THE THERMAL DECOMPOSITION OF CYCLOBUTANE AT LOW PRESSURES

by

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ABSTRACT

The thermal decomposition of cyclobutane is a homogeneous, unimolecular reaction; ethylene being the only product. The rate law :-

$$k = 10^{15.3} e^{-61,700/RT} \text{ sec.}^{-1}$$

was found to be obeyed in the pressure region 10 to 40 mm. and temperature range 398° to 450°C.

Cyclobutane undergoes a wall reaction to form propylene and 1-butene.

The high pressure rate constant falls off at low pressures and reaches a limiting low pressure rate when activation is maintained by collision with the walls of the reactor. The low pressure limiting rate decreases as the size of the reactor increases.

The fall off curves gave best agreement with values of the Slater parameter, n , between 5 and 8, and values of the Kassel parameter, s , between 3 and 7.

It was concluded that the ring vibrations are of major importance in the dissociation, and that the C—H bond vibrations are relatively unimportant.

No evidence for a tetramethylene biradical intermediate was found. The reaction mechanism probably involves the simultaneous splitting of two opposite C—C bonds.

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INTRODUCTION

1. Previous work.

The thermal decomposition of cyclobutane is a homogeneous, unimolecular reaction; ethylene being the only product. The first order rate constant falls off at low pressures, as expected for a unimolecular reaction. The low pressure rate constant can be restored to its high pressure value by the addition of an inert gas.

Genaux and Walters¹ studied the decomposition in the temperature range 430° to 480°C. and at initial pressures from about 30 to 400 mm. They carried out the reaction in several packed and unpacked Pyrex vessels, with various surface treatments, and observed no difference in rate. They concluded the reaction to be first order and homogeneous.

Kern and Walters² studied the reaction at 449°C. and at initial pressures from 0.2 to 80 mm. They observed a fall off in rate constant with decreasing pressure; the rate constant at 0.2 mm. being approximately half that at 80 mm. They concluded that the reaction did not involve a free radical chain mechanism as it was not inhibited by the addition of radical scavengers such as nitric oxide, toluene or propylene.

Genaux, Kern and Walters³ studied the decomposition over the temperature range 420° to 468°C. with initial pressures

from 1 to 996 mm. They found the rate law :-

$$k = 4.0 \times 10^{15} e^{-62,500/RT} \text{ sec.}^{-1}$$

to be obeyed down to about 20 mm. pressure. Below this the rate decreased with decreasing pressure. The rate constant at low pressures was raised by the addition of hydrogen, ethylene or ethane. Additional evidence for the absence of free radicals was provided by the fact that cyclobutane had no effect on the rate of decomposition of formaldehyde or the rate of polymerization of ethylene; two reactions which are known to be accelerated by the presence of free radicals.

Pritchard, Sowden and Trotman-Dickenson⁴ studied the decrease in rate constant over the pressure range 100 to 0.057 mm. at temperatures between 448.2° and 448.6°C. They obtained a lower value for the limiting high pressure rate constant, k_{∞} , than Genaux, Kern and Walters; $3.9 \times 10^{-4} \text{ sec.}^{-1}$ compared to $4.86 \times 10^{-4} \text{ sec.}^{-1}$, at 449°C. They also measured the efficiency of various gases in maintaining the high pressure decomposition rate.

There is considerable disagreement in the values of n , the effective number of normal vibration modes that contribute to extension of the reaction coordinate in Slater's theory, and s , the effective number of oscillators contributing to dissociation in Kassel's theory, that have been reported for cyclobutane. Rabinovitch and Michel⁵ give a value of $n_{\text{expt.}} = 20$, (which is equivalent to $s = 20$); whereas Powell⁶ gives a value of $s_{\text{expt.}} = 5$, (which is equivalent to $n = 8$). Both values are based on the

experimental data of Walters and his coworkers, and of Pritchard, Sowden and Trotman-Dickenson.

2. This work.

The main purpose of this work was to obtain a more accurate estimate of the values of n and s for cyclobutane. By observing the rate constants down to lower pressures than had been previously reported, it was hoped to obtain a more accurate idea of the shape of the fall off curve and hence to reduce the uncertainty in the comparison of the experimental curves with the theoretical curves for n and s .

No unambiguous evidence for the occurrence of any side reactions in the decomposition of cyclobutane has been reported. But completely clean unimolecular reactions are rare and it is possible that a second unimolecular reaction is taking place concurrently to form traces of C_3 , C_4 and C_5 compounds. This reaction may occur to a very small extent at high pressures but it might become more important as the pressure is lowered.

In this experiment the reaction products were analysed on a Golay column using a flame ionization detector. This system is theoretically capable of detecting 10^{-13} g./cc. of sample in the carrier gas. Therefore it was hoped to find evidence for or against the occurrence of any side reactions.

Genaux, Kern and Walters³ measured the rate by following the pressure change during the reaction, which is a more accurate

method than gas chromatographic analysis, but gives no indication of minor side reactions. They analysed the products from a few runs at about 120 mm. pressure, on a mass spectrometer and found traces of propane, C_4 compounds and C_5H_8 .

Pritchard, Sowden and Trotman-Dickenson⁴ assumed that there were no minor side reactions and measured the rate by absorption of the ethylene on a mercuric acetate bead.

Genaux and Walters¹ have shown that there is no significant surface effect on the reaction at high pressures. This may not be true at low pressures, however. Therefore in this experiment the reaction was carried out in several reactors with different surface-to-volume ratios, to see if there was any surface effect on the rate of the reaction or on the products formed.

EXPERIMENTAL

1. Materials.

Cyclobutane was prepared by the photolysis of cyclopentanone using a 450 watt, medium pressure, mercury arc lamp. The cyclopentanone was supplied by Eastman Organic Chemicals. The main products of the photolysis are carbon monoxide, ethylene and cyclobutane. Blacet and Miller⁷ have suggested the mechanism:-

The cyclobutane used in the high pressure experiments was the by-product of an experiment on the photolysis of cyclopentanone by Dr. Butler and Mr. Drake.* It was purified on

* Unpublished work.

a Beckmann Megachrom Preparative Gas Chromatograph. The purity of the sample was 98.6%. It contained 0.7% ethylene and 0.7% of a C_5 compound, probably 2-pentene, together with traces of C_3 , C_4 and C_5 compounds.

This sample was repurified for use in the low pressure experiments, using a Perkin Elmer model 154-C Vapor Fractometer, with a four-metre polyethylene glycol column, (column R), at room temperature. The purity of the sample obtained was 99.1%, the ethylene impurity being reduced to 0.01%. This sample was used for the first thirteen runs in the one-litre reactor. It was then repurified again, by the same method, and a 99.7% pure sample obtained. This sample was used for the remainder of the runs in the one-litre reactor and for the runs in the 100 ml. reactor.

A second sample of cyclobutane was prepared for the low pressure experiments in the five-litre reactor. Cyclopentanone vapour was photolysed for about half an hour and all the products, except for carbon monoxide, were condensed in a trap cooled with liquid nitrogen. The products collected from about forty photolyses were purified on the Perkin Elmer Vapor Fractometer under the same conditions as described above. The sample obtained was 99.9% pure.

Research grade ethylene was kindly donated by Dr. Halpern, who obtained it from the Matheson Company of Canada Ltd. The ethylene used in the low pressure pyrolyses was purified on

the Perkin Elmer Vapor Fractometer, under the same conditions as above. A 97% pure sample was obtained, the main impurity being about 3% of benzene. There were no C_3 , C_4 or C_5 compounds present.

The gases were stored in two-litre Pyrex vessels, with cold fingers, attached to the vacuum line. (See Figure I on page 8.) Care was taken to exclude any non-condensable impurities when the gases were placed in the storage vessels.

2. Furnace, and temperature measurement.

Three different reaction vessels were used. They were made from spherical Pyrex flasks and were approximately 100 ml., one-litre and five-litres in volume. The reaction vessel was heated in a furnace consisting of three concentric copper drums of diameters 24, 28 and 40 cm., and heights 24, 28 and 45 cm., respectively. The wall of the second drum was covered with asbestos paper and wound with nichrome heating wire. The space between the second and the outer drum was packed with vermiculite. The outer drum was wound with copper piping through which cold tap-water circulated. The temperature of the furnace was regulated by means of a variac and voltage regulating transformer. Usually it did not change by more than 0.6°C . in a two hour run.

When the first reaction vessel was changed it was found that the two inner drums were badly corroded. They were then replaced by steel ones.

FIG. I THE APPARATUS

Chromel-alumel thermocouples were used to measure the temperature. They were placed in wells, made of 8 mm. glass tubing, which projected about 3 cm. into the reactor. Only one thermocouple was used for the 100-ml. reactor. This thermocouple and three others were used for the one- and five-litre reactors. The four thermocouples were arranged tetrahedrally around the reactor. The reference junction was placed in melting ice, and the e.m.f. was measured using a Leeds and Northrup student-type potentiometer, which gave readings to within 0.2 of a millivolt ($0.5^{\circ}\text{C}.$). The corresponding temperature was found from Leeds and Northrup conversion tables. The four thermocouples were tested originally by placing them in the furnace (without a reactor) and measuring the e.m.f. at different temperatures. All four consistently gave the same readings. When the reference junction was interchanged with one of them, it too gave identical readings.

In the case of the one-litre reactor; the two uppermost thermocouples usually read $1^{\circ}\text{C}.$, (or less), higher, and the next-to-bottom one read $2^{\circ}\text{C}.$, (or less), higher than the bottom one. For the five-litre reactor; the uppermost thermocouple consistently read $1^{\circ}\text{C}.$ higher, and the two middle ones read $3^{\circ}\text{C}.$ higher than the bottom one. The temperature of the gas in the vessel was taken to be the average of the four. When the temperature changed during a run the average temperature was taken.

The low pressure runs were carried out at about $449^{\circ}\text{C}.$, as this was the temperature used by previous workers. At this

temperature a suitable decomposition of about 30% could be obtained in thirty minutes to two hours.

The reactors were seasoned before use by leaving a few cm. pressure of ethylene in them for several days at 449°C., or higher temperatures.

The order in which the experiments were performed was as follows : decompositions at pressures between about 40 and 10 mm. were carried out first in the 100 ml. reactor at various temperatures between 398°C. and 450°C., so that the energy of activation and the pre-exponential factor could be calculated. Then the one-litre reactor was installed and decompositions at about 449°C. and initial pressures from 1 mm. down to 10^{-3} mm. were studied. A few runs were done using ethylene at low pressures to see if any decomposition occurred. When the one-litre reactor cracked it was replaced by a 100 ml. one and a second series of low pressure cyclobutane pyrolyses were carried out. A third series was carried out in the five-litre reactor, to see if a decrease in the surface-to-volume ratio made any difference to the shape of the fall off curve.

3. Pressure measurement.

Pressure measurements down to 0.6 mm. were made using a wide-bore, mercury manometer. The two arms of the manometer were made of 18 mm. glass tubing and were joined at the base by capillary tubing, to regulate the flow of mercury. Measurements

of lower pressures were made on a McLeod gauge. The level of the mercury meniscus in both cases was measured using a cathetometer. The total volume of the bulbs of the McLeod gauge was measured by filling them with water from a burette. The volumes of the smaller bulbs were calibrated by comparison with the manometer, in the pressure region where the two overlapped. The diameters of the two capillary tubes used in the McLeod gauge were measured with the cathetometer.

4. Sampling

The glass tubing connecting the reactor to the vacuum line was out of the furnace and therefore the gas in it was not at the reaction temperature. This was corrected for at the end of a run by expanding the gas in the reactor into a dead space of about 30 ml. The reactor tap was then shut and the dead space evacuated. A sample was taken by expanding the gas in the reactor into a 250 ml. glass sample bulb. The sample was analysed by gas chromatography.

The reactor tap was usually held open for about 15 to 20 seconds while sampling the gas at low pressures. At pressures of about a micron, diffusion effects become important. As the molecular weight of ethylene is half that of cyclobutane it will diffuse $\sqrt{2}$ times faster than cyclobutane. Therefore unless equilibrium is established in the time taken to sample the gas, the gas sampled will not be representative of the gas in the

reactor. To check this, several runs were sampled using sampling times of up to ten minutes and larger sampling bulbs of one and two litres. Several samples were also taken by diluting the gas in the reactor with up to 10 mm. of prepurified nitrogen, just prior to sampling. The rate constant was found to be the same for all the sampling methods tried.

5. Analysis.

Analyses were made on a Perkin Elmer model 154-0410 Flame Ionization Accessory Kit to the model 154-C Vapor Fractometer. The Golay U column, which is a 150 foot, squalane coated, stainless steel, capillary column of internal diameter 0.010 inches, was used. The column temperature was maintained at 0°C. by using an ice-bath.

The carrier gas was prepurified nitrogen and was supplied by the Matheson Company of Canada Ltd.

The rate of gas flow through a long capillary column is very low and very small samples must be used to avoid capacitance effects and a large vapour spread at the head of the column. This was effected by splitting the stream of carrier gas and sample upstream of the column. The gas flowed past a #0 restriction at a carrier gas pressure of 12 p.s.i., and only one five-hundredth of the sample passed into the column for analysis.

A flame ionization detector was used. Hydrogen at 10 p.s.i. and air at 30 p.s.i. were diluted with the carrier gas from the

column and ignited to give a flame about 2 mm. high. The flame jet served as the positive electrode and a platinum wire, set 1 mm. away, as the negative electrode. A potential of two hundred volts was applied between the electrodes. The sample molecules in the flame underwent thermally induced ionization and produced a current, proportional to the concentration of sample in the carrier gas stream. This current was amplified electronically and the signal from the amplifier was recorded on a Leeds and Northrup model G Speedomax recorder, adapted for use on a one or a five millivolt range. The detector was found to be sensitive to atmospheric conditions; if placed in a draught it produced a lot of background noise, but if the lab. windows were shut a steady baseline was usually obtained.

The usual procedure followed for an analysis was to expand the gas in the sample bulb into a Toepler pump and then compress it into a capillary loop. The stream splitting tap was opened and a few seconds later the carrier gas was diverted through the loop. After about forty seconds the carrier gas was rediverted to its original path and after a minute the stream splitting tap was shut, to conserve gas.

The low pressure samples were diluted with nitrogen before analysis.

Preliminary calibrations were performed with mixtures of cyclobutane and ethylene in known ratios, and at various pressures. The peak heights recorded were found to be in direct ratio to the

partial pressures, within experimental error. Calibrations could be reproduced to within $\pm 4\%$ at higher pressures, but at lower pressures of the order of a micron, the error was about 15%.

About six analyses were made on the higher pressure runs, but only two or three were possible for the lower pressure runs. The analyses of the higher pressure samples differed by about 4% and the analyses of the lower pressure samples by about 6%. Few analyses differed by more than 10%. The average value was used in the calculation of the rate constant. The differences in the analyses were probably due to difficulties in mixing the sample.

The system was flushed with nitrogen before each analysis, and a blank analysis was carried out to see if there were any residual products from a previous analysis remaining in the system.

RESULTS

1. Calculation of the results.

The principal reaction taking place in the decomposition of cyclobutane is :-

Since this is first order, the rate of decomposition is :-

$$-\frac{d[\text{C}_4\text{H}_8]}{dt} = k [\text{C}_4\text{H}_8] \quad (2)$$

On integrating :-

$$\ln [\text{C}_4\text{H}_8] = -k t + C \quad (3)$$

If $[\text{C}_4\text{H}_8]_0$ is the concentration of cyclobutane when $t = 0$, then :-

$$\ln \frac{[\text{C}_4\text{H}_8]}{[\text{C}_4\text{H}_8]_0} = -k t \quad (4)$$

The material balance :-

$$[\text{C}_4\text{H}_8]_0 = [\text{C}_4\text{H}_8] + \frac{1}{2} [\text{C}_2\text{H}_4] \quad (5)$$

will hold at any time.

Combining (4) and (5) gives :-

$$k = \frac{1}{t} \ln \left(1 + \frac{[C_2H_4]}{2[C_4H_8]} \right) \quad (6)$$

The rate constant for reaction (1) was calculated by finding the $[C_2H_4]$ to $[C_4H_8]$ ratio from the recorded peak heights of the analysis, and substituting this and the duration of the run, in seconds, into equation (6).

2. High pressure results.

The high pressure data is given in Table I on page 18, and is plotted in Figure II on page 19.

The decomposition of cyclobutane in the pressure range 10 to 40 mm. and temperature range 398° to 450°C., was found to obey the rate law :-

$$k = 10^{15.3 \pm 0.8} e^{- (61,700 \pm 2,300)/RT} \text{ sec.}^{-1}$$

This was calculated from the data in Table I using a least squares method. The limits of error are given at the 95% confidence level.

The value is lower than that reported by Genaux, Kern and Walters³, of :-

$$k = 10^{15.60} e^{- 62,500/RT} \text{ sec.}^{-1}$$

This is probably due to the fact that in the pressure range 10 to 40 mm., the rate is beginning to fall below the high pressure limiting rate,

The concentrations of the impurities in the starting material did not alter appreciably during a run, and no new compounds were observed in the products. The 0.7% ethylene present in the starting material was corrected for in the calculation of the rate constant.

The rate constant was measured over a range of conversions from 3% to 81% and was found to be independent of conversion, thus establishing that the reaction was truly first order, (see Table I).

TABLE I. HIGH PRESSURE DATA OBTAINED IN THE 100ml. REACTOR

TEMPERATURE in °C.	TIME in minutes.	% conversion	$k \times 10^5$ in sec. ⁻¹
450.2	41.5	66	43.0
449.2	33.9	60	45.5
449.0	10.0	22	40.7
448.9	56.2	81	48.5
448.8	29.8	47	35.9
448.8	8.5	24	53.9
438.5	33.6	34	20.6
425.8	190.0	33	9.58
425.2	67.0	33	9.94
422.5	18.0	11	10.1
419.8	30.0	13	7.52
418.8	114.8	33	5.94
416.7	54.4	15	5.00
411.2	60.1	13	3.76
404.0	17.0	3	2.50
401.2	35.0	4	1.87
398.6	758.0	54	1.69
398.6	336.0	27	1.58
398.6	70.0	8	1.96
398.6	52.0	6	1.99

FIG. II TEMPERATURE DEPENDENCE OF THE HIGH PRESSURE RATE CONSTANT

3. Lower pressure results.

The runs at lower pressures were carried out at temperatures within 10° of 449°C . The rate constants were corrected to 449°C using the temperature dependence of the high pressure rate constant.

In many of the low pressure pyrolyses in all three reactors a C_3 and a C_4 compound were detected in the products. Their retention times were compared with the retention times of known C_3 and C_4 compounds on the same column, and it was concluded that they were probably propylene and 1-butene. Down to about 10^{-2} mm. pressure the amount of these compounds formed was small and the correction to the rate constant on the assumption that they were formed from cyclobutane or from ethylene was negligible. At pressures below this, however, their concentration increased and in some cases the concentration of propylene exceeded that of ethylene.

The cyclobutane samples of purity 99.1% and 99.7%, contained a C_5 compound, probably 2-pentene, as the main impurity. The 99.9% pure sample contained a C_4 compound, probably cis- or trans-2-butene (It was a different compound from that formed in the pyrolyses.) The concentration of these impurities decreased during a run, but there was no correlation between their decrease and the amount of propylene or 1-butene that was formed.

Several ethylene pyrolyses were carried out under the

same conditions as a cyclobutane pyrolysis. The ethylene sample was 97% pure. The main impurity was about 3% of benzene, and this did not decompose during a run. It contained no C_3 , C_4 or C_5 compounds. The results are shown in Table V on page 29. The C_3 and C_4 compounds formed had identical retention times with those formed in the cyclobutane pyrolyses, but their concentration was less than that obtained from cyclobutane under the same conditions. In the first two pyrolyses several other C_3 , C_4 and C_5 compounds were observed. These were not detected in cyclobutane pyrolyses.

The rate constants for the runs at pressures above about 10^{-2} mm. were uncorrected for the formation of propylene and 1-butene. Those at lower pressures were corrected on the assumption that these compounds were formed by a wall reaction of cyclobutane only. (The formation of propylene and 1-butene is discussed in section 3 of the Discussion.) It was assumed that the stoichiometry of these reactions was :-

When the rate constants for these runs were calculated, the final concentration of cyclobutane was corrected to the value it would have had if there had been no wall reaction,

i.e. ($[\text{cyclo-C}_4\text{H}_8] + \frac{3}{4} [\text{C}_3\text{H}_6] + [\text{1-C}_4\text{H}_8]$).

This lead to the following expression for the rate constant :-

$$k = \frac{1}{t} \ln \left(1 + \frac{[\text{C}_2\text{H}_4]}{2 \left([\text{cyclo-C}_4\text{H}_8] + \frac{3}{4} [\text{C}_3\text{H}_6] + [\text{1-C}_4\text{H}_8] \right)} \right)$$

The low pressure data is given in Tables II to V on pages 23 to 29. It is plotted in Figures IV, V and VI,

TABLE II. LOW PRESSURE DATA OBTAINED IN THE ONE-LITRE REACTOR

PRESSURE	TIME	TEMPERATURE	%	C_2H_4	C_3H_6	C_4H_8	$k \times 10^5$	$k \times 10^5$
in cm.	in sec.	in °C.	conversion	$(\frac{1}{1+3/4 C_3H_6+C_4H_8})$	$(\frac{1}{1+3/4 C_3H_6+C_4H_8})$	$(\frac{1}{1+3/4 C_3H_6+C_4H_8})$	in sec. ⁻¹	in sec. ⁻¹
1.26x10 ⁻¹	777	462.2	45	1.65			77.6	35.2
1.26x10 ⁻¹	1996	446.4	40	1.31			25.2	29.5
0.79x10 ⁻¹	1060	444.4	24	0.639			26.2	34.5
2.79x10 ⁻²	1430	446.0	23	0.609			18.6	22.3
2.70x10 ⁻²	1414	446.2	22	0.576			17.9	21.2
2.35x10 ⁻²	1467	446.2	23	0.606	0.002		18.0	21.4
1.48x10 ⁻²	1092	447.5	13	0.306			12.9	14.1
1.37x10 ⁻²	2187	442.7	34	1.04			19.5	28.1
1.17x10 ⁻²	2461	444.2	31	0.905			15.2	20.4
1.00x10 ⁻²	787	447.5	13	0.300			17.8	19.5
9.66x10 ⁻³	964	447.2	11	0.257			12.6	14.1
6.67x10 ⁻³	1023	446.4	11	0.236			10.9	12.8
5.19x10 ⁻³	2028	448.8	19	0.482	0.019	0.013	10.6	10.7
4.01x10 ⁻³	2806	445.3	20	0.515	0.009	0.007	8.18	10.3
3.11x10 ⁻³	2305	442.4	18	0.440	0.025	0.014	8.64	12.9

TABLE II. (continued)

PRESSURE in cm.	TIME in sec.	TEMPERATURE in °C.	% conversion	C_2H_4	C_3H_6	C_4H_8	$k \times 10^5$	$k \times 10^5$
				$(\text{C}_2\text{H}_4 + \frac{3}{4}\text{C}_3\text{H}_6 + \text{C}_4\text{H}_8)$	$(\text{C}_3\text{H}_6 + \frac{3}{4}\text{C}_4\text{H}_8)$	(C_4H_8)	in sec. ⁻¹	in sec. ⁻¹
⁻³ 1.74x10	1000	448.0	7	0.139	0.045	0.016	6.76	7.26
⁻⁴ 9.63x10	1052	446.8	6	0.122			5.63	6.45
⁻⁴ 5.34x10	1041	444.0	6	0.123	0.114		5.69	7.73
⁻⁴ 1.22x10	3607	445.5	8	0.169	0.105	0.037	2.25	2.78
⁻⁴ 1.02x10	1894	444.2	4	0.085	0.265	0.066	2.19	2.94

TABLE III. LOW PRESSURE DATA OBTAINED IN THE 100 ml. REACTOR

PRESSURE	TIME	TEMPERATURE	%	C_2H_4	C_3H_6	C_4H_8	$k \times 10^5$	$k \times 10^5$
in cm.	in sec.	in °C.	conversion	$(\frac{1}{2}C_3H_6 + C_4H_8)$ $(\frac{1}{4}C_3H_6 + C_4H_8)$ $(\frac{3}{4}C_3H_6 + C_4H_8)$			in sec. ⁻¹	in sec. ⁻¹
4.314	510	448.8	24	0.642			53.9	54.6
3.115	600	449.0	22	0.552			40.7	40.7
⁻¹ 9.64x10	2490	450.2	66	3.83			43.0	40.0
⁻¹ 0.75x10	4400	447.3	67	4.07			25.0	27.7
⁻² 4.12x10	3540	448.5	54	2.38			22.1	22.8
⁻² 3.06x10	2316	447.2	31	0.910			16.2	18.1
⁻² 2.30x10	3062	447.7	35	1.09			14.2	15.4
⁻³ 4.71x10	3923	449.2	33	0.983	0.011	0.006	10.2	10.3
⁻³ 2.10x10	2257	447.8	17	0.418	0.054	0.031	8.40	9.04
⁻³ 1.89x10	4102	441.4	18	0.428	0.035		4.73	7.55
⁻³ 1.64x10	5540	446.8	35	1.09			7.85	8.98
⁻³ 1.40x10	3520	448.7	21	0.540	0.012		6.79	6.92
⁻³ 1.2x10	2522	447.0	14	0.319	0.027	0.015	5.87	6.63
⁻³ 1.10x10	5000	448.5	28	0.789	0.016	0.006	6.64	6.89
⁻⁴ 5.00x10	7217	441.0	23	0.591	0.071	0.030	3.59	5.81

TABLE III. (continued)

PRESSURE in cm.	TIME in sec.	TEMPERATURE in °C.	% conversion	C_2H_4	C_3H_6	C_4H_8	$k \times 10^5$	$k_{449^\circ} \times 10^5$
				$(n + \frac{3}{4}C_3H_6 + C_4H_8)$	$(n + \frac{3}{4}C_3H_6 + C_4H_8)$	$(n + \frac{3}{4}C_3H_6 + C_4H_8)$	in sec. ⁻¹	in sec. ⁻¹
3.08×10^{-4}	7244	446.7	30	0.874	0.320		5.00	5.76
3.03×10^{-4}	6000	447.0	23	0.591	0.199		4.32	4.88
2.2×10^{-4}	6678	447.0	25	0.664	0.235		4.29	4.85
1.2×10^{-4}	7402	447.1	21	0.574	0.416		3.20	3.59
1.0×10^{-4}	4945	440.5	12	0.278	0.278		2.63	4.44
6.5×10^{-5}	6306	446.8	22	0.553	0.428		3.87	4.43
5.4×10^{-5}	4456	447.2	17	0.402	0.348		4.11	4.59

TABLE IV. LOW PRESSURE DATA OBTAINED IN THE FIVE-LITRE REACTOR

PRESSURE in cm.	TIME in sec.	TEMPERATURE in °C.	%	conversion	C_2H_4	C_3H_6	C_4H_8	$k \times 10^5$	$k \times 10^5$
					$(\square + \frac{3}{4}C_3H_6 + C_4H_8)$	$(\square + \frac{3}{4}C_3H_6 + C_4H_8)$	$(\square + \frac{3}{4}C_3H_6 + C_4H_8)$	in sec. ⁻¹	in sec. ⁻¹
1.05x10 ⁻¹	2434	448.1	51		2.08			29.3	30.9
4.30x10 ⁻²	3600	450.1	62		3.00			25.5	23.9
1.06x10 ⁻²	4200	449.5	41		1.40			12.6	12.2
7.24x10 ⁻³	4000	449.9	34		1.01			10.2	9.71
2.89x10 ⁻³	4626	448.7	23		0.588			5.57,	5.68
2.22x10 ⁻³	8455	447.1	38		1.22	0.011	0.003	5.63	6.32
1.43x10 ⁻³	4600	450.2	20		0.491			4.85	4.51
1.41x10 ⁻³	3758	448.4	16		0.391	0.087	0.096	4.76	4.97
6.12x10 ⁻⁴	4370	442.1	11		0.347	0.010	0.003	2.65	4.03
3.93x10 ⁻⁴	5053	449.0	18		0.435	0.080	0.018	3.89	3.89
3.87x10 ⁻⁴	8850	449.2	30		0.836	0.024	0.012	3.95	3.89
2.05x10 ⁻⁴	4974	449.3	14		0.304			2.84	2.79
1.90x10 ⁻⁴	6200	448.2	15		0.344	0.118		2.56	2.69

TABLE IV. (continued)

PRESSURE in cm.	TIME in sec.	TEMPERATURE in °C.	% conversion	C_2H_4	C_3H_6	C_4H_8	$k \times 10^5$	$k \times 10^5$
				$(\square + \frac{3}{4}C_3H_6 + C_4H_8)$	$(\square + \frac{3}{4}C_3H_6 + C_4H_8)$	$(\square + \frac{3}{4}C_3H_6 + C_4H_8)$	in sec. ⁻¹	in sec. ⁻¹
1.75x10 ⁻⁴	4973	448.5	14	0.334	0.015	0.007	3.11	3.22
1.63x10 ⁻⁴	8692	449.4	26	0.698	0.153	0	3.45	3.36
8.99x10 ⁻⁵	6914	448.2	6	0.122	0.976	0.073	0.858	0.901
8.78x10 ⁻⁵	4157	449.0	10	0.222	0.048		2.53	2.53
8.38x10 ⁻⁵	6660	448.2	19	0.478	0.133	0.008	3.22	3.38
8.14x10 ⁻⁵	9880	446.0	21	0.519	0.199	0.046	2.34	2.81
6.5 x10 ⁻⁵	4400	449.0	12	0.266	0.266	0.029	2.83	2.83
5.42x10 ⁻⁵	3664	450.7	19	0.458	0.167		5.62	5.07
5.07x10 ⁻⁵	5918	448.2	14	0.322	0.031		2.52	2.65
4.57x10 ⁻⁵	5650	448.8	22	0.558	0.279		4.36	4.41
2.46x10 ⁻⁵	9650	450.3	27	0.724	0.284		3.20	2.96
1.68x10 ⁻⁵	5540	449.4	12	0.267	0.978		2.89	2.92

TABLE V. DATA FROM ETHYLENE PYROLYSES IN THE ONE-LITRE REACTOR

PRESSURE	TIME	TEMPERATURE	% C ₃ H ₆	% C ₄ H ₈
in cm.	in sec.	in °C.	relative to the initial concentration of ethylene	
4.7×10^{-2}	13,570	449.2	0.059	0.354
4.2×10^{-2}	9,639	444.7	0.048	0.054
1.2×10^{-2}	1,707	446.6	0.095	0.260
1.8×10^{-3}	102,419	449.3	2.54	
1.5×10^{-3}	2,831	450.1	0.92	0.44
3.7×10^{-4}	2,403	446.6	1.50	0.81
5.4×10^{-5}	58,810	447.2	0.51	

In the 2nd run, in the above table, 0.019 % trans-2-butene, 0.016% cis-2-butene and 0.14% of a C₅ compound were also observed. In the 3rd run, 0.20% trans-2-butene and 0.21% cis-2-butene were observed. The first 3 runs may be compared to a) the 6th run in Table II. The 4th and 5th runs may be compared to b) the 16th run in Table II. The 6th run may be compared to c) the 18th run in Table II. The 7th run may be compared to d) the 21st run in Table IV.

PRESSURE	TIME	TEMPERATURE	% C ₃ H ₆	% C ₄ H ₈
in cm.	in sec.	in °C.	relative to the initial concentration of cyclo-C ₄ H ₈	
a) 2.4×10^{-2}	1467	446.2	0.20	
b) 1.7×10^{-3}	1000	448.0	4.2	1.5
c) 5.3×10^{-4}	1041	444.0	11.4	
d) 5.4×10^{-5}	3664	450.7	16.7	

DISCUSSION

1. Unimolecular reaction theories.

a. The Lindemann-Hinshelwood Mechanism.

The Lindemann-Hinshelwood mechanism is the basis of all the successful theories of unimolecular reactions.

The molecules are assumed to be activated by collision. If a molecule were to dissociate the moment it became activated the rate of the reaction would depend on the collision rate and hence on the concentration. No first order kinetics would be observed.

Lindemann postulated a time-lag between the activation of a molecule and its decomposition. It is not assumed that the time-lag will be the same for all molecules of the same species under the same conditions. The extent of the time-lag will depend on the vibrations of the molecule. A simple molecule with few vibrations will have a time-lag less than its collision frequency, at normal pressures, and therefore will undergo second order reactions.

If an activated molecule is polyatomic it may either be deactivated by a second collision or it may dissociate. Both courses are independent and occur at random. If the rate of reaction is k_1 , then the probability of an activated molecule dissociating in a short time Δt , is $k_1 \Delta t$. The probability that it

will suffer a second collision is ωt , where ω is the collision frequency. Slater^{8a} has shown that the absolute probability that an activated molecule will dissociate rather than be deactivated, is given by :-

$$\frac{k_1}{\omega + k_1} \quad (1)$$

The rate of deactivation at high pressures where an equilibrium exists between the activated molecules and the rest of the molecules, is $c f$, where c is the concentration and f is the statistical equilibrium probability of the activated state. At high pressures the rate of deactivation is very much greater than the rate of reaction and hence it can be equated with the rate of activation. Therefore the number of molecules dissociating in unit time is

$$\frac{c f \omega k_1}{\omega + k_1} \quad (2)$$

Therefore the rate constant

$$k = \frac{-1}{C} \frac{dC}{dt} \quad (3)$$

is given by :-

$$k = \frac{f \omega k_1}{\omega + k_1} \quad (4)$$

At high concentrations, $\omega \rightarrow \infty$, and k approaches the value k_1 . Therefore the high pressure rate will be first order.

At low concentrations, $\omega \rightarrow 0$, and k tends to the form

$$k \approx f \omega$$

Therefore the reaction will become second order as the pressure decreases.

The assumption that all activated molecules react at the same rate k_1 leads to a simpler pressure dependence of the rate constant than is observed experimentally. If it is assumed that the higher the energy an activated molecule possesses above the critical value necessary for dissociation, the faster it will react, then better agreement is observed with experiment.

The general formula (4), can be extended. If $k_E \Delta t$ is the probability of dissociation of a molecule with energy E in the short time Δt , and f_E is the statistical equilibrium probability of the molecules with energy E , then the expression becomes :-

$$k = \sum \frac{\omega f_E k_E}{\omega + k_E} \quad (5).$$

b. The Kassel Theory.⁹

The molecule, in the classical Kassel theory, is thought of as a set of oscillators which are coupled by small forces, such that energy can flow between them. The activated molecule will dissociate when sufficient energy flows into the critical oscillator affecting the bond which is to break. The Lindemann time-lag is interpreted as the time taken for sufficient energy to flow into the critical oscillator.

The chance that an activated molecule has an energy E , which is greater than or equal to the critical energy E_0 , in a particular oscillator, is the chance that it will have less than $E - E_0$ in the other oscillators. This is given by :-

$$[(E - E_0)/E]^{s-1} \quad (6)$$

where s is the number of oscillators affecting the dissociation, i.e. $(s-1)$ is the number of oscillators from which energy flows to the critical oscillator. The specific rate, the proportion of molecules with energy E (greater than E_0) that dissociate per second, is

$$k_E = A ([E - E_0]/E)^{s-1} \quad (7)$$

where A is a proportionality constant which can be thought of as the rate of energy flow into the critical oscillator. In practice the experimental pre-exponential factor is substituted.

The proportion of molecules with energy in the range E to

$E + dE$, is given by :-

$$f(E) dE = \frac{1}{(s-1)!} \left(\frac{E}{kT} \right)^{s-1} e^{-E/kT} \frac{dE}{kT} \quad (8)$$

Substitution of (7) and (8) in the general formula (5), and letting $\omega \rightarrow \infty$, leads to the high pressure rate constant :-

$$\begin{aligned} k_{\infty} &= \frac{A}{(s-1)! (kT)^s} \int_{E_0}^{\infty} (E-E_0)^{s-1} e^{-E/kT} dE \\ &= A e^{-E_0/kT} \end{aligned} \quad (9)$$

which is of the Arrhenius form.

The rate at any pressure is given by :-

$$k = \frac{A e^{-E_0/kT}}{(s-1)!} \int_0^{\infty} \frac{e^{-x} x^{s-1} dx}{1 + [x/(b+x)]^{s-1} A/\omega} \quad (10)$$

where $b = E_0/kT$.

The fall off of the rate constant with decreasing pressure can be found from (9) and (10) :-

$$\frac{k}{k_{\infty}} = \frac{1}{(s-1)!} \int_0^{\infty} \frac{x^{s-1} e^{-x} dx}{1 + [x/(b+x)]^{s-1} A/\omega} \quad (11)$$

Although the rate constant cannot be calculated a priori from Kassel's theory, the theory is valuable in that it enables the parameter s , to be found from a comparison of the theoretical and experimental fall off curves. If the number of oscillators, s ,

that contribute to dissociation is known, a reasonable dissociation mechanism, compatible with the structure of the molecule, can generally be found. If there are several possible mechanisms for a reaction, it may help to decide between them.

c. The Slater Theory.⁸

The molecule, in Slater's theory, is thought of as a set of harmonic oscillators which are uncoupled so that there can be no transfer of energy between them. This is the antithesis of Kassel's postulate.

The molecular vibrations are described by a suitable series of internal coordinates, q_r , which may be distances or angles in the molecule, or a combination of the two. The vibrations of the molecule are analysed into normal coordinates Q_i , which are related to the internal coordinates by the linear transformation:-

$$q_r = \sum_{i=1}^n \alpha_{ri} Q_i \quad (12)$$

$$= \sum_{i=1}^n \alpha_{ri} \sqrt{\mathcal{E}_i} \cos. 2\pi(\nu_i t + \psi_i) \quad (13)$$

where $\mathcal{E}_i$ is the energy, ν_i the frequency of vibration and ψ_i the phase of the i th. normal mode. The α_{ri} are termed amplitude

factors. Each internal coordinate can therefore be regarded as a superposition of n normal modes. The amplitude factors determine the contribution of each normal mode to a particular internal coordinate.

Reaction occurs when the reaction coordinate, which may be one of the internal coordinates or a combination of several of them, is extended beyond a critical value, q_0 . The reaction coordinate will be affected by all the normal modes of vibration of the molecule, but some may make a negligible contribution as the corresponding amplitude factors may be very small. The Slater parameter, n , is the effective number of normal modes that contribute to extension of the reaction coordinate.

The energies of the normal modes are constant between collisions. Reaction occurs when the n normal modes come sufficiently into phase to cause extension of the reaction coordinate to the critical value q_0 . The Lindemann time-lag is the time taken for this to come about.

The high pressure rate constant derived from the general formula (5), is

$$k_{\infty} = \sum f_E k_E \quad (14)$$

The proportion of molecules with energy in the range E_i to $E_i + dE_i$ in the i th. mode of vibration is given by :-

$$e^{-E/kT} dE_1 \dots \dots \dots dE_n / (kT)^n \quad (15)$$

where $E = \sum_1^n \epsilon_i$

The specific dissociation rate $k(\epsilon_1, \dots, \epsilon_n)$ of a molecule with these internal energies, is the chance per second that the reaction coordinate reaches the critical value, q_0 . It is given by:

$$k(\epsilon_1, \dots, \epsilon_n) = 1/2 \lim_{\tau \rightarrow \infty} [G_q(\tau)/\tau] \quad (16)$$

where G_q is the number of zeros of $q - q_0$ in the time $(0, \tau)$, q being the reaction coordinate. The factor of $1/2$ is necessary as q can only approach q_0 from a value less than q_0 .

Substituting (15) and (16) in the general formula (15) gives :-

$$k_\infty = \int \dots \int_0^\infty (1/2 \lim_{\tau \rightarrow \infty} [G_q(\tau)/\tau]) e^{-E/kT} \frac{d\epsilon_1 \dots d\epsilon_n}{(kT)^n} \quad (17)$$

This can be integrated to give a high pressure rate constant of the form:-

$$k_\infty = \nu e^{-E_0/kT} \quad (18)$$

where the pre-exponential factor, ν , is a weighted mean value of the vibrational frequencies of the molecule. It can be expressed:

$$\nu^2 = \frac{\sum_{oi} \alpha_{oi}^2 \nu_i^2}{\sum_{oi} \alpha_{oi}^2} \quad (19)$$

where the subscript $_o$ denotes the reaction coordinate.

Substitution of (15) and (16) in the formula for the general rate constant (5), leads to the expression for the rate constant at any pressure :-

$$k = \frac{\nu e^{-E_0/kT}}{[(n-1)/2]!} \int_0^{\infty} \frac{x^{(n-1)/2} e^{-x} dx}{1 + x^{(n-1)/2} \theta^{-1}} \quad (20)$$

where θ is a function of the concentration.

The pressure dependence of the rate constant can be expressed :-

$$\frac{k}{k_{\infty}} = \frac{1}{[(n-1)/2]!} \int_0^{\infty} \frac{x^{(n-1)/2} e^{-x} dx}{1 + x^{(n-1)/2} \theta^{-1}} \quad (21)$$

If the experimental activation energy is known, and if a detailed spectroscopic study of the molecule has been carried out to enable a vibrational analysis to be made, then in Slater's theory it is possible to calculate the rate of reaction at any pressure and the number of normal modes of vibration that contribute to extension of the reaction coordinate.

d. Comparison of the Kassel and Slater fall off parameters.

Schlag, Rabinovitch and Schneider¹⁰ have compared the Kassel and Slater fall off parameters, s and n .

The two equations describing the fall off behaviour

can be written :-

$$\text{Kassel : } I_s(\theta') = \frac{k}{k_\infty} = [\Gamma(s)]^{-1} \int_0^\infty \frac{x^{s-1} e^{-x} dx}{1+[x/(b+x)]^{s-1} \theta'^{-1}}$$

$$\text{Slater : } I_n(\theta) = \frac{k}{k_\infty} = [\Gamma((n+1)/2)]^{-1} \int_0^\infty \frac{x^{(n-1)/2} e^{-x} dx}{1+x^{(n-1)/2} \theta^{-1}}$$

These are of the same form if $(b+x)$ in the Kassel equation is replaced by the approximation b , and if b^{s-1} is then formally incorporated in θ .

From calculations in the upper region $k/k_\infty > 0.08$, taking b to be 40, Schlag, Rabinovitch and Schneider found that up to about $s = 4$, the relationship $s = (n+1)/2$ was valid. Above this s increases more rapidly than n , so that at about $s = 18$, n and s are equal.

2. The pre-exponential factor.

The pre-exponential factor of the Arrhenius equation :-

$$k = A e^{-E/RT}$$

lies in the range 10^{12} to 10^{14} sec.^{-1} for most reactions. The pre-exponential factors for the decomposition of cyclobutane and its derivatives are of the order of 10^{15} sec.^{-1} . (See Table VII)

According to Slater's theory the pre-exponential factor is a weighted mean value of all the vibrational frequencies of the molecule, and hence it should lie in the normal range of vibration frequencies of 10^{12} to 10^{14} sec.^{-1} . If the molecule has certain symmetry properties the theoretical value of the pre-exponential factor may be greater than 10^{14} . For example in the case of cyclopropane, Slater^{8b} took as the reaction coordinate a diminution of the distance of a hydrogen from a non-adjacent carbon, and calculated the mean frequency for a single coordinate to be $3.33 \times 10^{13} \text{sec.}^{-1}$. Because of its symmetry, cyclopropane has twelve equivalent reaction coordinates. The pre-exponential factor is therefore twelve times the mean frequency for a single coordinate: $4.0 \times 10^{14} \text{sec.}^{-1}$. The experimental value is $15 \times 10^{14} \text{sec.}^{-1}$ (11).

If the same reaction coordinate were taken for cyclobutane the pre-exponential factor would be sixteen times the mean frequency for a single coordinate, and a value of the pre-exponential factor which would be in reasonable agreement with experiment

could be calculated. But Srinivasan and Kellner¹² have shown that no hydrogen migration occurs in the decomposition of cyclobutane, so that a reaction coordinate involving a hydrogen is improbable. Other feasible reaction coordinates, such as the extension of a C—C bond or the increase in a C—C—H angle, can only lead to pre-exponential factors four or eight times the mean frequency for a single coordinate. The calculated value will therefore be lower than the experimental one.

Thiele and Wilson¹³ have extended Slater's unimolecular rate expression for high pressures to include the case where reaction occurs when two reaction coordinates exceed a critical value simultaneously. They calculate the pre-exponential factor to be given by an energy-weighted average of the two Slater frequencies for the individual reaction coordinates. This does not lead, however, to any increase in the value of the theoretical pre-exponential factor, which is still considerably less than experimental value.

Steel¹⁴ has proposed a formula for the rate of a reaction at high pressure where the critical energy needed for reaction is present in z of the s oscillators. It can be based on the Kassel or the Slater viewpoint as it is immaterial whether the oscillators are coupled or uncoupled. If z is 2, as is possible for cyclobutane, the expression reduces to :-

$$k_{\infty} = \lambda \cdot [(E_0/kT) + 1] e^{-E_0/kT}$$

Where λ is the frequency of reaction of molecules which contain the critical energy localized within the z critical oscillators. It is of the order of 10^{12} to 10^{14} .

For cyclobutane the factor $([E/kT] + 1)$ is 45. However for the two critical coordinates to rupture simultaneously they must be in phase. Steel estimates the probability of this to be about 25%. Therefore the factor for cyclobutane will reduce to about 11. This could lead to a value for the pre-exponential factor in agreement with experiment if λ were of the order of 10^{14} .

The pre-exponential factor in the transition state theory can be expressed :-

$$A = \frac{K e k T}{h} e^{\Delta S^*/R}$$

where K is a transmission coefficient and ΔS^* is the entropy of activation. An abnormally high pre-exponential factor can thus be interpreted as resulting from an increase in the entropy of the molecule on going to the transition state. For cyclobutane this would lead to an entropy of activation of about 9 e.u. at 449°C . (assuming a transmission coefficient of unity).

Walters et al.³ have calculated the entropy change in the reaction at 700°K to be 43 e.u. Therefore the transition state will be much closer to cyclobutane in structure than to ethylene. A reasonable structure for the transition state is one in which two opposite C—C bonds are lengthened slightly and the other

two are shortened and have a partial double bond character.

3. Minor Products.

In many of the lower pressure pyrolyses of cyclobutane a C₃ and a C₄ compound were detected in the reaction products. Their retention times corresponded with those of propylene and 1-butene. Their rate of formation compared to that of ethylene increased as the pressure was lowered.

These compounds could have been formed by a second unimolecular reaction of cyclobutane, or by a wall reaction of either cyclobutane or ethylene, or from a reaction of the impurities in the starting material.

The last possibility can be rejected. The main impurities were less than 0.1% of a C₄ compound, probably cis- or trans-2-butene, in the 99.9% pure sample and about 0.7% and 0.3% of a C₅ compound, probably 2-pentene, in the 99.1% and 99.7% pure samples, respectively. Butenes and pentenes decompose by a radical mechanism and therefore more than two products would be expected if the decomposition of the impurities were important. In addition, different compounds would be expected

from the reactions of different impurities. The concentrations of the impurities did decrease slightly during a run but there was no correlation between their decrease and the amount of propylene or 1-butene formed. Certainly the reactions of the impurities could not explain the greater formation of these compounds with decreasing pressure.

One of the objects of this work was to find evidence for or against the occurrence of a second unimolecular reaction of cyclobutane. If this second reaction had a value of n , the Slater fall off parameter, less than that for the main reaction, then the greater relative concentrations of propylene and 1-butene at lower pressures cannot be accounted for. If it had a value of n greater than that for the main reaction its high pressure limiting rate would start to fall off at lower pressures than that of the main reaction. If the reactions were occurring concurrently the second reaction could become more important as the pressure was lowered. This situation can be pictured :-

The formation of propylene and 1-butene became important at about 10^{-2} mm. pressure. If they were formed by a second unimolecular reaction of cyclobutane then the point in the diagram at which the two curves cross would occur at about 10^{-2} mm. pressure. The experimental rate constants at this pressure are in the region 5 to $9 \times 10^{-5} \text{ sec.}^{-1}$ (depending on the size of the reactor). Therefore a minimum value for the limiting high pressure rate constant of the second reaction is $5 \times 10^{-5} \text{ sec.}^{-1}$. This value is only ten times less than the limiting high pressure rate constant for the main reaction. Therefore about 10% of propylene and 1-butene would be expected at high pressures. Actually less than five parts in 10^4 of these compounds were observed at pressures greater than a millimetre. A second unimolecular reaction is therefore very improbable.

Thus the formation of propylene and 1-butene must be due to a wall reaction of cyclobutane or ethylene. Both propylene and 1-butene were formed in the pyrolysis of ethylene, but the amount formed was less than that formed from cyclobutane under the same conditions. For example 1.5% of propylene, relative to the initial concentration of ethylene, was formed in the one litre reactor at 3.7×10^{-3} mm. pressure and a temperature of 446.6°C. , in 2403 seconds. Whereas 11.4%, relative to the initial concentration of cyclobutane, was formed in the same reactor at 5.3×10^{-3} mm. pressure and 444.0°C. in 1041 seconds. In addition several other compounds were observed in a few of the ethylene

pyrolyses that were not detected in cyclobutane pyrolyses.

It was concluded that the propylene and 1-butene were formed mainly from a wall reaction of cyclobutane, but possibly with a minor contribution from a wall reaction of ethylene.

When the rate constants were corrected on the assumption that propylene and 1-butene were formed from cyclobutane only the fall off curve was found to level out at about 10^{-3} mm. pressure and the points lay reasonably on the curve. If they were corrected on the basis of a wall reaction of ethylene the curve started to rise again at pressures below about 10^{-3} mm. and there was considerable scatter of the points.

4. The low pressure limiting rate, k_0 .

The low pressure data is plotted in Figs. IV, V and VI. The three curves fall below the high pressure limiting level as the pressure is decreased and then start to level out again at about 10^{-1} to 10^{-2} mm. pressure. The curves plotted from the data obtained in the 100 ml. and five-litre reactors level out completely at about 10^{-3} mm. to give low pressure limiting rate constants, k_0 , of $4.6 \times 10^{-5} \text{ sec.}^{-1}$ and $2.9 (\pm 0.3) \times 10^{-5} \text{ sec.}^{-1}$ respectively. No data below 10^{-3} mm. pressure was obtained for the one-litre reactor, so no value of k_0 was obtained. It could be estimated from the way in which the curve started to level out

that the value of k_0 would be between the values obtained for the other two reactors.

It seems reasonable that the fall off curve will start to level out when the mean free path of a cyclobutane molecule approaches the same order of magnitude as the dimensions of the reactor. When the molecules are being activated by collision with the walls of the reactor rather than with each other the rate of reaction will be independent of pressure and the curve will level out completely. The mean free path of a cyclobutane molecule will be about the diameter of the 100 ml. reactor at 10^{-5} mm. pressure. At this pressure a cyclobutane in an infinite reactor would undergo about a hundred collisions per second. The experimental curve for the 100 ml. reactor levelled out at a pressure corresponding to a collision rate of about 10^4 sec.⁻¹.

If the size of the reactor is increased the value of k_0 should decrease. The decrease might be expected to be in the ratio of the surface-to-volume ratios of the reactors. The relative surface-to-volume ratios of the 100 ml., the one-litre and the five-litre reactors were about 1.00 : 0.47 : 0.28 (to within 15%). The ratio of k_0 for the 100 ml. and five-litre reactors was 1.0 : 0.61, or a minimum value of 1.0 : 0.54, which is half that expected.

5. Comparison of the theoretical and experimental fall off curves.

In the Kassel theory the parameter affecting the shape of the fall off curve is s , the number of oscillators that contribute to dissociation. In the Slater theory the parameter is n , the number of normal vibration modes that contribute to extension of the reaction coordinate.

Schlag, Rabinovitch and Schneider¹⁰ have evaluated Kassel's integral

$$I_s(\theta') = k/k_\infty = [\Gamma(s)]^{-1} \int_0^\infty \frac{x^{s-1} e^{-x} dx}{1 + [x/(b+x)]^{s-1} (\theta')^{-1}}$$

for a range of values of s, θ' and b .

Slater^{8c} has evaluated his integral

$$I_n(\theta) = k/k_\infty = \left[\frac{\Gamma(n+1)}{2} \right]^{-1} \int_0^\infty \frac{x^{(n-1)/2} e^{-x} dx}{1 + x^{(n-1)/2} \theta^{-1}}$$

for a range of values of n and θ .

An attempt was made to fit the Kassel curves for $s = 3, 7, 11, 15, 21$ and 26 , and the Slater curves for $n = 3$ up to 16 , to the experimental fall off curves. The value of $b, (E_0/RT)$, was taken to be 44 , which corresponds to 442°C . The values of k_0/k_∞ obtained from the experimental fall off curves were added to the values of $I_s(\theta')$ and $I_n(\theta)$ to correct for the activation of the molecules by collision with the walls of the reactor. Plots of $\log[I_n(\theta) + k_0/k_\infty]$ versus $\log(\theta)$, and $\log[I_s(\theta') + k_0/k_\infty]$ versus $\log(\theta')$ were drawn

for the values of n and s given above, on the same scale as the experimental plots of $\log k/k_\infty$ versus $\log p$. The theoretical curves were superposed on the experimental ones and the values of n and s that gave best agreement were found. The results are shown in Table VI.

The fit of the theoretical curve is very sensitive to the value of k_∞ . The best method of obtaining k_∞ is by extrapolation of the curve k^{-1} versus $p^{-1/2}$ (5). Unfortunately not many points in the pressure region of 1 to 10 mm. were taken and this made accurate extrapolation difficult. The plots of k^{-1} versus $p^{-1/2}$ are shown in Fig. III. By extrapolation of these plots to infinite pressure and comparison with the data of Genaux, Kern and Walters, and of Pritchard, Sowden and Trotman-Dickenson a value of $4.6 \times 10^{-4} \text{ sec.}^{-1}$ was taken for k_∞ for the experiments in the 100 ml. and one-litre reactors. A value of $k_\infty = 4.9 \times 10^{-4} \text{ sec.}^{-1}$ was chosen for the runs in the five-litre reactor, because the temperature may have been closer to 450°C .

Genaux, Kern and Walters obtained a value for k_∞ of $4.86 \times 10^{-4} \text{ sec.}^{-1}$ and Pritchard, Sowden and Trotman-Dickenson obtained a value of $3.9 \times 10^{-4} \text{ sec.}^{-1}$.

The best fit with the Kassel curves was obtained with values of s of 7, 7 or 3, and 3 for the one-litre, the 100ml. and the five-litre reactors respectively.

Kern and Walters used a cylindrical reactor of volume

TABLE VI. EXPERIMENTAL VALUES OF n AND s.

REFERENCE	REACTOR	s	$\theta'/p_{\text{mm.}}$	n	$\theta/p_{\text{mm.}}$
This work	100 ml.	7 or 3	5×10^{-6} or 5×10^{-3}	8	200
"	one-litre	7	4×10^{-6}	8	250
"	five-litre	3	5×10^{-3}	5	10
Kern and Walters ²	490 ml.	7	1×10^{-5}	9	1000
Pritchard, Sowden and Trotman - Dickenson ⁴	two-litre	7 or 3	1×10^{-6} or 8×10^{-3}	9	1400

FIG. III k^{-1} vs. $p^{-1/2}$, for pressures down to 10^{-2} mm.

490 ml. Their fall off curve was closest in shape to the one obtained in the 100 ml. reactor and gave the best fit with $s = 7$.

Pritchard, Sowden and Trotman-Dickenson used a two-litre reactor. Their fall off curve lay in between that obtained in the one-litre reactor and that obtained in the five-litre reactor. It corresponded with $s = 7$ and $s = 3$.

Powell⁶ states that the data of Pritchard, Sowden and Trotman-Dickenson and that of Walters and co-workers matches the curve for $s = 5$, which is consistent with the above.

It seems therefore that the value of s lies between 3 and 7; a larger value being unlikely.

With the Slater curves, the best fit was obtained using values of n of 8 for the 100 ml. and the one-litre reactors and 5 for the five-litre reactor.

The data of Pritchard, Sowden and Trotman-Dickenson, and that of Walters and co-workers agree with $n = 9$.

FIG. IV FALL OFF PLOT, $\log k/k_\infty$ vs. $\log p$ mm., at 449°C. in the one-litre reactor.

The points are fitted for the Kassel curve $s = 7$, (including k_0/k_∞).

FIG V FALL OFF PLOT, $\log k/k_\infty$ vs. $\log P$ mm., at 449°C in the 100ml. reactor.

The points are fitted for the Slater curve $n = 8$, (including k_0/k_∞).

FIG. VI FALL OFF PLOT, $\log k/k_{\infty}$ vs. $\log p$ mm., at 450°C . in the five-litre reactor.

The points are fitted for the Slater curve $n=5$, (including k_0/k_{∞}).

6. Related reactions.

Cyclopropane undergoes a thermal, unimolecular isomerization to form propylene. The reaction therefore involves the migration of a hydrogen. Slater^{8b} took as the reaction coordinate the diminution in the distance between a hydrogen and a non-adjacent carbon, and obtained good agreement between his calculations and the experimental data of Pritchard, Sowden and Trotman-Dickenson.¹¹

If cyclobutane decomposed by a similar mechanism to cyclopropane the product of the reaction might be expected to be a butene, probably 1-butene, rather than ethylene. Only traces of 1-butene are formed in the high pressure decomposition and these can be attributed to a wall reaction of cyclobutane. Srinivasan and Kellner¹² have shown that hydrogen migration does not occur in the decomposition of cyclobutane. They studied the decomposition of cyclobutane-1,1,2,2-d₄ and found the products to be C₂H₄, C₂H₂D₂ and C₂D₄ in the ratio 1 : 2 : 1. If hydrogen migration occurred C₂H₃D and C₂HD₃ should be formed also. The fact that the ratio of C₂H₄ to C₂H₂D₂ to C₂D₄ is 1 : 2 : 1 shows that cyclobutane-1,1,2,2-d₄ decomposes at an equal rate by two methods, both involving the rupture of two

opposite C—C bonds.

The derivatives of cyclobutane, whose thermal decompositions have been studied, give products which are consistent with the splitting of the ring across two opposite C—C bonds. This is shown in Table VII.

The bond dissociation energy for a C—C bond in the cyclobutane ring has been estimated by several methods. Most of them give values in agreement with the experimental activation energy, but they involve many assumptions and generalizations.

Pritchard, Sowden and Trotman-Dickenson⁴ have calculated values of 60 Kcal. and 59 Kcal. by the following methods.

a). The heat of formation of a tetramethylene biradical can be calculated from the heat of formation of n-butane, the C—H bond dissociation energy and the heat of combination of hydrogen atoms:

The C—C bond dissociation energy of cyclobutane is the difference in the heats of formation of cyclobutane and tetramethylene:

$$\begin{aligned}D(\text{C—C}) &= +66 - 6.3 \text{ Kcal/mole} \\ &= 60 \text{ Kcal./mole.}\end{aligned}$$

TABLE VII. THE THERMAL DECOMPOSITION OF CYCLOBUTANE DERIVATIVES

COMPOUND	PRODUCTS	A in sec. ⁻¹	E in Kcal.	Refer- ence.
C_2H_4	4.0×10^{15}	62.5	3
-1,1,2,2-d ₄	$C_2H_4 + C_2H_2D_2 + C_2D_4$ in the ratio 1:2:1			12
$C_2H_4 + CH_3CH=CH_2$	2.4×10^{15}	61.2	18
$C_2H_4 + CH_3CH_2CH=CH_2$	3.6×10^{15}	62.0	19
$C_2H_4 + CH_2=C=CH_2$	1.2×10^{15}	61.5	20
$C_2H_4 + CH_2=CO$	3.6×10^{14}	52.0	21
cis-	C_3H_6 $C_2H_4 + CH_3CH=CHCH_3$ (cis and trans)	3.0×10^{15} 3.7×10^{15}	60.4 63.0	22
trans-	C_3H_6 $C_2H_4 + CH_3CH=CHCH_3$ (cis and trans)	2.8×10^{15} 2.9×10^{15}	61.6 63.4	23
$C_2H_4 + CH_2=CHCOCH_3$	3.4×10^{14}	54.5	24
C_2F_4 C_3F_6	1.0×10^{16} 1.6×10^{17}	74.3 87.0	25

b). The heat of formation of a strainless cyclobutane molecule would be four times that of a methylene group. The strain energy in the cyclobutane ring is given by the difference between the actual heat of formation of cyclobutane and that of 'strainless' cyclobutane.

$$\begin{aligned}\text{Strain energy} &= 6.3 - (-4.9 \times 4) \text{ Kcal./mole.} \\ &= 26 \text{ Kcal./mole.}\end{aligned}$$

If the normal value for a C—C bond dissociation energy is taken to be 85 Kcal./mole. Then the bond dissociation energy of cyclobutane will be: $85 - 26 = 59$ Kcal./mole.

It has been postulated by Burwell¹⁵ that the thermal isomerization of α - and β -pinene involves the splitting of the four membered ring as the initial step. The activation energy of the isomerizations can be equated with the bond dissociation energies involved in the splitting of the four membered ring to form a biradical. The experimental activation energies are 44 and 49 Kcal./mole. for α - and β -pinene respectively. Pritchard, and Trotman-Dickenson¹⁶ postulate that cyclobutane bears the same relationship to α - and β -pinene as propane does to 4,4-dimethylpentene.

α -pinene β -pinene

cyclobutane

propane

4,4-dimethyl-
pentene

The difference in the bond dissociation energies of the latter pair is 28 Kcal./mole. If the difference in the bond dissociation energies of the pinenes and of cyclobutane is also 28 Kcal./mole, then the bond dissociation energy of cyclobutane will be $46 + 28 = 74$ Kcal./mole. This is considerably higher than the experimental activation energy.

In reply, Seubold¹⁷ states that the four membered ring in the pinenes should be more stable than cyclobutane as it is a substituted ring. He calculates the strain energy for the four membered ring in the pinenes to be 11 Kcal./mole., compared to 26 Kcal./mole. for cyclobutane. Hence the bond dissociation energy for cyclobutane should be : $46 + 26 - 11 = 61$ Kcal./mole., which agrees with the activation energy.

7. Mechanism of the decomposition of cyclobutane.

Most unimolecular reactions that have been studied in the region where the rate constant decreases with decreasing pressure, have experimental values of n fairly close to the total number of normal vibrational modes of the molecule; $3N - 6$ for a non-linear molecule containing N atoms. Experimental values of n and s for a number of compounds are given in Table VIII.

Cyclopropane was found to have a value of $n = 13$. The total number of vibrational modes in cyclopropane is 21, compared to 30 for cyclobutane. As cyclobutane has more vibrational modes than cyclopropane it might be expected to have a greater value of n .

The results of this experiment show that the value of n for cyclobutane is of the order of 5 to 8. The decomposition of cyclobutane involves no hydrogen migration, whereas the isomerization of cyclopropane does. Therefore it is possible that the C—H vibrations are relatively unimportant in the decomposition of cyclobutane. If the vibrations of the carbons alone is considered, the number of normal vibrational modes is 6, which agrees with the experimental value of n . It seems probable, therefore, that it is the ring vibrations that are important in the dissociation, and that the C—H vibrations are relatively unimportant.

The structure of cyclobutane is still uncertain. The two possible structures are one in which the ring is planar, D_{4h}

TABLE VIII. EXPERIMENTAL VALUES OF n AND s FOR A NUMBER OF COMPOUNDS.

COMPOUND	TOTAL NUMBER OF VIBRATION MODES	$n_{\text{expt.}}$	$s_{\text{expt.}}$	Reference
NO_2Cl	6	6	5	26
trans- $\text{C}_2\text{H}_2\text{D}_2$	12	10		27
cyclopropane	21	13	6	11
N_2O_5	15	14 - 15	5	28
cis- C_4H_8	30	28		5
trioxymethylene	30	20	5	29
octafluorocyclobutane	30	20		25

The experimental values of n , except for octafluorocyclobutane, are those given by Rabinovitch and Michel⁵, The experimental values of s , are those given by Powell.⁶

symmetry, and one in which the ring is puckered and there is minimum repulsion between the hydrogen atoms, D_{2d} symmetry. The planar structure may have an out of plane bending vibration and the puckered structure may undergo inversion through the planar structure. Electron diffraction measurements favour the puckered structure^{30,31}, and I.R. measurements tend to favour the planar structure^{32,33,34}. Pitzer and co-workers³⁴ have suggested that although the puckered structure should be more stable, the potential barrier for inversion is probably low so that at room temperature a considerable proportion of the molecules will have a planar equilibrium structure. At 449°C., therefore, cyclobutane will probably have a planar equilibrium structure.

Schafer, Monter and Wolff-Mitscherlich³⁵ have worked out a normal vibration analysis of cyclobutane, assuming D_{4h} symmetry. The six normal modes of vibration of the ring are shown in Fig. VII.

There are several possible ways in which the reaction may occur : one C—C bond may be broken forming a tetramethylene biradical which later splits to form two molecules of ethylene; or two opposite C—C bonds may be broken simultaneously; or a mechanism intermediate between the two may occur.

FIG.VII THE SIX NORMAL MODES OF VIBRATION OF THE CYCLOBUTANE RING.

If a tetramethylene biradical is an intermediate in the reaction it may either have a normal lifetime and reactivity (like an alkyl radical) or it may have a very short lifetime.

The first possibility is unlikely. Many of the standard tests for the presence of free radicals have been applied to the decomposition of cyclobutane and its derivatives and none have proved positive. Walters and his co-workers have added radical scavengers such as propylene, toluene and nitric oxide and observed no difference in the rate of the reaction. They have also tried adding cyclobutane to reactions which are known to be accelerated by free radicals, such as the polymerization of ethylene and the decomposition of formaldehyde, without success. More conclusive evidence for the absence of a normal free radical is provided by the fact that no other products besides ethylene are observed, except for those which can be attributed to a wall reaction (see section 3 of the discussion). A normal free radical would be expected to add to ethylene and also abstract hydrogen from cyclobutane, to form a whole gamut of products by reactions such as :-

Tetramethylene has been postulated as an intermediate in the photolysis of cyclopentanone, to account for the formation of polymeric compounds and higher olefins and cyclohexane. It is likely, though, that this mechanism is incorrect and that these products are due to the secondary photolytic decomposition of 4-pentenal³⁶.

No polymeric compounds were detected in the decomposition of cyclobutane and the walls of the reactors looked perfectly clean after many decompositions.

Several estimates of the activation energy of the reaction

have been made. Bawn and Milsted³⁷ calculated a value of 15 Kcal./mole., using a value of 73 Kcal./mole for the aliphatic C—C bond dissociation energy. Benson³⁸ has estimated it to be 4 Kcal./mole. He calculated the bond dissociation energy at 450°C. to be 58.5 Kcal./mole., which is 4 Kcal./mole less than the experimental activation energy.

The activation energy for the addition of an alkyl radical to ethylene is about 7 Kcal. and for hydrogen abstraction from cyclobutane is about 9 Kcal.³⁹ Therefore if the activation energy for the decomposition of tetramethylene were 15 Kcal many products would be expected. Even if the activation energy were 4 Kcal. the rate constant for the addition of tetrameth-

ylene would be about ten times less than the rate constant for the dissociation of tetramethylene (assuming a similar pre-exponential factor for the two reactions), at 449°C . Appreciable amounts of products other than ethylene would be expected.

The values that have been calculated for the bond dissociation energy of cyclobutane are in agreement with the experimental activation energy, (see section 6 of the Discussion). It is possible that the fission of tetramethylene requires no activation energy. Its lifetime would then be extremely short. Walters and his co-workers³ have estimated the entropy change for the formation of tetramethylene to be about 15 e.u. This is greater than the experimental entropy of activation of 9 e.u. Therefore if tetramethylene is formed in the reaction it should be an intermediate and not the activated complex. They suggest that the activated complex may undergo a transformation into the biradical which would then have only a momentary existence.

The period of time for which an intermediate must exist before it can be classified as a separate species is a philosophical question. The collision frequency of a cyclobutane molecule is about 10^9 per second at 449°C . and 126mm. pressure. Walters and his co-workers³ have analysed products from a decomposition at this pressure and 438°C . on a mass spectro-

meter and found no significant products besides ethylene. Therefore if the biradical exists its lifetime must be less than 10^{-9} sec. If the lifetime of the radical is very short it can be regarded as being merely a bump on the potential energy surface, and not as a separate entity. This mechanism is then essentially the same as that in which two bonds rupture simultaneously.

It can be concluded that the mechanism of the thermal decomposition of cyclobutane does not involve a stable tetramethylene biradical. It may involve a transient biradical, but a more probable mechanism is the simultaneous rupture of two opposite C—C bonds. It is the vibrations of the ring carbon atoms that are important in the dissociation; those of the C—H bonds are relatively unimportant.

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