

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Thermal Decomposition of Cyclobutane^{1,2}

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The homogeneous thermal decomposition of cyclobutane has been studied over the temperature region from 420 to 468° with initial pressures from 1 to 996 mm. At a given temperature the first-order rate constant remains essentially unchanged as the pressure is increased from 100 to 996 mm. The variation of the rate with temperature may be expressed as $k = 4.0 \times 10^{15} e^{-62,500/RT}$ sec.⁻¹. With a pressure of 1 mm. the rate constant is approximately two-thirds of the value for experiments above 100 mm. Addition of 54 mm. of hydrogen, ethane or ethylene to 1 mm. of cyclobutane raises the rate constant.

Preliminary results concerning the thermal decomposition of cyclobutane at pressures from 30 to 400 mm. over the temperature interval from 430 to 480° have been reported in an earlier communication,³ and in a second publication⁴ the data from experiments at lower initial pressures have been presented. The present report provides additional information concerning (a) the characteristics of the reaction over a wider pressure range, (b) the effect of added inert gases and (c) the activation energy of the reaction.

Experimental

The samples of cyclobutane were prepared by the photochemical decomposition⁵ of cyclopentanone and were purified by distillation in a Podbielniak column. The fraction used for this study had a boiling point of $12.7 \pm 0.2^\circ$ (cor. to 760 mm.) in agreement with the value of 12.6° calculated from Heisig's results.⁶ Infrared absorption curves were used to check on the purity also. With some of the cyclobutane it was observed that the last portions of the stored sample gave an absorption at 13.4μ slightly greater than that present in the first samples³ which were in accord with the published infrared curves.^{5b,7} Treatment with activated sulfuric acid⁸ followed by contact with moist pellets of potassium hydroxide removed the substance responsible for the absorption. However, both the treated and untreated samples showed the same kinetic results. Similarly a treatment of the cyclobutane samples with silver oxide or with freshly distilled sodium did not affect the rate. Furthermore, cyclobutane separated by distillation from the reaction mixture obtained in earlier pyrolytic experiments gave rates of decomposition in agreement with that for unpyrolyzed cyclobutane.

Hydrogen was obtained from the Ohio Chemical and Manufacturing Company and in order to remove traces of oxygen the gas was passed over copper at 500–520°. The ethane used was the research grade of the Phillips Petroleum Company. The sources, purities and treatments of the other substances were the same as those given in the previous report.⁴

The apparatus which consisted of a Pyrex reaction vessel, furnace, equipment for temperature measurement and control, and a vacuum system was of the type already described.⁹ For convenience the experiments at pressures

above 80 mm. were usually performed in one apparatus and the experiments at 80 mm. and below were performed in a second apparatus similar in design. Pressures of 80 mm. and above were ordinarily measured with either a single arm or a U-tube capillary manometer containing mercury; pressure measurements between 80 and 1 mm. were made by means of large-bore mercury manometers read with a cathetometer. For a number of experiments in the 1 mm. region a small McLeod gage was used to measure the pressure.

Results and Discussion

Products.—In order to establish the stoichiometry of the reaction at pressures in the neighborhood of 120 mm. the reaction mixtures were separated into two fractions, one volatile at -137° , the other volatile at room temperature. Mass spectrometric analysis¹⁰ of these fractions gave the following results: (a) for the more volatile fraction in the third experiment in Table I, ethylene, 99.86%; propane, 0.05%; cyclobutane, 0.07%; other C₄⁺ compounds, 0.02%; (b) for the less volatile fraction, from the second experiment in Table I cyclobutane, $99.3 \pm 0.1\%$, with apparently some C₃H₆ also present, and from the last experiment in Table I, cyclobutane, 99.2% and ethylene, 0.8%. Analyses of the products from the first, third, fourth and last experiments in Table I showed that more than 98–99% of the more volatile fraction could be absorbed in activated sulfuric acid.⁸ Moreover, when the reaction products collected from a series of experiments at pressures above 100 mm. were fractionated in a Podbielniak column, plateaus in the distillation curve were obtained only at -105 and 12.6° (757 mm.) corresponding to ethylene and cyclobutane, respectively.

If it is assumed that the only reaction is the conversion of cyclobutane into ethylene, the amount of the more volatile fraction (ethylene) and the amount of the less volatile fraction (cyclobutane) in the reaction mixture during the decomposition can be calculated from the measurements of the

TABLE I
COMPARISON OF THE OBSERVED AND CALCULATED COMPOSITIONS OF THE REACTION MIXTURE

Temp., °C.	P ₀ , mm.	ΔP/P ₀ , %	Volatile at Calcd.	Cc. of gas at N.T.P.		Volatile at 25° Calcd.	Obsd.
				Obsd.	Calcd.		
427	123	30	20.6	22.1
438	126	26	18.3	18.2	25.2	24.3	..
438	126	27	18.5	18.0
449	123	50	33.7	32.1
449	140	58	44.0	44.3	15.3	15.4	..
458	129	29	20.1	20.2	23.9	24.5	..

(10) The analyses were performed by the Consolidated Engineering Corporation.

(1) This work has been supported by a grant from the Celanese Corporation of America.

(2) Abstracted in part from the M.S. thesis submitted by Charles T. Genaux.

(3) C. T. Genaux and W. D. Walters, *THIS JOURNAL*, **73**, 4497 (1951).

(4) F. Kern and W. D. Walters, *Proc. Natl. Acad. Sci.*, **38**, 937 (1952).

(5) (a) S. W. Benson and G. B. Kistiakowsky, *THIS JOURNAL*, **64**, 80 (1942); (b) T. P. Wilson, *J. Chem. Phys.*, **11**, 369 (1943).

(6) G. B. Heisig, *THIS JOURNAL*, **63**, 1698 (1941).

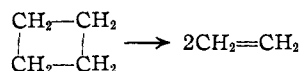
(7) (a) J. D. Roberts and C. W. Sauer, *ibid.*, **71**, 3925 (1949); (b) American Petroleum Institute Research Project 44, Infrared Spectral Data, Carnegie Institute of Technology, Pittsburgh, Pennsylvania, Serial No. 1158.

(8) (a) W. J. Gooderham, *J. Soc. Chem. Ind. (London)*, **57**, 388T (1938); (b) H. Tropesch and W. J. Mattox, *Ind. Eng. Chem., Anal. Ed.*, **6**, 404 (1934).

(9) D. W. Vanas and W. D. Walters, *THIS JOURNAL*, **70**, 4035 (1948).

total pressure. In several experiments the reaction mixture was removed after a definite time of reaction and separated into two fractions the volumes of which were measured. A comparison of the observed and calculated values is given in Table I.

The results of the analyses and the data in Table I show that at pressures of 125 mm. the reaction¹¹ is essentially



and that pressure measurements may be used to follow the rate of the decomposition at least during the early stages of the reaction. This conclusion is in agreement with that reached in the low pressure experiments.⁴

With respect to the over-all pressure increase for the reaction it was observed in a series of six experiments at initial pressures of about 100 mm. covering the temperature region 427–482° that all of the values for the ratio of the final to the initial pressure fell within the range 1.97–2.00 corrected for dead space. A value of 2.00 ± 0.02 was obtained for experiments at initial pressures of 1–20 mm.⁴

Kinetics.—As has been reported previously,^{3,4} the decomposition of cyclobutane has been found to proceed homogeneously under the conditions used in the present study.¹² Table II presents the results of the majority of the experiments carried out over the pressure range 1 to 996 mm. at temperatures from 420 to 468°. The first-order rate constants have been calculated from the quarter-times (25% pressure increase) obtained from the pressure–time curves. It is to be noted that in the use of the pressure data for rate calculations dead space corrections were applied whenever necessary. For convenience in the comparison of different experiments, a correction of 0.6% per tenth of a degree has been made on the rate constants of the experiments above 80 mm. to adjust them to the temperatures indicated in Table II. The average of the deviations of the actual experimental temperatures from those given was about 0.2°. In only a few of the experiments at 80 mm. and below did the temperature differ more than 0.1° from that given in Table II and in these cases the appropriate small corrections were applied.

That the decomposition of cyclobutane is first order in the range from 100 to 1000 mm. is evident from the constancy of the values of the rate constant for experiments at different initial pressures. Moreover, when the data from 100 mm. experiments carried to completion are employed for plots of $\log(2P_0 - P_t)$ vs. time, a linear behavior is obtained until at least 90–95% of the cyclobutane has de-

(11) In an unsuccessful attempt to prepare cyclobutane by heating the calcium salt of cyclobutane carboxylic acid with lime, H. G. Colman and W. H. Perkin, Jr., *J. Chem. Soc.*, **51**, 228 (1887), obtained ethylene as the major constituent of the gases produced in the reaction. They suggested that the ethylene had been formed from cyclobutane.

(12) Packing the vessel to increase the surface to volume ratio about thirty-fold did not alter the rate at a pressure of 10 mm. or above, and gave an increase of not more than 10% at 1 mm. Reducing the S/V ratio by the use of a 12-liter bulb in place of the usual 0.5-liter bulb does not change the rate at 1 mm.

TABLE II
RATE OF DECOMPOSITION OF CYCLOBUTANE

Numbers in parentheses indicate the number of experiments from which the average value was calculated. Letters designate the following treatments of cyclobutane prior to decomposition: A, activated H₂SO₄; B, concd. H₂SO₄; C, sodium; D, moist KOH; E, Ag₂O; F, Na₂SO₃ solution; G, pre-pyrolysis.

<i>P</i> ₀ , mm.	10 ⁴ <i>k</i> , sec. ⁻¹ Temp., 449°		<i>P</i> ₀ , mm.	10 ⁴ <i>k</i> , sec. ⁻¹ Temp., 420°	
742	4.91		16.4	0.78	(2)
525	4.87	A			Temp., 427°
405	4.78	(2)	996	1.21	
297	4.88		822	1.23	A, D
140	5.00	G	127	1.25	A, C
132	4.92	(3)	115	1.22	
126	4.90	A			Temp., 438°
126	4.95	(3)	787	2.48	
90	4.78		133	2.52	A, F, D
80	4.98	(5)	124	2.49	E
51	4.94	(2)	112	2.44	B
19	4.78	(4)	15.6	2.40	(3)
15.4	4.68	(7)			Temp., 459°
9.6	4.49	(6)	166	9.4	A, D
5.2	4.24	(7)	129	9.0	A
1.09	3.30	(14)	126	9.0	G
			119	8.6	
		With 54 mm. added gas Temp., 449°	15.2	8.5	(3)
		Add. gas	4.8	7.5	(4)
1.0	4.23 ^a	H ₂			Temp., 468°
1.0	4.40 ^a	C ₂ H ₆ ^b	117	15.0	A, E
1.0	4.49 ^a	C ₂ H ₄	91	14.2	

^a Average of four or more experiments. ^b In this case, 55 mm. of added gas.

composed. By the use of this type of plot values of the rate constant were calculated from the slopes of the lines for eighteen of the experiments above 80 mm., and these rate constants agreed with values calculated from the quarter times within an average deviation of less than 1%.

The data from experiments at pressures below 20 mm. (Table II) show that the rate constant decreases in value as the initial pressure is lowered. In order to summarize the data concisely the low pressure values represent the averages of experiments performed in the present work and in the earlier study at the pressures indicated. In no case did the initial pressure differ from the tabulated average pressure more than 10%, and for the experiments with cyclobutane alone at 80 mm. and below the average deviation of the rate constant never exceeded 2%. The present average value for the specific reaction rate at 1 mm. at 449° is about 2% lower than the average of the results given earlier.⁴ In the present investigation additional experiments have been performed to evaluate with greater precision the dead space correction, which is subject to some uncertainty due to the diffusion that occurs more readily at low pressures. As a result it has been concluded that the earlier values of the rate constants for experiments at 1 mm. and below should be lowered by 1.5%.

In an extension of the preliminary work in which 5 mm. of cyclobutane was decomposed in the presence of 60 mm. of different inert gases, experiments have now been performed with 1 mm. of

cyclobutane in the presence of about 54 mm. of hydrogen, ethane or ethylene. The data in Table II show that the addition of an inert gas raises the rate constant, but the efficiencies of the inert gases used are considerably lower than that of cyclobutane itself.

The results from the individual experiments at different temperatures with approximately 120 mm. initial pressure have been plotted as $\log k$ vs. $10^3/T$ in Fig. 1. On the basis of the Arrhenius representation of the reaction rate constant, $k = Ae^{-E/RT}$, the activation energy which has been obtained for the 120 mm. experiments can be given as 62.5 kcal. per mole. In an attempt to find the best value of the activation energy several techniques including the least squares method have been tried; from the estimated experimental error the specification of the activation energy more closely than the nearest 0.5 kcal. does not appear warranted. The average rate constants for the 15 mm. experiments at different temperatures, which are also plotted in Fig. 1, ordinarily lie somewhat below the line drawn through the 120 mm. points. An activation energy of 62 kcal. per mole was obtained from the 15 mm. results. In view of the experimental error the slightly lower value at the lower pressures may not be of significance. By the use of the activation energy obtained from Fig. 1 the variation of the rate constant with temperature can be expressed as $k = 4.0 \times 10^{15} e^{-62,500/RT}$ sec.⁻¹.

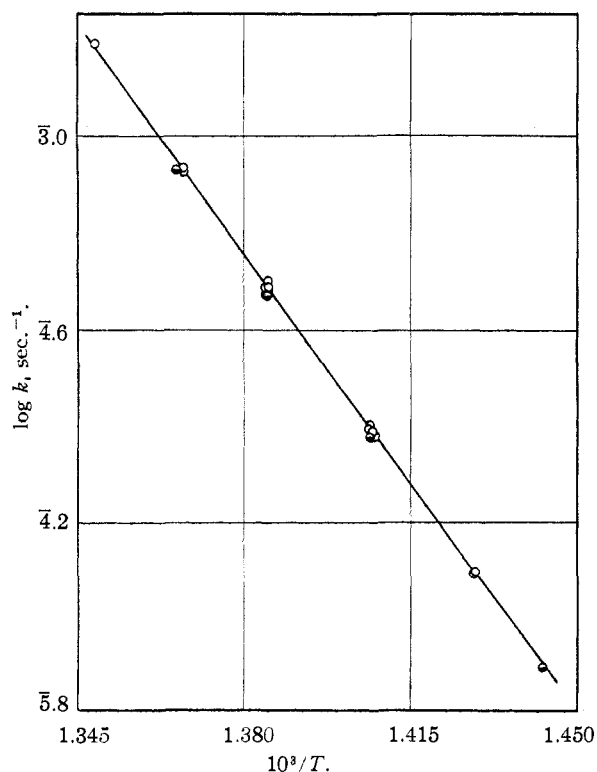


Fig. 1.—Change in rate with temperature: O, experiments with initial pressure of ~ 120 mm.; \bullet , 15 mm.

Mechanism.—The decomposition of cyclobutane does not appear to be occurring to a significant extent by a free radical chain mechanism since the addition of nitric oxide, propylene, or toluene does

not appreciably inhibit the reaction.^{5,4} However, several experiments in addition to those already reported⁴ were performed in an attempt to ascertain whether or not radicals are present during the decomposition of cyclobutane. Since both the decomposition of formaldehyde¹³ and the polymerization of ethylene¹⁴ are known to be accelerated by free radicals, cyclobutane at a pressure of 8.6 mm. was decomposed in the presence of 150 mm. of formaldehyde at 468°, and in other experiments small amounts of cyclobutane (~ 35 mm.) were decomposed in the presence of 700 mm. of ethylene at 450°. Neither the decomposition of formaldehyde nor the polymerization of ethylene was altered significantly in rate. In another experiment a mixture of 10 mm. of cyclobutane and 680 mm. of hydrogen was allowed to remain at 438° until half of the cyclobutane had decomposed. In this experiment there was the possibility that if a tetramethylene biradical were an intermediate during the decomposition of cyclobutane, the biradical might be able to react with hydrogen to form *n*-butane. The less volatile fraction of the reaction mixture which was separated and subjected to mass spectrometric analysis contained only 0.1% *n*-butane. Since this amount is almost within the experimental error and does not exceed the amount of *n*-butane found in some of the experiments in the absence of hydrogen, the experiment does not give any positive evidence for the presence of a tetramethylene biradical.

Discussion.—On the basis of the experimental results presented above the homogeneous thermal decomposition of cyclobutane would appear to be a unimolecular reaction which eventually decreases in rate as the pressure is lowered. From the viewpoint of the transition-state theory the fact that the frequency factor in the rate expression is greater than 10^{13} sec.⁻¹ indicates that the entropy of activation is positive, as would be expected for a reaction involving the breaking of a ring.¹⁵ When the experimental frequency factor is set equal to $\kappa e(kT/h)e^{\Delta S^\ddagger/R}$ and the transmission coefficient κ is assumed to be one, the entropy of activation at 449° can be calculated to be +9 cal./deg. mole.

By the use of the experimental and calculated thermodynamic data available in the literature¹⁶ for cyclobutane and ethylene various thermodynamic quantities can be calculated for the overall decomposition of one mole of cyclobutane into two moles of ethylene. At 700°K. the calculated standard free energy change is -11 kcal. with the corresponding equilibrium constant of 3×10^3 atm. Therefore, under the conditions used for the study of the rate of decomposition the system at equilibrium should be far on the side of ethylene in agreement with the results observed experi-

(13) Results of Dr. J. E. Longfield obtained in this Laboratory.

(14) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1946, pp. 150-155; F. O. Rice and W. D. Walters, *THIS JOURNAL*, **63**, 1701 (1941).

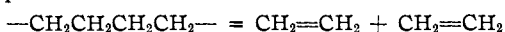
(15) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 297.

(16) T. L. Cottrell, *Trans. Faraday Soc.*, **44**, 716 (1948); J. Coops and S. Kaarsemaker, *Rec. trav. chim.*, **69**, 1364 (1950); National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Series III.

mentally. Since the entropy change for the reaction which was calculated to be +43 cal./deg. mole at 700°K. is much larger than the experimental entropy of activation given above (neglecting the small difference in temperature), the activated complex appears to have a structure much closer to cyclobutane than to the products.

Since it is possible that a short-lived tetramethylene biradical may be an intermediate in the reaction, it was of interest to estimate the difference in the entropy between a cyclobutane molecule and the fully formed biradical in order to compare this entropy difference with the entropy of activation. Although the uncertainty in the calculated entropy value for the biradical is appreciably greater than that for cyclobutane on account of the less exact information concerning its structure, estimates made by the use of Pitzer's method,¹⁷ as well as other methods, indicate that the entropy change for the formation of the biradical is at least +15 cal./deg. mole. Since this is larger than the observed entropy of activation, it appears that the structure of the activated complex does not correspond to that of the fully formed biradical (not coiled). However, the activated complex may subsequently undergo a transformation into the biradical.

Bawn and Milsted¹⁸ have discussed the stability of hydrocarbon biradicals and have estimated the energy of activation to be about 15 kcal./mole for the process



If the frequency factor associated with this activation energy of decomposition is in the region 10^{10} – 10^{13} sec.⁻¹ and if the tetramethylene biradical does

(17) K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940).

(18) C. E. H. Bawn and J. Milsted, *Trans. Faraday Soc.*, **35**, 889 (1939).

not react with molecules more readily than the methyl radical does,¹⁹ it can be calculated that for the conditions used in the experiments in the present work almost all of the tetramethylene radicals would decompose before they could react either with added hydrogen or with another molecule of cyclobutane.²⁰ Although no indication of the presence of a biradical as an intermediate has been obtained, one cannot conclude from the available data that a tetramethylene biradical is not formed momentarily during the decomposition.²¹ However, there is no evidence to show that the presence of a biradical would mean that the rate measured would not correspond to that of a simple unimolecular process.

Acknowledgment.—The authors wish to thank Dr. Frank Buff and Dr. C. E. H. Bawn for helpful discussion and Dr. G. W. Rathjens, Jr., for information and comments concerning the entropy of cyclobutane at 286°K.

NOTE ADDED IN PROOF:—The observed activation energy for the cyclobutane decomposition would not be in disagreement with the values of 58 and 60 kcal./mole for *D* (C–C) which have been calculated by F. H. Seubold, Jr., *J. Chem. Phys.*, **21**, 1616 (1953), and by H. O. Pritchard, R. G. Sowden and A. F. Trotman-Dickenson, *Proc. Roy. Soc. (London)*, **218A**, 416 (1953), respectively. The latter article also presents data on the effect on inert gases on the decomposition.

(19) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951); T. G. Majury and E. W. R. Steacie, *Disc. Faraday Soc.*, No. 14, 45 (1953).

(20) The possibility that a trimethylene biradical may react with a molecule of cyclopropane in the thermal decomposition of cyclopropane has been suggested by E. S. Corner and R. N. Pease, *THIS JOURNAL*, **67**, 2067 (1945).

(21) In the pyrolysis of cyclobutene the initial step appears to involve the rupture of only one bond since preliminary experiments by F. Kern and W. Cooper in this Laboratory indicate that an important reaction is the isomerization to butadiene.

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Kinetics of the Decarboxylation of Phenylmalonic Acid in Aqueous Solution¹

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The rate of decarboxylation of phenylmalonic acid has been measured in aqueous solution at 45° over a range of concentration and *pH*. The singly charged anion decomposes more rapidly than the un-ionized acid while the doubly charged anion appears to be stable. The acid ionization constants of phenylmalonic acid at 25° are 2.65×10^{-3} and 9.4×10^{-6} .

Recent studies of carbon isotope effects on rates of decarboxylation reactions² indicate that the change in rate on substitution of C¹⁴ is more than double that on substitution of C¹³. In connection with attempts to elucidate the cause of this anomaly some measurements were made of the rate of decarboxylation of phenylmalonic acid in aqueous solution. These are reported in the present paper.

The mechanism of decarboxylation reactions in general has been shown in recent years to exhibit a

plurality of character.³ In the case of malonic acids decarboxylation in aqueous solution is considered to involve the unimolecular decomposition of the un-ionized acid and its anions. The kinetics of decarboxylation of many substituted malonic acids have been studied, for example, by Bernoulli⁴ and co-workers, who obtained apparent first-order rate constants without, however, analyzing the contributions to the rate due to the acid and anions. The only quantitative study of the relative rates

(1) This work was assisted by the American Petroleum Institute through Research Project 50.

(2) For example, P. E. Yankwich and E. C. Stivers, *J. Chem. Phys.*, **21**, 61 (1953).

(3) For a recent review see B. R. Brown, *Quart. Rev. Chem. Soc.*, **5** [2], 141 (1951).

(4) A. L. Bernoulli and H. Jakubowitz, *Helv. Chim. Acta*, **4**, 1018 (1921).