

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER, ROCHESTER, NEW YORK]

The Thermal Decomposition of *trans*-1,2-Dimethylcyclobutane^{1,2}

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The thermal decomposition of *trans*-1,2-dimethylcyclobutane has been studied in the pressure region 13–375 mm. at 430° and over the temperature range 390–440° for pressures of 15–19 mm. Two types of ring cleavage occur, the more important one yielding two molecules of propylene and the other producing ethylene and a mixture of *trans*-2-butene and *cis*-2-butene. Each process is a homogeneous, first order reaction which is not inhibited by the addition of nitric oxide or propylene. The rates of the two ring cleavages of *trans*-1,2-dimethylcyclobutane were found to be slower than the corresponding reactions of the *cis*-1,2-dimethylcyclobutane. The first order rate constant for the reaction yielding propylene can be expressed as $k_1 = 2.8 \times 10^{15} \exp(-61,600/RT)$ sec.⁻¹ and the rate constant for the formation of ethylene is $k_2 = 2.9 \times 10^{15} \exp(-63,400/RT)$ sec.⁻¹. The ring cleavage is accompanied by a slower isomerization forming *cis*-1,2-dimethylcyclobutane. Analyses of the pyrolytic reaction mixtures have been used for the estimation of the rate constants for the forward and reverse geometrical isomerizations.

In a related study on *cis*-1,2-dimethylcyclobutane³ two modes of thermal decomposition and also a *cis*-*trans* isomerization were observed. The predominant ring cleavage process of the *cis* compound yields two molecules of propylene and the less important cleavage yields a molecule of ethylene and a molecule of 2-butene. The pyrolysis of the *trans*-1,2-dimethylcyclobutane has been investigated to determine the effect of a change in the geometrical structure upon the kinetic aspects of the decomposition. In addition to the study of the ring cleavage reactions, it was of interest to use the analytical data from the experiments with the 1,2-dimethylcyclobutanes to estimate the rates of the *cis*-*trans* isomerizations of these compounds.

Experimental

Materials and Apparatus.—*trans*-1,2-Dimethylcyclobutane was synthesized⁴ from a mixture of 2-methylcyclobutane carboxylic acid and its ethyl ester.⁵ The mixture, presumably containing both *cis* and *trans* isomers, was used as a starting material without purification. It was reduced with lithium aluminum hydride, the resultant alcohol was esterified with *p*-toluenesulfonyl chloride and the tosyl ester was reduced with lithium aluminum hydride to the hydrocarbon.^{6,7} The reaction product was fractionated at a reflux ratio of 20:1 or greater in a 75-cm. column with Lecky-Ewell packing and nine fractions were collected. Two middle fractions, which were shown to be 94–96% pure by gas chromatography, distilled in the range 56.1–56.5° at 744 mm. Kazanskiĭ and Lukina⁸ have reported the boiling point of *trans*-1,2-dimethylcyclobutane to be 56.8–56.9° at 760 mm. The higher boiling fractions from the distillation were shown by gas chromatography to contain an appreciable quantity of the *cis* isomer. All samples used in the kinetic experiments and for the physical measurements were carefully purified by a large scale gas chromatographic method, yielding samples which were at least 99.7% pure.

Carbon-hydrogen analysis by W. Manser (Zurich) gave values of 85.42% C and 14.63% H (theor. 85.62% C and 14.38% H). The index of refraction, n_D^{20} 1.3896, and the freezing point, $\sim -121^\circ$, are in good agreement with the literature values⁸ of 1.3893 and -122.5° , respectively. The other substances used in this work, as well as the experi-

mental technique and equipment, were the same as those reported earlier.³

Analysis of the Products.—The products of the decomposition (ethylene, propylene, *trans*-2-butene and *cis*-2-butene) and the product of the isomerization (*cis*-1,2-dimethylcyclobutane) were identified and analyzed by a combination of infrared spectroscopy, gas chromatography and absorption in sulfuric acid. The ring cleavage products obtained from the pyrolysis of *trans*-1,2-dimethylcyclobutane are the same as those found from the *cis* isomer but not in the same proportions. In most of the experiments the reaction mixtures were separated into three fractions by differences in volatility as mentioned previously.³ Fraction I contained the gas non-condensable at -196° (usually less than 0.1% of the total decomposition products), fraction II contained ethylene, propylene and 2-butenes, and fraction III contained *trans*-1,2-dimethylcyclobutane together with a small amount of the *cis* isomer. A special experiment showed that subsequent reaction of the decomposition products was negligible under the conditions used for the rate studies.

In Table I are data obtained by analysis of the products from experiments at 430°. The reaction products were

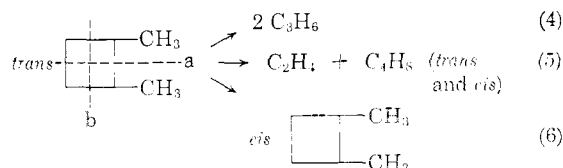
TABLE I

ANALYSIS OF THE PRODUCTS FROM THE THERMAL DECOMPOSITION OF *trans*-1,2-DIMETHYLCYCLOBUTANE AT 430°

P ₀ , ^a mm.	ΔP, mm.	Pressure of components in the reaction mixture, mm.					C ₆ H ₁₂
		C ₃ H ₆	C ₂ H ₄	C ₄ H ₈ <i>trans</i>	C ₄ H ₈ <i>cis</i>	C ₆ H ₁₂	
17.9	2.46	3.89	0.56	0.51	0.07	15.6	
16.9	2.39	3.76	.55	.49	.07	14.4	
16.6 ^b	2.41	3.83	.56	.50	.07	14.0	
18.7 ^c	2.59	4.02	.59	.51	.06	16.0	
19.0 ^c	2.58	4.00	.57	.49	.06	16.5	
94.8 ^d	12.8	19.9	2.9	2.6	.3	80.4	
375 ^d	53.1	86.8	12.5	11.5	1.5	330	
15.2 ^e	2.25		4.58 (C ₂ , C ₃ , C ₄)			12.9	

^a Initial pressure given only to 0.1 mm. to save space. ^b 0.12 mm. NO added. ^c Packed reaction vessel. ^d 319 ml. unpacked vessel; other experiments, 487 ml. unpacked vessel. ^e 7.3 mm. propylene added.

analyzed also in seventeen other experiments covering the temperature range 390–460°. On the basis of the observed products it appears that three reactions occur simultaneously in the pyrolysis of *trans*-1,2-dimethylcyclobutane



Cleavage along "a," which is the most important of the three reactions, yields two molecules of propylene, cleavage along "b" yields a molecule of ethylene and a molecule of 2-butene, and a geometrical isomerization produces *cis*-1,2-di-

(1) Financial support was received from the National Science Foundation.

(2) Abstracted from the Ph.D. thesis submitted by H. R. Gerberich, who held a Monsanto Fellowship during 1957–1958 and a Union Carbide Fellowship during 1958–1959.

(3) H. R. Gerberich and W. D. Walters, *J. Am. Chem. Soc.*, **83**, 3935 (1961).

(4) Synthesis performed by D. T. Culley in this Laboratory.

(5) Purchased from Reaction Products, Inc., Painesville, Ohio.

(6) D. S. Noyce and D. B. Denney, *J. Am. Chem. Soc.*, **74**, 5912 (1952).

(7) H. Pines and N. E. Hoffman, *ibid.*, **76**, 4417 (1954).

(8) B. A. Kazanskiĭ and M. Yu. Lukina, *Doklady Akad. Nauk S.S.S.R.*, **94**, 889 (1954).

methylcyclobutane. The analytical data indicate that reactions 4, 5, and 6 are the only significant reactions. For a series of twenty-three experiments one-half the pressure of decomposition products (columns 3-6 in Table I) is 1.00 ± 0.01 times the pressure increase, ΔP ; one-half the pressure of decomposition products added to the pressure of undecomposed 1,2-dimethylcyclobutane (column 7) is 1.00 ± 0.01 times P_0 . As would be expected from equation 5, the total pressure of 2-butenes (*cis* and *trans*) is essentially equal to the pressure of ethylene. These experimental equalities hold over the experimental ranges of temperature and pressure and do not appear to be changed by addition of nitric oxide or propylene or by reaction in a packed vessel. The experiments were usually carried to 13-15% decomposition. Gas chromatographic analysis of the undecomposed 1,2-dimethylcyclobutanes has shown that the composition is about 98% *trans* and 2% *cis*-1,2-dimethylcyclobutane after about one-eighth decomposition. The *cis* isomer decomposes faster than the *trans* isomer and to minimize the effect of its presence, rate measurements were confined to the first 12.5% decomposition. Moreover, a small correction has been applied to the rate constants presented in the subsequent sections to compensate for the effect of the *cis* isomer.

In one experiment *trans*-1,2-dimethylcyclobutane was allowed to react for a time equivalent to 7 half-lives. When appropriate correction was made for the "dead space," the final pressure attained a value of 1.99 times the initial pressure.

Results for the Ring Cleavage

Order of the Reaction.—Plots of ΔP versus time show no induction period and the curves possess the shape expected for a first order reaction. To determine the order of the reaction experiments were made at initial pressures which were varied 29-fold. These results are summarized in Fig. 1. The first order character is shown by the fact that the rate constant (k') based on the pressure increase remains unaltered over the entire range of pressures at 430°. Further confirmation of the order was obtained from the linearity of plots of $\log [P_0/(P_0 - \Delta P)]$ versus time. Rate constants calculated from the slopes of the logarithmic plots agreed to within 0.5% of those calculated from the time of 12.5% pressure increase. For experiments carried beyond 15% decomposition plots of $\log [P_0/(P_0 - \Delta P)]$ vs. time showed a small increase in slope because a significant amount of the faster decomposing *cis*-1,2-dimethylcyclobutane (formed by isomerization) was present.

Since analyses were performed on the reaction mixture after about one-eighth decomposition, the rates of the individual ring cleavage reactions 4 and 5 could be obtained. The rate constants k_4 and k_5 were calculated as

$$k_4 = [1/2 P_{C_3H_6} / (1/2 P_{C_3H_6} + P_{C_2H_4})] k' \quad (7)$$

$$k_5 = [P_{C_2H_4} / (1/2 P_{C_3H_6} + P_{C_2H_4})] k' \quad (8)$$

The rate constants k_4 and k_5 , which are also shown in Fig. 1, are independent of pressure over the investigated range. Likewise, as the data in Fig. 1 indicate, the first order rate constants are not changed appreciably by packing the vessel to increase the S/V about 35-fold or by addition of nitric oxide or propylene, which can inhibit many free radical chain reactions.

Effect of Temperature.—The temperature was varied between 390 and 440° at 10° intervals. To illustrate the effect of temperature, experiments with initial pressures near 16 mm. at 390, 410 and 440° are shown in Table II.

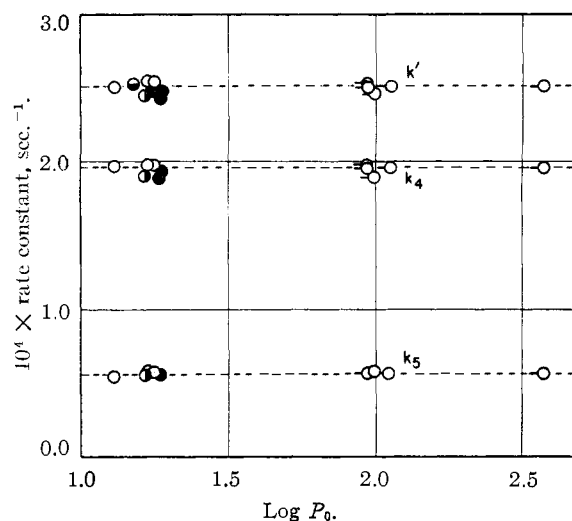


Fig. 1.—First order rate constants for the decomposition of *trans*-1,2-dimethylcyclobutane at 430° with different initial pressures (P_0): ---, the average value of the points shown for the pure substance in an unpacked vessel; \odot , 7.3 mm. propylene added; \bullet , 0.12 mm. NO added; \bullet , packed reaction vessel; \circ , unpacked vessel, 319 ml.; volume of unpacked vessel in other experiments was 487 ml.

A slight change in product distribution with temperature is indicated by the data given in Table II. The ratio $1/2 P_{C_3H_6} / P_{C_2H_4}$ changes from a value of about 3.8 at 390° to about 3.4 at 440° corresponding to a slightly higher activation energy for reaction 5 than for reaction 4. In reaction 5 the amount of *cis*-2-butene formed compared to *trans*-2-butene is small and no change in the ratio with temperature (outside the experimental error) could be established.

For the experiments in Table II, as well as experiments at other temperatures, two methods were employed to evaluate the over-all rate constant

TABLE II
DECOMPOSITION OF *trans*-1,2-DIMETHYLCYCLOBUTANE AT VARIOUS TEMPERATURES

P_0 , mm.	$10^4 k'$, sec. ⁻¹ from $p-t$ curve	$10^4 k'$, sec. ⁻¹ from anal.	$1/2 P_{C_3H_6} / P_{C_2H_4}$	$P_{cis-C_4H_8} / P_{trans-C_4H_8}$
390°				
15.38	0.175	0.172	3.8	0.13
16.53	.173	.177	3.8	.13
15.45	.173	.169	3.7	.11
410°				
17.22	0.69	0.69	3.5	0.13
17.23	0.68	0.69	3.6	0.13
440°				
16.11	4.7	4.6	3.5	0.14
15.93	4.6	4.8	3.4	0.12

k' , for ring cleavage. One method involved the calculation of the first order rate constant from the time for 12.5% pressure increase, and the other method depended upon the composition of the reaction mixture determined analytically after a definite time of reaction, t . In the second method the expression used for the computation of the rate constant was

$$k' = (1/t) \ln [(P_{C_6H_{12}} + 1/2 P_{C_3H_6} + P_{C_2H_4}) / P_{C_6H_{12}}] \quad (9)$$

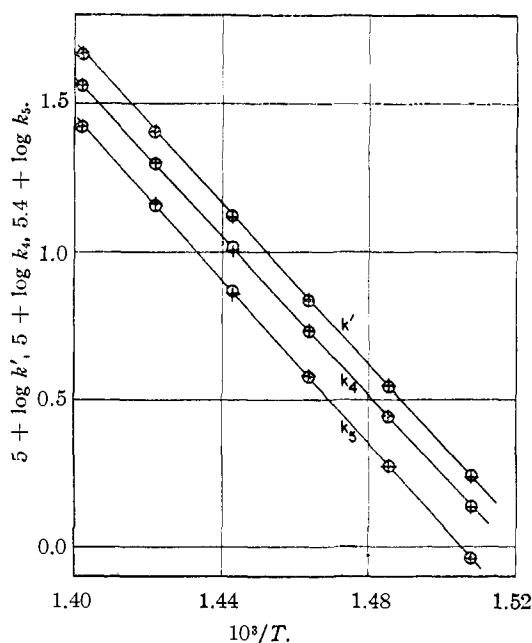


Fig. 2.—Effect of temperature upon the ring cleavage reactions of *trans*-1,2-dimethylcyclobutane: +, rate constants calculated from gas chromatographic analyses; O, values calculated for k' from manometer readings; for k_4 and k_5 the points shown as O were calculated by the use of expressions (7) and (8).

which is independent of manometer readings. Inspection of the values of k' shown in Table II reveals that the two methods give concordant values. It was found that the results of the two methods agreed within $\pm 2\%$ average deviation for experiments at all temperatures used in the present study.

The rate constants k' , k_4 and k_5 for pressures near 16 mm. at all temperatures are given in Fig. 2 in terms of a log (rate constant) vs. $1/T$ plot. To present the data concisely the following procedure has been used. For the two or more experiments at each temperature an average value of k' was calculated from the time of 12.5% pressure increase, and an average value of k' was computed from the analyses of the reaction mixtures. Both values for k' at each temperature are shown in Fig. 2. For the experiments at a given temperature values for k_4 were calculated on the basis of relationship 7 with k' obtained from manometer readings, and the average value at each temperature is plotted in Fig. 2. For each experiment a second value for k_4 was calculated from relationship 7 with k' obtained from reaction mixture analyses. Similarly two values of k_5 were calculated for each temperature. Examination of Fig. 2 shows that there is good agreement between the rate constant values which involve manometer readings and those calculated solely from analyses. Activation energies for the over-all ring cleavage and for reactions 4 and 5 were obtained from the slopes of log (rate constant) vs. $1/T$ plots and by least squares procedures. The activation energies (shown in Table III) with deviations not exceeding 0.5 kcal./mole will encompass all the activation energies and their standard deviations which were found by the

treatment of the data in different ways. Entropies of activation at 430° have been calculated in accordance with the transition state theory from the expression for the frequency factor $A = \kappa e(k_B T/h) \exp(\Delta S^*/R)$ with κ , the transmission coefficient, assumed to be one. For a comparison of the ring cleavage reactions observed for *trans*-1,2-dimethylcyclobutane and also the ring cleavage reactions of *cis*-1,2-dimethylcyclobutane³ the Arrhenius parameters, entropies of activation, and rate constants at 430° are summarized in Table III.

TABLE III
RATE DATA FOR THE RING CLEAVAGE REACTIONS OF *trans*
AND *cis*-1,2-DIMETHYLCYCLOBUTANE

Process	$10^{18} A$, sec. ⁻¹	ΔS^* , e.u.	E_a , kcal./ mole	$10^4 k$ at 430° , sec. ⁻¹
Over-all <i>trans</i> decomposi- tion	4.7	9.5	62.0	2.57
Reaction 4	2.8	8.5	61.6	2.00
Reaction 5	2.9	8.5	63.4	0.58
Over-all <i>cis</i> decomposi- tion	4.8	9.5	60.8	6.0
Reaction 1	3.0	8.6	60.4	5.0
Reaction 2	3.7	9.0	63.0	0.95

Discussion of the Ring Cleavage.—The data in Table III indicate that the symmetrical cleavage of *trans*-1,2-dimethylcyclobutane into two molecules of propylene (reaction 4) requires a lower activation energy than the unsymmetrical cleavage into ethylene and 2-butene (reaction 5). The pre-exponential factors for reactions 4 and 5 are not significantly different and the faster rate for the symmetrical cleavage is the result of the lower energy of activation (about 1.8 kcal./mole). The preferential formation of propylene from the *trans*-1,2-dimethylcyclobutane, which results in 78% propylene in the decomposition products at 430° , is not quite as great as that for *cis*-1,2-dimethylcyclobutane, which gives 83% propylene in the decomposition products at 430° .

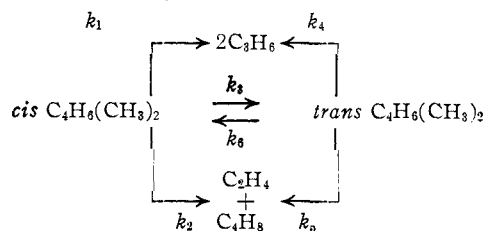
The values summarized in Table III make possible a comparison of the corresponding reactions for *cis*- and *trans*-1,2-dimethylcyclobutane. The rate constants shown in the last column indicate that for each type of ring cleavage the *trans*-1,2-dimethylcyclobutane reacts more slowly than the *cis* isomer. Thus the steric relationship of the two methyl groups affects both the rate of ring cleavage and the ratio of symmetrical to unsymmetrical ring cleavage. The difference in rate for the *cis* and *trans*-1,2-dimethylcyclobutanes depends primarily upon the difference in activation energy. For the symmetrical ring cleavage (4, 1), which is the more important type of ring cleavage, the *trans*-1,2-dimethylcyclobutane has an activation energy approximately 1.2 kcal./mole higher than that for the *cis* compound. The calculated entropies of activation for the ring cleavage reactions of the two 1,2-dimethylcyclobutanes are essentially the same and have positive values close to those observed for the decomposition of the mono-substituted alkylcyclobutanes.⁹

(9) R. E. Wellman and W. D. Walters, *J. Am. Chem. Soc.*, **79**, 1542 (1957); M. N. Das and W. D. Walters, *Z. physik. Chem. (Frankfurt)*, **15**, 22 (1958); S. M. E. Kellner and W. D. Walters, *J. Phys. Chem.*, **65**, 466 (1961).

Another aspect of these studies is the extent to which the 2-butene formed retains the configuration of the parent molecule. In the decomposition of *trans*-1,2-dimethylcyclobutane the 2-butene formed is about 89% *trans* at 390–420°, whereas in the decomposition of the *cis* isomer the 2-butene is 64% *cis*. In neither case is the original configuration retained completely, but it is more nearly so with *trans*-1,2-dimethylcyclobutane. Furthermore in neither case does the proportion of the 2-butenes correspond to the equilibrium composition for which values have been reported in the range 43–47% *cis*-2-butene near 417°.¹⁰ In view of the partial retention of configuration by the 2-butenes formed, if a biradical has a momentary existence during the reaction, it decomposes before the steric configuration reaches the equilibrium condition.

cis-trans Isomerization

The present study and the one reported earlier have shown that the pyrolyses of the 1,2-dimethylcyclobutanes proceed mainly by ring cleavage, but a *cis-trans* isomerization occurs to a lesser extent. Each pyrolytic experiment was designed primarily for the study of the decomposition, and the reaction times were chosen so that the percentage of decomposition would be about 13–15%. Under such reaction conditions the amount of isomerization is small; for example, the measured amount of *trans* isomer formed is 3.5–4% of the unreacted *cis*-1,2-dimethylcyclobutane. In the pyrolysis of the *trans* isomer the amount of isomerization occurring during the usual reaction time was about 2%. Therefore, the accuracy with which the percentage of isomerization was determined by means of the gas chromatographic procedure did not approach that attained for the analyses of the ring cleavage products. Nevertheless, it was of interest to use the analytical data for the calculation of the rates of the geometrical isomerization reactions. The rate constants (k_3 and k_6) for the isomerization were computed on the basis of the following kinetic scheme from relationships derived according to a method outlined by Frost and Pearson.¹¹



Order of Reaction and Homogeneity.—In experiments covering the pressure range 11–393 mm. at 420° for the *cis* isomer, the first order rate constant k_3 at different pressures had the same value within an experimental error of $\pm 5\%$, and for the *trans* isomer with pressures of 17–375 mm. at 430° the first order rate constant k_6 remained unchanged (all values lying within a range of $\pm 8\%$ except one). Likewise an increase in the surface to volume

(10) H. H. Voge and N. C. May, *J. Am. Chem. Soc.*, **68**, 550 (1946); W. F. Anderson, J. A. Bell, J. M. Diamond and K. R. Wilson, *ibid.*, **80**, 2384 (1958).

(11) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 173–177.

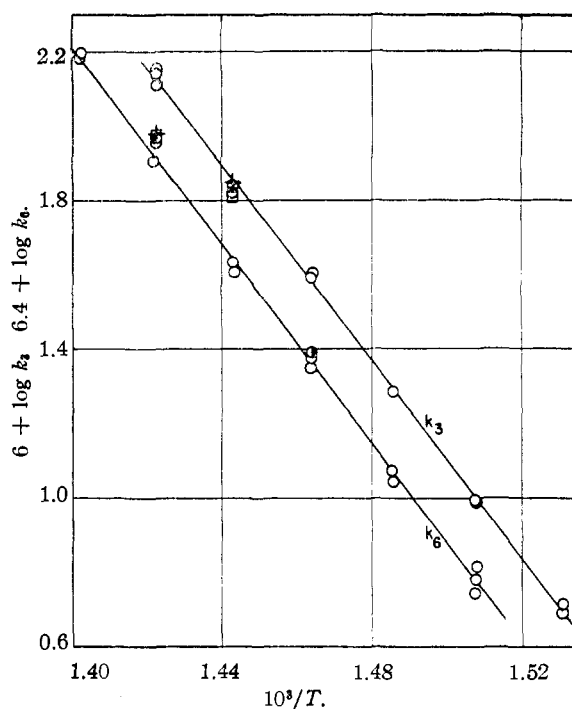


Fig. 3.—First order rate constants for the geometrical isomerization of *cis*-1,2-dimethylcyclobutane (k_3) and *trans*-1,2-dimethylcyclobutane (k_6) at various temperatures: O, initial pressure 11–21 mm.; \bullet , 0.52 mm. NO (or 5.9 mm. propylene) added; \circ , 0.34 mm. NO added; \ominus , 7.5 mm. propylene added; \square , packed reaction vessel; +, initial pressure, ~ 385 mm.

ratio by a factor of 35 did not alter k_3 or k_6 appreciably. That the rate constants are not significantly dependent upon the initial pressure or upon the surface to volume ratio is evident from an inspection of Fig. 3 in which some of the data are given. In other experiments in which radical-chain inhibitors, namely, nitric oxide and propylene, were added the calculated rate constants were essentially the same as those obtained in the absence of inhibitors (see Fig. 3).

Effect of Temperature.—The rate of isomerization was examined from 380 to 430° for the *cis* isomer and from 390 to 440° for the *trans* isomer. The activation energies were evaluated both by the graphical method and by least squares analysis. The isomerization rates observed in the present study may be represented by the following expressions: $k_3 = 6.4 \times 10^{14} \exp(-60100/RT)$ sec.⁻¹ and $k_6 = 3.7 \times 10^{14} \exp(-61300/RT)$ sec.⁻¹. The least squares analysis indicated a deviation of 0.5 kcal./mole for the data for the *cis* isomer and 0.9 kcal./mole for the *trans* isomer. The higher activation energy (about 1 kcal./mole) for the *trans* isomer is approximately the same as the difference observed between the activation energies of the symmetrical ring cleavages (4 and 1) of the 1,2-dimethylcyclobutanes. The faster rate of isomerization observed for the *cis* isomer compared to that of the *trans* isomer indicated that the equilibrium constant (*cis/trans*) is close to 0.24 at 420°.

Discussion of the *cis-trans* Isomerization

A comparison of the present results in the cyclobutane series may be made with the finding of

Flowers and Frey¹² on similar cyclopropane derivatives. Their data for the geometrical isomerization of 1,2-dimethylcyclopropane gave a value of 1.07 kcal./mole for the ΔH of the *trans* to *cis* isomerization, with an equilibrium constant of 0.41 at 399°. A structural isomerization yielding four C₅ olefins was found to be slower than the geometrical isomerization. The greater proportion of 2-pentenenes in the products from *cis*-1,2-dimethylcyclopropane compared to the products from the *trans* isomer was attributed to the repulsion of the methyl groups.

Although the activation energies of the *cis-trans* isomerization reactions of the 1,2-dimethylcyclobutanes are almost the same or slightly lower than the activation energies for the symmetrical ring cleavage reactions 1 and 4, the rates of isomerization are smaller than the rates of the ring cleavages. The slower rates of isomerization appear to be caused by the fact that the pre-exponential factors for the isomerizations are approximately an order of magnitude smaller than those of the ring cleavages. The apparent entropies of activation for the geometrical isomerizations at 430° were estimated from the relationship $A = \kappa e(k_B T/h) \exp(\Delta S^*/R)$. If κ is taken as 1, the apparent entropy of activation, ΔS^* , is 5.5 e.u. for reaction 3 and 4.4 e.u. for reaction 6.¹³ The lower apparent entropies of

(12) M. C. Flowers and H. M. Frey, *Proc. Roy. Soc. (London)*, **A257**, 122 (1960); **A260**, 424 (1961).

activation for the *cis-trans* isomerizations (3 and 6) compared to the ring cleavage reactions (1, 2, 4, and 5) may be the result of a situation where any activated complex for isomerization has a somewhat lower entropy than the type of activated complex required for ring cleavage. On the other hand, if a biradical were formed as a very short-lived intermediate¹⁴ in both isomerization and ring cleavage, the differences in rates of the subsequent steps leading to isomerization or ring cleavage could produce differences in the observed over-all rates. It should be noted that depending on the C-C bond broken initially more than one type of biradical could conceivably be formed.

Acknowledgment.—The authors wish to thank the Esso Education Foundation for the grant to the Department of Chemistry which provided the gas chromatograph used in this work. They also wish to thank Mr. Carl Whiteman, Jr., for making the infrared measurements and the least squares calculations.

(13) With $\kappa = 0.5$, the values of ΔS^* would be 6.9 and 5.8 e.u. for reactions 3 and 6, respectively.

(14) In a consideration of the 1,2-dideuteriocyclopropane isomerization data (see E. W. Schlag and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **82**, 5996 (1960)) recently S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961), has discussed such a mechanism for the pyrolysis of cyclopropane and suggested it for cyclobutane. F. T. Smith, *ibid.*, **29**, 235 (1958), has postulated an internal rotation (rather than a ring opening) for the geometrical isomerization of 1,2-dideuteriocyclopropane.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, ROCHESTER, NEW YORK]

The Vapor Phase Decomposition of 2,5-Dihydrofuran¹

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The decomposition of 2,5-dihydrofuran between 342 and 409° has been found to be a first order homogeneous process yielding equal amounts of hydrogen and furan as the only products. Addition of nitric oxide, propylene or toluene had no effect upon the rate of decomposition. The calculated first order rate constants were observed to remain unchanged, in this study, over the pressure range 5–46 mm. and at pressures from 57 to 270 mm. in earlier work in this Laboratory. From experiments with initial pressures of 10–12 mm. the rate constant was calculated to be $5.3 \pm 0.1 \times 10^{12} \exp.(-48,500/RT)$ sec.⁻¹.

Experiments² conducted some years ago in this Laboratory showed that the thermal decomposition of 2,5-dihydrofuran takes place at 400–470° and that furan is an important product. Furan was detected first² by the Liebermann-Burchard reaction,³ and its presence was confirmed by infrared absorption measurements.^{2,4} In a series of exploratory experiments⁴ near 400° with initial pressures of 125–270 mm. the reaction mixture was removed after 50–60% pressure increase and the gas, non-condensable at –195°, was measured. The measured amounts of this gas averaged within 4% of the values expected from the observed pressure increase on the basis that the reaction yields only furan and hydrogen. No evidence was obtained

for the presence of aldehydes in the products. Pressure-time curves for the decomposition in a constant volume system indicated that the reaction is a first order process over the pressure range 57–270 mm. and experiments at 370–410° gave a value of about 48 kcal./mole for the activation energy.⁴

Recently α -alkyl-2,5-dihydrofurans have been passed over broken silica and activated charcoal at 470–480° and have been found to give α -alkylfurans and hydrogen.⁵

In order to determine the stoichiometry of the decomposition and to ascertain the kinetic parameters more accurately, a study of the decomposition of a highly purified sample of 2,5-dihydrofuran has been undertaken.

Experimental

Materials.—Three different samples of 2,5-dihydrofuran were used in these experiments. Samples A and B were kindly given to us by Dr. Raymond Paul, Société Des Usines Chimiques, Rhone-Poulenc, Paris. Sample A, which

(1) Financial support was received during a portion of this work from a Shell Research Grant to the Department of Chemistry.

(2) Performed by H. I. Machoukin as part of his senior research problem for the B.S. degree, 1955.

(3) V. E. Levine and E. Richman, *Proc. Soc. Exptl. Biol. Med.*, **31**, 582 (1934).

(4) Results of Anna Morlang in connection with her senior research problem for the B.S. degree, 1956.

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