

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. F. Trotman-Dickenson, *Proc. Roy. Soc. (London)*, **A218**, 416 (1953).

(1) Supported by Atomic Energy Commission Contract AT(45-1)-432.

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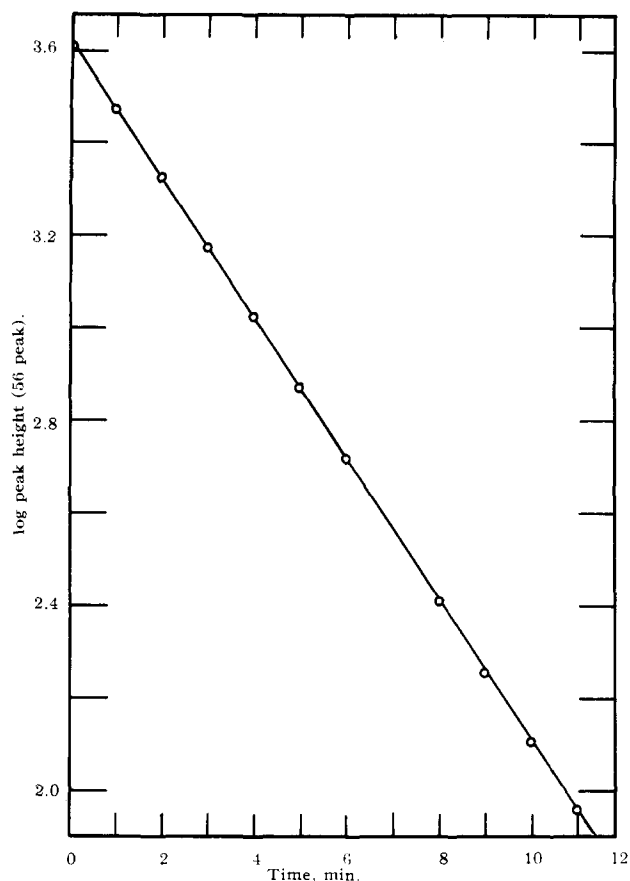


Fig. 1.—Representative kinetic run: Initial pressure, 1350 μ ; T , 500.1°; k , 5.66×10^{-3} sec. $^{-1}$. Time covers about six half-lives.

pressure and have studied the collisional activation efficiency of a considerable variety of added gases.

Experimental

The cyclobutane was purchased from the Fabian Chemical Co., Montreal. Mass spectrometric and gas chromatographic analysis showed the material to contain 3% of *n*-butane as the only detectable impurity.

The *n*-butane was removed gas chromatographically using a large column 2 in. in diameter and 12 ft. long packed with the detergent "Tide."

The mass spectrometer was a conventional Nier-type 60° deflection mass spectrometer constructed in this Laboratory. The spectrometer tube was mounted in a separate chassis with minimum equipment around it so that the thermostat containing the reaction vessel could be positioned as closely as possible to the spectrometer tube. The accelerating voltage (2500 v.) and magnet supplies were electronically regulated to 1 part in 10^4 and the room was thermostated to better than 1° by an air conditioning unit to improve the regulation and stability of the supplies. The filament emission in the ion source was regulated to about 0.1%. The electrometer was a very nearly 100% feedback amplifier with an input impedance of 10^{12} ohms and an output impedance of about 3×10^4 ohms providing a voltage gain of unity but a power gain of 3×10^7 . The amplifier was linear as the resistors and had a sensitivity of about 3 or 4×10^{-16} amp. per scale division of the Leeds and Northrup Micromax recorder driven by the output.

The leaks were all Pyrex and were constructed in this Laboratory. No metal surfaces were exposed to the reacting system. All leaks were tested over the pressure range for which they were used to ensure linearity of response of the spectrometer, *i.e.*, that the flow through them was molecular.

Several reaction flasks with corresponding leaks were used to cover various pressure ranges. In the highest range a 1-l. flask was used. Two 2-l. flasks were used in the intermediate and lower ranges and three 13-l. flasks were used for the measurements at the lowest pressures.

Loss of gas *via* leak-out to the spectrometer was entirely negligible at the higher pressures. It became significant, however, at the lower pressures. Leak-out was first order and is represented by the equation from kinetic theory (eq. 1)

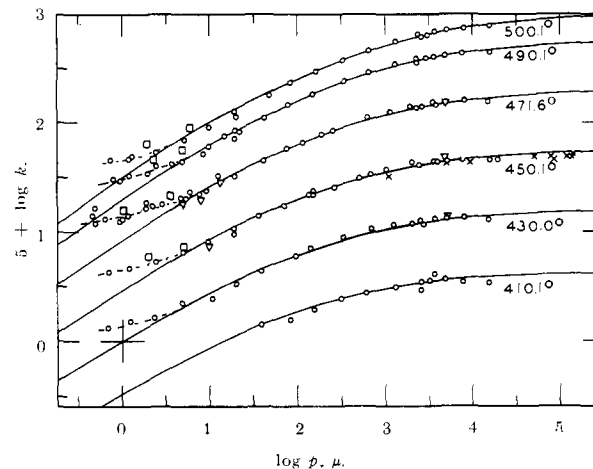


Fig. 2.—Pressure dependence of the rate constant. Solid curves calculated from the Kassel integral: ∇ , added gas runs; \square , packed flask runs; \times , data of Walters, *et al.*,^{3,4} measured at 449°. These data were *not* corrected to 450.1°.

$$-\frac{dN}{dt} = \frac{\bar{c}A}{4V}N = k'N \quad (1)$$

where N is the number of molecules in the flask, \bar{c} is their average thermal velocity, A is the area of the leak, and V is the volume of the vessel. Since A was never known with any accuracy, the value of k' was measured directly using *n*-butane as the gas at temperatures where its own decomposition was negligible. The values of k' were corrected to the molecular weight of cyclobutane and the temperatures used for the decompositions using the parameters in the above equation. Leak-out constants so determined varied from 0.1×10^{-3} sec. $^{-1}$ to 3.0×10^{-3} sec. $^{-1}$ and were applied as corrections wherever significant. The largest corrections never comprised over 30% of the measured rate constants at the very lowest pressures and in nearly all cases were much smaller than this.

Initial pressures for each run were calculated by expansion between known volumes, making correction for the difference in temperatures and requiring material balance. The volume ratios used were large enough that any errors due to thermal transpiration were reduced to negligible amounts. Initial pressures outside the reaction vessel before expansion were measured directly by a mercury manometer for higher pressures or by a micromanometer, manufactured by Consolidated Electroynamics Corp., for lower pressures.

The kinetic measurements were made by focusing the spectrometer on the 56 peak and plotting its intensity continuously as a function of time directly on a Leeds and Northrup Micromax recorder.

The dead space did not exceed 15 cc. and resulted in a negligible correction for all the flasks used.

The thermostat was an air bath so designed that the heaters were not in the same compartment with the reaction flask. The air was stirred rapidly by a fan, recirculating the air over the heaters and back over the reaction vessel. The bulk of the power necessary to maintain the operating temperature was supplied directly from the power lines *via* a Variac. The remainder of the power was fed to hand-wound heaters of low heat capacity by a GL-5557 thyatron. The sensing element in the thermostat was a nickel wire resistance thermometer which was wired as one arm of a resistance bridge. A 60-cycle signal was fed to the bridge and the output signal was amplified, and its phase shifted 90° by a suitable capacitance circuit. This signal controlled the firing cycle of the thyatron so that power was fed to the control heaters in proportion to the error of the temperature from the mean temperature. By this means, the temperature at one point in the thermostat could be controlled to $\pm 0.05^\circ$ as measured by a Leeds and Northrup platinum resistance thermometer, calibrated by the National Bureau of Standards, and a Mueller bridge. Gradients across the effective working volume of the thermostat were several times larger than this but were not larger than 0.3°. Presumably gradients across the flask (inside) were less than this.

Temperatures were also measured by an alumel-chromel thermocouple in a thermocouple well sealed into the reaction flask close to the molecular leak. The thermocouple was calibrated at 0, 100°, and at the boiling point of mercury. Since the thermocouple and platinum resistance thermometer (the latter outside the flask) always agreed to better than 0.05°, during most of the measurements the use of the thermocouple was discontinued.

TABLE I
 FIRST-ORDER RATE CONSTANTS FOR CYCLOBUTANE DECOMPOSITIONS

p, μ	Flask	$k \times 10^6,$ sec. ⁻¹	p, μ	Flask	$k \times 10^6,$ sec. ⁻¹	p, μ	Flask	$k \times 10^6,$ sec. ⁻¹	p, μ	Flask	$k \times 10^6,$ sec. ⁻¹
683.3°K.						744.8°K. (contd.)					
15800	A	3.39	1380	B	3.12	2000	A	141	3.01	D	17.7
7740	A	3.49	636	B	2.76	1210	B	128	2.34	C	17.0
5050	A	3.66	330	B	2.44	636	B	112	2.00 ^a	E	18.7
3780	A	4.14	160	B	1.95	257	B	84.6	1.90	D	16.3
3310	A	3.63	87.2	B	1.57	194	B	77.0	1.19	C	13.9
2700	B	2.98	41.1	B	1.41	119	B	65.6	1.04 ^d	E	13.0
2630	A	3.54				77.9	B	57.8	0.99	D	12.2
703.2°K.						763.3°K.					
15900	A	13.1	143	B	7.29	40.5	B	44.5	0.66	C	13.0
8150	A	13.8	98.5	B	6.08	20.2	C	32.2	0.52	D	11.9
5200	A	13.5	40.0	B	4.41	18.0	B	31.7	0.47 ^c	E	13.9
3760	A	13.3	20.4	B	3.42						
2820	B	11.8	11.4	C	2.45	16100	A	452	20.4	D	87.3
2550	A	12.8	5.00	C	2.21	7600	A	435	20.2	C	70.2
2040	A	12.0	2.36	C	1.63	4870	A	420	15.0	D	75.3
1230	B	11.8	1.23	C	1.53	3640	A	397	10.1	C	60.4
703	B	10.7	0.71	C	1.32	3000	A	394	8.82	D	51.9
337	B	8.93				2970	B	370	5.02	C	43.9
723.3°K.						773.3°K.					
20100	A	44.6	163	B	23.3	2460	A	389	3.78	D	42.0
16300	A	45.7	160	A	22.8	1350	B	343	2.54	C	39.8
7860	A	45.3	137	B	21.9	653	B	291	2.02	D	34.3
5160	A	45.1	72.0	B	17.2	337	B	240	1.25	C	32.4
4090	A	43.5	38.0	B	14.3	153	B	183	0.97	D	29.4
3700	A	44.9	19.8	C	9.62	85.7	B	148	.81	C	30.3
2540	B	41.3	19.1	B	10.6	41.0	B	109	.50	D	16.7
2060	A	43.5	10.0	C	8.28	22.8	B	83.2			
1075	B	36.8	5.05	C	6.42						
695	A	33.5	2.48	C	5.31	16200	A	774	86.6	B	233
509	B	31.4	1.21	C	4.66	8140	A	736	50.2	B	176
273	B	25.2	0.72	C	4.32	5140	A	715	20.8	C	114
744.8°K.						773.3°K.					
16200	A	156	13.2	D	32.8	3720	A	671	19.8	B	127
8240	A	158	9.40	C	24.0	3070	A	643	10.1	C	89.6
4040	A	148	8.03 ^b	E	22.0	2680	B	611	5.05	C	68.6
3680	A	154	6.18	D	23.0	2420	A	644	2.50	C	53.0
2750	B	140	5.56	C	20.6	1350	B	566	1.30	C	49.5
2350	A	140	4.96 ^c	E	20.7	669	B	454	1.23	C	47.0
						334	B	374	0.74	C	45.7
						168	B	292			

Nominal flask sizes: A, 1 l.; B, 2 l.; C, 2 l. (different flask and different leak than B); D, 13 l.; E, new 13-l. flask and new leak. ^a 1st run in new flask, E. ^b 2nd run in new flask, E. ^c 1st run after seasoning flask E in C₂H₄. ^d 2nd run after seasoning flask E in C₂H₄. ^e 3rd run after seasoning flask E in C₂H₄.

Results

Figure 1 shows a plot of the logarithm of the peak height of the 56 peak as a function of the time for a representative run. It is seen that the plot is accurately linear over at least six half-lives and has been found to be so over three more half-lives, showing that the actual rate of disappearance of cyclobutane was accurately first order over the whole course of the decomposition. This was true at all pressures. The standard deviations of the slopes for the faster runs were generally 1% or less. For the slower runs the scatter was greater, generally not greater than 2 or 3%. Reproducibility of duplicate runs was poorer by about a factor of two and a few deviations of 10% were observed.

Table I shows the results of 136 runs made at six temperatures in the range 410 to 500°. Table II shows the results of 15 runs made either in a flask packed with enough Pyrex glass wool to increase the surface area at least 20-fold or with certain foreign gases added. The data are represented in Fig. 2 in the form of a plot of $\delta + \log k$ vs. $\log p$, where p is the initial

pressure in microns. In plotting the points for the added gas runs, the total pressure was used.

Mass spectrometric and gas chromatographic measurements indicated that the product was about 99.8% ethylene. The gas chromatograms using a silicone column showed two very small additional peaks whose retention times corresponded to propane and *n*-butane, although no certain identification was made. The peak area corresponding to propane was about three times that of the other peak and the sum of the two was estimated to be about 0.2% of the ethylene peak. An average of several measurements showed that not more than 0.03% of the gas remaining after ten or more half-lives was left after condensation in liquid air. Thus, no appreciable amount of H₂ was produced. The peak intensity at the 56-peak dropped to zero after 10–15 half-lives. There was no evidence of isomerization to 1-butene at any pressure.

Discussion

The experimental data were fit by the Kassel integral⁶ (eq. 2)

(6) L. S. Kassel, *J. Phys. Chem.*, **32**, 225 (1928).

$$k = \frac{k_{\infty}}{(RT)^s \Gamma(s)} \int_0^{\infty} \frac{z^{s-1} e^{-z/RT} dz}{1 + \frac{ART}{a\beta N} \left[\frac{z}{z + E_0} \right]^{s-1}} \quad (2)$$

where $z = E - E_0$, the energy in excess of the activation energy. E_0 is the activation energy, $A = k_{\infty} e^{+E_0/RT}$, s is the effective number of vibrational modes contributing to the decomposition, $a = 4\sigma^2(\pi kT/m)^{1/2}$, σ being the collision diameter, and β is the pressure.

TABLE II
PACKED FLASK AND ADDED GAS RUNS

Temp., °K.	Flask ^a	p, μ	$k \times 10^6$, sec. ⁻¹
Packed flask runs			
724.3	F	5.04	7.53
724.3	F	2.03	5.86
744.8	F	3.75	21.9
744.8	F	1.06	15.7
763.2	F	5.03	55.7
763.2	F	2.36	46.7
773.1	F	6.10	89.2
773.1	F	1.98	64.9
Nitric oxide (50 mole %)			
703.2	A	5150	13.8
723.3	C	10.4	7.50
744.8	A	5180	154
744.8	C	5.25	17.6
Propylene (50 mole %)			
723.3	A	4910	49.2
Air (10 mole %)			
744.8	C	8.51	19.9
Water vapor (20 mole %)			
744.8	C	14.1	28.5

^a Flask F, 13 l., packed with Pyrex glass wool to increase surface 20-fold.

IBM 704 computers at Los Alamos, New Mexico, and later an IBM 1620 at the University of Oregon, were coded to compute values of this integral by numerical integration.

Using initial estimates of E_0 and A from the data at our highest pressures, values of the integral were computed for a series of values of s and σ at one temperature. Fits were made visually on large-scale plots. An excellent fit at one temperature was obtained using $s = 18$ and $\sigma = 6 \text{ \AA}$. With all the parameters thus assigned, calculation at the other temperatures revealed that the calculated curves were closer together throughout the whole pressure range than were the experimental curves. This indicated that the initially chosen value of E_0 was too small as might have been expected. New integrals with larger values of E_0 were computed and excellent fits were obtained at all temperatures in the pressure range 16 mm. to 20 μ .

These computed integrals are shown as the solid curves in Fig. 2. The final values of the parameters and the computed values of the integrals are tabulated in Table III.

Attempts to extrapolate k to infinite pressure *via* a plot of $1/k$ vs. $1/p$ yielded too low a value of E_0 also. It appears that there are inherent errors in this extrapolation and it seems far better to adopt a value of E_0 which will yield a good theoretical fit over as wide a pressure range as possible. Thus, we choose $E_0 = 63,200$ cal./mole as a much more reliable value. This value is to be compared to that reported by Walters and co-workers,^{3,4} obtained by measurements at higher pressures by the pressure change method. They obtained $E_0 = 62,500$ cal./mole.

TABLE III

$E_0 = 63,200 (\pm 300)$ cal./mole
 $s = 18$
 $\sigma = 5.8 \text{ \AA}$
 $A = 7.02 (\pm 0.10) \times 10^{15}$

p, μ	$(s + \log k)$ at 7°K.					
	683.3°	703.2°	723.3°	744.8°	763.2°	773.3°
1.00	-0.476	+0.014	0.476	0.937	1.037	1.501
3.16	- .252	.246	.717	1.188	1.565	1.763
10.0	- .053	.455	.935	1.415	1.800	2.003
31.6	+ .119	.638	1.127	1.617	2.011	2.217
100	.265	.793	1.293	1.793	2.195	2.406
316	.383	.921	1.430	1.940	2.350	2.566
1000	.474	1.020	1.539	2.059	2.477	2.698
3160	.539	1.094	1.620	2.149	2.575	2.800
10000	.582	1.143	1.677	2.213	2.646	2.875
∞	.632	1.204	1.750	2.301	2.748	2.985

From the value $A = 7.02 \times 10^{15}$ sec.⁻¹ and the relation⁷

$$A = e(kT/h)e^{+\Delta S^*/R}$$

a value of ΔS^* of 10.2 cal./deg. at 450° is calculated.

From the variation of the fits with change in E_0 we estimate the precision in this parameter to be ± 300 cal. and the precision in A to be about $\pm 0.10 \times 10^{15}$ sec.⁻¹.

It is significant to note that the data of Pritchard, Sowden, and Trotman-Dickenson⁵ at one temperature show a faster fall-off of k with pressure than do the present data and they would require an anomalously small value of the parameter s to fit their data.

It is inherent in the derivation of the Kassel integral that the assumption is made that all activated molecules are deactivated at the first subsequent collision (unless decomposition intervenes). It is not at all clear that this assumption is valid. On the one hand, evidence from ultrasonic measurements⁸ indicate that many collisions are required to de-excite vibrationally excited molecules. On the other hand, for kinetic purposes in decomposition reactions, deactivation need mean the loss of only a relatively small fraction of the vibrational energy for the molecule to be deactivated, *i.e.*, unreactive. This observation tends to support the idea of 100% efficient deactivation by collision.

To find out if the Kassel theory could throw any light on this question, new values of the integral were calculated for $s = 30$, the total number of modes possible for cyclobutane. The value of σ was then decreased to obtain the best possible fit to the experimental data. A value $\sigma = 0.45 \text{ \AA}$ was finally chosen. The values of the Kassel integral calculated with these parameters are shown in Table IV. Comparisons with values in Table III shows that these values also fit the experimental data down to about 20 μ within the limits of the scatter and do so as well as the values with $s = 18$ and $\sigma = 5.8 \text{ \AA}$. The ratio $(5.8/0.45)^2 = 166$ can be interpreted as meaning that nearly 200 collisions are needed to deactivate a molecule and that all modes are involved in the decomposition. This assumption fits the data just as well as the assumption of 100% deactivation efficiency and a lesser number of modes being effective. It is apparent that direct measurements of rate constants cannot distinguish between these two extremes, at least in the available pressure range. The

(7) S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

(8) Many investigators have found collision numbers in the range 10^4 to 10^6 for decay of vibrationally excited CO₂. For an extensive review, see T. L. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases," Butterworth and Co. (Publishers) Ltd., London, 1961. Also see F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **84**, 4215 (1962), for an extensive discussion of energy transfer.

TABLE IV

$E_0 = 63,200$ cal./mole
 $s = 30$
 $\sigma = 0.45$ Å.
 $A = 7.02 \times 10^{18}$ sec.⁻¹

p, μ	$(5 + \log k)$ at 5°K.					
	683.3°	703.2°	723.3°	744.8°	763.2°	773.3°
1.00	-0.343	+0.125	0.564	0.999	1.344	1.524
3.16	-.148	.333	.783	1.229	1.585	1.770
10.0	+.025	.518	.980	1.439	1.805	1.996
31.6	.175	.680	1.155	1.626	2.002	2.199
100	.301	.819	1.305	1.790	2.177	2.379
316	.404	.933	1.432	1.928	2.326	2.534
1000	.484	1.023	1.533	2.042	2.450	2.664
3160	.542	1.091	1.611	2.131	2.549	2.768
10000	.581	1.139	1.667	2.197	2.623	2.847
∞	.632	1.204	1.750	2.301	2.750	2.985

two sets of curves calculated with $s = 18$ and $s = 30$ are not identical, however, the latter having slightly less curvature. The two sets of curves would be increasingly farther apart at still lower pressures, the one for $s = 30$ being above the one for $s = 18$ at lower pressures. If measurements could be made to yet lower pressures, without trouble from surface effects, it might be possible to distinguish between these two points of view and to throw some light on the question of efficiency of collisional deactivation.

Perhaps the most interesting point about the data is the departure of the data from theory below 20 μ . At all temperatures the rate constants appear to be too high. In fact, a close examination of Fig. 2 suggests that the experimental data show an inflection point at approximately 10 μ .

Since at this pressure it is approximately true for a 13-l. spherical flask that half the collisions of each molecule are with the walls and half are intermolecular, one immediately suspects a surface reaction.

A flask was packed with enough washed Pyrex wool to increase the surface area by at least 20-fold. The measurements in this flask are shown in Table II and as squares on Fig. 2. Rate constants from half these runs fall within the limits of the scatter of the constants from the runs in unpacked flasks. The largest deviation observed was 20% increase in k . This argues that, for the unpacked flasks, not more than 1% of the reaction was a reaction on the wall. Further, it is not possible to distinguish data obtained at low pressures in 2-l. and in 13-l. flasks. It does not seem reasonable that so little wall reaction could account for the observed deviation of the experimental rate constants from the Kassel curves by more than a factor of two at 0.5 μ .

To find if the wall was conditioned⁹ by previous re-

actions in the flask, a factory-new flask (flask E) was prepared and two runs were made at low pressures. Then the flask was conditioned by filling it with 15 mm. of cyclobutane and heating overnight at 745°K. Then the next three runs were made at low pressures. No significant differences were observed in the values of k obtained. These five runs are indicated in Table I.

It has been suggested by Rabinovitch¹⁰ that a possible explanation of the low pressure behavior of k could be that cyclobutane decomposes *via* two paths. If one path involves a different number of oscillational modes than does the other, then one rate constant would decrease with pressure at a different rate than the other. The two curves might cross at about 10 μ .

The two paths might be (1) rupture of one bond and then rupture of the second a number of oscillational cycles later and (2) simultaneous rupture of two bonds, *i.e.*, within about one vibrational cycle. The latter might be visualized as involving more oscillational modes and so k for this process should decrease more slowly than k for the first process. This implies that the higher pressure process would proceed *via* the tetramethylene free radical.

Decompositions carried out with added gases, particularly NO, showed no inhibition of the reaction. The rate corresponded to the rates in pure cyclobutane if the constants were plotted using the total pressure instead of the partial pressure of cyclobutane. The effect of added water vapor was investigated due to the impossibility of removing the last traces of water vapor from glass vessels. Neither water vapor nor air changed the rate constants, compared on a total pressure basis.

Lack of inhibition by NO does not argue for the absence of free radicals and so against the mechanism given earlier. It only argues that the free radicals, if present, do not react with the parent molecule. The data suggest that the collisional efficiencies for activation of the parent molecule by all these added gases is quite high, nearly as high as for cyclobutane itself.

If the decomposition does proceed *via* two competitive mechanisms, this would argue in favor of a high collisional deactivational efficiency and the participation of less than the maximum number of oscillational modes in the mechanism chiefly responsible for the decomposition above 20 μ .

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