be first order throughout a given experiment. Experimentally this prediction is verified and at all initial pressures each run remains first order throughout the run. Another important prediction of this simplified form of unimolecular reaction theory is that the rate constant varies with varying initial pressure. This prediction has also been confirmed experimentally by this research because the experimental rate constant was found to decline with declining initial pressures. Figure 1 shows the pressure dependence of  $k_{uni}$  plotted in logarithmic form. At high pressures theoretically the line asymptotically approaches  $\log k_{\infty}$ . At low pressures, the line has a theoretical slope of unity, corresponding to the region in which the relationship

$$k_0 = (k_{uni})_{p=0} = k_2(M)$$

is applicable. It is very difficult to collect experimental data in this region because it appears that the more complicated a molecule is the lower the pressure region at which the slope of  $\log k$  vs.  $\log p$



becomes unity. This is exemplified by Schneider and Rabinovitch (1962) who studied the thermal unimolecular isomerization of methylisocyanide (6 atoms, 12 normal modes) to acetonitrile from 10,500 torr down to 0.16 torr. They came closer to the two theoretical limits of high and low pressures than any other single study that had been done although the slope of  $\log k$  vs.  $\log p$  at their low pressures was less than 1 by about 10%. Theoretical calculations on the unimolecular thermal decomposition of azomethane (10 atoms, 24 normal modes) were done by Clark in 1958. The calculations showed that at pressures of  $10^{-12}$  torr the slope of the  $\log k$  vs  $\log p$  plot was less than unity by about 6%. At the present state of the art it is impossible to make measurements at these low pressures. The lower pressure limit for experimental measurements is about  $10^{-4}$  torr.

#### Classical Microscopic Theories

The first microscopic theory of unimolecular reactions was developed by Hinshelwood in (1926). He used a rather simple molecular model in which he assumed that:

- (i) The problem could be treated classically;
- (ii) The energy of activation was supplied by binary collisions in which vibrational energy was available for activation;



(iii) for activation it was sufficient to have the minimum energy  $E_0$  in the molecule as a whole;

(iv) the fraction  $W$  of reactant molecules which contain energy per mole in excess of  $E_0$  is given by the classical equilibrium distribution for a system of molecules having  $s$  vibrational modes which contribute to the activation process.

$$W = \frac{\exp(-E_0/RT) (E_0/RT)^{s-1}}{\Gamma(s)} \quad (1.6)$$

where  $\Gamma(s)$  is the gamma function and the higher-order terms are negligible for values of  $E_0/RT$  which are usually involved,  $E_0/RT \gg 1$ . Hinshelwood's theory predicts a straight line plot for  $1/k_{\text{exp}}$  vs.  $1/p$  and it represents an analytical formulation of the Lindemann time-lag theory. It does not in general account satisfactorily for the observed variation of the rate constant with pressure because, in general, a plot of  $1/k_{\text{exp}}$  vs.  $1/p$  from experimental data is found to be curved. This failure is largely due to the rather unrealistic assumption that the excess of energy in these bonds above the activation energy does not increase the probability of reaction.

To overcome these difficulties Kassel (1928) proposed a classical theory in which the molecule is represented as a system of weakly coupled harmonic oscillators. Kassel assumed that a molecule

must possess at least the activation energy in a single vibrational bond as a necessary condition for decomposition and, further, that the excess energy in the molecule above the activation energy enhances the probability of reaction by increasing the chance that the bond in question will possess the necessary threshold energy increment. If a molecule contains total vibrational energy of magnitude  $E/N_0$ , ( $E > E_0$ ), distributed among  $2s$  quadratic terms associated with  $s$  vibrational modes, the temperature-independent probability per unit time for decomposition was shown by Kassel to be

$$b_E = A \left( \frac{E - E_0}{E} \right)^{s-1} \quad (1.7)$$

where  $A$  is a constant of proportionality. It is shown to be the frequency factor for the Arrhenius equation applied at high pressures.

$$A = k_{\infty} \exp(E_0/RT)$$

Kassel used the strong collision assumption and derived an expression for  $k_{\text{exp}}$  in the following way. The strong collision assumption states that all collisions of activated molecules lead to deactivation. This assumption is justified because the concentration of activated molecules in the system is very small such that collisions between

activated molecules can be ignored. Another reason in favor of the strong collision assumption is that it takes the removal of only a few percent of the energy of most of the activated molecules to deactivate them. Using this assumption, a system of molecules at collisional equilibrium is represented by



If it is imagined that the reaction is not "allowed" to proceed, the rate of deactivation of the activated molecules is

$$a_{\text{eq}}^* = a n^2 W$$

Here  $n_{\text{eq}}^*$  is the equilibrium concentration of the activated molecules,  $n$  is the concentration of all the molecules in the system, both in molecules per cc., and

$$a = 4 \sigma^2 (\pi k T / m)^{1/2} .$$

The rate of activation must equal to the rate of deactivation.

$$\text{rate of activation} = a n^2 W$$

Now if the reaction is "allowed" to take place, the rate of activation is assumed to be the same as before. The rate of loss of activated molecules however is simply given by the following expression

$$\text{rate of loss of activated molecules} = an^* + b_E n^*$$

Then 
$$an^2 W = an^* + b_E n^*$$

giving 
$$n^* = an^2 W / (an + b_E) \quad (1.9)$$

But 
$$k_{\text{exp}} = \int_{E_0}^{\infty} k_E dE = \int_{E_0}^{\infty} \frac{b_E n^*}{n} dE \quad (1.10)$$

substituting for  $n^*$  from Equation (1.9), Equation (1.10) becomes

$$k_{\text{exp}} = \int_{E_0}^{\infty} \frac{b_E}{n} \frac{an^2 W dE}{(an + b_E)}$$

$$\int_{E_0}^{\infty} \frac{b_E W dE}{1 + \frac{b_E RT}{a N_0 p}} \quad (1.11)$$

where  $n = p/kT = N_0 p/RT$ .

Substituting for  $b_E$  from Equation (1.7) and  $W$  from Equation (1.6),

Kassel got the following relationship for  $k_{\text{exp}}$

$$k_{\text{exp}} = \frac{k_{\infty}}{[(s)] (RT)^s} \int_{E_0}^{\infty} \frac{(E-E_0)^{s-1} \exp(-(E-E_0)/RT) dE}{1 + \frac{ART \left(\frac{E-E_0}{E}\right)^{s-1}}{aN_0p}} \quad (1.12)$$

Experimental values of  $k_{\text{exp}}$  can be compared with Equation (1.12) by obtaining  $k_{\infty}$  at a given temperature directly from experiment and  $E_0$  from a plot of  $\ln k_{\infty}$  vs.  $d(1/T)$ . A preliminary value of  $s$  is then selected which is less than the maximum possible value,  $(3n - 6)$ , where  $n$  is the number of atoms in the non-linear decomposing molecule. The hard-sphere collision diameter is best estimated from viscosity measurements if they are available. In the absence of viscosity data the value of the collision diameter for cyclobutane derivatives is estimated using a method due to Bondi (1964). In most cases it is found that the Kassel theory provides a satisfactory agreement with experiment and it is used here, in a modified form, to discuss the results of this research.

The reason for the modification is that experimental rate constants at pressures below 10 microns (1 torr = 100.0 microns) were found to approach a constant value. This is due to the fact that at such low

pressures the activation and deactivation of gas molecules as a result of collisions with the walls of the reaction vessel are significant. The modified form of the theory is due to Swinehart and Thomas (1964, 1969). They obtained a relationship for  $k_{\text{exp}}$  in the same way as Kassel did with the additional terms due to collisions with the walls of the reaction vessel. They obtained the expression for  $k_{\text{exp}}$  in the following way.

If collisions with the wall involve only energy exchange (not reaction) two new parameters can be introduced, namely  $\lambda$  and  $\lambda'$ . These stand for the intermolecular vibrational deactivation collision efficiency and wall collision efficiency respectively. At collisional equilibrium if it is imagined that no reaction is "allowed" to take place, from Equation (1.8), the rate of deactivation of activated molecules is

$$\lambda a n_{\text{eq}}^* W + \lambda' \frac{1}{4} n_{\text{eq}}^* W \bar{c} \left( \frac{S}{V} \right)$$

where  $\left( \frac{S}{V} \right)$  is the surface-to-volume ratio of the reaction flask and  $\bar{c}$  the average thermal speed of the molecule. Here again the strong collision assumption is made. If this is the same as the rate of activation even when a chemical reaction is "allowed" to occur, the following relationship can be written

$$\lambda a n^* + \lambda' \frac{1}{4} n^* \bar{c} \left( \frac{S}{V} \right) + b_E n^* = \lambda a n^2 W + \lambda' \frac{1}{4} n W \bar{c} \left( \frac{S}{V} \right) \quad (1.14)$$

Solving for  $n^*$

$$\begin{aligned}
 n^* &= \frac{\lambda a n^2 W + \lambda' \frac{1}{4} n W \bar{c} \left( \frac{S}{V} \right)}{\lambda a n + \lambda' \frac{1}{4} \bar{c} \left( \frac{S}{V} \right) + b_E} \\
 &= \frac{n W}{1 + \frac{b_E}{\lambda a n + \lambda' \frac{1}{4} \bar{c} \left( \frac{S}{V} \right)}} \quad (1.15)
 \end{aligned}$$

Substituting for  $n^*$  from Equation (1.15),  $W$  from Equation (1.6) and  $b_E$  from Equation (1.7) into Equation (1.10), Swinehart and Thomas obtained

$$k = \frac{k_\infty}{\sqrt{(s)} (RT)^s} \int_{E_0}^{\infty} \frac{(E-E_0)^{s-1} \exp(-(E-E_0)/RT) d(E-E_0)}{1 + \frac{A R T \left( \frac{E-E_0}{E} \right)^{s-1}}{\lambda N_0 a p + \frac{\lambda'}{4} \bar{c} R T \left( \frac{S}{V} \right)}} \quad (1.16)$$

which is used to discuss the results of this research. It can not be used to predict  $k_{\text{exp}}$  in advance because there is no way of selecting many of the parameters. The usual practice is to select  $k_\infty$  to fit the high pressure experimental data and then select the other parameters to fit all the experimental rate constants.

History of Low Pressure Studies  
of Cyclobutane Derivatives

The aim of experimental physical chemistry, I think, is to provide data on all the possible chemical compounds over all the possible ranges of experimental variables. This research project is a small contribution undertaken to provide kinetic data regarding the low pressure pyrolysis of ethylcyclobutane.

In previous studies in this laboratory, the gas phase thermal decomposition of several cyclobutane derivatives have been shown to be unimolecular reactions. The first order rate constants became pressure dependent at about one torr and fall off with decreasing pressure. At pressures around 10 microns, significant departure from the expected fall-off begins to occur and by 1 micron the rate constant seems to be leveling off to a limiting low pressure value. This low pressure departure from unimolecular reaction theory can be explained by the fact that the walls of the reaction vessel contribute to the collisional deactivation of the excited cyclobutane molecule in accordance with the Thomas-Swinehart (1964, 1969) modifications of the Kassel integral. Among the compounds studied in this laboratory were cyclobutane Vreeland (1963), methylenecyclobutane Burkhardt (1962), methylcyclobutane Thomas (1964) and 1, -2-dimethylcyclobutane Conn (1966); hence a study of ethylcyclobutane is in line with



the traditional studies in this laboratory. Thomas (1964) and Conn (1966) have detected isomerization of the substituted cyclobutane molecules they studied. Thus a study of ethylcyclobutane pyrolysis followed by careful analysis of the reaction products may throw further light on the reaction mechanism of substituted cyclobutane rings leading to isomerizations.

#### Previous Work on Ethylcyclobutane

Wellman and Walters (1957) had earlier studied the thermal decomposition of ethylcyclobutane over the pressure range 7-400 torr at 450° C. They found that the reaction products were exclusively ethylene and 1-butene, that the kinetics appeared to be first-order, homogeneous and probably unimolecular up to at least 40% of the reaction. Nitric oxide, propylene and toluene had no effect on the rate of the reaction. Their experimental values for the Arrhenius parameters were

$$A = 3.6 \times 10^{15} \text{ sec}^{-1}$$

and  $E_0 = 62.0 \pm 1.0 \text{ kcal mole}^{-1}$ .

## CHAPTER TWO

### MATERIALS AND EQUIPMENT

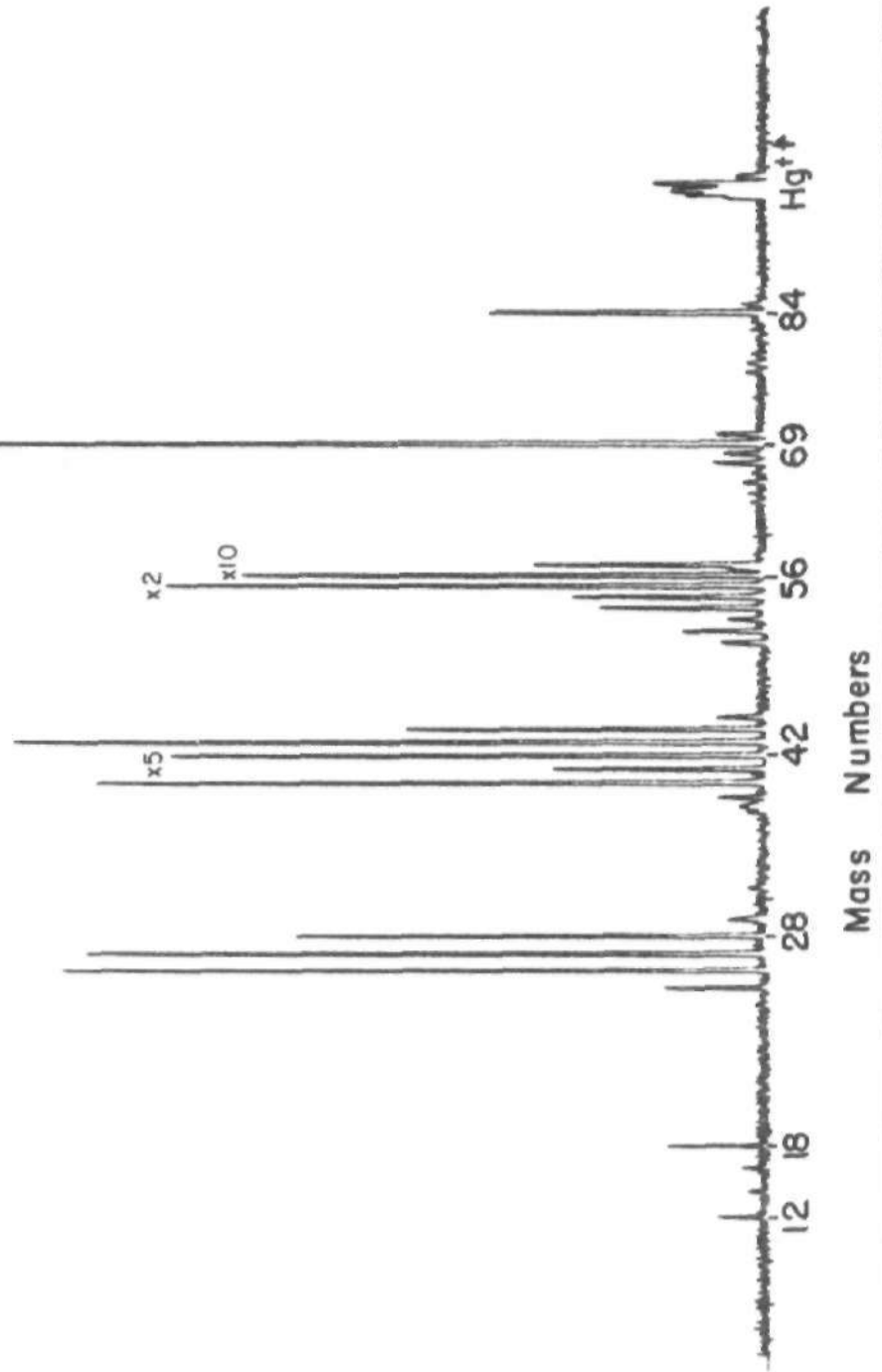
#### Materials

The sample of ethylcyclobutane used in this research was bought from the Chemical Samples Company, Columbus, Ohio. The ethylcyclobutane was gas chromatographically tested for purity using a column of dibutylphthalate, which was found by Conn (1966) to be a very effective means of separating cyclobutane compounds from other types of compounds. The ethylcyclobutane was found to contain no other detectable peak using the Beckmann/GC-2 gas chromatograph. Impurities amounting to about 0.2% could be easily identified with this chromatograph. The ethylcyclobutane thus used in this study was better than 99.8% pure and during the course of the study, periodic checks were made to ensure the purity of the material.

Mass spectrum of the ethylcyclobutane was then recorded, Figure 2, and compared to a standard ethylcyclobutane spectrum from American Petroleum Institute, Mass Spectral Data (1960). The numbers over several of the peaks indicate the factor by which the peak height must be multiplied so as to give the true peak height.

Figure 2.- Mass Spectrum of Ethylcyclobutane

Accl. Volt. = 2300V. Bomb. Volt. = 50V. Trap = 16.5  $\mu$ A Case = 98  $\mu$ A  
Stab. = 10mA Leak 50 Press. = 5.6  $\mu$



Also note the presence of mass spectral peak due to water at 18 and the second order mercury ( $\text{Hg}^{++}$ ) spectrum. The relative peak heights obtained from the spectrum, after being adjusted for background mass spectral peaks, are contained in Table I. The other materials used in this work were, methane, ethylene, 1-butene, cis- and trans-2-butenes, cis-2-pentene, trans-2-pentene, cis-2-hexene, trans-2-hexene, cyclopentene, 3-methyl-1-pentene and 2-ethyl-1-butene. All of them were purchased commercially and were used for reference purposes. Nitric oxide was used in this work for added-gas runs. The nitric oxide came from a tank supplied by the Matheson Company. It was passed slowly through a trap filled with glass beads cooled with a dry ice-trichloroethylene slurry to remove traces of nitrogen dioxide contained in the tank.

### Equipment

#### Mass Spectrometer

The mass spectrometer used in this research has been described in great detail by McCoy (1956), Clark (1958), Whatley (1961), and Vreeland (1963). Lowden (1972) has also discussed the most recent modifications in the mass spectrometer.

The instrument is a standard Nier type with  $60^\circ$  deflection with a carbonized tungsten or a rhenium filament for the emission of the

TABLE I  
 MASS SPECTRUM OF ETHYLCYCLOBUTANE\*

m/e	Observed Peak Height (mm)	Background (mm)	Net Peak Height (mm)	Relative Peak Height (%)
12	6.0	--	6.0	0.9
15	2.0	--	2.0	0.3
16	3.0	2.5	0.5	0.1
18	13.3	11.4	1.9	0.3
25	13.2	--	13.2	2.0
26	93.0	--	93.0	13.4
27	89.5	--	89.5	13.0
28	62.0	8.5	53.5	7.7
29	4.8	--	4.8	0.7
38	6.2	--	6.2	0.9
39	89.5	--	89.5	13.0
40	28.0	--	28.0	4.0
41	392.5	--	392.5	56.7
42	99.5	--	99.5	14.4
43	47.2	--	47.2	6.8
44	7.2	3.2	4.0	0.6
50	5.5	--	5.5	0.8
51	10.5	--	10.5	1.5
52	4.2	--	4.2	0.6
53	21.5	--	21.5	3.1
54	25.0	--	25.0	3.6
55	158.0	--	158.0	22.8
56	692.0	--	692.0	100.0
57	30.3	--	30.3	4.4
67	6.5	--	6.5	0.9
68	5.0	--	5.0	0.7
69	113.4	--	113.4	16.4
70	6.2	--	6.2	0.9
84	36.5	--	36.5	5.3

\* Bombarding voltage = 50 volts, acceleration voltage = 2,300 V, trap current = 16.5  $\mu$ A, case current = 9.8  $\mu$ A, stabilizing current = 10 mA, pressure of sample = 5.6  $\mu$ , leak 50, ambient temperature.

bombarding electrons. The energy of these bombarding electrons was approximately 50 electron volts. The ion source of the mass spectrometer was connected by a glass tube to an all glass leak sealed into the center of the spherical reaction vessel. In this way, the reaction mixture is continuously sampled as the reaction proceeds. The ions emerging from the ion source were accelerated by a potential difference of 2,300 volts  $\pm$  0.1 volt and sorted magnetically according to their mass to charge ( $m/e$ ) ratio. A beam of ions with a selected  $m/e$  value could be brought to focus on the collector by adjusting the magnetic field which was controlled by a constant current power supply. The power supply is regulated at  $\pm$  0.005%. The collector was connected to an electrometer whose output was displayed by either a galvanometer or a Leeds and Northrup Speedomax-G recording potentiometer.

Three filaments were used during this research, one made with carbonized tungsten and the other two with rhenium. Under the operating conditions the carbonized tungsten filament was found to have a longer life time. As a consequence of varying source geometry with each new filament and different positions of the source magnet, the dependence of the peak height on source voltages changed from time-to-time. Thus whenever a new filament was installed on the spectrometer a determination of the functional dependence of mass

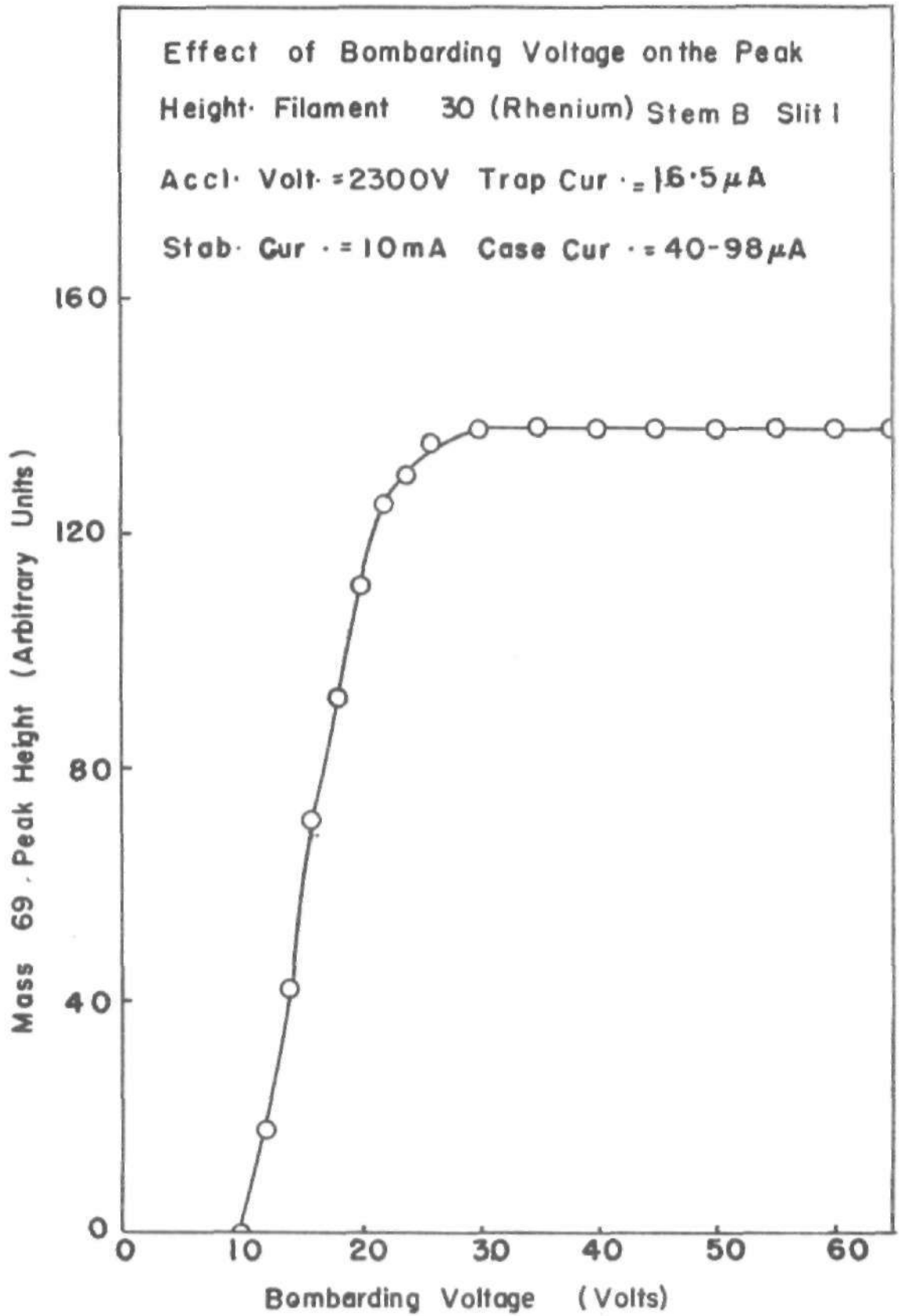
spectral peak height on the bombarding voltage at fixed trap and stabilizing currents had to be made to enable a suitable choice for the bombarding voltage for the kinetic runs. The best value was one which gave a minimum peak height change for small fluctuations of bombarding voltages as shown in Figure 3.

### Gas Chromatograph

The analytical gas chromatograph was essentially that described by Vreeland (1963), and Conn (1966). Two columns, one of fifteen feet dibutylphthalate on chromosorb and the other one of eleven feet silver nitrate were used in series in most of the analytical measurements. An activated molecular sieves column was also used to detect methane. The molecular sieves column was activated by heating at  $250^{\circ}\text{C}$  (120 volts A.C., 5 amps) for 2-4 hours in the vacuum line. A Leeds and Northrup Speedomax-G recorder fitted with a Leeds and Northrup No. 9835-A preamplifier (0-50 microvolts) was used to display the chromatograms. In all cases helium was used as the carrier gas. A three-way stopcock mounted on a "cold finger" trap immersed in liquid nitrogen was used to freeze unknown peaks out of the effluent carrier gas when the gas flow was diverted through the trap. All other peaks were vented to the atmosphere.

Cracking patterns of peaks collected in this way were obtained

Figure 3.- Peak Ht. Vs Bomb. Volt. <sup>22</sup>





on the mass spectrometer and usually this sufficed to identify unknown compounds amounting to several parts in ten thousand or more. Comparison of gas chromatographic retention times with known samples served to confirm the mass spectrometric analyses.

#### Preparation of Silver Nitrate Column

Freshly distilled 1, 3-propane-diol was saturated with powdered silver nitrate in subdued light. Twenty-five millilitres of freshly distilled absolute methanol was used to dilute five millilitres of the silver nitrate solution. Ten grams of chromosorb-P, non-acid washed, 30-60 mesh was baked out at  $120^{\circ}$  C for two hours and then cooled to room temperature. The diluted silver nitrate solution was then added to the chromosorb and after a few minutes of stirring the liquid was poured off. The treated chromosorb was spread out to dry thoroughly in subdued light. After drying, it was packed into a piece of plastic tubing and taped to protect the chromosorb from light. The tubing was 11 feet long and had an internal diameter of 1/8 inch.

#### The Thermostat

Kinetic measurements require very accurate and constant temperature control throughout the reaction time. The temperature of the reaction vessel used in this work was maintained constant to

$\pm 0.05^{\circ}$  C at any one point by the air-bath thermostat described by Clark (1958). Temperature gradients across the bath were found to be about  $1.5^{\circ}$  C. Air was rapidly circulated over heaters and around the flask by a fan. Temperature fluctuations in the thermostat were sensed by a nickel resistance thermometer which was one arm of a resistance bridge. If the bridge was out of balance, it resulted in an A. C. voltage signal being sent to a phase shift thermo-regulator. The thermo-regulator controlled the firing cycle of a pair of thyatron tubes which supplied 10-20% of the power to the thermostat. The bulk of the power was supplied to a set of chromatox heaters by a variac operating from the power mains.

The actual temperature of the thermostat was measured by a platinum resistance thermometer which was mounted vertically in the thermostat. The thermometer was calibrated by the National Bureau of Standards and was used in conjunction with a Leeds and Northrup Mueller Bridge, Type G1. The regulated temperature was set by varying the adjustable resistance in the bridge according to the readings of the platinum resistance thermometer. Temperature readings were made at frequent intervals during kinetic runs.

#### Gas Handling System

The gas handling system which was used to supply the gas to the

reaction vessel and to measure the gas pressure is shown in Figure 4. High vacuum stopcocks were used after lubricating with Consolidated Electrodynamics Corporation vacuum grease. Minimum amount of grease was used since the grease seemed to absorb hydrocarbons. Teflon needle valves with lightly greased "O" rings were also used in some parts of the gas handling system as shown in Figure 4.

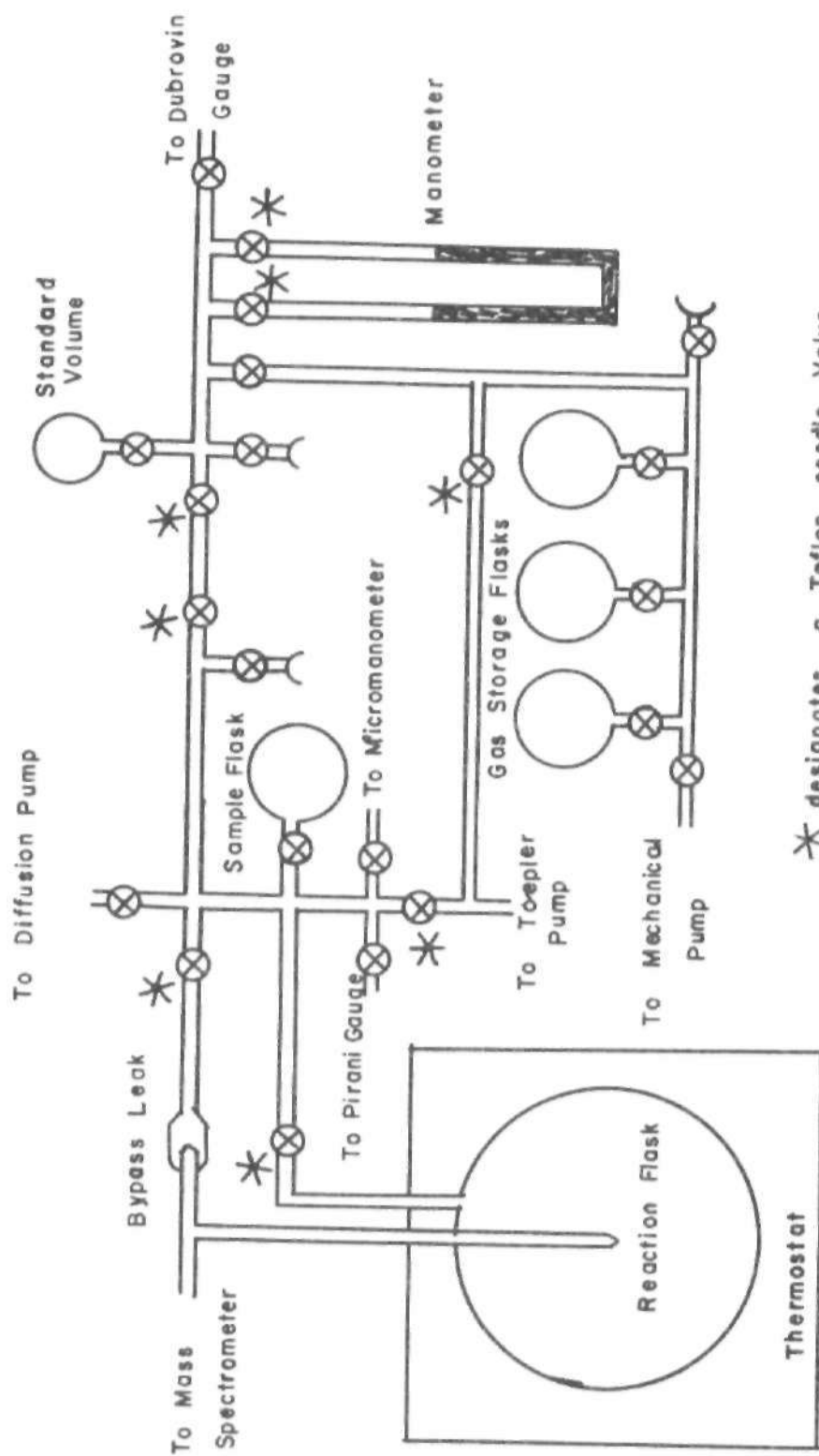
The various volumes in the vacuum rack were previously calibrated by the use of two reference flasks. A small 212.4 cc flask and another one of volume 2,170 cc. Both reference flasks were themselves calibrated by weighing the contained water. The calibration of the other volumes was then carried out by admitting dry air into a reference flask, measuring its pressure with a mercury manometer and then expanding this air into the volume to be measured and noting the final pressure. Application of Boyle's law then yielded the volume desired. The pumping system for the gas handling system consisted of a mercury diffusion pump backed by a rotary oil pump.

#### Reaction Flasks, Leaks and Leak-out Constants

The reaction flasks used in this work were made from standard pyrex round bottom laboratory flasks as shown in Figure 5. Four flasks were used in this research. Two 13,000 cc for the pressure

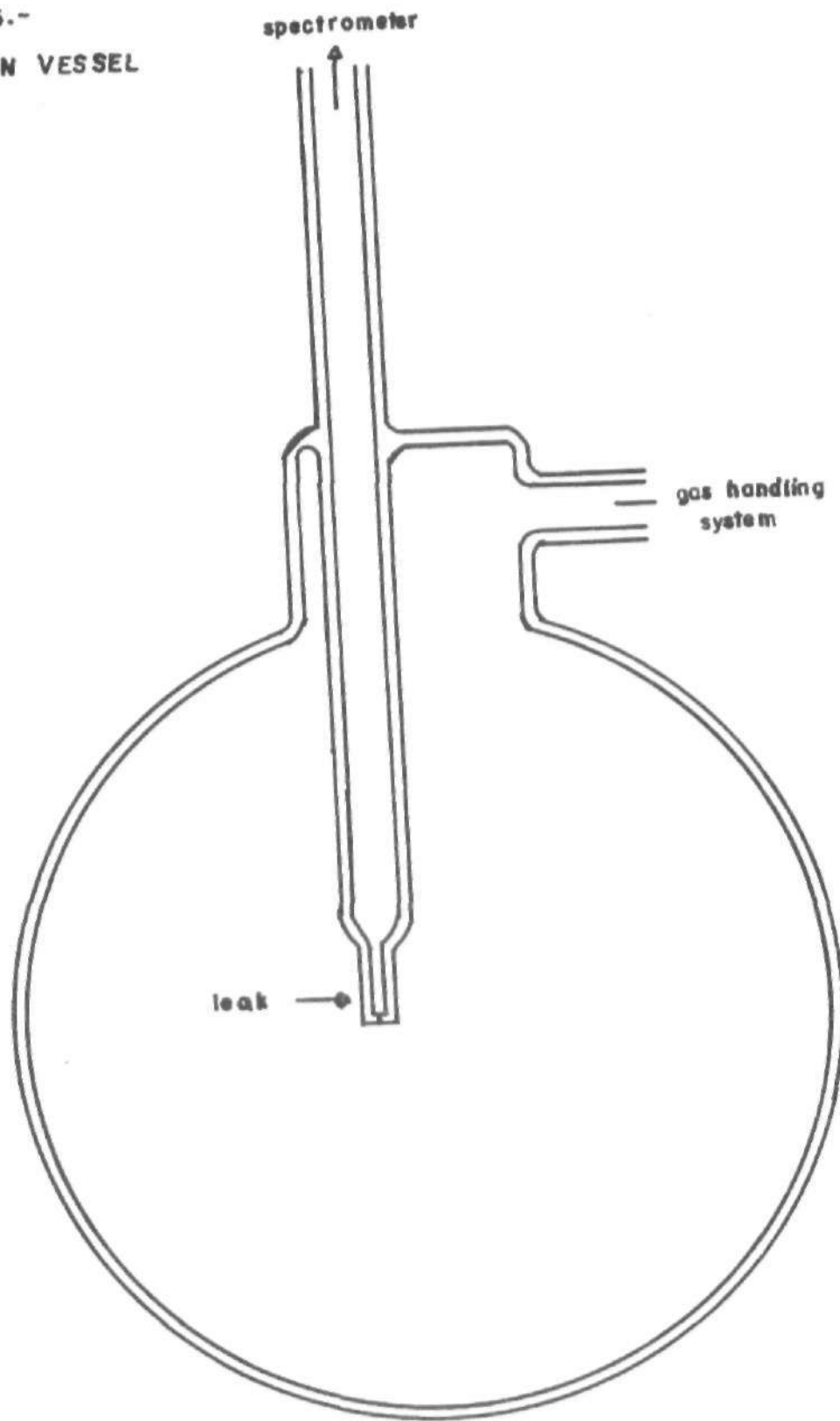
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Figure 4- Sample System



\* designates a Teflon needle Valve

FIGURE 5.-  
REACTION VESSEL



ranges 0.1 to 25 microns and 6-400 microns. A third 1,000 cc flask was used to cover the high pressure region, 250-1,500 microns. The fourth flask used had a volume of 13,000 cc but was filled with glass wool to increase the surface-to-volume ratio. A glass diaphragm molecular leak was mounted in the geometrical center of the flask. The construction of these leaks was described by Clark (1958).

The rate of flow of gas through a molecular leak is proportional to the pressure behind the leak. The rate of loss of material due to this effect is a first-order process. With a first-order thermal reaction, the overall process is also first-order.

It was necessary to measure the leak-out constant for each flask-leak combination and then subtract this from the observed rate constant to obtain the rate constant for the thermal reaction alone. The leak-out constants for all the 13,000 cc flasks were measured using n-butane at  $350^{\circ}\text{C}$  ( $623^{\circ}\text{K}$ ) and monitoring the peak  $m/e = 58$ . For the high pressure flask (1,000 cc) the leak-out rate constant was not measured since it was very much smaller than the experimental rate constant and consequently could be ignored without significant error. The leak-out constant was only of importance in the very low pressure region and at lower temperatures of the reaction. The correction needed there was

$$k_{10}(M, T) = k_{10}(58, 623) \cdot \left( \frac{58T}{623M} \right)^{1/2} \quad (2.1)$$

T is the temperature of the reaction in °K and M the molecular weight of the reaction compound. Table II shows the leak-out constants for all the flasks used in this work.

TABLE II  
FLASKS AND LEAK-OUT CORRECTIONS

Flask	Leak	Volume of Flask (litre)	$k_{10}$ at 623.2°K $\text{sec}^{-1}$	Error %	$\left(\frac{S}{V}\right)_{\text{cm}^{-1}}$	Notes*
6	7	12.73	1.24E-5	0.4	0.209	1
3	46	12.72	2.04E-6	2.7	0.209	2, 5
10	32	1.19	2.65E-7	10.0	0.464	3
8	52	12.50	2.52E-5	0.7	2.2	1, 4

\* Notes:

1. Low pressure flask-leak combination.
2. Intermediate pressure flask-leak combination.
3. High pressure flask-leak combination.
4. Packed with 30.01 g Corning number 800 glass fiber.
5. Added-gas runs carried out in this flask.

The reaction flask had a side arm which was sealed to the sampling system through a teflon needle valve. The sense of the valve was such that the needle was facing the reaction flask. This was done to avoid the reaction mixture from coming into contact with any grease

during the run. The needle valve was placed as close to the flask as possible to provide a minimum of unheated dead space.

### Pressure Measuring Devices

Three different devices were used to measure the initial reaction pressures during the course of this work. For low pressure runs a Consolidated Electrodynamics Corporation micromanometer was used. Precision of measurements was 0.3% or 0.03 microns whichever is larger. From 10 microns and larger, the percent error was nearly constant. The percentage error rose rapidly as the pressure became lower than 10 microns. For example at 1 micron the error was 3%. The upper limit was set by the instrument manufacturer at 500 microns. The vacuum rack was so designed and calibrated that the initial pressure of a sample of gas could be measured in a known volume. This volume of gas was then expanded into the reaction flask and the final pressure in the known volume measured. If the initial number of moles of gas in the expansion volume is equal to the number of moles of gas in the reaction vessel plus that in the expansion volume after the expansion, the pressure of gas in the reaction vessel is given by

$$P_{RF} = (P_1 - P_2) \left( \frac{V_{exp} T_{RE}}{V_{RF} T_{exp}} \right) \quad (2.2)$$



The subscripts  $RF$  and  $exp$  refer to the reaction flask and the expansion volume respectively, while  $P_1$  and  $P_2$  refer to the initial and the final pressures of the gas in the expansion system. Equation (2.2) is independent of thermal transpiration. Whenever possible the micromanometer was used to measure both the initial and the final pressures for an expansion. For the pressure range 200-500 microns, it was assumed that the pressure inside the reaction vessel was equal to that outside it inspite of temperature differences. The micromanometer was thus used to measure the initial pressures of the reaction. Thermal transpiration was ignored in all measurements of initial pressures of reaction from 200 microns up.

Pressures between 500-10,000 microns, being outside the range of the micromanometer, were measured by putting the sample of gas into a calibrated volume  $V_{cal}$  at a temperature  $T_{exp}$  and at a pressure  $P_1$ . This volume was connected to the reaction flask by glass tubing of volume  $V_{conn}$  and whose temperature was  $T_{exp}$ . After the stopcock to the calibrated volume and the teflon needle valve to the reaction flask were opened and a steady pressure obtained, it was assumed that the pressure in the connecting tubing was equal to the pressure inside the reaction flask. The pressure of the gas inside the flask at the beginning of the reaction is given by

$$P_{RF} = \left( \frac{P_1 V_{cal}}{T_{exp}} \right) / \left( \frac{V_{RF}}{T_{RF}} + \frac{V_{cal} V_{conn}}{T_{exp}} \right) \quad (2.3)$$

Initial reaction pressures above 10,000 microns were measured directly using a wide bore mercury manometer and a cathetometer.

At the completion of most of the kinetic runs the final pressure in the reaction flask was measured to provide rough estimates of the ratio of the initial pressure to the final pressure. In these instances the reaction vessel was connected to the appropriate pressure measuring device and the needle valve opened. After the pressure and the temperature of the external system were measured, the ideal gas equation was used to correct for the expansion of the gas. If  $P_{ext}$  was the observed final pressure,  $V_{ext}$  the volume external to the flask into which the gas expanded,  $T_{ext}$  was the temperature of the external volume, and  $P_f$  was the corrected final pressure, the correct ideal gas equation which was used here is

$$P_f = P_{ext} \left( 1 + \frac{V_{ext} T_{RF}}{V_{RF} T_{ext}} \right) \quad (2.4)$$

## CHAPTER THREE

## EXPERIMENTAL PROCEDURE

Choice of Mass Spectral Peak  
for Following Reactions

It was necessary to choose a mass spectral peak with which to follow the progress of the thermal decomposition of the ethylcyclobutane using the mass spectrometer. The peak chosen was required to indicate the concentration of the ethylcyclobutane with time as the reaction proceeded. There should be no interference from the major products of the reaction as this would complicate matters. The best choice therefore was the parent peak of the ethylcyclobutane,  $m/e$  84. On inspecting the mass spectrum of ethylcyclobutane Figure 2, it turned out that this peak is only 5.3% of the base peak ( $m/e$  56) of the ethylcyclobutane spectrum. The base peak of the spectrum could not be used because it corresponded to the parent ion of 1-butene, one of the major products of the reaction. Mass spectral peak  $m/e$  69 was found to be 16.4% of the base peak and could not come from the major products of the reaction. Hence this peak was selected for following the progress of the reaction in order to allow measurements to be made at lower ethylcyclobutane pressures with a given flask-leak combination.

The parent peak of ethylcyclobutene was used to follow the reaction at higher pressures in a given flask-leak combination.

After several runs were made it was recognized that the correction factor (see Chapter Four) depended on the mass spectral peak used to follow the reaction. Hence several sets of runs were made at the same temperatures and pressures and the resultant rate constants compared (see Table VIII).

#### Routine Kinetic Runs

The routine kinetic run is, but for slight modifications, almost exactly the same as that described by Conn (1966). The thermal decomposition of ethylcyclobutane was followed by monitoring the 69 or the 84 m/e peak in the mass spectrum of the reaction mixture. After the kinetic data has been recorded in the high and intermediate pressure ranges, the reaction mixture might be pumped out by the Toepler pump or frozen in liquid nitrogen for later gas chromatographic analysis. The procedure followed in a typical run is described in this section. It has been included to make the experimental details available for reference.

Before a run could be started, much preliminary work was necessary to ensure stability of the apparatus during the run:

- (a) The high voltage, magnet and micromanometer power supplies

were warmed-up several hours before use. During heavy use, these circuits were maintained on 24 hours a day warm-up. The mass spectrometer laboratory was thermostated to  $\pm 0.5^{\circ}$  C to help stabilize the power supplies.

(b) The spectrometer filament emission was turned up to operating conditions and the electrometer and the recorder were turned on at least 2 hours before run time.

(c) The trap on the spectrometer vacuum system was filled with dry ice at least an hour before run time to establish a constant pumping rate during the run.

(d) An initial pressure was chosen for the run and an appropriate expansion procedure was determined.

(e) The thermostat was adjusted to the reaction temperature and the regulation was checked for about 30 minutes.

(f) An appropriate chart speed was chosen so that one half-life of reaction would be recorded on about 6-12 inches of chart paper.

(g) The mass spectrometer was focused on the 69 or the 84 mass spectral peak, depending on which peak was to be used to follow the reaction, by admitting a small sample of ethylcyclobutane to the by-pass leak. The magnet current and the accelerating voltage were adjusted until the 69 or the 84 m/e beam was centered in the collector

slit. The magnet current was chosen so that the accelerating voltage used was nearly 2,300 volts. After the sample was pumped from behind the by-pass leak, the electrometer was balanced and the background 69 or 84 peak height was measured.

(h) About once a week an ice point was determined for the platinum resistance thermometer.

(i) The ion-gauge was flamed and the spectrometer out-gassed at least every other day.

(j) For low pressure measurements, the build up of water vapor inside the closed-off reaction flask was occasionally checked to be sure that it was not too excessive. This was done by closing off the reaction flask from the pumps and observing the 18 m/e peak for a time period equivalent to the reaction time to see how much it grows during this time.

Since the preliminary steps were quite time consuming, it proved advantageous to make many runs in succession without shutting down the spectrometer. After the preparations were completed, the run was started and recorded. The following list gives the sequence of events and the data recorded:

1. The initial pressure in the sample system was measured and recorded, as was the temperature of the sample system rack.

2. The recorder chart drive was started.
3. The teflon needle valve between the sample system and the reaction flask was opened.
4. The timer was started and the electrometer was rebalanced, if necessary.
5. The reaction flask needle valve was closed when the 69 or the 84 m/e peak reached a maximum. This took about 30 seconds for the low pressure region and about 10 seconds at higher pressures.
6. The final pressure in the sample system was measured and recorded.
7. The temperature of the thermostat, the case current, the bombarding voltage, the spectrometer filament current, the magnet current and the line voltage were recorded. Each of these readings was checked periodically as the reaction went on.
8. When the peak height as monitored by the recorder decayed suitably, another shunt setting was selected and appropriate base line checks made.
9. At intervals during the run a base line was determined.
10. When sufficient data were recorded, the chart drive was stopped and the chart speed was changed to that suitable for recording a mass spectrum (about 30 inches per hour).
11. The mass spectrum of the reaction products was recorded.

12. The final pressure at the end of the run was measured. The reaction products were collected in a sample tube cooled with liquid nitrogen.

13. After the collection was completed, the mass spectrum of the product gases non-condensable at liquid nitrogen temperature was recorded.

14. In some cases the Toepler pump was used to collect the reaction mixture so that the reaction products non-condensable at liquid nitrogen temperature could be collected and analyzed using the gas chromatograph.

15. The reaction flask was pumped on for at least 30 minutes before the next run was started.

#### Routine Gas Chromatographic Runs

The gas chromatograph was warmed-up by turning on the helium flow, the filament current, and the recorder circuits. Two to three hours of warm-up was essential if the instrument was to be used at full sensitivity. The gas chromatographs of the reaction products were run by warming the sample tube to room temperature and expanding the gas into the injection system of the chromatograph. The procedure used is listed below:

- a. About 20 minutes was allowed for warm-up of the sample tube.



b. The injection system was pumped down to three microns of pressure or less with the diffusion pump.

c. The product mixture, or part of it, was distilled into the sample loop, using liquid nitrogen to cool the loop.

d. The sample loop was allowed to warm-up to room temperature.

e. The sample was injected into the column by reversing the stopcocks.

f. The signal was attenuated appropriately so that each peak was visible on the recording paper.

g. The flow rate of the helium carrier gas, the gas chromatograph filament current, the chart speed of the recording paper, and the operating temperature of the chromatograph were recorded.

#### Nitric Oxide Added-Gas Runs

The nitric oxide-ethylcyclobutane gas mixtures were prepared by adding measured pressures of the gases to separate calibrated volumes of a gas mixing device, Opler and Smith (1953). The two compartments were then connected on both ends to form a closed loop. Inversion of the apparatus caused sliding pistons to force the gases back and forth between the two compartments, thus mixing them. Nitric oxide added-gas runs were made in the same manner as normal

runs.

### Peak Height Measurements

Mass spectral peak heights were obtained by measuring the deflection of the recorder pen from the base line. A smooth curve was drawn through the recorded trace with a flexible spline. At equally spaced intervals on the time scale the distance between the curve and the base line was taken as the peak height. An example of this technique is shown in Figure 6.

### Rate Constant Determination

The experimental rate constants were derived from the peak height (PH) data by finding the slope in a  $\ln (PH - \alpha PH_0)$  vs. time (t) plot. The isomerization coefficient ( $\alpha$ ) was chosen so that the plot was linear. The isomerization coefficient was calculated using a computer program which produced a fit by minimizing the variance. The program listing is contained in the Appendix. It calculated the standard deviation in the slope of the line thus fitted, Youden (1951). The isomerization coefficient was found to be 2.5-3.0% for the mass spectral peak  $m/e = 69$  and 7.5-11% for  $m/e = 84$ . Figure 7 shows a plot of the data for a single experiment. The peak heights vs. time curves for both the corrected and the uncorrected points are shown.

Figure 6.- Peak Height Vs. Time

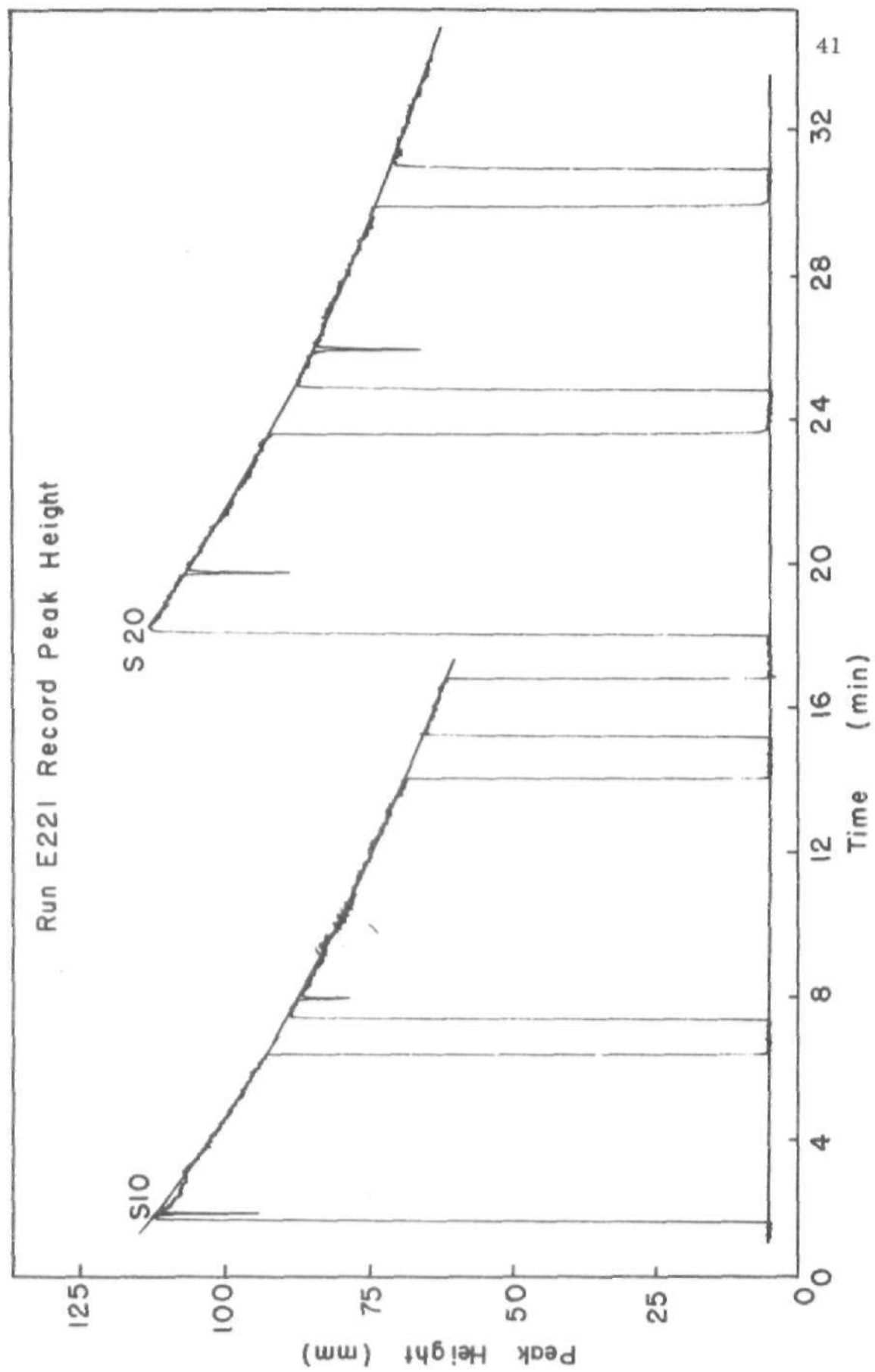
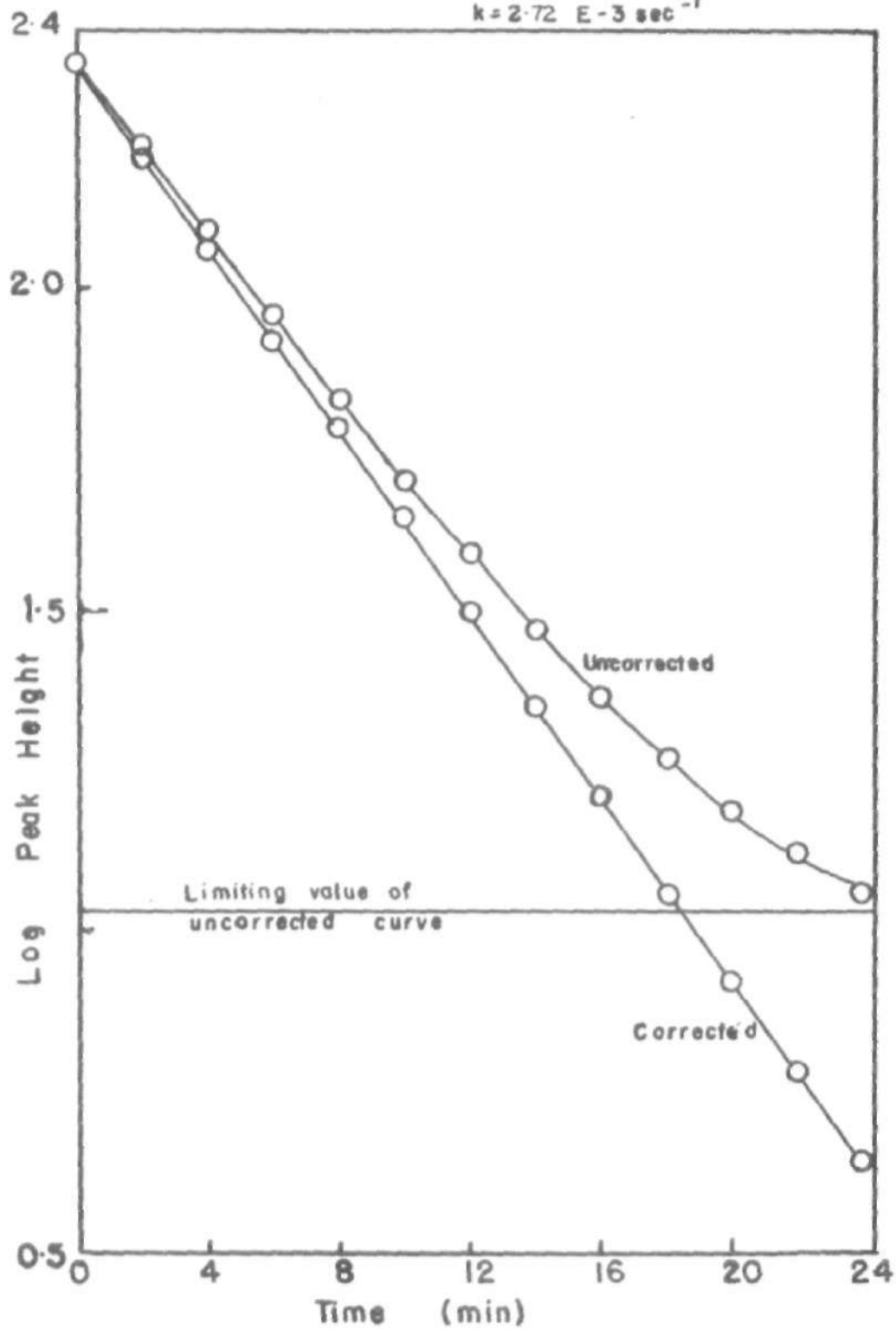


FIGURE 7.-Log(Peak Height) Vs-Time

EXPERIMENT E 052  $P_0 = 32.3 \mu$   $T = 7532^\circ K$ 

$$k = 2.72 \text{ E-}3 \text{ sec}^{-1}$$



## CHAPTER FOUR

## RESULTS

Kinetic Results from Unpacked Flasks

Table III contains the experimental rate constants obtained from the unpacked flasks. In a large majority of the kinetic runs the mass spectrometer was used to monitor the 69 m/e peak in the spectrum of the ethylcyclobutane. However in some cases the 84 m/e peak was used to follow the reaction. The entries for each run are the run number, the flask-leak combination, pressure (p) in microns and rate constant (k) in seconds<sup>-1</sup>, corrected for both leak-out and isomerization, expressed in the standard computer notation. The letter E represents a base 10 exponential, for example, E 3 is symbolic for 10<sup>3</sup>. The standard deviation in k, and the size of the isomerization correction ( $\alpha$ ) in percent of the initial mass spectral peak height are also tabulated. Where a dash (-) is entered for the isomerization correction, there was nothing subtracted from the initial mass spectral peak height, because the reaction was not followed for a long enough time to establish the extent of isomerization. Common logarithms of the pressure (log p) and that of the rate

TABLE III  
RATE CONSTANTS FROM UNPACKED FLASKS

Experiment Number	Flask-Leak	Pressure (Microns)	$k(\text{sec}^{-1})$ E-4	-Error (%)	$\alpha$ (%)	Log(P)	5 + log(k)	m/e
T = 673, 2°K (400°C)								
E124	6-7	0.26	0.159	0.51	--	-0.585	0.201	69
E122	6-7	0.96	0.142	0.48	--	-0.018	0.154	69
E121	6-7	1.64	0.166	0.38	--	0.215	0.221	69
E120	6-7	2.61	0.188	0.49	--	0.417	0.273	69
E119	6-7	4.87	0.184	0.63	--	0.688	0.265	69
E070	3-46	6.53	0.194	0.30	2.6	0.815	0.289	69
E118	6-7	8.69	0.181	0.43	--	0.940	0.258	69
E069	3-46	10.1	0.210	0.22	2.8	1.001	0.322	69
E127	6-7	11.5	0.193	0.96	10.1	1.060	0.284	84
E068	3-46	17.0	0.219	0.22	2.8	1.231	0.340	69
E067	3-46	24.8	0.228	0.22	2.9	1.394	0.359	69
E066	3-46	40.0	0.239	0.22	2.9	1.602	0.380	69
E064	3-46	63.3	0.254	0.23	2.7	1.801	0.404	69
E062	3-46	90.1	0.255	0.19	2.9	1.955	0.407	69
E061	3-46	130.	0.263	0.20	2.6	2.116	0.420	69
E060	3-46	145.	0.290	0.22	2.8	2.163	0.462	69
E057	3-46	154.	0.264	0.39	--	2.188	0.422	69
E059	3-46	228.	0.278	0.49	3.7	2.357	0.443	69
E058	3-46	320.	0.246	0.26	--	2.505	0.391	69
E161	10-32	734.	0.271	0.22	3.6	2.860	0.432	69
E159	10-32	2540.	0.261	0.87	9.5	3.405	0.416	84
E157	10-32	5170.	0.239	0.34	9.0	3.713	0.378	84
E156	10-32	12500.	0.241	0.17	10.2	4.095	0.382	84

TABLE III--Continued

Experiment Number	Flask-Leak	Pressure (Microns)	$k(\text{sec}^{-1})$ E-4	Error (%)	$\alpha$ (%)	Log(P)	5 + log(k)	m/e
T = 693, 2°K (420°C)								
E115	6-7	0.17	0.427	0.42	--	-0.770	0.630	69
E114	6-7	0.27	0.437	0.43	--	-0.569	0.641	69
E116	6-7	0.38	0.475	0.33	3.4	-0.420	0.677	69
E113	6-7	0.69	0.485	0.32	3.0	-0.161	0.686	69
E112	6-7	1.13	0.520	0.17	2.6	0.053	0.716	69
E111	6-7	1.68	0.554	0.47	2.5	0.225	0.744	69
E110	6-7	2.56	0.589	0.23	2.9	0.408	0.770	69
E109	6-7	3.71	0.639	0.26	3.0	0.569	0.806	69
E131	6-7	5.79	0.666	0.12	10.	0.763	0.824	84
E023	3-46	6.16	0.687	0.17	1.7	0.790	0.837	69
E108	6-7	8.59	0.699	0.46	2.8	0.934	0.844	69
E130	6-7	9.96	0.729	0.25	9.0	0.998	0.862	84
E129	6-7	10.1	0.734	1.1	9.7	1.003	0.866	84
E022	3-46	10.6	0.786	0.10	3.3	1.026	0.895	69
E021	3-46	14.6	0.812	0.37	2.7	1.163	0.910	69
E020	3-46	29.8	0.859	0.11	2.8	1.475	0.934	69
E019	3-46	43.0	0.917	0.10	2.9	1.633	0.962	69
E018	3-46	67.0	0.970	0.16	2.9	1.826	0.987	69
E017	3-46	104.	0.987	0.98	2.8	2.018	0.994	69
E016	3-46	174.	1.04	0.13	2.9	2.242	1.016	69
E015	3-46	227.	1.06	0.13	2.7	2.443	1.025	69
E152	10-32	331.	0.953	0.26	2.3	2.520	0.979	69
E014	3-46	420.	1.18	0.30	4.2	2.623	1.070	69
E153	10-32	718.	1.02	0.16	2.6	2.856	1.008	69
E154	10-32	2530.	1.00	0.18	9.8	3.403	1.001	84
E151	10-32	4530.	0.997	0.32	10.3	3.556	0.999	84
E155	10-32	13900.	0.954	0.43	11.0	4.143	0.979	84

TABLE III--Continued

Experiment Number	Flask-Leak	Pressure (Microns)	$k(\text{sec}^{-1})$ E-4	Error (%)	$\alpha$ (%)	Log(p)	$5 + \log(k)$	m/e
T = 713.2°K (440°C)								
E102	6-7	0.16	1.26	0.53	--	-0.769	1.102	69
E103	6-7	0.39	1.37	0.57	--	-0.409	1.137	69
E104	6-7	0.79	1.58	0.19	2.5	-0.102	1.198	69
E105	6-7	1.50	1.79	0.20	2.8	0.176	1.252	69
E106	6-7	2.00	2.08	0.17	2.8	0.301	1.319	69
E096	6-7	2.86	1.98	0.34	2.7	0.428	1.297	69
E095	6-7	3.57	2.04	0.33	2.6	0.553	1.310	69
E013	3-46	5.69	2.25	0.16	2.5	0.755	1.351	69
E092	6-7	6.35	2.28	0.19	2.9	0.803	1.357	69
E134	6-7	6.46	1.88	0.16	8.5	0.810	1.274	84
E091	6-7	7.61	2.27	0.32	2.6	0.881	1.356	69
E107	6-7	8.64	2.37	0.18	3.0	0.937	1.374	69
E132	6-7	9.81	2.00	0.43	9.2	0.992	1.301	84
E007	3-46	9.90	2.36	0.50	1.0	0.996	1.373	69
E011	3-46	15.1	2.69	0.24	2.8	1.180	1.439	69
E006	3-46	20.8	2.89	0.47	2.8	1.319	1.460	69
E005	3-46	34.6	2.86	1.00	3.1	1.540	1.456	69
E003	3-46	59.3	2.93	0.38	7.6	1.773	1.467	84
E002	3-46	90.5	3.24	0.23	7.7	1.957	1.511	84
E012	3-46	155.	3.44	0.47	3.2	2.191	1.536	69
E008	3-46	208.	3.51	0.16	3.3	2.318	1.545	69
E009	3-46	287.	3.57	0.10	3.8	2.458	1.553	69
E147	10-32	334.	3.44	0.15	3.8	2.527	1.536	69
E010	3-46	421.	3.45	0.55	3.5	2.624	1.538	69
E150	10-32	737.	3.65	0.18	3.1	2.870	1.562	69
E149	10-32	1340.	3.60	0.20	2.8	3.128	1.556	69
E148	10-32	2340.	3.77	0.20	11.2	3.369	1.576	84
E146	10-32	4920.	3.75	0.15	10.8	3.692	1.574	84
E164	10-32	1320.	3.43	0.25	11.2	4.120	1.536	84



TABLE III--Continued

Experiment Number	Flask-Leak	Pressure (Microns)	$k(\text{sec}^{-1})$ E-4	Error (%)	$\alpha$ (%)	Log(P)	$5 + \log(k)$	m/e
T = 733, 2°K (460°C)								
E082	6-7	0.17	3.75	0.22	--	-0.770	1.574	69
E083	6-7	0.27	4.21	0.10	2.3	-0.569	1.624	69
E094	6-7	0.40	4.32	0.20	2.5	-0.398	1.636	69
E084	6-7	0.65	4.60	0.30	2.4	-0.187	1.663	69
E085	6-7	1.09	4.93	0.26	2.4	0.037	1.693	69
E086	6-7	1.71	5.34	0.12	2.5	0.235	1.728	69
E087	6-7	2.43	5.67	0.11	2.6	0.386	1.754	69
E088	6-7	3.91	6.23	0.12	2.6	0.592	1.795	69
E032	3-46	5.72	7.01	0.13	3.3	0.757	1.846	69
E089	6-7	6.30	6.96	0.19	2.7	0.799	1.843	69
E090	6-7	7.76	7.19	0.49	2.8	0.890	1.857	69
E135	3-46	8.71	6.27	0.22	9.5	0.940	1.798	84
E034	3-46	10.5	8.02	0.49	3.2	1.023	1.904	69
E031	3-46	13.0	8.11	0.10	2.6	1.114	1.909	69
E030	3-46	21.3	8.51	0.11	2.0	1.327	1.930	69
E029	3-46	37.4	9.50	0.10	2.8	1.577	1.978	69
E028	3-46	66.6	10.2	0.19	2.7	1.824	2.010	69
E027	3-46	101.	10.9	0.15	2.9	2.001	2.038	69
E026	3-46	185.	12.4	0.68	3.4	2.266	2.094	69
E033	3-46	177.	11.4	0.12	2.9	2.248	2.058	69
E025	3-46	301.	11.9	0.95	2.9	2.479	2.074	69
E143	10-32	354.	11.7	0.10	3.2	2.548	2.068	69
E024	3-46	448.	12.5	0.14	3.0	2.651	2.095	69
E145	10-32	624.	11.7	0.22	3.0	2.795	2.069	69
E144	10-32	1220.	11.9	0.64	2.9	3.087	2.076	69
E142	10-32	2580.	12.2	0.11	9.8	3.411	2.086	84
E141	10-32	5050.	12.2	0.20	9.9	3.703	2.085	84
E163	10-32	13500.	12.1	0.14	10.2	4.130	2.081	84

TABLE III--Continued

Experiment Number	Flask-Leak	Pressure (Microns)	$k(\text{sec}^{-1})$ E-4	Error (%)	$\alpha$ (%)	Log(P)	5 + Log(k)	m/e
T = 753, 2°K (480°C)								
E081	6-7	0.17	11.3	0.25	2.3	-0.770	2.051	69
E080	6-7	0.26	11.5	0.21	2.6	-0.585	2.059	69
E079	6-7	0.41	11.6	0.23	2.6	-0.387	2.062	69
E078	6-7	0.68	12.5	0.19	2.5	-0.168	2.098	69
E077	6-7	1.10	13.7	0.15	2.6	0.041	2.136	69
E072	6-7	1.80	15.5	0.15	6.9	0.255	2.190	84
E076	6-7	2.50	15.8	0.18	2.7	0.398	2.200	69
E075	6-7	4.72	18.3	0.12	2.2	0.674	2.263	69
E055	3-46	6.19	18.7	0.16	--	0.792	2.272	69
E074	6-7	6.21	20.0	0.26	2.7	0.793	2.301	69
E073	6-7	10.5	21.7	0.16	7.1	1.022	2.336	84
E054	6-7	10.9	21.8	0.15	2.1	1.037	2.339	69
E053	3-46	19.7	24.6	0.14	2.4	1.294	2.391	69
E052	3-46	32.3	27.2	0.10	2.5	1.509	2.434	59
E051	3-46	45.2	28.6	0.10	2.6	1.655	2.456	69
E050	3-46	62.0	30.4	0.33	2.4	1.792	2.483	69
E035	3-46	64.0	29.9	0.18	2.7	1.806	2.476	69
E049	3-46	95.1	32.2	0.10	2.1	1.792	2.483	69
E048	3-46	161.	33.8	0.16	2.4	2.208	2.508	69
E056	3-46	249.	35.5	0.21	2.7	2.396	2.529	69
E139	10-32	348.	35.0	0.13	3.1	2.396	2.544	69
E047	10-32	367.	38.8	0.46	8.3	2.564	2.589	84
E140	10-32	600.	36.6	0.44	2.9	2.778	2.564	69
E138	10-32	988.	38.1	0.24	2.9	2.995	2.581	69
E137	10-32	2400.	38.5	0.43	3.1	3.381	2.586	69
E136	10-32	5270.	37.2	0.10	10.	3.722	2.571	84
E162	10-32	14000.	38.3	0.10	10.8	4.147	2.563	84

constant plus a constant ( $5 + \log k$ ) are also listed on the table. Finally the mass spectral peak used to follow the reaction is also listed. Figure 8 shows a plot of ( $5 + \log k$ ) vs.  $\log (p)$  for the data.

#### Kinetic Results from Packed Flask

In the plot of  $\log (k)$  vs.  $\log (p)$ , at the low pressure end, it was found that the rate constants are bigger than they should be from the Kassel theory. This made it necessary to investigate the possibility of some sort of surface effect. One of the simpler things that can be done to investigate the role of the surface in the reaction is to add more surface. If the reaction is proceeding principally on the surface, the rate of the reaction should increase by approximately the same factor as the surface-to-volume ratio has been increased. A 13 litre pyrex reaction flask containing leak 52 was packed with pyrex glass wool, Thomas (1964). The surface-to-volume ratio for this flask was approximately ten times that of the unpacked 13 litre flasks. The data collected on the decomposition of ethylcyclobutane in the packed flask are contained in Table IV and displayed in Figure 8. Clearly the added surface area does have an effect. At low pressures, 0.2 microns, the observed rate coefficients are about 50% bigger than those at corresponding pressures in the unpacked flasks. The rate constants at a higher pressure, about 9 microns, are about

Figure 8.-Kinetics Data

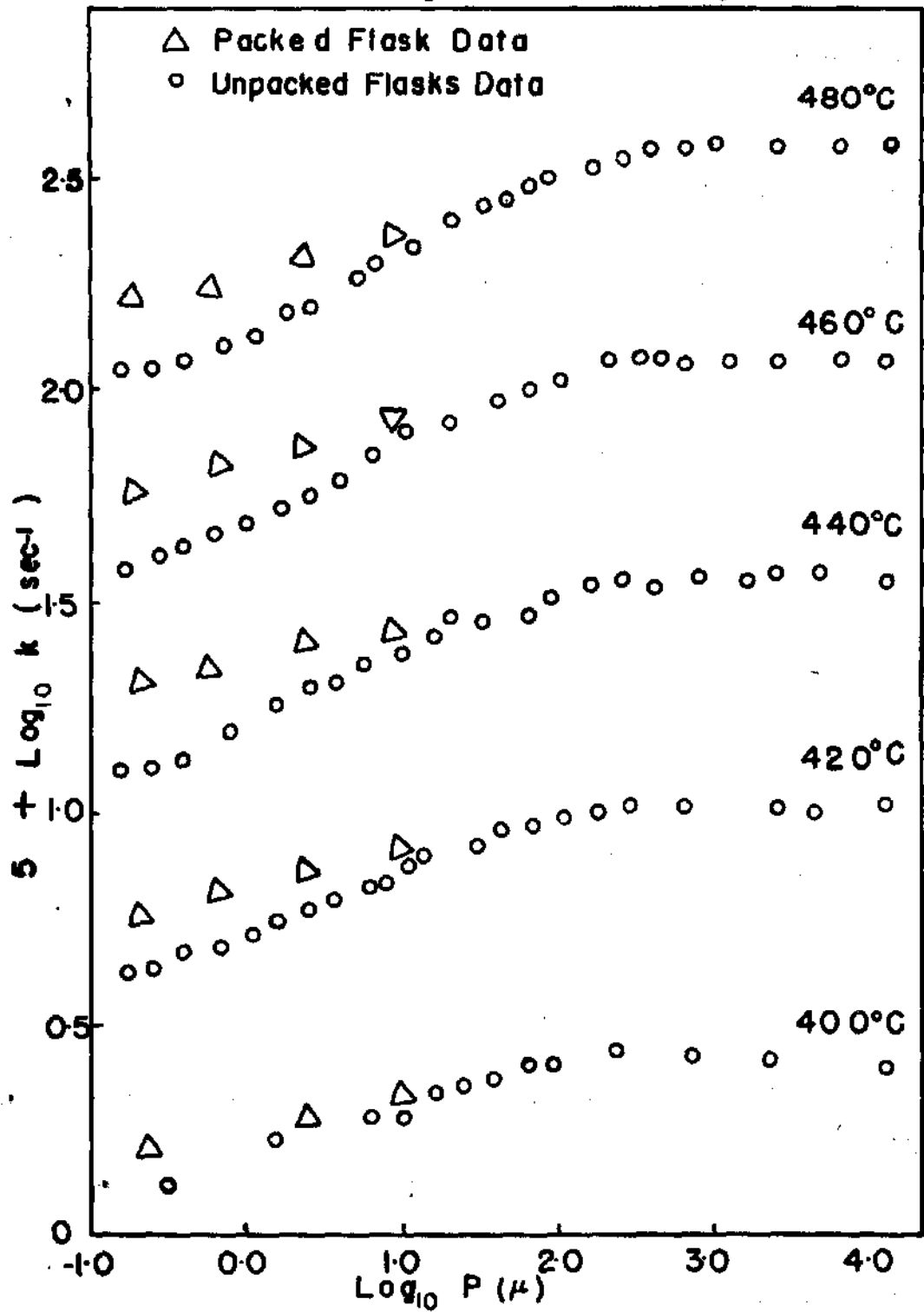


TABLE IV  
RATE CONSTANTS FROM PACKED FLASK  
FLASK 8 LEAK S2

Experiment Number	Pressure (Microns)	$k(\text{sec}^{-1})$ E-4	Error (%)	$\alpha$ (%)	Log(P)	5 + log(k)	m/e
T = 673, 2°K (400°C)							
E217	0.17	0.166	0.47	--	-0.770	0.218	69
E219	0.20	0.188	0.72	--	-0.699	0.274	69
E216	0.76	0.196	0.13	2.5	-0.120	0.292	69
E215	2.70	0.136	0.17	3.4	0.431	0.134	69
E218	9.05	0.250	0.28	7.5	0.957	0.398	84
T = 693, 2°K (420°C)							
E211	0.22	0.569	0.54	--	-0.678	0.755	69
E213	0.66	0.656	0.75	1.6	-0.180	0.817	69
E214	0.67	0.656	0.80	3.3	-0.174	0.817	69
E210	2.42	0.731	0.40	3.5	0.384	0.864	69
E212	9.92	0.799	0.30	7.4	0.997	0.903	84
T = 713, 2°K (440°C)							
E206	0.21	2.07	0.93	--	-0.677	1.315	69
E207	0.55	2.20	0.29	2.3	-0.60	1.342	69
E208	2.40	2.57	0.48	3.7	0.380	1.409	69
E209	8.98	2.68	0.17	7.9	0.953	1.428	84
T = 733, 2°K (460°C)							
E205	0.19	5.87	0.63	--	-0.722	1.768	69
E204	0.64	6.64	0.16	2.6	-0.194	1.822	69
E203	2.31	7.34	0.10	2.7	0.364	1.866	69
E202	8.74	8.61	0.26	7.2	0.942	1.935	84
T = 753, 2°K (480°C)							
E200	0.18	16.5	0.52	--	-0.745	2.218	69
E199	0.26	17.7	0.33	2.0	-0.206	2.247	69
E198	2.31	21.4	0.17	2.5	0.364	2.330	69
E201	7.97	23.6	0.19	6.4	0.901	2.374	84

25% bigger than those in the unpacked flasks. The packed flask rate constants approached the results obtained in the unpacked flasks at still higher pressures i. e. , about 30 microns.

Mass spectrometric and gas chromatographic analyses of the products of the reactions carried out in the glass wool packed reaction flask showed no change in product composition. In addition, the value of the correction factor necessary to account for isomerization reaction was not detectably different in the packed flask.

Kinetic Results from Nitric Oxide  
Added-Gas Runs

The addition of nitric oxide was found to inhibit thermal decomposition reactions that proceed via chain mechanisms, Staveley and Hinshelwood (1937). Hence it was advisable to investigate the thermal decomposition of ethylcyclobutane in the presence of nitric oxide. Table V contains the experimental rate constants for a series of nitric oxide added-gas runs at an initial ethylcyclobutane pressure of approximately 10 microns. Figure 9 shows a plot of the measured rate constants vs. percent of nitric oxide.

The mass spectrum of the products after the reaction appeared not to differ from those of reactions run at similar pressures of ethylcyclobutane without nitric oxide, except for the mass spectral peaks due to the nitric oxide.

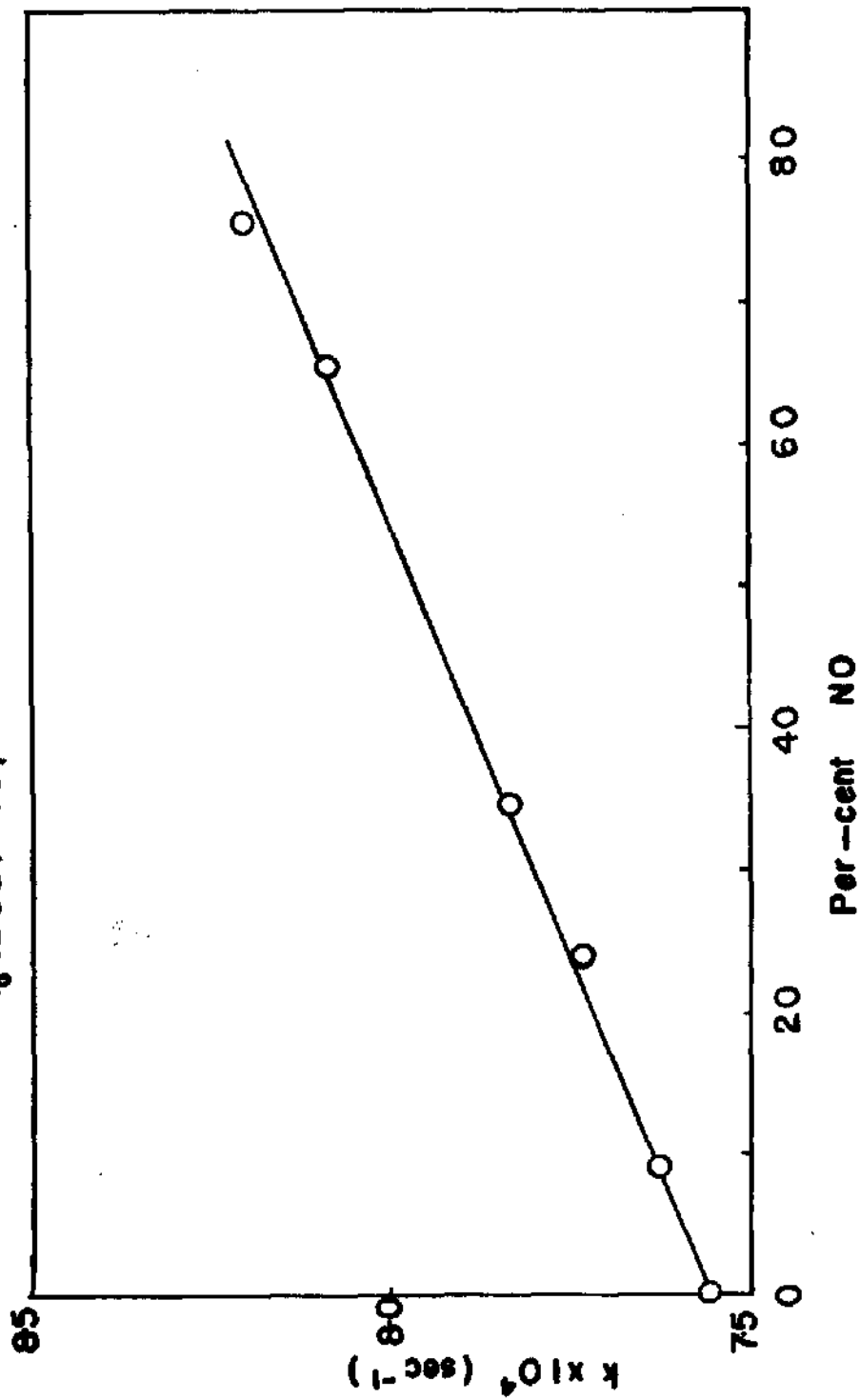
TABLE V

RATE CONSTANTS FROM NITRIC OXIDE ADDED-GAS RUNS  
 ETHYLCYCLOBUTANE PRESSURE = 10.5 ( $\pm$  0.5) MICRONS  
 FLASK 3 LEAK 46 m/e = 69 T = 733.2°K (460°C)

Experiment Number	Total Pressure (Microns)	Ethylcyclobutane Pressure (Microns)	Nitric Oxide Pressure (Microns)	Mole % Nitric Oxide	k(sec <sup>-1</sup> ) E-4	Error %	$\alpha$
E071	11.0	11.0	0.0	0.00	7.56	0.16	2.7
A002	11.2	10.1	1.1	9.25	7.63	0.19	2.7
A003	13.2	10.0	3.2	24.1	7.74	0.15	2.6
A004	15.8	10.3	5.5	34.8	7.84	0.17	2.6
A005	21.1	10.6	10.5	49.6	8.11	0.24	2.6
A006	29.6	10.1	19.5	65.6	8.09	0.26	2.6
A007	41.8	10.3	31.5	75.4	8.20	0.25	2.5
A001	52.9	11.0	41.9	79.1	8.33	0.21	2.7

Figure 9.- Nitric Oxide as Added Gas

$P_0(\text{ECB}) = 10 \mu$   $T = 73.32^\circ \text{K}$



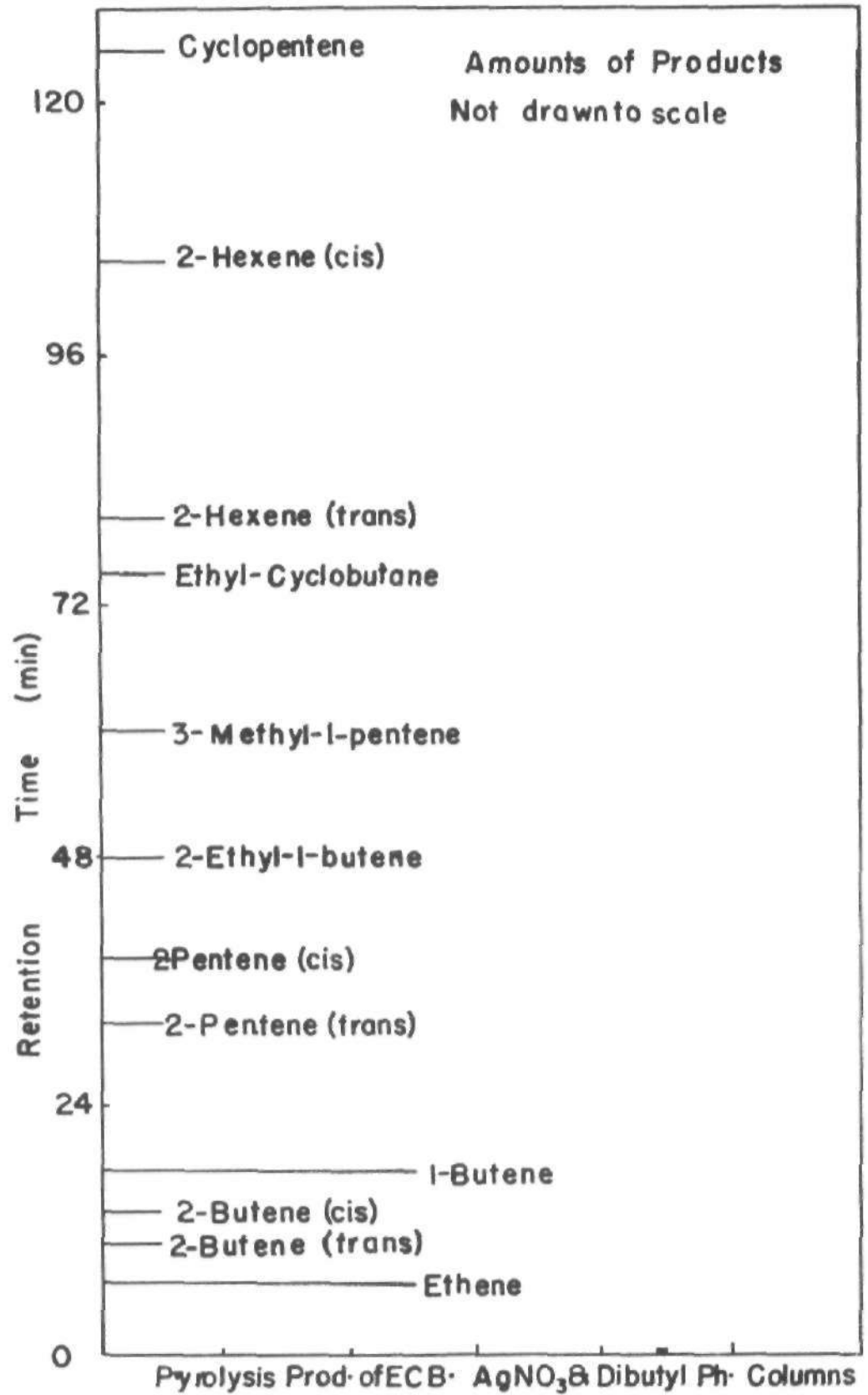


### Reaction Products

The major products of the thermal decomposition of ethylcyclobutane were found to be ethylene and 1-butene. Small amounts of other compounds were also found in the reaction mixture. These were cyclopentene, cis- and trans-2-hexene, 3-methyl-1-pentene, 2-ethyl-1-butene, cis- and trans-2-pentene, cis- and trans-2-butene and methane. An example of the separation which was afforded by a combination of a 15 foot dibutylphthalate and an eleven foot silver nitrate columns in series for a reaction product mixture of ethylcyclobutane is shown in Figure 10. The lengths of the horizontal lines do not indicate the quantities of the respective products. Thus the ethylcyclobutane both isomerized and decomposed under the conditions of this research.

The amount of reaction product per reaction was generally too small to analyze gas chromatographically. This made it necessary to collect reaction products from several experiments in a sample tube and then run the gas chromatograph of the composite runs. The relative amounts of ethylene, 1-butene, 2-butene, 2-hexene and ethylcyclobutane were determined gas chromatographically. The transformation of gas chromatographic peak areas into meaningful relative pressures required a plot of gas chromatographic peak areas versus sample size over the range of sample sizes found in the reaction mixtures. Such

Figure 10.-Products Analysis



plots are shown in Figure 11 for the main products of the reaction. The plots indicate that the sensitivity of 1-butene is about 20% more than that of ethylene at high sample pressures (10 torr and up). At lower sample pressures however, the sensitivities are equal, within the experimental error of the measurements. The size of sample used during the analysis of the pyrolysis product was about 10 torr. This means that for the reaction products, the area under the 1-butene curve should be greater than that of the ethylene by about 20% since they were produced in equal amounts during the reaction.

As shown in Figure 10, the pyrolysis of ethylcyclobutane produced no less than twelve products. The ethylene and the butene were not completely resolved from one another. The resolution was such that the base line was never fully restored from one peak to another. This resulted in uncertainties of the order of 20% in the determination of the peak areas of the ethylene and the 1-butene, which in turn made the peak area of the 1-butene roughly equal to that of the ethylene. Table VI shows the distribution of the reaction products in mole percent of the total reaction products simply as ratios of peak areas.

It is to be noted that the 2-butenes came from the thermal isomerization of 1-butene (Conn, 1966), whereas the mechanism via which the 2-pentenes and the cyclopentene were produced is still uncertain.

Figure II. Calibration Curves for Ethene & 1-Butene.  $\text{AgNO}_3$  and Dibutyl Phthalate Columns in Series. Room Temp.

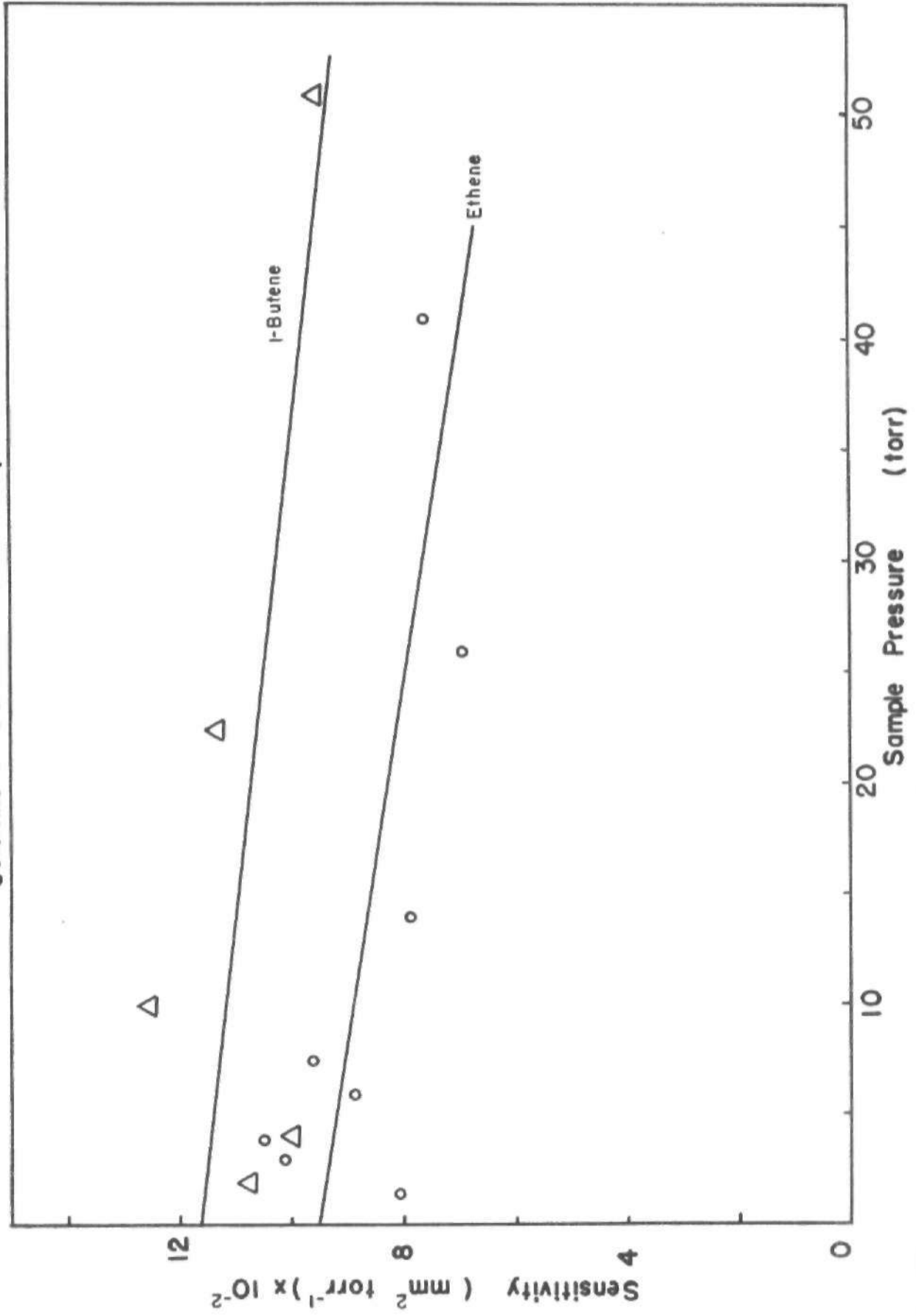


TABLE VI  
 QUANTITATIVE ANALYSIS OF ETHYLCYCLOBUTANE PYROLYSIS  
 PRODUCTS HOMEMADE CHROMATOGRAPH  
 15' DIBUTYLPHTHALATE + 11' AgNO<sub>3</sub>  
 COLUMNS IN SERIES AT ROOM  
 TEMPERATURE

Percent of Compound	Pressure Region			
	Intermediate*	Intermediate	High	High**
% Ethylene	48.0	50.0	49.0	45.0
% Cis- and trans-2- butene	0.6	0.8	0.4	1.0
% 1-Butene	48.0	46.0	49.0	50.0
% Cis- and trans- 2-pentene	0.03	0.04	0.09	0.2
% 3-Methyl-1-pentene + 2-Ethyl-1-butene	0.04	0.04	0.04	0.2
% Ethylcyclobutane	2.0	2.0	0.2	1.0
% Cis- and trans-2- hexene	1.0	1.0	0.5	1.2
% Cyclopentene	0.4	0.1	0.3	0.6
Total of All Minor Reaction Products	2.1	2.0	1.3	3.2

\* Pressure range 5-400 microns.

\*\* Pressure range 330-14,000 microns.

## CHAPTER FIVE

## DISCUSSION

Introductory Remarks

Kinetic results on the thermal decomposition of cyclobutane Vreeland and Swinehart (1963), and methylcyclobutane Thomas, Conn and Swinehart (1969) showed the respective reaction products to be ethylene and ethylene plus propylene. The reactions were found to be first-order and not inhibited by the presence of nitric oxide, propylene and toluene. The first-order rate constant fell off as the initial pressure was lowered. The addition of inert gasses and increasing the surface-to-volume ratio of the reaction vessel were found to raise the value of the rate constants towards the high pressure values. It was therefore of interest to study the thermal decomposition of ethylcyclobutane at low pressures in order to ascertain whether the decomposition of a related compound would be similar and to observe any effect of the change of structure upon the characteristics of the reaction.

The experimental results of this research have shown that the thermal decomposition of ethylcyclobutane at low pressures is a

homogeneous, first-order reaction which forms mainly ethylene and 1-butene. Small amounts of side products were also formed. This decomposition is quite similar to the thermal decompositions of methylcyclobutane Thomas (1964), and 1,2-dimethylcyclobutane Conn (1966), with respect to the type of ring cleavage and the kinetics of the reaction.

#### Surface Effect

As seen from Table IV a ten fold increase in surface-to-volume ratio of the reactions vessel resulted only in about 50% increase in the rate of reaction. It was also found that the rate constant in the packed flask approached those from the unpacked flask at about 30 microns of pressure.

If the surface of the reaction vessel were catalyzing the reaction, a ten fold increase in the surface-to-volume ratio should increase the rate of reaction by ten fold, not 50%. Moreover since the packed flask rate constants became equal to those of unpacked flask at a sufficiently high pressure, it was concluded that the thermal decomposition of ethylcyclobutane is homogeneous and activation and deactivation of the reactant molecules occurred through collisions of these molecules with the glass surface. Thus the added surface increased the effective pressure of the reaction in a manner similar to an added inert gas.

### Free Radical Reactions

Experimenting with azomethane- $d_6$  and nitric oxide Chang and Rice (1969) have reported that as the concentration of nitric oxide increased and the pressure of azomethane- $d_6$  remained constant the rate constant of azomethane- $d_6$  reaction first decreased and then slowly increased. The minimum in their series of experiments occurred at a concentration of about 10 mole percent nitric oxide or less. They interpreted this observation as indicating a free radical chain reaction in azomethane- $d_6$ .

This test for a free radical chain reaction was applied to the thermal decomposition of ethylcyclobutane. Figure 9 is a plot of  $k$  vs. percent nitric oxide at an ethylcyclobutane pressure of 10.5 ( $\pm 0.5$ ) microns. Nitric oxide was added to the ethylcyclobutane in the range 10 to 80 mole percent without producing a minimum in the plot of  $k$  vs. % nitric oxide. A straight line through all the points extrapolated into the rate constant found for pure ethylcyclobutane at the same temperature and pressure. Essentially this extrapolation eliminates the possibility that there was a minimum at lower nitric oxide mole percentage which was overlooked.

Since there was no observable inhibition in the presence of added nitric oxide, no evidence has been found for a free radical chain mechanism. Any radicals that may be produced are quite short-lived.



Accounting for Isomerization

As was seen from a plot of the data from a single experiment Figure 7 there was a curvature in the  $\log(\text{PH})$  vs. time plots for runs that were followed for a time period longer than one half-life of the reaction time. The curvature is due to the formation during the run of small amounts of ethylcyclobutane isomers via side reactions. These side reactions produced four isomers namely cis- and trans-2-hexene, 3-methyl-1-pentene and 2-ethyl-1-butene.

Treatment of the data to account for the isomerization reactions is based on the assumption that the isomers are formed directly from ethylcyclobutane by unimolecular reactions. The proposed reaction scheme is



where E stands for ethylcyclobutane and Is stands for the isomers.

The rate equations for this scheme are

$$-d\text{E}/dt = (k_d + k_i) \text{E} \quad (5.3)$$

$$d\text{Is}/dt = k_i \text{E} \quad (5.4)$$

Integrating Equation (5.3) from  $t = 0$  to  $t = t$

$$E = E_0 \exp(-(k_d + k_i)t) \quad (5.5)$$

Substituting for  $E$  from Equation (5.5) into Equation (5.4) and integrating from  $t = 0$  to  $t = t$

$$Is = (k_i / (k_d + k_i)) E_0 (1 - \exp(-(k_d + k_i)t)) \quad (5.6)$$

Now the mass spectrometric peak height followed is the sum of the peak heights due to the isomers as well as the ethylcyclobutane.

Therefore

$$PH(m/e) = S_{E, m/e} E + S_{Is, m/e} Is \quad (5.7)$$

where  $S_{E, m/e}$  and  $S_{Is, m/e}$  are the sensitivities for mass number  $(m/e)$  followed during the reaction. Since

$$PH_0(m/e) = S_{E, m/e} E_0 \quad \text{at } t = 0 \quad (5.8)$$

and

$$PH_\infty(m/e) = S_{Is, m/e} I_{s\infty} \quad \text{at } t = \infty \quad (5.9)$$

Equation (5.7) may be written as

$$PH_t(m/e) = PH_0(m/e) \exp(-(k_d + k_i)t) + PH_\infty(m/e)(1 - \exp(-(k_d + k_i)t)) \quad (5.10)$$

or

$$(\text{PH}_t(m/e) - \text{PH}_\infty(m/e)) = (\text{PH}_o(m/e) - \text{PH}_\infty(m/e)) \exp(-(k_d + k_i)t) \quad (5.11)$$

$$\text{Hence} \quad -d(\ln(\text{PH}_t(m/e) - \text{PH}_\infty(m/e)))/dt = k_d + k_i \quad (5.12)$$

A plot of the difference between the peak height measured at any time and a constant correction term equal to the peak height remaining after virtual completion of the decomposition, vs. time, should yield a straight line whose slope is the sum of the two rate constants  $k_d + k_i$ .

In practice the exact value of  $\text{PH}_\infty(m/e)$  was determined by finding empirically the value of a constant term which, when subtracted from all peak heights, gave the best fit to a straight line rather than by actually measuring the residual peak height at mass 69 or 84 after ten half-lives or so. The empirical constant term was expressed as a percentage of the initial peak height ( $\text{PH}_o$ ), and represented by  $\alpha(m/e)$ . The precision of the values given for the isomerization constant,  $\alpha(m/e)$ , is not very high. The standard deviation for  $\alpha(69)$  is 16% while that of  $\alpha(84)$  is 15%. The precision with which  $\alpha(m/e)$  could be determined depended on a number of factors. First the number that was subtracted from each peak height to linearise the plot of  $\log(\text{PH})$  vs. time plot could be varied by  $\pm 3-5\%$  of its

own value without any substantial change in the slope of the straight line thus obtained. The uncertainty in this number diminishes as the number of half-lives increases over which the reaction was followed. For example, if the reaction was followed for six half-lives the number to be subtracted could be determined to about  $\pm 1\%$  of its own value. For reaction followed for one half-life, this number could not be determined at all. Secondly, the value of  $PH_0$  (m/e) was uncertain by  $\pm 1\%$  since it was determined by extrapolation to time zero, which is itself somewhat uncertain. Finally during slow runs instrumental fluctuations introduce scatter in the  $\log(PH)$  vs. time plots, and this results in greater uncertainties in the subtracted constant.

From Table IV, it is apparent that the correction term required to bring the points onto a straight line is not temperature or pressure dependent. The average value of  $\alpha(69)$  is 2.8% of the initial peak height ( $PH_0$ ). When the mass spectral peak 84 is used to follow the reaction, the correction term was found to be 9.3% of the initial peak height ( $PH_0$ ), on the average. The difference in the two percentages is a result of the difference in sensitivities.  $S_{E, m/e}$  and  $S_{Is, m/e}$  for the ethylcyclobutane and the isomers of ethylcyclobutane for the mass spectral numbers 84 and 69 as shown by Table VII. Here the sensitivities for the isomers is taken to be that of the 2-hexenes since

the other two isomers are produced in very much smaller amounts than the 2-hexenes. See Table VI.

TABLE VII  
SENSITIVITIES\* OF MASS SPECTRAL PEAKS 69 AND 84 IN  
ETHYLCYCLOBUTANE AND 2-HEXENE

m/e	ethylcyclobutane sensitivity mm. micron <sup>-1</sup>	2-hexene sensitivity mm. micron <sup>-1</sup>
69	18.7	19.3
84	6.2	26.8

\* Accl. volt = 2,300 v, bomb volt = 50 v, trap current = 16.5  $\mu$ A, case current = 90  $\mu$ A, stabilizing current = 10 mA, leak 50, pressure = 7.0 ( $\pm$  0.4) microns.

The rate constants were found to be independent of the mass spectral peak used to follow the reaction. This view is confirmed by the fact that when several experiments were performed at given sets of pressures and temperatures, the same rate constants, within experimental error, were obtained using both mass numbers 69 and 84. The results are shown in Table VIII.

#### Mechanism of Ethylcyclobutane Pyrolysis

The thermal decomposition of cyclobutane and that of the substituted cyclobutane compounds may occur via at least two different

TABLE VIII

COMPARISON OF RATE CONSTANT AT SIMILAR TEMPERATURES  
AND PRESSURES USING  $m/e = 69$  AND 84

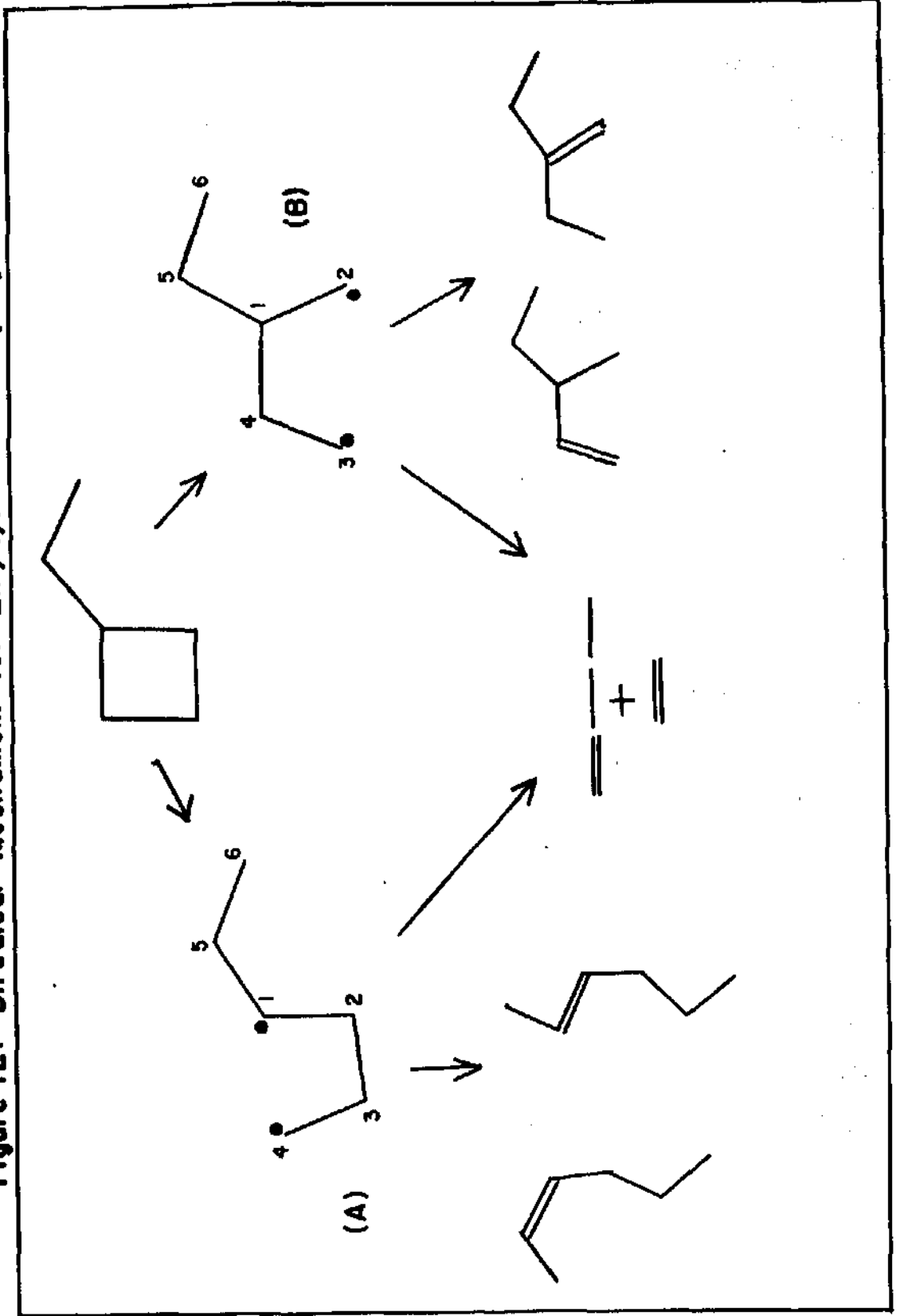
Experiment Number	Flask-Leak Combination	Pressure (microns)	$k(\text{sec}^{-1})$ E-4	Error %	$\alpha$ (%)	Log(P)	5 + log k	m/e
T = 673, 2°K (400°C)								
E070	3-46	6.53	0.194	0.30	2.6	0.815	0.289	69
E128	6-7	7.35	0.200	0.56	12.1	0.866	0.301	84
T = 693, 2°K (420°C)								
E131	6-7	5.79	0.666	0.12	9.1	0.763	0.824	84
E023	3-46	6.16	0.687	0.17	1.7	0.790	0.837	69
E108	6-7	8.59	0.699	0.46	2.8	0.934	0.844	69
E130	3-46	9.96	0.729	0.25	9.0	0.998	0.863	84
E129	3-46	10.1	0.734	1.10	9.7	1.00	0.866	84
E022	6-7	10.6	0.786	0.10	3.3	1.25	0.895	69
T = 713, 2°K (440°C)								
E132	6-7	9.81	2.00	0.43	9.1	0.992	1.301	84
E007	3-46	9.90	2.36	0.50	1.0	0.996	1.372	69
T = 753, 2°K (480°C)								
E073	6-7	10.5	21.7	0.16	7.1	1.022	2.336	84
E054	3-46	10.9	21.8	0.15	2.2	1.037	2.339	69
E139	6-7	348.	35.0	0.13	3.1	2.542	2.438	69
E047	3-46	367.	38.8	0.46	8.3	2.564	2.588	84

mechanisms, one is a concerted process via which the two opposite carbon-carbon bonds of the cyclobutane system break simultaneously Burkhardt (1962). The other mechanism is in terms of diradical intermediates.

The strength of the carbon-carbon bond (Pauling, 1960) in ethane is  $83.1 \text{ kcal mole}^{-1}$ . The energy needed to simultaneously break two carbon-carbon bonds in the cyclobutane ring system is therefore equal to  $166.2 \text{ kcal mole}^{-1}$  minus the strain energy of the cyclobutane ring. Since the strain energy is about  $26 \text{ kcal mole}^{-1}$ , it follows that about  $140 \text{ kcal mole}^{-1}$  of energy is needed for the concerted process. The activation energy for the pyrolysis of ethylcyclobutane was found to be  $62.5 \text{ kcal mole}^{-1}$ , which is too small for the concerted process. Also the concerted mechanism, if applied to the thermal decomposition of ethylcyclobutane, does not explain the observed isomerization of ethylcyclobutane to cis- and trans-2-hexenes, 3-methyl-1-pentene and 2-ethyl-1-butene. Hence it was concluded that the concerted mechanism does not apply to the pyrolysis of ethylcyclobutane.

The mechanism shown in Figure 12 is consistent with the information available on the decomposition of the ethylcyclobutane and cyclobutane derivatives in general. The mechanism involves the formation of diradical intermediates which exist for a sufficiently long

Figure 12.- Diradical Mechanism for Ethylcyclobutane Pyrolysis

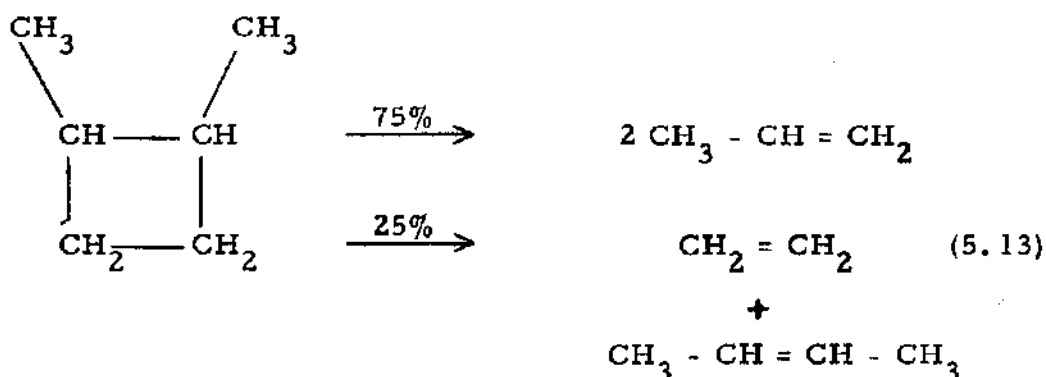




period of time that rotation about carbon-carbon bonds can occur, resulting in isomerization. The scheme explains the formation of the observed ethylcyclobutane isomers as well as that of the ethylene and 1-butene which are the main products of the reaction. It may be demonstrated by means of scale models of the diradical intermediate (A) in Figure 12 that either of the two hydrogen atoms attached to the carbon atom numbered five ( $C_5$ ) in the diradical (A) may be brought into contact with  $C_4$  by simple rotations about carbon-carbon bonds in the molecule, without stretching or bending any of these bonds. Hydrogen atom transfer from  $C_5$  to  $C_4$  then leads directly to the formation of cis- and trans-2-hexenes.

A transfer of one hydrogen atom from  $C_4$  to  $C_2$  in the diradical intermediate (B) in Figure 12 gives rise to 3-methyl-1-pentene while a hydrogen atom transfer from  $C_1$  to  $C_3$  gives rise to 2-ethyl-1-butene. The amount of the 2-hexenes is about 22 times more than that of the 3-methyl-1-pentene or the 2-ethyl-1-butene. This reflects the ease with which the transfer of the respective hydrogen atoms could be made as well as a preference of breaking the carbon-carbon bond next to the ethyl group over breaking that carbon-carbon bond which is furthest from it. This type of phenomenon was noted by Conn (1966). He found that the major product of pyrolysis of cis- and trans-1-2-dimethylcyclobutane was obtained by breaking the

carbon-carbon bond joining the two substituted carbon atoms. The minor reaction products came from breaking the carbon-carbon bonds joining the carbon atoms that are least substituted. The products distribution is shown below.



The diradical mechanism, besides being able to account qualitatively for all the observed pyrolytic reactions of cyclobutane, cyclopropane and their derivatives, has also been found to be qualitatively consistent with the experimental kinetic data. O'Neal and Benson (1968) have recently completed a quasi-equilibrium thermodynamic calculations based on a transition state approach using the diradical as an intermediate for the pyrolytic reactions of several cyclobutane and cyclopropane derivatives. Arrhenius parameters so estimated appeared to be in reasonable agreement with the experimentally determined values. These calculations have further strengthened the belief in the formation of diradicals in the pyrolysis of cyclobutane

and its derivatives.

The major objection to the diradical mechanism is that free radicals have never been trapped in cyclobutane or substituted cyclobutane thermal decomposition systems. As an example, the addition of nitric oxide did not abnormally alter the rates of decomposition of ethylcyclobutane nor were nitric oxide addition compounds observed in the mass spectra of the reaction products. However, Seubold (1954) has pointed out that the absence of addition reactions with additives does not rule out the presence of diradicals since diradicals would be expected to recombine at a much faster rate than they would abstract a hydrogen atom from toluene or add to nitric oxide. The former process must have a low steric factor and a reasonably large activation energy; the latter process is slow because even methyl radicals recombine about one thousand times faster than they add to nitric oxide.

The conclusions reached here are therefore that the thermal decomposition of ethylcyclobutane takes place via diradical intermediates since this mechanism satisfactorily accounts for all the reaction products, including the isomers of ethylcyclobutane. The structural isomerization appeared to be slow in comparison with the decomposition reaction.

## CHAPTER SIX

APPLICATION OF KASSEL THEORY TO  
ETHYLCYCLOBUTANE

The modified Kassel integral Equation (6.1) which takes into account the activation and deactivation of molecules by collision with the wall (Thomas, Conn and Swinehart (1969)) was used to fit the ethylcyclobutane data.

$$k = \frac{A \exp(-E_0/RT)}{[s]^2 (RT)^2} \int_0^{\infty} \frac{Z^{s-1} \exp(-Z/RT) dz}{1 + \frac{A \left(\frac{Z}{Z+E_0}\right)^{s-1}}{\frac{4\lambda\sigma^2 P}{k_1 T} \left(\frac{\pi kT}{m}\right)^{1/2} + \frac{\lambda' \bar{c}}{4} \left(\frac{S}{V}\right)}} \quad (6.1)$$

where

- A = The Arrhenius frequency factor in  $\text{sec}^{-1}$  at the high pressure limit
- $E_0$  = The activation energy in calories  $\text{mole}^{-1}$  at the high pressure limit
- s = The effective number of oscillators in the molecule
- R = The universal gas constant in calories  $\text{deg}^{-1} \text{mole}^{-1}$
- $k_1$  = The Boltzman constant in cc microns  $\text{deg}^{-1} \text{molecule}^{-1}$
- k = The Boltzman constant in ergs  $\text{deg}^{-1}$
- T = The absolute temperature
- Z =  $E - E_0$ , the excess energy in calorie  $\text{mole}^{-1}$
- $\lambda$  = The intermolecular collision deactivation efficiency
- $\lambda'$  = The wall collision deactivation efficiency
- P = The initial pressure of the parent molecule in microns of Hg
- $\sigma$  = The collision diameter of the parent molecule in cm
- m = The mass of the parent molecule in grams
- $\bar{c}$  =  $(8kT/\pi m)^{1/2}$ , the mean molecular speed
- $\Gamma$  = The gamma function
- $\left(\frac{S}{V}\right)$  = The surface-to-volume ratio in  $\text{cm}^{-1}$  for the reaction flask

The value adopted for  $\sigma$  was consistent with  $\sigma = 5.85 \text{ \AA}$  used by Thomas (1964) for methylcyclobutane and a correction due to the additional methyl group in ethylcyclobutane. The methyl group volume contribution  $22.7 \text{ \AA}^3$  found by Bondi (1964) was added to the methylcyclobutane volume to give the ethylcyclobutane volume, which was used to obtain  $\sigma$  treating the molecule as a sphere.

$$V = \pi \sigma^3 / 6 \quad (6.2)$$

The result was  $\sigma = 6.25 \text{ \AA}$ .

The surface-to-volume ratio of the unpacked reaction flask was taken to be  $0.212 \text{ cm}^{-1}$  on the assumption that the reaction flask is composed of a sphere of volume 12,600 cc plus a cylindrical volume of 130 cc to correct for the neck and the side arm of the reaction flask. The packed flask was that used by Conn (1966) when it had a surface-to-volume ratio of  $4.77 \text{ cm}^{-1}$ . Kinetic measurements from this flask were found to produce rate constants that were lower than expected for a surface-to-volume ratio of  $4.77 \text{ cm}^{-1}$ . Hence after the reaction flask was removed from the thermostat the glass wool was inspected. It was found to have settled in about 60% of the volume of the flask. Under these conditions the surface-to-volume ratio of the packed flask was calculated to be  $2.2 \text{ cm}^{-1}$ .

The adjustable parameters in the modified Kassel integral are

A,  $E_0$ ,  $s$ ,  $\lambda$  and  $\lambda'$ . Initial estimates of these variables were obtained in the following way.

The Arrhenius parameters were chosen to agree with the high pressure rate constants of Wellman and Walters for the initial modified Kassel integral calculations. These were

$$E_0 = 62.0 \text{ kcal mole}^{-1}$$

and  $A = 3.6 \times 10^{15} \text{ sec}^{-1}$

A value of  $s = 29$  and  $\lambda = 0.70$  were selected, to start with, in agreement with those for cis-1,2-dimethylcyclobutane, Conn (1966).

The value adopted for  $\lambda'$  was unity on the assumption that the interior surfaces of the reaction vessel should be able to transfer any amount of energy to or from molecules that strike the surfaces.

Using a PDPIO computer program the calculations for the rate constants were done numerically. The calculated rate constants were then compared with the experimental rate constants at all temperatures and pressures that were used in this research.

When the first set of calculations was done it was found that the values of A and  $E_0$  from the high pressure data of Wellman and Walters (1957) were too small and thus did not give a good Kassel fit. These were slightly increased and the calculations done again. Now there was a good fit at high pressures (above 30 microns) and at all the

reaction temperatures. At the low pressure end of the isotherms however, the values of the calculated rate constants were found to be lower than the experimental values. Hence the values of  $s$  and  $\lambda$  were increased in order to raise the lower end of the isotherms to get a better Kassel fit at all reaction temperatures and pressures. The final values of the parameters of the Kassel integral which gave the best fit between experimental rate constants and those calculated from the modified Kassel theory are shown in Table IX.

TABLE IX  
PARAMETERS OF THE KASSEL INTEGRAL  
FOR ETHYLCYCLOBUTANE

Parameter	$A(\text{sec}^{-1})$	$E_0(\text{cal mole}^{-1})$	$\sigma(\text{\AA})$	$\lambda'$	$\lambda$	$s$
Value	5.5E15	6.25E4	6.25	1	0.75	30

Table X contains a summary of the Kassel parameters obtained for several other unimolecular reactions for comparison with those obtained for ethylcyclobutane.

Table XI contains the calculated values of the rate constants for the modified Kassel integral for the unpacked flasks while Table XII contains the packed flask calculated data.

Figure 13 shows the agreement between theory and experiment. The circles represent experimental points while the curves were drawn



TABLE X  
VALUES OF KASSEL INTEGRAL PARAMETERS FOR SELECTED REACTIONS

Molecule	Number of Normal Modes	A (Sec <sup>-1</sup> )	E <sub>0</sub> (kcal/mole)	s	λ	λ'	σ (Å)	Ref.*
Ethylcyclobutane	48	5.5E15	62.5	30	0.75	1.00	6.25	a
Trans-1,2-dimethyl cyclobutane	48	4.53E15	62.0	30	0.70	1.00	6.25	b
Cis-1,2-dimethyl cyclobutane	48	2.76E15	60.0	29	0.70	1.00	6.25	b
Spirohexane	42	8.7E13	58.5	22	1.00	1.00	6.0	c
Methylcyclobutane	39	10.64E15	63.1	26	0.70	1.00	5.85	d
1,4-Cyclohexadiene	36	9.6E11	42.5	22	0.2	1.00	6.0	c
Glyoxal	12	1.38E13	52.6	10.3	0.097	1.00	4.5	e

\* a = this research, b = Conn (1966), c = Gay (1968), d = Thomas, Conn and Swinehart (1969), and e = Lowden (1972).

TABLE XI

CALCULATED VALUES OF RATE CONSTANTS FROM THE MODIFIED KASSEL INTEGRAL  
FOR UNPACKED FLASKS USING PARAMETERS OF TABLE IX AND  $\left(\frac{S}{V}\right) = 0.212 \text{ cm}^{-1}$

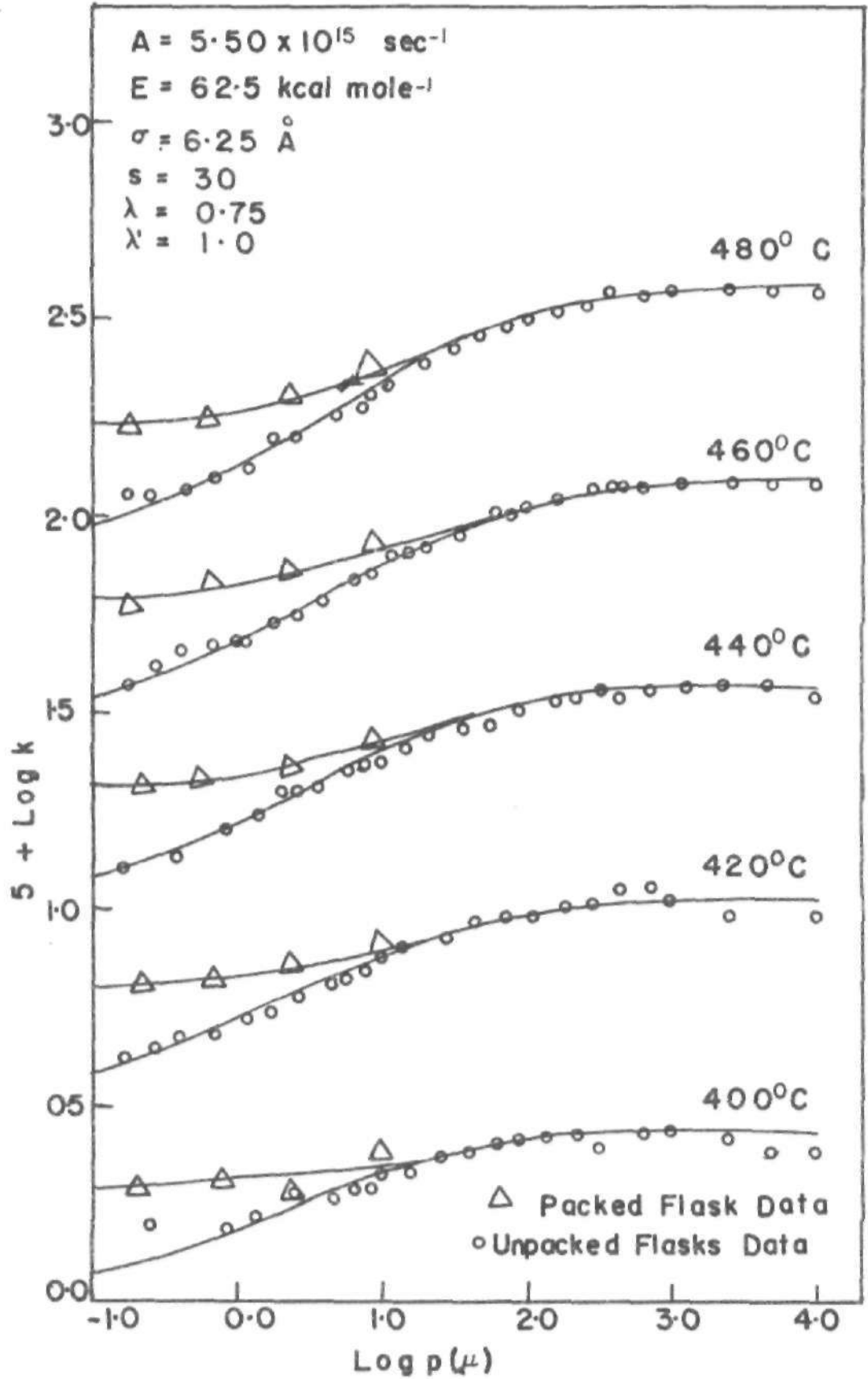
Pressure (P) (microns)	log (P)	5 + log k <sub>Kassel</sub> (sec <sup>-1</sup> )				
		T = 673.2°K	693.2°K	713.2°K	733.2°K	753.2°K
0.1	-1.0	0.0697	0.5967	1.0875	1.5451	1.9722
1.0	0.0	0.1867	0.7245	1.2258	1.6935	2.1303
10.0	1.0	0.3290	0.8861	1.407	1.8943	2.3506
100.0	2.0	0.4105	0.9837	1.5218	2.0273	2.5035
1000.0	3.0	0.4407	1.0227	1.5708	2.0876	2.5753
10000.0	4.0	0.4480	1.0328	1.5845	2.1058	2.5989

TABLE XII

CALCULATED VALUES OF RATE CONSTANTS FROM THE MODIFIED KASSEL INTEGRAL FOR THE  
 PACKED FLASK USING PARAMETERS FROM TABLE IX AND  $\left(\frac{S}{V}\right) = 2.2 \text{ cm}^{-1}$

Pressure (P) (microns)	log(P)	$S + \log k$ (sec) <sup>-1</sup>				
		T = 673.2°K	693.2°K	Kassel 713.2°K	733.2°K	753.2°K
.1	-1.0	0.2546	0.8027	1.3148	1.7938	2.2417
1.0	0.0	0.2724	0.8225	1.3364	1.8171	2.2667
10.0	1.0	0.3404	0.8998	1.4231	1.9133	2.3721
100.0	2.0	0.4110	0.9845	1.5228	2.0287	2.5039
1000.0	3.0	0.4407	1.0227	1.5708	2.0878	2.5753
10000.0	4.0	0.4479	1.0328	1.5845	2.1061	2.5989

Figure 13- Kassel Integral Fitted to Kinetics Data



from the calculated results. Inspection of Figure 13 then, showed that the theoretical curves represent the experimental data quite well.

From the variation of the fits with change in  $E_0$ , the precision in this parameter was found to be  $\pm 0.3$  kcal. The experimentally determined value of the activation energy was in good agreement with the difference between the energy of C-C bond (83.1 kcal) and the strain energy of the ethyl cyclobutane ring ( $\sim 23$  kcal). Hence it was concluded that the activation energy of this reaction was the energy needed to open the ethylcyclobutane ring. The precision in the frequency factor was about  $\pm 0.10 \times 10^{15} \text{ sec}^{-1}$  and the frequency factor itself is roughly equal to the highest vibration frequency of the molecule. The entropy of activation was calculated by setting the expression  $e(kT/h)e^{\Delta S^*/R}$  equal to the experimental frequency factor. The calculated value of  $\Delta S^*$  at  $450^\circ\text{C}$  is 11.0 cal/deg. mole. This is a positive value as might be expected for a reaction involving ring cleavage.

The variation of the fits with change in  $s$  was only sensitive to integral values of  $s$ . In this way the effective number of internal degrees of freedom that can store energy in the activated complex was found to be 30. Theoretically  $s=48$  in ethylcyclobutane molecule. This means that all the modes do not contribute energy to the critical mode of the reaction with equal efficiency. Finally the value of  $\lambda = 0.75$  found for ethylcyclobutane lends further supports to the strong collision assumption.

## APPENDIX

PROGRAM FOR EXTRACTION OF RATE CONSTANTS  
FROM MASS SPECTRAL DATA

C PLOTS LN(PH) VS TIME TO CALCULATE K.  
 C VERSION 10, 29 DEC, 1971  
 C THIS PROGRAM IS NOW SET UP TO ATTEMPT TO LINEARIZE THE  
 C FIT OF THE DATA TO A STRAIGHT LINE BY MINIMIZING THE  
 C STANDARD DEVIATION IN THE SLOPE.  
 C THIS PROGRAM IS SET UP TO HANDLE A MAXIMUM OF 100 DATA  
 C POINTS PER DATA SET.  
 C CARD 1 OF EACH SET SHALL CONTAIN TEMPERATURE IN  
 C DEGREES C COL 12-14 (F3.0), INITIAL PRESSURE IN  
 C MICRONS COL 22-27 (F6.0), LEAK-OUT CONSTANT AT MASS  
 C 58 COL 56-63 (E8.3), NUMBER OF POINTS TO OMIT COL  
 C 70-71 (I2), RUN ID COL 73-77 (A1, I4), AND SEQ  
 C NUMBER COL 78-80 (I3)  
 C CARD 2 OF EACH SET SHALL CONTAIN VOLUME OF REACTION  
 C FLASK COL 1-6 (F6.0), EXPANSION VOLUME COL 7-12  
 C (F6.1), TEMPERATURE OF EXPANSION VOLUME IN DEGREES  
 C C COL 13-17 (F5.1), INITIAL EXPANSION PRESSURE COL  
 C 18-24 (F7.0), FINAL EXPANSION PRESSURE COL 25-31  
 C (F7.0), FINAL PRESSURE OF REACTION IN EXPANDED SYSTEM  
 C COL 32-38 (F7.0), FINAL EXPANSION VOLUME COL 39-44  
 C (F6.1), FINAL EXPANSION TEMPERATURE COL 45-49 (F5.1),  
 C LENGTH OF REACTION IN MIN COL 50-54 (I5), PORT TEMP  
 C OF FLASK WAS MONITORED COL 56 (A1), LEAK IN FLASK  
 C COL 58-59 (A2), FACTOR BY WHICH TIME FROM CARDS IS  
 C TO BE DIVIDED TO GET REAL REACTION TIME COL 60-61  
 C (F2.0), STANDARD DEVIATION IN LEAK-OUT CONSTANT (AS  
 C PERCENT) COL 62-66 (F5.4), VOLUME IN WHICH COMPOUND  
 C WAS CONTAINED IF NOT IN EXPANSION VOLUME COL 67-71  
 C (F5.2), RUN ID AND SEQ NUMBER SAME AS BEFORE.  
 C CARD 3 OF EACH DATA SET WILL CONTAIN NUMBER OF MINUTES  
 C THAT ELAPSED AFTER START OF REACTION BEFORE THE ZERO  
 C POINT WAS SELECTED FOR PUNCHING DATA CARDS COL 1-5  
 C (F5.0), FLASK ID COL 7 AND 8 (A2), PEAK HEIGHTS  
 C CORRECTED TO SHUNT 20 (F6.1) BEGINNING IN COLUMN 9,  
 C PEAK HEIGHT MONITORED DURING RUN IN COLUMNS 69-71  
 C (I3), RUN ID IN COLUMNS 73-80 AS BEFORE. THE FORMAT  
 C FOR THIS CARD IS (F5.0,1X,A2,NNF6.1,T69,I3,1X,A1,I4,  
 C I3). NN ARE TWO DIGITS THAT ARE GENERATED BY THE

C PROGRAM FROM THE VALUE OF NPH THAT WAS INPUT.  
 C CARDS 2 AND 3 WILL NOT BE EXPECTED IF CARD 1 CONTAINS  
 C AN "L" IN COL 73 FOR THIS WILL BE A LEAK-OUT RUN.  
 C IF COL 73 CONTAINS AN "A", THIS IMPLIES THAT IT IS AN  
 C ADDED GAS RUN. AN EXTRA CARD WILL BE EXPECTED AFTER  
 C THE FIRST CONTAINING ADDED GAS ID AND MOLE FRACTION  
 C REACTANT. THE INITIAL PRESSURE IN THE FIRST CARD  
 C SHALL BE TOTAL PRESSURE IN THE REACTION VESSEL.  
 C THIS CARD IS READ AND PRINTED ALPHAMERICALLY AND  
 C MUST BE SEQUENCE NUMBERED.  
 C TO RESTART MAIN PROGRAM PUNCH "RESTART" IN COL 1-7 OF  
 C A CARD AND INSERT THIS CARD WHERE A FIRST CARD OF A  
 C DATA SET WOULD BE EXPECTED.  
 C IF COLUMN 71 OF A TITLE CARD CONTAINS ANYTHING OTHER  
 C THAN A BLANK OR ZERO IT IS ASSUMED THAT THIS IS A  
 C LEAK-OUT RUN AND THE RATE CONSTANT WILL BE CALCULATED  
 C FROM A STRAIGHT LINE FIT TO THE DATA  
 C IT IS ASSUMED THAT ALL LEAKOUTS ARE MEASURED AT 350 C  
 C AND FOR N-BUTANE.

REAL KLO, K(2), N, LN10, IP, MASS, LN2, LOG(3,100),  
 1 LOGP, LOGKP5(2)  
 INTEGER O, AG, CC, BLANK, ONE, CONVT, CALC  
 LOGICAL TEST  
 DIMENSION TIME(5), S(5), HT(5), CHAR(55), TIM(100),  
 1 PH(100), SHUNT(100), PHS20(100), DIFF10(3,100),  
 2 SLOP(2), SDS(100), SDK(2), P(2), DELTA(100), FMT(8),  
 3 ME(10), PHME20(10), SLOPE(3), B(2), PHS20E(100),  
 4 INPUT(16)  
 DATA L, AG, REST, BLANK, ONE, ZERO, FMT/'L', 'A',  
 1 'REST', ' ', '1', 0.0, '(F5.0', ',1X,A', '2', '  
 2 'F6.1', ' ', 'X', 'I3,1X', ',A1,I', '4,I3)'/  
 TYPE 50  
 50 FORMAT (' ENTER INPUT DEVICE, OUTPUT DEVICE (2I2) ',  
 1 \$)  
 ACCEPT 51, II, IO  
 51 FORMAT (2I2)  
 IF ((IO .NE. 16) .AND. (IO .NE. 17)) GO TO 143  
 TYPE 35  
 35 FORMAT (' ENTER BUFFER LENGTH (I) ', \$)  
 ACCEPT 36, NWD  
 36 FORMAT (I)  
 IF ((NWD .EQ. 128) .OR. (NWD .EQ. 0)) GO TO 143  
 CALL OBUFF (IO, 2, NWD)  
 143 TYPE 37  
 37 FORMAT (' ENTER NUMBER OF PEAK HEIGHTS TO BE INPUT (I)'  
 1 ', '\$)  
 ACCEPT 36, NPH

```

TYPE 38
38 FORMAT (' ENTER M/E VALUES FOR PEAK HEIGHT, ONE TO A',
1 ' LINE (I)'/)
ACCEPT 36, (ME(I), I = 1, NPH)
ENCODE (5,39,FMT(3)), NPH
39 FORMAT ('2', I3)
I = 68 - 8 - NPH * 6
ENCODE (3,40,FMT(5)), I
40 FORMAT (I3)
TYPE 70, FMT
70 FORMAT (1X, 8A5)
LN2 = ALOG(2.)
LN10 = ALOG(10.)
TLO = 350. + 273.16
C
113 TYPE 94
94 FORMAT (' ENTER MASS OF COMPOUND (F) = ', $)
ACCEPT 95, MASS
95 FORMAT (F)
TYPE 96
96 FORMAT (' ENTER CPD ID (10A4)'/)
ACCEPT 27, (CHAR(I), I = 21, 30)
TYPE 10
10 FORMAT (' ENTER DATE (7A4)'/)
ACCEPT 27, (CHAR(I), I = 31, 37)
27 FORMAT (10A4)
110 READ (II,71,END=111) INPUT
71 FORMAT (16A5)
DECODE (80,1,INPUT), T, IP, KLO, O, CALC, IDA, IDB, IDC
DECODE (80,90,INPUT), (CHAR(I), I = 1, 20)
1 FORMAT (11X,F3.0,7X,F6.0,28X,E8.3,6X,I2,I1,A1,I4,I3)
90 FORMAT (20A4)
IF (CHAR(1) .EQ. REST) GO TO 113
TYPE 28, IDA, IDB
28 FORMAT (1X, A1, I4)
CONVT = 0
CC = BLANK
TEST = .TRUE.
TFUDGE = 1.
WRITE (IO,11) (CHAR(I), I = 21, 37)
11 FORMAT ('1COMPOUND = ', 10A4// ' DATE OF PROCESSING = ',
1 7A4//)
IF (CALC .NE. 0) GO TO 102
IF (IDA .NE. AG) GO TO 114
READ (II,15) (CHAR(I), I = 38, 55), ID1, ID2, ID3
15 FORMAT (18A4, A1, I4, I3)
IF (.NOT.((ID1 .EQ. IDA).AND.(ID2 .EQ. IDB).AND.
1 (ID3 .GT. IDC))) GO TO 101
IDC = ID3
WRITE (IO,16) (CHAR(I), I = 38, 55)
16 FORMAT (' ', 18A4)

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114 WRITE (IO,2) (CHAR(I), I = 1, 20)
  2 FORMAT (1X, 20A4// ' TIME (MIN) PH (MM) SHUNT',
  1 ' PH.(S=20) PH ADJUST LOG PH DIFF')
  IF (IDA .EQ. L) GO TO 102
  READ (II,12) VR, VX, TX, P1, P2, PF, VFX, TFX, MIN,
  1 PORT, LEAK, TFUDGE, SDKLO, VCPD, ID1, ID2, ID3
  12 FORMAT (F6.0, F6.1, F5.1, 3F7.0, F6.1, F5.1, I5, 1X,
  1 A1, 1X, A2, F2.0, F5.4, F5.2, 1X, A1, I4, I3)
  IF ((ID1 .EQ. IDA).AND.(ID2 .EQ. IDB).AND.(ID3 .GT.
  1 IDC)) TO TO 112
101 TYPE 4
  4 FORMAT (' CARD OUT OF SEQUENCE, END.')
  END FILE IO
  STOP
112 IDC = ID3
  READ (II,FMT) TBS, FLASK, (PHME20(I), I = 1, NPH), MEF,
  1 ID1, ID2, ID3
  IF (.NOT.((ID1 .EQ. IDA).AND.(ID2 .EQ. IDB).AND.
  1 (ID3 .GE. IDC))) GO TO 101
  IDC = ID3
  KLO = KLO * SQRT((T + 273.16) * 58.12/(TLO * MASS))
  IF (TFUDGE .EQ. ZERO) TFUDGE = 1.
102 N = 0
  J = 0
100 READ (II,3) (TIME(I), HT(I), S(I), I = 1, 5), ID1,
  1 ID2, ID3
  3 FORMAT (5(F4.0, 1X, F5.1, 1X, F3.0), 2X, A1, I4, I3)
  IF (.NOT.((ID1 .EQ. IDA).AND.(ID2 .EQ. IDB).AND.
  1 (ID3 .GT. IDC))) GO TO 101
103 IDC = ID3
  DO 105 I = 1, 5
  IF (TIME(I) .EQ. -99.) GO TO 106
104 A = HT(I) * 20./S(I)
  J = J + 1
  TIM(J) = TIME(I)/TFUDGE
  PH(J) = HT(I)
  SHUNT(J) = S(I)
  PHS20(J) = A
  PHS20E(J) = A * EXP(KLO * TIM(J) * 60.)
105 CONTINUE
  GO TO 100
106 N = J - 0
  NUM = 1
  DELTA(1) = 0.
  DELTA(2) = 0.
  ND = 2
  IF (CALC .NE. 0) GO TO 137
120 SX1 = 0.
  SX2 = 0.
  SXX1 = 0.
  SXX2 = 0.

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SXY1 = 0.
SXY2 = 0.
SY1 = 0.
SY2 = 0.
NP = (J - 0)/2
IPP = 0 + NP
DO 118 I = 1, IPP
Y = ALOG(PHS2OE(I) - DELTA(NUM))
LOG(NUM,I) = Y
IF (I .LE. 0) GO TO 118
X = TIM(I) * 60.
SX1 = SX1 + X
SXX1 = SXX1 + X * X
SXY1 = SXY1 + X * Y
SY1 = SY1 + Y
118 CONTINUE
KP = IPP + 1
DO 119 I = KP, J
Y = ALOG(PHS2OE(I) - DELTA(NUM))
LOG(NUM,I) = Y
X = TIM(I) * 60.
SX2 = SX2 + X
SXX2 = SXX2 + X * X
SXY2 = SXY2 + X * Y
119 SY2 = SY2 + Y
D1 = NP * SXX1 - SX1 * SX1
D2 = (J - IPP) * SXX2 - SX2 * SX2
A1 = (SY1 * SXX1 - SXY1 * SX1)/D1
A2 = (SY2 * SXX2 - SXY2 * SX2)/D2
B1 = (NP * SXY1 - SX1 * SY1)/D1
B2 = ((J - IPP) * SXY2 - SX2 * SY2)/D2
SX = SX1 + SX2
SXX = SXX1 + SXX2
SXY = SXY1 + SXY2
SY = SY1 + SY2
DX = N * SXX - SX * SX
SLOPE(NUM) = (N * SXY - SX * SY)/DX
B(NUM) = (SY * SXX - SXY * SX)/DX
SS = 0.
DO 116 JP = 1, J
DIFF = B(NUM) + SLOPE(NUM) * TIM(JP) * 60. -
1 LOG(NUM,JP)
DIFF10(NUM,JP) = DIFF/LN10
IF (JP .LE. 0) GO TO 116
117 SS = SS + DIFF * DIFF
116 CONTINUE
SS = SS/(N - 2.)
K(NUM) = -SLOPE(NUM)
SLOP(NUM) = -SLOPE(NUM)
SLOPE(NUM) = -SLOPE(NUM)
SDS(NUM) = 100. * SQRT(SS * N/DX)/SLOP(NUM)

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IF (IDA .EQ. L) GO TO 122
SDK(NUM) = SQRT((SLOP(NUM) * SDS(NUM))**2 + (KLO *
1 SDKLO)**2)/K(NUM)
DD = EXP(A2 + B2 * TIM(J) * 60.) - EXP(A1 + B1 *
1 TIM(J) * 60.)
NUM = NUM + 1
IF (NUM .GE. 3) NUM = 2
DELTA(NUM) = DELTA(NUM) + DD * 1.1
IF (ABS(DD) .GT. 0.003 * PHS2OE(J)) GO TO 120
DELTA(NUM) = DELTA(NUM) - DD * 1.1
IF (DELTA(NUM) .EQ. ZERO) NUM = 1
VAR = 0.1 * PHS2OE(J)
123 IF (DELTA(NUM) .LT. ZERO) GO TO 124
IF (ABS(DELTA(NUM)) .LE. 0.001 * PHS2OE(J)) GO TO 124
IRT = 1
DC = DELTA(NUM) + VAR
GO TO 125
126 IRT = 2
ID1 = NVAL
DC = DELTA(NUM) - VAR
GO TO 125
127 ID2 = NVAL
IF ((SDS(ID2) .LT. SDS(NUM)).AND.(SDS(ID2) .LT.
1 SDS(ID1))) GO TO 129
IF ((SDS(ID1) .LT. SDS(NUM)).AND.(SDS(ID1) .LT.
1 SDS(ID2))) GO TO 130
VAR = VAR * 0.1
DO 128 JP = 1, J
LOG(2,JP) = LOG(3,JP)
128 DIFF10(2,JP) = DIFF10(3,JP)
SLOPE(2) = SLOPE(3)
IF (VAR .LT. 0.0001) GO TO 135
GO TO 123
129 NUM = ID2
GO TO 123
130 NUM = ID1
GO TO 123
125 DO 131 JP = 1, ND
NVAL = JP
IF (DC .EQ. DELTA(JP)) GO TO (126, 127), IRT
131 CONTINUE
ND = ND + 1
IF (ND .GT. 100) GO TO 136
DELTA(ND) = DC
NVAL = ND
SX = 0.
SXX = 0.
SXY = 0.
SY = 0.
DO 132 JP = 1, J

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Z = PHS2OE(JP) - DELTA(ND)
IF (Z .LE. ZERO) GO TO 108
Y = ALOG(Z)
GO TO 109
108 Y = -1.E12
109 LOG(3,JP) = Y
IF (JP .LE. 0) GO TO 132
X = TIM(JP) * 60.
SX = SX + X
SXX = SXX + X * X
SXY = SXY + X * Y
SY = SY + Y
132 CONTINUE
DX = N * SXX - SX * SX
B(2) = (SY * SXX - SXY * SX)/DX
SLOPE(3) = (N * SXY - SX * SY)/DX
SS = 0.
DO 133 JP = 1, J
DIFF = B(2) + SLOPE(3) * TIM(JP) * 60. - LOG(3,JP)
DIFF10(3,JP) = DIFF/LN10
IF (JP .LE. 0) GO TO 133
SS = SS + DIFF * DIFF
133 CONTINUE
SS = SS/(N - 2.)
SLOPE(3) = -SLOPE(3)
SDS(ND) = 100. * SQRT(SS * N/DX)/SLOPE(3)
IF (Z .LE. ZERO) SDS(ND) = 1.E20
GO TO (126, 127), IRT
135 K(2) = SLOPE(2)
SDK(2) = SQRT((SLOPE(2) * SDS(NUM))**2 + (KLO *
1 SDKLO)**2)/K(2)
SDS(2) = SDS(NUM)
DELTA(2) = DELTA(NUM)
NUM = 2
IF (NUM .EQ. 2) WRITE (IO,21)
21 FORMAT ('+', 79X, 'LOG PH      DIFF')
122 DO 121 JP = 1, J
P(1) = LOG(1,JP)/LN10
IF (NUM .EQ. 2) P(2) = LOG(2,JP)/LN10
200 WRITE (IO,5) CC, TIM(JP), PH(JP), SHUNT(JP),
1 PHS2O(JP), PHS2OE(JP), (P(I), DIFF10(I,JP),
2 I = 1, NUM)
5 FORMAT (A1, F9.2, F11.1, F8.0, 2F12.2, 2(F10.5, F13.5))
121 CONTINUE
IF (IDA .EQ. L) GO TO 107
WRITE (IO,6) CC, K(1), SDS(1)
6 FORMAT (//A1, 'RATE CONSTANT 1 (CORR FOR LEAK-OUT)',
1 8X, '=' , E16.8, ' STD DEV SLOPE = ', F9.4, '%')
IF (NUM .EQ. 2) WRITE (IO,29) CC, K(2), SDS(2)
29 FORMAT (A1, 'RATE CONSTANT 2 (CORR FOR LEAK-OUT & ISOM',
1 ') = ', E16.8, ' STD DEV SLOPE = ', F9.4, '%')

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IF (IDA .EQ. L) GO TO 110
WRITE (IO,7) CC, SDKLO, SDK(1)
7 FORMAT (A1, 'STD DEV KLO = ', F9.4, '% STD DEV K1 = ',
1 F9.4, '%')
IF (NUM .EQ. 2) WRITE (IO,30) SDK(2)
30 FORMAT ('+', 52X, 'STD DEV K2 = ', F9.4, '%')
HL = (LN2/K(NUM))/60.
HLN = MIN/HL
WRITE (IO,8) CC, NUM, HL, MIN, HLN
8 FORMAT (A1, 'HALF LIFE', I2, ' = ', F10.3,
1 ' MIN REACTION FOLLOWED FOR', I5, ' MIN = ', F5.2,
2 ' HALF LIVES.')
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WRITE (IO,14) CC, VR, VX, TX
14 FORMAT (A1, 'REACTION VOLUME = ', F7.0, 4X,
1 ' EXPANSION VOLUME = ', F7.1, 4X, ' EXPANSION TEMPERAT',
2 ' URE = ', F5.1)
IF (VCPD .EQ. ZERO) GO TO 217
VTOT = VCPD + VX
WRITE (IO,19) CC, VCPD, VTOT
19 FORMAT (A1, 'VOLUME FROM WHICH CPD EXPANDED = ', F7.2,
1 4X, 'TOTAL VOLUME EXTERNAL TO REACTION FLASK = ',
2 F8.2)
217 WRITE (IO,24) CC, P1, P2, IP
24 FORMAT (A1, 'P1 = ', F12.3, 4X, 'P2 = ', F12.3, 4X,
1 ' INITIAL PRESSURE OF REACTION = ', F12.3)
IF (PF .EQ. ZERO) GO TO 150
WRITE (IO,25) CC, PF
25 FORMAT (A1, 'AT END OF REACTION FINAL PRESSURE MEASU',
1 ' RED WAS = ', F12.3)
IF (TFX .NE. ZERO) GO TO 115
TFX = TX
WRITE (IO,17) CC
17 FORMAT (A1, 'TEMPERATURE OF VOLUME IN WHICH FINAL',
1 ' PRESSURE WAS MEASURED HAS NOT BEEN ENTERED, IT',
2 ' HAS BEEN SET EQUAL TO EXPANSION TEMPERATURE.')
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115 PCORR = PF * (1. + (VFX/VR) * (T + 273.16))/
1 (TFX + 273.16)
PR = PCORR/IP
WRITE (IO,13) CC, PCORR, PR
13 FORMAT (A1, 'FINAL PRESSURE OF REACTION (CORR FOR ',
1 ' EXPANSION) = ', F12.3, 4X, 'FINAL PRESSURE/INITIAL ',
2 ' PRESSURE = ', F6.3)
WRITE (IO,18) CC, VFX, TFX
18 FORMAT (A1, 'FINAL EXPANSION VOLUME = ', F7.1, 4X,
1 ' FINAL EXPANSION TEMPERATURE = ', F5.1)
150 CONTINUE
WRITE (IO,26) CC, KLO, PORT, LEAK, FLASK
26 FORMAT (A1, 'KLO (CORR FOR MASS & TEMPERATURE) = ',
1 E16.8, 4X, 'PRT PORT = ', A1, 4X, 'LEAK ', A2,
2 ' IN FLASK ', A2)

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PHI = EXP(B(NUM) + TBS * (SLOPE(NUM) + KLO) * 60.) +
1 DELTA(NUM)
WRITE (IO,41) CC, MEF, PHI
41 FORMAT (A1, 'THE PEAK HEIGHT THAT WAS MONITORED ',
1 'DURING THIS REACTION (M/E = ', I3, ') EXTRAPOLATED',
2 ' TO TIME WHEN RXN STARTED (S=20) = ', F10.3,
3 ' APPROX')
DO 141 I = 1, NPH
IF (PHME20(I) .EQ. ZERO) GO TO 141
PR = PHME20(I)/PHI
WRITE (IO,42) CC, ME(I), PR
42 FORMAT (A1, 'PH (M/E = ', I3, ')/INITIAL PH MONITORED',
1 ' PEAK = ', F8.4, ' (AT END OF RUN)')
141 CONTINUE
LOGP = ALOG(IP)/LN10
LOGKP5(1) = ALOG(K(1))/LN10 + 5.
IF (NUM .EQ. 2) LOGKP5(2) = ALOG(K(2))/LN10 + 5.
WRITE (IO,20) CC, LOGP, LOGKP5(1)
20 FORMAT (A1, 'LOG(INITIAL PRESSURE) =', F9.5, 4X,
1 'LOG(K1) + 5 =', F9.5)
IF (NUM .EQ. 2) WRITE (IO,31) LOGKP5(2)
31 FORMAT ('+', 62X, 'LOG(K2) + 5 =', F9.5)
WRITE (IO,22) CC, DELTA(NUM)
22 FORMAT (A1, 'NUMBER THAT HAD TO BE SUBTRACTED FROM',
1 ' ALL PEAK HEIGHTS TO YIELD BEST ST LINE = ', F8.3)
IF (CONVT .EQ. 1) WRITE (IO,23)
23 FORMAT ('+', T92, 'PROGRAM FAILED TO CONVERGE IN 100',
1 ' TRIES')
GO TO 110
124 NUM = 1
GO TO 122
136 CONVT = 1
GO TO 135
111 TYPE 9
9 FORMAT (' THE END.')
IF ((IO .NE. 16) .AND. (IO .NE. 17)) GO TO 142
END FILE IO
END FILE IO
UNLOAD IO
142 STOP
137 SX = 0.
SXX = 0.
SY = 0.
SKY = 0.
DO 138 I = 1, J
X = TIM(I) * 60.
Y = PHS20(I)
IF (I .LE. 0) GO TO 138
SX = SX + X
SXX = SXX + X * X
SY = SY + Y

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SXY = SXY + X * Y
138 CONTINUE
DX = N * SXX - SX * SX
SLOPE(1) = (N * SXY - SX * SY)/DX
B(1) = (SY * SXX - SXY * SX)/DX
SS = ZERO
DO 139 I = 1, J
DIFF = B(1) + SLOPE(1) * TIM(I) * 60. - PHS20(I)
DIFF10(1,I) = DIFF
IF (I .LE. 0) GO TO 139
SS = SS + DIFF + DIFF
139 CONTINUE
SS = SS/(N - 2.)
SDS(1) = 100. * SQRT(SS * N/DX)/SLOPE(1)
SDI = 100. * SQRT(SS * SXX/DX)/B(1)
K(1) = -SLOPE(1)/B(1)
SDK(1) = SQRT(SDS(1)**2 + SDI**2)
WRITE (IO,32) (CHAR(I), I = 1, 20)
32 FORMAT (1X, 20A4// ' TIME (MIN) PH (MM) SHUNT',
1 ' PH (S=20) DIFF')
DO 140 I = 1, J
140 WRITE (IO,33) TIM(I), PH(I), SHUNT(I), PHS20(I),
1 DIFF10(1,I)
33 FORMAT (F10.2, F11.1, F8.0, F12.2, F8.2)
SDS(1) = SDK(1)
107 WRITE (IO,34) K(1), SDS(1)
34 FORMAT (// ' KLO = ', E16.8, ' STD DEV K = ', F9.4, '%')
GO TO 110
END

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