Unimolecular Reactions of Methylcyclobutane at Low Pressures

Timothy F. Thomas, Paul J. Conn, and D. F. Swinehart[1]

Contribution from the Department of Chemistry, University of Oregon, Eugene, Oregon 97403. *Received June 2, 1969*

Abstract: The thermal decomposition of methylcyclobutane has been investigated over the temperature range 410–490° and a pressure range 1×10^{-4} to 10 Torr by a mass spectrometric technique. The principal products are ethylene and propylene, but isomerization to 1-pentene accounts for 0.5–1.8% of the reaction. The reaction shows evidence of activation and deactivation by wall collisions below 10 μ. A modified form of the Kassel integral is presented which fits the data very well, using E_0 = 63.1 kcal/mole and an effective 26 oscillational modes. It is found that the collisional deactivation efficiencies for intermolecular and wall collisions are in the ratios 0.7 and 1.0.

Das and Walters[2] and Pataracchia and Walters[3] have reported investigations of the decomposition of methylcyclobutane over the pressure range 3×10^{-3}–417 Torr and Arrhenius parameters $A = 4.4 \times 10^{15}$ sec^{-1} and $E_0 = 62.0 \pm 0.5$ kcal/mole. The reaction products were principally ethylene and propylene, the reaction was homogeneous, and the first-order rate constant was practically invariant at pressures above 1 Torr.

Reported herewith is a more comprehensive study of this reaction extending the pressure range from the lower limit of Das and Walters to 1×10^{-4} Torr and the temperature range from 410 to 490°.

The method used to follow the reaction was that of Vreeland and Swinehart.[4] A molecular leak was sealed directly into the reaction flask which fed a tiny fraction of the reacting mixture into the ion source of a mass spectrometer where the intensity of the parent peak of methylcyclobutane at m/e 70 was monitored continuously during a run on a strip-chart recorder. This intensity was a direct measure of the partial pressure of the parent molecule irrespective of the nature or pressure of product molecules except for a small perturbation noted below.

Experimental Section

The methylcyclobutane was prepared by the hydrogenation of methylenecyclobutane over platinum in glacial acetic acid as solvent.[5] The product was purified by passage through an 8-ft length of 1.25-in. o.d. aluminum tubing packed with silicone stopcock grease adsorbed on Chromosorb using helium as the carrier gas. The product was collected in a liquid nitrogen trap and the impurities were vented to the atmosphere. Analytical gas chromatograms showed no observable impurities except for 0.1% *n*-pentane.

The mass spectrometer, associated equipment, leaks, thermostat, and temperature-measuring equipment were described by Vreeland and Swinehart.[4] In particular, temperatures were measured with a platinum resistance thermometer certified by the National Bureau of Standards.

Five reaction flasks and leaks were used in this work. All had volumes a little less than 13 l. except for one 1-l. flask used at the highest pressures.

Gas was introduced into the reaction vessels by expansion between known volumes at known temperatures. Pressures were measured in the external volume before and after expansion using a Consolidated Electrodynamics Corp. micromanometer, a Dubrovin gauge, or a mercury manometer and cathetometer according to the pressure range in each case. Thermal transpiration became increasingly important as the pressure decreased. By requiring a material balance, *i.e.*, by equating the number of moles of gas before and after expansion, the following equation was derived

$$p = \frac{V_o T_r}{V_r T_o}(p_i - p_f) \tag{1}$$

where V_o and T_o are the volume and temperature of the gas pipet outside the thermostat; V_r and T_r are the volume and temperature of the reaction flask. p_i and p_f are the initial and final pressures in the pipet. Knowing the volumes and temperatures and measuring p_i and p_f for each run gave a calculated pressure, p, in the flask independent of thermal transpiration. Dead-space corrections were not applied since the dead space was only about 15 ml for a reaction flask of about 12,600 ml.

Since gas was lost continuously to the spectrometer, leak-out corrections were applied by subtracting the leak-out constants from the measured constants to obtain the true rate constants. The leak-out is represented by eq 2 from kinetic theory, where p is the

$$-\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{\bar{c}A'}{4V}p = k_{1.\mathrm{o}}p \tag{2}$$

partial pressure of the parent molecules in the flask, $\bar{c}$ their average thermal speed, A' the area of the leak, and V the volume of the vessel. $k_{1.\mathrm{o}}$ was measured directly using an inert gas, generally *n*-butane at 350° where its decomposition was not measurable. This measured $k_{1.\mathrm{o}}$ was corrected to the temperature of reaction and the molecular weight of the parent molecule by means of the parameters in eq 2.

Results

Table I shows the results of 110 runs made at five temperatures from 410 to 490°. Table II shows the results of 18 runs in a flask packed with enough Pyrex glass wool to increase the surface area more than 20-fold. Table III shows similar results of five runs in a flask packed with glass tubing. Table IV shows the results of 10 runs with various gases added to the methylcyclobutane.

Figure 1 shows a typical plot of the logarithm of the peak height *vs.* time for one run, at 195 μ and 490°, and shows the correction for the isomerization to 1-pentene (see below).

Discussion

Plots of the logarithm of the peak heights *vs.* time were quite linear over one half-life, but longer runs over three to six half-lives showed curvature corresponding to an apparent slowing of the reaction. The peak intensities did not go to zero after ten or more half-lives indicating that some substance other than methylcyclobutane was contributing to the peak in-

---

[1] To whom inquiries should be addressed.

[2] M. N. Das and W. D. Walters, *Z. Physik. Chem.* (Frankfurt), **15**, 22 (1958).

[3] A. F. Pataracchia and W. D. Walters, *J. Phys. Chem.*, **68**, 3894 (1964).

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

[5] D. E. Applequist and J. D. Roberts, *ibid.*, **78**, 4012 (1956).

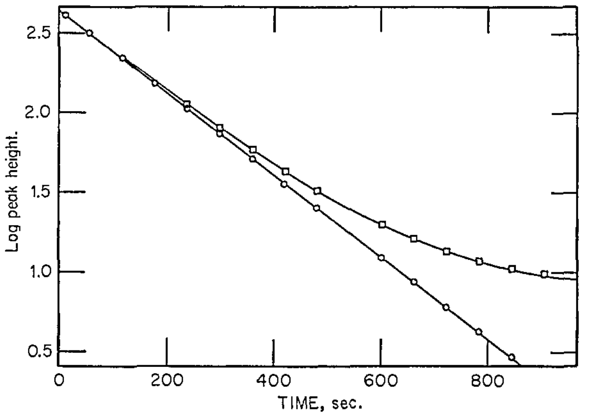


Figure 1. Plot of log peak height *vs.* time for a typical run: □, uncorrected plot; ○, plot made by subtracting 1.7% of the initial peak height from all points, *i.e.*, R = 1.7% (temperature = 762.5°K, initial pressure = 195 μ, $k = 6.01 \times 10^{-3}$ sec^{-1}). The run covers seven half-lives.

tensity at *m/e* 70. Gas chromatography revealed a small peak in addition to those of ethylene and propylene and comprising about 1% of the sum of those substances and absent in a chromatogram of the original compound. Comparison of the retention time and mass spectrum of this peak with an authentic sample identified this substance as 1-pentene.

Since most runs were not carried for more than three to five half-lives, correction for this isomerization was made by subtracting a constant from all peak heights, chosen to yield a straight line as shown in Figure 1. This subtractive constant could not be varied by more than 0.1–0.2% without showing noticeable curvature in the plots. The constant (for each run) amounted to about 1.8% of the initial peak height at the higher pressures and temperatures and fell to 0.5% or less at the lowest pressures. The constant, expressed as a percentage of the initial peak intensity, is shown for each run as R in Tables I–IV. The corrected rate constant is that for the total rate of loss of methylcyclobutane and is the sum of the rate constants for decomposition and isomerization.

Plots of the logarithm of the corrected rate constant *vs.* logarithm of the initial pressure for each run shown in Figures 2 and 3 show that the rate constant does not continue to fall uniformly as the pressure is decreased, and the rate constant is increased substantially at low pressures by increasing the surface-to-volume ratio. It should be noted that the rate constant is not increased in proportion to the surface-to-volume ratio. Thus the data cannot be fit by a classical Kassel integral,[6] shown in eq 3. Such behavior has

$$k = \frac{k_\infty}{(RT)^s\Gamma(s)}\int_0^\infty \frac{z^{s-1}e^{-z/RT}dz}{1 + \frac{ART}{apN}\left(\frac{z}{z+E_0}\right)^{s-1}} \qquad (3)$$

been observed before with varying degrees of certainty[7–9] for various reactions, and the suggestion has been made that energy exchange with the walls might be the cause.

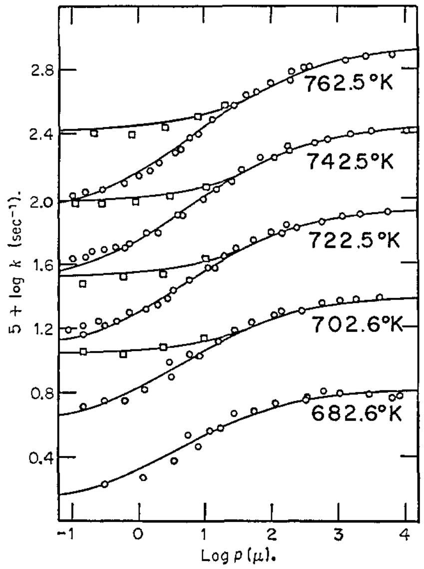


Figure 2. Plot of first-order rate constants at all experimental temperatures and pressures: ○, data from unpacked flasks; □, data from flask packed with glass wool. Solid curves were calculated from the integral in eq 11.

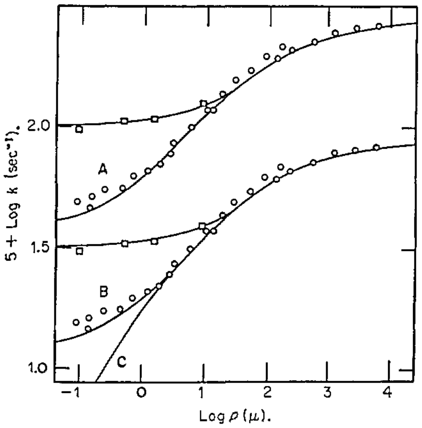


Figure 3. Lower isotherm, B, at 722.5°K and curves calculated from integral in eq 11 using E_0 = 63,100 cal, $A = 1.064 \times 10^{16}$ sec^{-1}, σ = 5.85 Å, s = 26, λ' = 1.00, and λ = 0.70: upper branch, S/V = 4.77 cm^{-1}; lower branch, S/V = 0.207 cm^{-1}. Upper isotherm, A, consists of same data displaced upward by 0.5 log unit; curves calculated from integral in eq 11 and same parameters as in lower isotherm except s = 39, λ' = 0.018, λ = 0.013. Curve C was calculated from the uncorrected Kassel integral.

We wish to assert this point of view most emphatically. Thus, while the reaction shows no evidence of occurring *on* the wall, exchange of vibrational energy occurs between the wall and molecule on collision with the wall. The energized molecule then decomposes *in the gas phase.* A modification of the Kassel integral to incorporate this idea is presented herewith.

It is assumed that the rate of formation of activated molecules at any pressure is equal to the rate of deactivation which would obtain were the reacting system at collisional equilibrium, *i.e.*, if there were no reaction to products.

Let λ' be the probability of an activated molecule, with vibrational energy $\geqq \epsilon_0$, losing enough energy to become deactivated on collision with the walls, and λ

---

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

(7) J. N. Butler and R. B. Ogawa, *J. Am. Chem. Soc.*, 85, 3346 (1963).

(8) A. W. Kennedy and H. O. Pritchard, *J. Phys. Chem.*, 67, 161 (1963).

(9) F. J. Fletcher, B. S. Rabinovitch, K. W. Watkins, and D. J. Locker, *ibid.*, 70, 2823 (1966).

Table I. First-Order Rate Constants for Methylcyclobutane Decompositions[a]

p, μ	$k \times 10^5$ sec^{-1}	R, %	p, μ	$k \times 10^5$ sec^{-1}	R, %
		762.5°K			
6500	767.9	1.78	12.94	302.0	1.49
5837	767.5	1.72	7.898	247.2	1.39
2644	758.7	1.75	5.942	240.8	1.24
1275	712.7	1.75	4.394	198.3	1.25
371	646.7	1.75	3.518	192.8	0.80
322	641.4	1.80	2.047	163.9	0.77
195	600.7	1.70	1.481	147.7	0.68
190	547.3	1.75	1.019	135.4	0.66
99.9	515.8	1.55	0.609	123.9	0.66
59.22	452.8	1.1	0.288	113.6	0.58
41.88	434.3	1.7	0.153	109.3	0.53
26.81	371.9	1.67	0.101	104.8	0.50
		742.5°K			
10,770	258.0	1.55	4.545	78.4	1.00
3254	259.7	1.57	3.924	79.72	0.82
1571	248.9	1.57	1.996	61.95	0.73
688	232.8	1.37	1.323	61.55	0.62
440	224.1	1.51	0.776	51.13	0.36
190.3	195.3	1.49	0.764	52.44	0.42
186.4	210.0	1.57	0.629	50.12	0.25
106.7	177.5	1.52	0.460	50.70	0.30
67.71	179.3	1.53	0.300	48.06	0.37
36.63	149.8	1.53	0.199	49.83	0.29
25.89	128.6	0.40	0.161	42.89	0.28
15.25	112.3	1.29	0.101	42.80	0.26
9.62	98.79	1.19			
		722.5°K			
5930	82.99	1.4	5.91	31.43	0.86
2673	81.29	1.41	3.32	26.97	0.68
1188	78.16	1.36	2.833	24.51	0.30
576	71.29	1.35	1.941	22.22	0.48
208	66.07	1.36	1.274	20.79	0.29
166.6	68.17	1.30	0.742	19.70	0.32
145.2	59.43	1.35	0.467	17.55	0.30
97.52	62.55	1.33	0.312	16.24	0.30
53.83	54.36	1.32	0.247	17.41	0.30
29.91	49.01	1.50	0.148	16.21	0.30
19.05	42.98	1.10	0.140	14.53	0.30
13.92	37.09	0.79	0.091	15.47	0.29
11.07	37.05	1.14			
		702.6°K			
4309	24.37	1.30	15.67	13.45	1.01
1885	23.99	1.26	8.23	10.31	1.11
1064	23.43	1.30	5.972	10.74	0.69
594	22.64	1.37	3.139	7.73	0.97
284	20.44	1.30	2.928	9.65	0.46
141.6	20.19	1.33	1.258	6.52	0
110.5	18.97	1.30	0.622	5.61	0
101	18.87	1.26	0.308	5.63	0
49.3	17.24	1.21	0.144	5.08	0
28.34	15.29	1.20			
		682.6°K			
8770	6.099	1.33	26.42	4.73	1.07
6583	5.793	1.27	17.04	3.74	0.83
3084	6.169	1.24	12.03	3.62	0.74
1070	6.336	1.30	8.069	2.86	0.62
630	6.440	1.18	5.730	3.40	0.53
366	6.022	1.25	3.401	2.33	0.30
340.2	5.740	1.24	1.202	1.85	0
116.4	5.349	1.16	0.316	1.67	0
54.87	4.84	1.06			

[a] Surface-to-volume ratio = 0.207 cm^{-1}.

Table II. First-Order Rate Constants for the Decomposition of Methylcyclobutane in a Flask Packed with Glass Wool[a]

p, μ	$k \times 10^5$ sec^{-1}	R, %	p, μ	$k \times 10^5$ sec^{-1}	R, %
		762.5°K			
20.06	371.7	1.5	0.791	247.0	0.71
7.99	319.7	1.27	0.204	250.5	0.54
2.45	274.1	0.92			
		742.5°K			
10.52	117.0	0.75	0.275	91.86	0.47
2.94	103.1	0.65	0.117	92.79	0.49
0.928	93.41	0.60			
		722.5°K			
10.15	42.08	1.08	0.587	33.10	0.31
2.33	34.31	0.30	0.148	29.7	0.32
		702.6°K			
9.53	13.85	1.13	0.590	10.89	0.49
2.30	12.01	0.97	0.147	11.20	0.40

[a] Surface-to-volume ratio = 4.47 cm^{-1}.

Table III. First-Order Rate Constants for the Decomposition of Methylcyclobutane in a Flask Packed with Glass Tubing (722.6°K)[a]

p, μ[b]	p_{H_2O}, μ[c]	$k \times 10^5$ sec^{-1}	R, %
2.13	7.4	45.06	0
2.35	3.1	43.3	0.47
2.25	0.98	42.19	0.95
0.64	0.82	41.58	0.89
13.07	2.8	47.47	1.02

[a] Surface-to-volume ratio = 4.98 cm^{-1}. [b] Initial pressure of methylcyclobutane. [c] Pressure of water vapor (μ) at end of run.

Table IV. First-Order Rate Constants for the Decomposition of Methylcyclobutane (M) with Added Gases

T, °K	p(total), μ	$k \times 10^5$ sec^{-1}	R, %
	91.2% C_3H_6 + 8.8% M		
722.5	92.5	56.41	1.33
722.5	42.5	44.02	1.29
742.5	60.9	145.1	1.49
	91.1% C_2H_4 + 8.9% M		
742.5	78.0	151.8	1.45
722.5	91.1	49.05	0
722.5	42.9	41.83	0
	13.5% NO + 86.5% M		
722.5	57.51	54.27	1.27
722.5	34.23	45.28	0
	92.5% NO + 7.5% M		
722.5	105.3	47.63	2.10
722.5	47.6	36.5	1.99

be the corresponding probability on colliding with another molecule. Then the rate of deactivation (at equilibrium) is equal to the rate of activation as a function of the energy of the molecule and is given by

$$R_{\text{act}}(\epsilon) = \lambda a n^2 f(\epsilon) + (\lambda'/4) n f(\epsilon) \bar{c} (S/V) \quad (4)$$

where a is the collision frequency factor given by kinetic theory as $4\sigma^2(\pi kT/m)^{1/2}$, $\bar{c}$ is the mean molecular speed, $(8kT/\pi m)^{1/2}$, n is the initial number of molecules per cubic centimeter, and S and V are the surface area and volume, respectively. $f(\epsilon)$ is the distribution function for molecules with energy ϵ in s degrees of freedom

$$f(\epsilon)d\epsilon = (\epsilon/kT)^{s-1} \exp(-\epsilon/kT)(d\epsilon/kT)/(s-1)! \quad (5)$$

It should be noted that eq 4 presumably is valid only if packing in a flask is uniformly distributed throughout the volume. Now when reaction occurs, the number of activated molecules per cubic centimeter is $n^*(\epsilon)$ instead of $nf(\epsilon)$, and the rate of loss of activated molecules is

$$R_{\text{loss}}(\epsilon) = \lambda ann^*(\epsilon) + (\lambda'/4)n^*(\epsilon)\bar{c}(S/V) + b(\epsilon)n^*(\epsilon) \quad (6)$$

where $b(\epsilon)$ is the specific rate constant for reaction of activated molecules, with energy ϵ, to products. Setting $R_{\text{act}}(\epsilon) = R_{\text{loss}}(\epsilon)$ and solving for $n^*(\epsilon)$ we obtain

$$n^*(\epsilon) = \frac{nf(\epsilon)}{1 + \dfrac{b(\epsilon)}{\lambda an + (\lambda'/4)\bar{c}(S/V)}} \quad (7)$$

$b(\epsilon)$ is given by

$$b(\epsilon) = A\left(\frac{\epsilon - \epsilon_0}{\epsilon}\right)^{s-1} \quad (8)$$

where A is the Arrhenius frequency factor for high pressures. The rate of reaction is expressed by

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = \int_{\epsilon_0}^{\infty} b(\epsilon)n^*(\epsilon)\,\mathrm{d}\epsilon = k_{\text{obsd}}n \quad (9)$$

or

$$k_{\text{obsd}} = \int_{\epsilon_0}^{\infty} \frac{b(\epsilon)n^*(\epsilon)\,\mathrm{d}\epsilon}{n} \quad (10)$$

Putting (5), (7), and (8) into (10) and using $n = Np/RT$ and $z = E - E_0$ yields

$$k_{\text{obsd}} = \frac{A\exp(-E_0/RT)}{(RT)^s\Gamma(s)} \int_0^{\infty} \frac{z^{s-1}\exp(-z/RT)\,\mathrm{d}z}{1 + \dfrac{ART[z/(z + E_0)]^{s-1}}{\lambda aNp + (\lambda'/4)(S/V)\bar{c}RT}} \quad (11)$$

This integral is identical with the classical Kassel integral except for the S/V term. At high pressures the denominator goes to unity and k_{obsd} is independent of pressure. As the pressure is lowered k_{obsd} decreases until at sufficiently low pressure the (S/V) term becomes dominant and k_{obsd} approaches a constant lower limit. Thus plots of log k *vs.* log p acquire a sigmoid shape required by the experimental data

The Kassel integral has four parameters, namely A, E_0, s, and σ. The integral in eq 11 appears to have three more, λ, λ', and S/V. In reality only one has been added. $\lambda\sigma^2$ is really one parameter and (S/V) is capable of independent evaluation. So λ' is the only additional parameter.

To fit the data with values of this integral, it is necessary to select a value for σ. Lemaire and Livingston[10] have investigated the structure of methylcyclobutane by electron diffraction. Using their data the distance between the methyl carbon and the diagonally opposite ring carbon is 3.51 Å. The longest molecular diameter is along the line joining these two atoms and is obtained by adding the van der Waals radii of two carbon atoms since the hydrogens do not add to the dimension along this line due to their angular orientation. Using 1.70 Å for these radii[11] we obtain 6.91 Å which should serve as an upper limit to σ. From a calculation of molecular volumes[10] considering the contribution of the methyl group to the cyclobutane volume, we have chosen $\sigma = 5.85$ Å.

A value of the surface area of the unpacked flask was calculated geometrically assuming the flask to be a sphere.

The average fiber diameter of the Pyrex wool used to pack a flask was estimated using a calibrated reticule in the eyepiece of a microscope. About 100 random observations on many small samples by two independent observers yielded an average diameter of 9.7 ± 0.8 μ. The 12.5-l. flask was packed with 29 g of Pyrex wool. The density of Pyrex was taken as 2.23 g/cc and the surface area calculated geometrically.

Hobson[12] has studied the adsorption of N_2 on Pyrex at low temperatures and concluded that the surface is nearly "flat." He supported these results by electron microscopy, which showed a rolling surface with a periodicity of about 300 Å. Thus any correction to our calculated surface areas due to roughness is probably less than the error in our geometric calculations.

Values of the integral in eq 11 were calculated by IBM 360 computer for a substantial range of the values of the various parameters. The curves in Figure 2 were drawn using the calculated values of the rate constants from the integral. These values and the values of the parameters used are shown in Tables V and VI. The fit is good at all temperatures and pressures.

Table V. Calculated Value of the Rate Constant from the Integral in Eq 11[a]

	(5 + log k) at T°K				
p, μ	762.5°	742.5°	722.5°	702.6°	682.6°
0.1	1.963	1.556	1.121	0.656	0.155
1.0	2.151	1.736	1.293	0.820	0.311
10.0	2.453	2.021	1.559	1.067	0.539
100.0	2.699	2.246	1.764	1.252	0.703
1,000.0	2.848	2.378	1.878	1.351	0.786
10,000.0	2.916	2.435	1.925	1.388	0.816

[a] E_0 = 63.1 (±0.3) kcal/mole, A = 1.064 (±0.10) × 10^{16} sec^{-1}, σ = 5.85 Å, s = 26, S/V = 0.207, λ' = 1.00, λ = 0.70.

Table VI. Calculated Values of the Rate Constant from the Integral in Eq 11[a]

	(5 + log k) at T°K				
p, μ	762.5°	742.5°	722.5°	702.6°	682.6°
0.1	2.425	1.991	1.528	1.037	0.508
1.0	2.438	2.004	1.541	1.048	0.519
10.0	2.524	2.085	1.617	1.119	0.584
100.0	2.705	2.252	1.768	1.256	0.706
1,000.0	2.849	2.378	1.879	1.351	0.786
10,000.0	2.916	2.435	1.925	1.388	0.816

[a] Parameters same as in Table V except S/V = 4.475 cm^{-1}.

Initially it was assumed that λ' was unity. It seemed more reasonable to assume λ' to be unity than that λ should be unity. A wide spectrum of vibration frequencies is to be found in the solid wall. Thus a vibrating molecule can find any frequency it requires for delivering energy to or receiving energy from the wall on collision. Then λ was allowed to assume a value which fits the data. The fact that λ was found to be 0.7 supports the contention that intermolecular collisions are strong collisions. The precision of selection of a value for λ cannot be better than ±10%

---

[10] H. P. Lemaire and R. L. Livingston, *J. Am. Chem. Soc.*, 74, 5732 (1952).

[11] A. Bondi, *J. Phys. Chem.*, 68, 441 (1964).

[12] J. P. Hobson, *J. Chem. Phys.*, 34, 1850 (1961).

and may be poorer than that. These values of the λ's require s to be 26. The value reported by Pataracchia and Walters[8] from measurements at one temperature was $s = 23$.

The maximum value of s for a molecule of 15 atoms is 39. Therefore new integrals were calculated with $s = 39$, and λ and λ′ were adjusted to restore the fit, finding $\lambda' = 0.018$ and $\lambda = 0.013$. Comparison of the fit with these parameters at 449.3° is shown in Figure 3 using the calculated values in Table VII. It is apparent that the two sets of parameters account equally well for the data at this temperature. The isotherms calculated with $s = 39$ are a little bit closer together at the lower pressure limit than are those with $s = 26$. Thus the first set corresponds to deactivation at nearly every collision of an activated molecule while the second set would require 80 collisions to deactivate on the average.

Table VII. Calculated Values of the Rate Constants from the Integral in Eq 11[a]

p, μ	(5 + log k) at T°K				
	762.5°	742.5°	722.5°	702.6°	682.6°
0.1	1.923	1.538	1.123	0.677	0.193
1.0	2.112	1.718	1.292	0.836	0.340
10.0	2.417	2.000	1.552	1.072	0.553
100.0	2.670	2.228	1.754	1.250	0.706
1,000.0	2.829	2.365	1.871	1.347	0.786
10,000.0	2.907	2.429	1.922	1.387	0.816

[a] Parameters same as in Table V except $s = 39$, $\lambda = 0.013$, $\lambda' = 0.018$.

We incline to the former view with $s = 26$. In principle s must itself be an average and it would appear that, even if all modes of vibration feed energy into the critical mode, not all of them do so with equal efficiency. So it is reasonable that s be less than 39.

Thus a single set of parameters fits the data over a range of 10^5 in the pressure and 80° in the temperature including all data in packed and unpacked flasks.

It is worthy of note that the ratio λ/λ' is substantially independent of the value of s. Hence the conclusion that collisions between molecules and collisions with the walls are nearly equally efficient in deactivating activated molecules is independent of the value of the parameter which is most difficult to justify on *a priori* grounds. And this fact also provides convincing evidence that deactivation *via* intermolecular collisions is very efficient.

Similar data were reported for cyclobutane by Vreeland and Swinehart,[4] but they found very little increase in rate in a packed flask. In that case, the Pyrex glass wool was washed in benzene, alcohol, and water, in that order (but *not* in chromic acid cleaning solution). The water wash caused the wool to mat badly and it lost its fluffy characteristics. Although an attempt was made to pick the mats apart, success was marginal and the wool only "half-filled" the flask. On geometrical grounds, this packing should not cause as great an increase as it would have if the wool were distributed uniformly through the volume. Still, it is not clear that it should have given little or no increase at all as reported.

In the present case, the wool was washed in benzene and alcohol but not in water. On allowing the solvent to evaporate, the wool retained its fluffy characteristics and the packing "filled" the flask essentially completely. Several runs with cyclobutane with this packing showed increases in rate comparable to those observed here for methylcyclobutane. Thus it is clear that the deviations from the Kassel integral for cyclobutane at low pressures must be due to activation and deactivation by wall collisions also. It is not clear why the difference in washing the wool packing in the two cases produced such a drastic difference in effect on the rate.

At low pressures and at temperatures of 450–500° the outgassing of water vapor from the flask is a serious problem. The flasks in this study were outgassed at 530° for 1 week or more and the packed flask for 2 weeks before measurements were attempted. The outgassing was checked by closing the flask from the pumps and monitoring the water peak at m/e 18 for a period of time comparable to the projected reaction times. With shorter periods of outgassing, the pressure of water vapor would build up to values equal to or greater than the initial pressure of the reacting gas for the lowest pressure measurements.

A 13-l. flask was packed with 6-cm lengths of 10-mm o.d. Pyrex glass tubing, using over 1300 pieces, providing a surface to volume ratio even larger than for the glass-wool-packed flask, due principally to the decreased volume. This flask was outgassed essentially continuously at 500–530° for 6 months. Even after this long period, water was evolved into the evacuated space at a rate which made measurements of doubtful value. In fact, rough estimates from water collected in the cold trap indicated that after a couple of weeks, water was evolved at nearly a constant rate. It appears that we were outgassing the tubing through the entire thickness of the walls.[13] Thus we wish to suggest to workers in the field that, for measurements below 10 μ and temperatures of 450° and up, this point be checked lest their low-pressure measurements be literally "all wet." The point does not seem to have been considered before. In fact, no technique occurs to us, alternative to our own, which is capable of detecting water vapor in very small amounts in such an environment.

Five runs in this flask showing an estimate of the pressure of water vapor at the end of each run are shown in Table III. From the work of Todd, it would be desirable to pack with Vycor glass tubing rather than Pyrex tubing.

Figure 4 shows a plot of R, the correction term for each run and expressed as a percentage of the initial peak height, *vs.* the initial pressure at four temperatures. These values were selected from the longer runs where their estimation appeared more reliable. In spite of the scatter, it is clear that R decreases with pressure and temperature. From the three isotherms at the highest temperatures it was estimated that activation energy for isomerization was 4000 (±2000) cal higher than that for decomposition and that for high pressures

$$\frac{k_{\mathrm{i}}}{k_{\mathrm{d}}} = \left(0.27\begin{Bmatrix}+0.77\\ \hline -0.20\end{Bmatrix}\right)\exp[-(4000 \pm 2000)/RT]$$

---

[13] B. Todd, *J. Appl. Phys.*, 26, 1238 (1955).

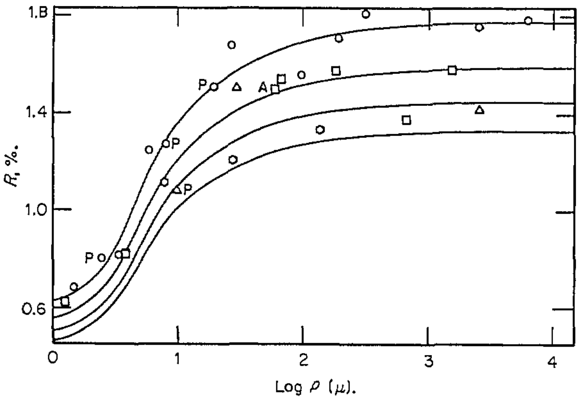


Figure 4. Plot of the correction term, R, in per cent of initial peak height for each run. The curves are isotherms (from top to bottom) at 762.5, 742.5, 722.5, and 702.6°K, respectively. The upper isotherm was drawn empirically to fit data, and the others were drawn with a constant 4000 cal as the difference in activation energy between the isomerization and decomposition reactions.

From the added gas runs shown in Table IV, relative activation efficiencies per molecule were calculated and are shown in Table VIII. Propylene is more efficient than ethylene and that of NO is smaller. It is approximately true, *i.e.*, within the limits of error of the estimates, that the sum of the efficiencies of propylene and ethylene is the same as that of methylcyclobutane itself. It is worthy of note that relatively small amounts of NO do not decrease the rate but do increase the rate. Presumably this indicates the absence of free-radical chains so that NO simply acts qualitatively as any other inert added gas.

Table VIII. Collisional Efficiencies per Molecule from Added Gas Runs[a]

Added gas	p_0, μ	p_a, μ	p_{eff}, μ	α
C_3H_6	8.11	84.41	59.7	0.61
C_3H_6	3.72	38.74	21.0	0.45
C_3H_6	5.34	55.60	34.2	0.52
C_2H_4	6.95	71.01	39.1	0.45
C_2H_4	8.11	82.98	50.6	0.29
C_2H_4	3.83	39.09	16.9	0.34
NO	7.94	97.36	28.8	0.21
NO	3.59	44.01	10.2	0.15

[a] p_0 = initial pressure of methylcyclobutane; p_a = initial pressure of added gas; p_{eff} = pressure of pure methylcyclobutane required to give same rate constant; $\alpha = (p_{eff} - p_0)/p_a$ = efficiency per molecule.

From the equation

$$A = e\left(\frac{kT}{h}\right)\exp(\Delta S^{\ddagger}/R) \qquad (12)$$

the value of $A = 1.064 \times 10^{16}\ \mathrm{sec}^{-1}$ and $T = 722.5$°K; the activation entropy is calculated to be $\Delta S^{\ddagger} = 11.0$ cal/deg. This value compares with the entropies of activation for cyclobutane[4] of 10.2 eu and for methylcyclobutane by Das and Walters[2] of 8.1 eu.

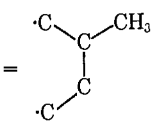
There are two possible diradical intermediates for the two reactions

$$M \rightleftharpoons J \longrightarrow C_2H_4 + C_3H_6$$

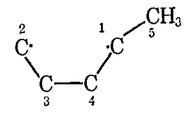
$$M \rightleftharpoons I \begin{cases} \longrightarrow C_2H_4 + C_3H_6 \\ \longrightarrow \text{1-pentene} \end{cases}$$

where

J =



I =



Scale models of I show that any of the hydrogen atoms of the methyl group may be brought close to C_2 by simple rotations about carbon–carbon bonds. Hydrogen-atom transfer from C_5 to C_2 then leads directly to the formation of 1-pentene. No such simple process is possible for J. Both diradicals may decompose to ethylene and propylene.

Acknowledgments. We wish to thank the Atomic Energy Commission for support and the National Science Foundation for a fellowship for one of us (T. F. T.).