

$k_{\text{dis}}/k_{\text{com}}$ is proportional to $T^{-0.85}$ for the reaction in isooctane and to $T^{-0.6}$ for that in glycol.

The balance of products was again low,^{4a} as in the photolysis of azoethane¹ and azomethane,^{4b} e.g., we could not account for about 20% of radicals when the reaction proceeded at -191° . Photolysis of $\text{CF}_3\text{N}_2\text{CF}_3$ in 2,3-dimethylbutane shows excellent balance of products at $T \geq -30^\circ$. At -191° the ratio $(\text{BF}_3\text{H} + 2\text{C}_2\text{F}_6)/\text{N}_2$ was again low (about 1.74).

All these observations resemble those reported for the interaction of ethyl radicals,¹ namely (1) the increase in $k_{\text{dis}}/k_{\text{com}}$ when glycol replaces isooctane as a solvent; (2) the increase of $k_{\text{dis}}/k_{\text{com}}$ with decreasing temperature which seems to be represented by a function T^{-a} ; (3) convergence of the $k_{\text{dis}}/k_{\text{com}}$ values at the lowest temperatures to a limit which seems to be common for all the investigated solvents. It appears,

(4) (a) In reply to the referee's question, we stress that the balance is expected to be low at higher temperatures and in the presence of scavengers, since the reaction of primary radicals with the solvent radicals and the scavenger gives products other than CH_4 , C_2H_4 , and C_2H_6 . Such reactions, we believed are unlikely at liquid nitrogen temperature, and therefore the low balance obtained in those experiments puzzles us. (b) R. E. Rebbert and P. Ausloos, *J. Phys. Chem.*, **66**, 2253 (1962).

therefore, that these characteristic features of the radical combination and disproportionation are typical of radical interactions in solution.

There is one interesting qualitative difference in the behavior of azoethane and methyl-ethyl azo compound. In the photolysis of solid azoethane the value of $k_{\text{dis}}/k_{\text{com}}$ was found to be lower than that obtained at the same temperature in other solvents. It was suggested¹ that this result may have been due to the crystal lattice effectively freezing the radical and preserving their initial orientation which favors the combination. In the methyl-ethyl system the $k_{\text{dis}}/k_{\text{com}}$ ratio was again lower in the solid azo compound than in other solvents, although to a much smaller degree. As this azo compound is not as symmetrical as azoethane, the crystal lattice may have had less influence on the orientation of the radicals and thus combination would not be favored to such an extent.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER 8, B. C.]

The Thermal Decomposition of Cyclobutane at Low Pressures

BY JAMES N. BUTLER AND ROSALIND BARR OGAWA¹

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The thermal decomposition of cyclobutane has been studied using gas chromatography for analysis at pressures from 43 mm. to 1.7×10^{-4} mm. at a temperature of 449° . Ethylene is the product of a homogeneous first-order decomposition. Propylene and 1-butene are formed in small amounts by zero-order reactions. The shape of the curve of first-order rate constant for ethylene formation as a function of pressure is consistent with the Kassel theory, if s is taken to be 14, or the Slater theory, if n is taken to be 16.

Introduction

The thermal decomposition of cyclobutane in the gas phase has been shown to be a homogeneous unimolecular reaction.²⁻⁵ The primary product is ethylene, although traces of C_3 , C_4 , and C_5 compounds have been detected.^{3,5} The first-order rate constant decreases at low pressures, as predicted by the Kassel or Slater theories⁶ of unimolecular reactions, but there has been some disagreement as to the shape of the fall-off curve. Values for the effective number of normal modes contributing to the decomposition have been quoted^{5,7,8} which vary from 8 to 20.

Experimental

The furnace and associated equipment have been described previously.⁹ Spherical reactors of 100-ml., 1-l., and 5-l. volumes were made from Pyrex flasks. One thermocouple was used in the small reactor, and four thermocouples in the large reactors. The temperature variation over the surface of the 5-l. reactor was less than 3° , and the drift in temperature during a 2-hr. run was less than 0.6° .

Cyclobutane was prepared by the photolysis of cyclopentanone¹⁰⁻¹² and purified by gas chromatography. The samples used

varied in purity from 99.1 to 99.9%, the principal impurity being a C_5 compound, probably 2-pentene. The samples contained less than 0.01% of ethylene and less than 0.01% of C_3 and C_4 compounds.

Pressures were measured with a wide-bore manometer and cathetometer, or with a McLeod gage. Thermal transpiration corrections were negligible compared to the other experimental errors at pressures above 0.05 mm. At low pressures, corrections based on Liang's equation¹³ were used. The parameter ϕ was estimated to be 20 by using Liang's correlation with collision diameter. The largest corrections (at 2×10^{-4} mm.) were 30%.

Samples were expanded into a 300-ml. bulb at room temperature at the conclusion of a run and analyzed by gas chromatography. The composition of the gas was the same within experimental error whether the sampling time was 20 sec. or 10 min. and whether the gas was expanded directly into the bulb or diluted first with approximately 1000 times as much nitrogen and then expanded into the bulb. This eliminates the possibility of a systematic error in the rate constant resulting from the fact that ethylene diffuses through a small opening at low pressures faster than cyclobutane.

Analysis was performed using a Perkin-Elmer Model 154-C vapor fractometer with flame ionization detector. A 150-ft. squalane-coated capillary column maintained at 0° separated all compounds from C_2 to C_5 except 1-butene and isobutene. Gas samples were diluted with nitrogen and transferred to a capillary sampling loop with a Toepfer pump. Quantitative analysis was made by measuring peak heights. Calibrations would be reproduced to within $\pm 4\%$. Between each sample, a blank analysis was performed to see if any residual products remained in the system.

Results

The principal product of the decomposition of cyclobutane was ethylene. At low pressures small amounts of propylene and 1-butene were also observed. The results obtained near 449° are listed in Table I.

(1) This paper is based on the M.Sc. Thesis of Rosalind Barr Ogawa, Birkbeck College, Malet St., London W. C. 1, England.

(2) C. T. Genaux and W. D. Walters, *J. Am. Chem. Soc.*, **73**, 4497 (1951); F. Kern and W. D. Walters, *Proc. Natl. Acad. Sci. U. S.*, **38**, 937 (1952).

(3) C. T. Genaux, F. Kern, and W. D. Walters, *J. Am. Chem. Soc.*, **75**, 6196 (1953).

(4) H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, *Proc. Roy. Soc. (London)*, **A218**, 416 (1953).

(5) R. W. Vreeland and D. F. Swinehart, *J. Am. Chem. Soc.*, **85**, 3349 (1963).

(6) N. B. Slater, "The Theory of Unimolecular Reactions," Cornell University Press, Ithaca, N. Y., 1959.

(7) R. E. Powell, *J. Chem. Phys.*, **30**, 724 (1959).

(8) B. S. Rabinovitch and K. W. Michel, *J. Am. Chem. Soc.*, **81**, 5065 (1959).

(9) J. N. Butler, *ibid.*, **84**, 1393 (1962).

(10) S. W. Benson and G. B. Kistiakowsky, *ibid.*, **64**, 80 (1942).

(11) F. E. Blacet and A. Miller, *ibid.*, **79**, 4327 (1957).

(12) R. Srinivasan, *ibid.*, **81**, 1546, 5541 (1959).

(13) S. C. Liang, *J. Phys. Chem.*, **57**, 910 (1953).

TABLE I
 EXPERIMENTAL RESULTS

Pres- sure, ^a mm.	Time, sec.	Temp., °C.	Ratio to cyclobutane—			$k_1 \times 10^5$, corrected to 449°	Pres- sure, ^a mm.	Time, sec.	Temp., °C.	Ratio to cyclobutane—			$k_1 \times 10^5$, corrected to 449°
			C ₂ H ₄	C ₃ H ₆	C ₄ H ₈					C ₂ H ₄	C ₃ H ₆	C ₄ H ₈	
5-l. reactor													
1.05	2434	448.1	2.08			31.0	0.117	2461	444.2	0.905		20.4	
0.430	3600	450.1	3.00			23.9	.100	787	447.5	.300		19.5	
.106	4200	449.5	1.40			12.2	.0966	964	447.2	.257		14.0	
.0725	4000	449.9	1.01			9.74	.0667	1023	446.4	.236		12.8	
.0292	4626	448.7	0.588			5.68	.0520	2028	448.8	.495	0.020	0.013	10.9
.0227	8455	447.1	1.23	0.011	0.003	6.38	.0402	2806	445.3	.522	.009	.007	10.4
.0148	4600	450.2	0.491			4.44	.0312	2305	442.4	.455	.026	.014	13.1
.0146	3758	448.4	.466	.103	.114	5.42	.0176	1000	448.0	.146	.047	.017	7.41
.00673	4370 ^b	442.1	.250	.010	.003	4.11	.00992	1052	446.8	.122			6.45
.00453	5053	449.0	.472	.087	.020	4.04	.00568	1041	444.0	.134	.125		8.12
.00445	8850	449.2	.862	.025	.012	3.94	.00153	3607	445.5	.191	.119	.042	2.97
.00254	4974	449.3	.304			2.81	.00130	1894	444.2	.115	.360	.090	3.42
.00238	6200	448.2	.378	.130		2.81							
.00221	4973 ^c	448.5	.340	.015	.007	3.27							
.00209	8692	449.4	.789	.173		3.56	43.14	510	448.8	0.642			55.3
.00121	6914	448.2	.626	5.00	.374	1.77	31.15	600	449.0	0.552			40.6
.00119	4157 ^c	449.0	.230	0.050		2.58	9.64	2490	450.2	3.83			40.0
.00115	6660 ^c	448.2	.536	.149	.009	3.57	0.75	4400	447.3	4.07			28.0
.00111	9880 ^b	446.0	.645	.247	.057	3.09	.412	3540	448.5	2.38			23.0
.00090	4400	449.0	.345	.345	.038	3.22	.306	2316	447.2	0.910			18.1
.00077	3664	450.7	.523	.191		5.44	230	3062	447.7	1.09			15.4
.00072	5918 ^c	448.2	.419	.040		3.35	.0476	3923	449.2	0.997	0.011	0.006	10.4
.00065	5650	448.8	.705	.353		4.90	0218	2257	447.8	.450	.058	.033	9.38
.00037	9650	450.3	.920	.361		3.40	.0197	4102	441.4	.439	.036		7.64
.00025	5540	449.4	1.00	3.68		4.04	.0172	5540	446.8	1.09			8.98
100-ml. reactor													
							.0148	3520	448.7	0.545	.012		6.95
							.0128	2522	447.0	.331	.028	.016	6.75
							.0118	5000	448.5	.803	.016	.006	6.96
1.26	777	462.2	1.65			35.2	.00581	7217	441.0	.644	.077	.033	6.05
1.26	1996	446.6	1.31			29.5	.00380	7244	446.7	1.15	.421		6.55
0.790	1066	444.4	0.639			34.2	.00374	6000	447.0	0.694	.234		5.27
.279	1430	446.0	.609			22.3	.00282	6678	447.0	.806	.285		5.31
.270	1414	446.2	.576			21.2	.00164	7402	447.1	.834	.605		4.56
.235	1467	446.2	.605	0.002		21.3	.00139	4945	440.5	.351	.351		4.96
.148	1092	447.5	.306			14.2	.00093	6306	446.8	.814	.630		5.30
.137	2187	442.7	1.04			27.6	.00078	4456	447.2	.544	.471		5.31

^a Corrected for thermal transpiration ^b Sampling time 5–10 min. ^c Reactor flooded with nitrogen before sampling.

Propylene and 1-butene appear to have been formed directly by decomposition of cyclobutane rather than by the subsequent reaction of ethylene. A series of experiments on the decomposition of ethylene under conditions comparable to those used for the decomposition of cyclobutane indicated that the rate of formation of propylene from cyclobutane was about 100 times as great as the rate of formation of propylene from ethylene.

The amounts of propylene and 1-butene formed were rather irreproducible, and different experiments performed under presumably the same conditions gave values which varied by about a factor of twenty. In spite of the large error, the pressure range covered was sufficiently wide to make it clear that the reactions forming these compounds were much more nearly zero order than first order. A few typical rate constants obtained in the 5-l. reactor at various pressures are given in Table II. The k_2 is the zero-order rate constant for the formation of propylene, and k_3 is the zero-order rate constant for the formation of 1-butene.

At a pressure of about 1 mm., the ratio of propylene to ethylene was about 5×10^{-4} , but at pressures of about 10^{-3} mm., the ratio of propylene to ethylene was near unity. The ratio of propylene to 1-butene varied from 1 to 15, but showed no obvious trend with pressure. In Table II are also given average values of the rate constants for the three different reactors used.

 TABLE II
 FORMATION OF PROPYLENE AND 1-BUTENE
 5-l. reactor, 449°

Pressure, mm. ^a uncor.	$10^2 k_2^b$	$10^3 k_3^b$	$C_3H_6^c /$ 1-C ₄ H ₈
	(C ₂ H ₄), mm./sec.	(1-C ₄ H ₈), mm./sec.	
1.05	2.8	1.5	2.0
2.22×10^{-2}	1.3	0.35	3.7
6.12×10^{-3}	1.1	.34	3.3
3.93×10^{-3}	4.3	.96	4.5
1.75×10^{-3}	0.4	.19	2.1
8.99×10^{-4}	9.3	.71	13.4
6.5×10^{-4}	2.9	.32	9.2
4.57×10^{-4}	1.4		
1.68×10^{-4}	2.0		
5-l. avg. (18)	2.0	0.3	6.6
1-l. avg. (18)	27.0	11.5	2.4
100-ml. avg. (14)	7.3	3.5	2.1

^a The number of points included in each average is shown in parentheses. ^b Limits of error on k_2 and k_3 are about a factor of two for the 5-l. vessel and a factor of five for the 1-l. and 100-ml. vessels. ^c Limits of error on the ratio are about a factor of two for all three vessels.

Any differences are within the limits of experimental error.

If the reaction forming ethylene is first order and the reactions forming propylene and 1-butene are zero

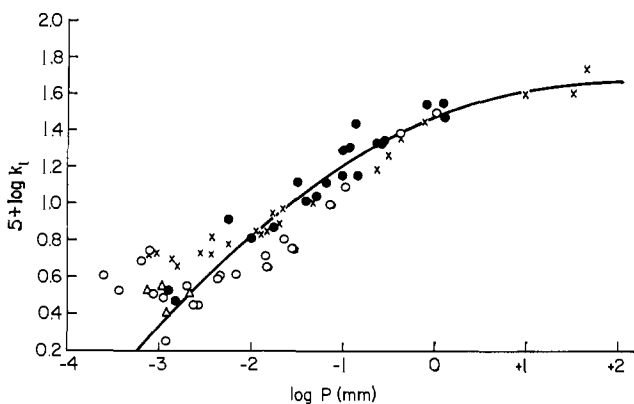


Fig. 1.—First-order rate constant for the formation of ethylene as a function of pressure. The curve is obtained by the Kassel theory with $s = 14$ or by the Slater theory with $n = 16$. O, 5-l. reactor; Δ , 5-l. reactor with N_2 added before sampling; \bullet , 1-l. reactor; \times , 100-ml. reactor.

order, the following integrated rate expressions are obtained

$$k_1 t = \ln \left(\frac{k_1 [\text{cyclo-C}_4\text{H}_8]_0 + k_2 + k_3}{k_1 [\text{cyclo-C}_4\text{H}_8] + k_2 + k_3} \right)$$

$$k_2 t = \frac{3}{4} [\text{C}_3\text{H}_6]$$

$$k_3 t = [1-\text{C}_4\text{H}_8]$$

where t is the time of reaction, and square brackets indicate partial pressures in mm. If the only products of the reaction are these three compounds, a material balance gives

$$[\text{cyclo-C}_4\text{H}_8]_0 = [\text{cyclo-C}_4\text{H}_8] + \frac{1}{2} [\text{C}_2\text{H}_4] + \frac{3}{4} [\text{C}_3\text{H}_6] + [1-\text{C}_4\text{H}_8]$$

These equations were used in an iterative procedure to obtain k_1 . Usually the term $k_2 + k_3$ was small, so that one iteration was sufficient to obtain k_1 within 1% error. No trend in k_1 was observed as the degree of decomposition was varied from 3 to 80%, indicating that the formation of ethylene was first order.

The k_1 was also calculated on the assumption that the reactions forming propylene and 1-butene were first order; the results differed insignificantly from the ones calculated assuming zero-order reactions.

The temperature dependence of k_1 in the range from 398 to 450° at pressures from 10 to 40 mm. was briefly studied, and the first-order rate constant was found to obey the expression

$$k_1 = 10^{15.3} \pm 0.8 e^{-61,7000 \pm 2900 \text{ cal.}/RT} \text{ sec.}^{-1}$$

which is consistent with the results obtained by previous workers.²⁻⁵ The first-order rate constant was also measured at temperatures near 449° in the pressure range from 43 down to 1.7×10^{-4} mm. The rate constant was corrected to 449° using the Arrhenius expression, and the results are listed in Table I.

Figure 1 shows the experimental values of k_1 as a function of pressure in the three reactors. The solid curve was calculated as described in the Discussion section. The high pressure limiting rate constant k_∞ was found to be $4.9 \times 10^{-4} \text{ sec.}^{-1}$, by extrapolating⁸ a plot of k_1^{-1} as a function of $p^{-1/2}$. This agrees with measurements made by Walters and co-workers³ at pressures up to 1000 mm. The data obtained by Vreeland and Swinehart⁵ by mass spectrometry are much more precise than our data, and fall within our limits of error.

Conclusions

The decrease in the first-order rate constant of a unimolecular reaction as the pressure is decreased may be described by the classical theories of unimolecular reactions.⁶ By choosing proper values of the adjustable

parameters, curves of comparable shape can be obtained from either the Kassel or the Slater theory.¹⁴ According to the Kassel theory, the rate constant at any pressure is given by

$$\frac{k}{k_\infty} = I_s \left(\frac{\omega}{A} \right) = \frac{1}{(s-1)!} \int_0^\infty \frac{x^{s-1} e^{-x} dx}{1 + \frac{A}{\omega} \left(\frac{x}{b+x} \right)^{s-1}}$$

where A is the pre-exponential factor in the Arrhenius expression for k_∞ , s is a fall-off parameter, identified as the number of effective oscillators, E_0 is the activation energy for k_∞ , $b = E_0/RT$, $\omega = (4\pi\sigma^2 NP/RT) \cdot (\pi RT/M)^{1/2}$ is the frequency of collisions at pressure P , σ is the collision diameter of the molecule.

The curve in Fig. 1 was calculated using the following values of the parameters: $A = 2 \times 10^{15} \text{ sec.}^{-1}$; $k_\infty = 4.9 \times 10^{-4} \text{ sec.}^{-1}$; $s = 14$; $E_0 = 61,700 \text{ cal.}$; and $\sigma = 5.5 \times 10^{-8} \text{ cm.}$ The collision diameter was assumed to be approximately the diameter of the molecule, since deactivation probably occurs on every collision, and s was adjusted to give the best fit to the data. Vreeland and Swinehart⁵ obtained the best fit to their data using $s = 18$, but they used higher values of A and E_0 . Their curve is nearly identical with the one in Fig. 1.

According to the classical form of Slater's theory, the rate constant at any pressure is given

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

The fall-off parameter n is the number of normal vibrational modes participating in the decomposition, and

$$\theta = \frac{\omega}{\nu} f_n b^{(n-1)/2}$$

where ν is one-fourth the pre-exponential factor A if the critical coordinate is the breaking of a carbon-carbon bond, and f_n is a factor which is usually between 10 and 10^3 for a fairly complex molecule.⁶ A curve indistinguishable from that drawn in Fig. 1 can be obtained if n is taken to be 16 and f_n is taken to be 120.

At pressures below 10^{-3} mm., the experimental rate constants are larger than those predicted theoretically. Furthermore, the rate constants measured in the 100-ml. reactor are larger than those measured in the 1-l. or 5-l. reactors and deviate from the theoretical curve at higher pressures. Although the data scatter badly, it appears as if a limiting rate is reached at sufficiently low pressures. A similar result was obtained by Vreeland and Swinehart.⁵

The most obvious explanation for a low-pressure limiting rate is that the molecules which decompose are activated by collisions with the walls of the vessel instead of by collisions with other molecules. At the pressure where the rate begins to level out the mean free path of a cyclobutane molecule is about the same order of magnitude as the diameter of the vessel. The fact that the low pressure limiting rate is higher in the smaller reaction vessel also supports this explanation.

However, Vreeland and Swinehart⁵ have measured the rate constant at pressures from 10^{-3} to 10^{-2} mm. in a vessel packed with glass wool, which increases its surface area by a factor of 20. They have found that the rate is no more than 20% higher in the packed vessel than in the unpacked vessel. This result argues against wall activation as an explanation of the low-pressure limiting rate, since it indicates that collisions with the wall are very much less efficient for activation than collisions with other molecules.

(14) E. W. Schlag, B. S. Rabinovitch, and F. W. Schneider, *J. Chem. Phys.*, **32**, 1599 (1960).

Two other factors which could cause an apparent leveling-out of the rate at low pressures can probably be discounted. The diameter of the connecting tubing was large enough that thermal transpiration corrections were small, and these corrections were made where necessary.

Another possible factor could be inhomogeneous sampling. Because cyclobutane has twice the molecular weight of ethylene, it would diffuse less rapidly, and a sample obtained at low pressures might be expected to be richer in ethylene than the mixture in the reactor. To test this idea, the time of sampling at 10^{-3} mm. pressure was varied from 20 sec. to 10 min., without any systematic variation being observed in the measured rate constant. In another series of tests at 10^{-3} mm. pressure, the reactor was filled with pre-purified nitrogen, just before sampling, to a pressure of about 10 mm. These points are indicated by triangles on Fig. 1. The rate constant was the same within experimental error as when no nitrogen was used. Thus the sampling procedure could not account for the low-pressure limiting rate.

Thus, the low-pressure limiting rate does not seem to have a simple explanation. It may merely be that under such conditions, the classical theory of unimolecular reactions no longer applies.

The reactions forming propylene and 1-butene are probably wall reactions, as indicated by the fact that they are zero order. Within experimental errors the rate constant in the 100-ml. vessel could be 10 times the rate constant in the 5-l. vessel (see Table II). If a homogeneous first-order reaction forming propylene or 1-butene occurs, its high pressure limiting rate is less than 5×10^{-4} times the rate of the reaction forming ethylene. Study of such a reaction would be very difficult because in any reactor of reasonable size, the surface reactions are more rapid than the homogeneous reaction. It is probable that no homogeneous reaction forming propylene or 1-butene occurs.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE UNIVERSITY OF OREGON, EUGENE, OREGON]

A Mass Spectrometric Investigation of the Thermal Decomposition of Cyclobutane at Low Pressures¹

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The decomposition of cyclobutane has been investigated over the temperature range 410 to 500° and a pressure range of 0.5 μ to 20 mm. by a mass spectrometric technique. The reaction is accurately first order over the whole range of pressures and temperatures. The experimental data are fit by the Kassel integral using $E_0 = 63,200$ cal./mole and an effective 18 oscillational modes. The data show an anomalous departure from curves calculated from the Kassel integral below 20 μ , the rate constants being too large. This is not a surface effect as judged from packed flask measurements and it is suggested that cyclobutane decomposes *via* two competing mechanisms.

Introduction

The bulk of the data in the literature on unimolecular decompositions has been obtained simply by following the total pressure change with time. If the stoichiometry of the reaction is simple and unique, data obtained by this method may be an accurate and reliable measure of the actual rate of decomposition of the parent molecule. However, if the reaction is, in fact, complicated by successive or parallel reactions among the products and/or the products and parent molecule, simply following the total pressure with time may be misleading and not be a measure of the actual decomposition rate at all. What is needed is a method of measuring the partial pressure of the parent molecule irrespective of processes which occur after the initial decomposition.

Most data exist in the pressure range approximately from 1 mm. to 1 atm. Data are seriously needed over a much wider pressure range and particularly at lower pressures.

Consider the following experimental technique designed to provide data satisfying these requirements. Suppose the molecular leak conventionally used to introduce gas samples into a mass spectrometer is removed from the spectrometer ion source and is sealed directly into a reaction vessel and connected to the ion source of a mass spectrometer by a longer path than is usually used. Suppose a decomposition reaction occurs in the reaction vessel. All products will have

molecular weights less than that of the product molecule and the peak intensity of the parent peak of the parent molecule will be a unique measure of the partial pressure of the parent molecule irrespective of the subsequent reactions among the products, providing only that two conditions are met. First, the products must not isomerize or polymerize to yield molecules of equal or larger molecular weight than the parent substance and, second, flow through the leak must be molecular flow and not viscous flow. Then the peak intensity of the parent peak will be directly proportional to the partial pressure of the parent substance.

This paper is written to report the application of this technique to the decomposition of cyclobutane in the pressure range from 0.5 μ to 20 mm. Future reports will be made on the investigation of more complex systems.

This reaction has been investigated by the pressure change method by Genaux and Walters³ and by Genaux, Kern, and Walters⁴ in the pressure range 1 to 996 mm. and over the temperature range 420 to 468°. They found that the reaction is homogeneous and yields ethylene stoichiometrically. They report that the rate constant at 1 mm. is approximately two-thirds of the value obtained at pressures above 100 mm. Pritchard, Sowden, and Trotman-Dickenson⁵ have studied the composition at one temperature (448.4°) down to 57 μ

(3) C. T. Genaux and W. D. Walters, *J. Am. Chem. Soc.*, **73**, 4497 (1951).

(4) C. T. Genaux, F. Kern, and W. D. Walters, *ibid.*, **75**, 6196 (1953).

(5) H. O. Pritchard, R. G. Sowden, and A. P. Trotman-Dickenson, *Proc. Roy. Soc. (London)*, **A218**, 416 (1953).

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(2) To whom inquiries should be addressed.