

its effect on the characteristics of conductometric,<sup>21-23</sup> potentiometric,<sup>5,23,24</sup> and spectrophotometric<sup>25</sup> neutralization curves. Romberg and Cruse<sup>5</sup> accounted quantitatively for the shape of their potentiometric titration curves on the basis of associated anions.

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

## The Thermal Decomposition of *cis*-1,2-Dimethylcyclobutane<sup>1</sup>

BY H. R. GERBERICH AND W. D. WALTERS

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The gas-phase thermal decomposition of *cis*-1,2-dimethylcyclobutane has been investigated for pressures near 15 mm. over the temperature region 380–430° and for initial pressures from 5.8 to 393 mm. at 420°. The products which were analyzed qualitatively by infrared absorption and quantitatively by gas chromatography indicated that the main decomposition process is a ring cleavage to yield two molecules of propylene. A second ring cleavage of lesser importance produces ethylene and a mixture of *cis*-2-butene and *trans*-2-butene. Both processes were found to be first order decompositions which could not be inhibited by nitric oxide or propylene. The first order rate constant for the reaction forming propylene can be expressed as  $k_1 = 3.0 \times 10^{15} \exp(-60400/RT)$  sec.<sup>-1</sup> and the rate constant for the cleavage into ethylene and 2-butene,  $k_2 = 3.7 \times 10^{15} \exp(-63000/RT)$  sec.<sup>-1</sup>. The ring cleavage is accompanied by a slower isomerization yielding *trans*-1,2-dimethylcyclobutane.

Earlier studies have shown that cyclobutane<sup>2</sup> and its monoalkyl substituted derivatives<sup>3</sup> decompose thermally into ethylene and a substituted ethylene. The ring cleavages are first order homogeneous reactions and are unaffected by the addition of nitric oxide, propylene or toluene. An investigation of *cis*-1,2-dimethylcyclobutane was of interest because there was the possibility of one ring cleavage process yielding two molecules of propylene and another reaction forming 2-butene and ethylene. This study was undertaken to determine the relative importance of two types of ring cleavage and to compare the pyrolysis of a *cis*-disubstituted cyclobutane with those of the monosubstituted cyclobutanes. The consideration of the isomerization of the *cis*-isomer into *trans*-1,2-dimethylcyclobutane will be given in a subsequent paper.

### Experimental

**Materials and Apparatus.**—*cis*-1,2-Dimethylcyclobutane was synthesized in a three-step process starting from the anhydride of *cis*-1,2-cyclobutanedicarboxylic acid.<sup>4</sup> The procedure<sup>5</sup> consisted in reduction of the anhydride to the diol with lithium aluminum hydride, followed by esterification with *p*-toluenesulfonyl chloride and subsequent reduction of the di-tosyl ester to the hydrocarbon with lithium aluminum hydride. The crude material was fractionated in a 75-cm. column with Lecky-Ewell packing while a 10 to 1 reflux ratio was maintained. Five fractions (~4 ml. each) which distilled over the range 66.3–67.1° at 748 mm. were taken, and for use in rate studies each of these fractions was subjected to further purification in a Perkin-Elmer 154B Vapor Fractometer. The infrared

spectra of the five purified samples were essentially identical. Quantitative analysis by gas chromatography indicated a purity of at least 99.7%. Carbon-hydrogen analysis<sup>6</sup> of the purified material yielded: C, 85.44, 85.59; H, 14.55, 14.50 (theor. C, 85.62; H, 14.38). The refractive index was  $n_D^{20}$  1.403. A second sample<sup>7</sup> of *cis*-1,2-dimethylcyclobutane was obtained by the reduction of 2-methylcyclobutanecarboxylic acid by a procedure similar to that mentioned above. In this case both *trans* and *cis* isomers were formed and the higher boiling *cis* isomer was separated by fractional distillation and gas chromatography. The infrared spectrum and the kinetic behavior of this second sample of the *cis* isomer were essentially identical with the sample prepared from the anhydride of *cis*-1,2-cyclobutanedicarboxylic acid.

Propylene (99.5%, Ohio), ethylene (99.5%, Ohio), *trans*-2-butene (99%, Matheson), *cis*-2-butene (99%, Matheson) and nitric oxide (98.7%, Matheson) were distilled from trap to trap under vacuum and degassed thoroughly before use.

The vacuum system, furnace and temperature control were of a relatively conventional type. The temperature which was regulated to within  $\pm 0.1^\circ$  during an experiment was measured with a platinum, platinum-13% rhodium thermocouple standardized regularly at the melting point of zinc (419.5°). The Pyrex glass reaction vessels used in the various phases of this investigation were cylindrical in shape and had these characteristics: vessel (A) 487 ml. capacity, low pressure experiments (below 40 mm. initial pressure); vessel (B), 319 ml. capacity, high pressure experiments (90–400 mm.); vessel (C), 430 ml. free volume, packed with thin-walled Pyrex tubing, surface-to-volume ratio about 35 times that of vessel (A).

The reaction system was one of almost constant volume. The pressure increase during a low pressure experiment was measured to  $\pm 0.01$  mm. on a wide bore manometer with the aid of a Gaertner M930-300 cathetometer. The pressure increase during a high pressure experiment was read directly from an ordinary mercury manometer. In all experiments the pressure data were corrected for the small "dead space" external to the reaction zone. Subsequent to the kinetic experiment the unreacted *cis*-1,2-dimethylcyclobutane and products were removed rapidly from the reaction vessel by expansion through a series of three cold traps, the coldest of which was at  $-196^\circ$ .

**Analysis of the Products.**—The products of the reaction were separated by their differences in volatility and analyzed by infrared spectroscopy, gas chromatography and

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

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(7) Preparation by D. T. Culley in this Laboratory.

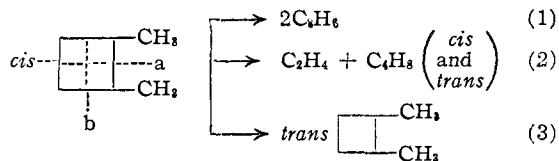
reaction with sulfuric acid. In most experiments the reaction products were divided into three portions: the material non-condensable at  $-196^\circ$  (I), the material volatile at  $-95^\circ$  but condensable at  $-196^\circ$  (II), and the material volatile at room temperature, but condensable at  $-95^\circ$  (III). The volumes of fractions I and II were measured in a gas buret. The material in fraction III was condensed at  $-196^\circ$  into a tube fitted with a micro-stopcock and weighed.

Fraction I seldom amounted to more than 0.2 volume % of fraction II and was not analyzed further. In several experiments fraction II was separated into three portions of different volatilities and the portions were tested for absorbability in activated sulfuric acid<sup>8</sup> or 87% sulfuric acid.<sup>9</sup> The data indicated that  $C_3$  and  $C_4$  unsaturated hydrocarbons along with ethylene are the main constituents of fraction II and account for 98-99% of this fraction. Two additional methods were used to identify the reaction products in fraction II. Gas chromatography revealed four components which had retention times identical with those of pure ethylene, propylene, *trans*-2-butene and *cis*-2-butene. Sufficient material for infrared measurements was obtained by the use of the combined products from six 400 mm. experiments carried to 50-60% pressure increase at 445-450°. Each of the four components of fraction II then was isolated by gas chromatography. The infrared spectra of these constituents corresponded closely to those of pure samples of ethylene, propylene, *trans*-2-butene and *cis*-2-butene. In the *trans*-2-butene portion there was some absorption at  $15\mu$  from a small amount of *cis* isomer which was not removed completely by the chromatographic separation.

Fraction III contained *cis*- and *trans*-1,2-dimethylcyclobutanes which accounted for at least 99.4% of the fraction at 14% decomposition. The infrared spectra of these components after the large scale separation were quite similar to the spectra for the corresponding pure compounds. A small deviation from complete purity may be due to a less satisfactory separation for the large amounts used and to minor products from subsequent reactions occurring at the longer times and higher pressures used for the collection of the products. The two isomers had these infrared absorption maxima: 3.47, 6.8-6.9, 7.25, 7.4-7.6, 9.75 and 10.47 $\mu$  for the *cis*- and 3.47, 6.8-6.9, 7.2-7.3, 7.5-7.6, 8.02, 9.1-9.2 and 10.28 $\mu$  for the *trans*-1,2-dimethylcyclobutane.

The quantitative determination of the compositions of fractions II and III was accomplished by gas chromatography. Nearly all gas chromatographic analyses were made using a column packed with Perkin Elmer "D" material. In the quantitative analysis of fraction III the peaks for the *cis* and *trans* isomers were well separated. For various analyses both the peak height and the area under the peak on the chromatogram were used to calculate the amount of each component in the fraction and were found to give concordant results. To check the validity of the analytical procedures, chromatograms of similar standard mixtures were determined frequently and compared with those of the reaction products.

On the basis of the products identified it appears that there are three reactions which occur simultaneously in the pyrolysis of *cis*-1,2-dimethylcyclobutane



Cleavage along "a" leads to two molecules of propylene, cleavage along "b" leads to a molecule of ethylene and a molecule of 2-butene (*cis* or *trans*), and a geometric isomerization produces *trans*-1,2-dimethylcyclobutane. The relative importance of these three reactions was determined by analyses performed on the products from twenty-three experiments under different experimental conditions. Some of the results at  $420^\circ$  are given in Table I. It was found that the decomposition to propylene predominates over

that to ethylene and the isomers of 2-butene. As expected from equation 2, the amount of ethylene is equivalent to the sum of the *cis*- and *trans*-2-butene. Gas chromatographic analyses also showed that in experiments with *cis*-1,2-dimethylcyclobutane after a time when 14% of the  $C_8H_{12}$  had undergone ring cleavage, the  $C_8H_{12}$  remaining undecomposed was not more than 3.6% *trans* isomer. Experiments at  $420^\circ$  carried out in the presence or absence of nitric oxide and with vessels of different surface to volume ratios (see Table I) gave reaction mixtures with unchanged proportions of propylene, ethylene and the 2-butenes.

TABLE I  
PRODUCTS FROM THE THERMAL DECOMPOSITION OF *cis*-1,2-DIMETHYLCYCLOBUTANE AT  $420^\circ$  UNDER VARIOUS EXPERIMENTAL CONDITIONS

$P_0$ , <sup>a</sup> mm.	$\Delta P$ , mm.	Pressure of the components in the reaction mixture in mm.				
		$C_2H_4$	$C_3H_6$	$C_4H_8$ , <i>trans</i>	$C_4H_8$ , <i>cis</i>	$C_8H_{12}$
10.9	1.48	2.54	0.23	0.08	0.15	..
12.3 <sup>b</sup>	1.74	2.89	.27	.10	.17	10.5
16.6	2.39	4.09	.37	.14	.25	14.2
14.1 <sup>c</sup>	2.03	3.48	.32	.12	.20	12.1
19.8 <sup>d</sup>	2.78	4.80	.44	.17	.29	17.1
19.1 <sup>d</sup>	2.63	4.49	.41	.15	.27	16.5
393 <sup>e</sup>	59.5	99.5	9.2	3.5	6.1	338
15.8 <sup>f</sup>	2.29	4.65 (total $C_2$ , $C_3$ , $C_4$ )				13.6

<sup>a</sup> Initial pressures given here only to  $\pm 0.1$  mm, to save space. <sup>b</sup> Sample of *cis* isomer prepared from 2-methylcyclobutane carboxylic acid, other experiments with material obtained from the anhydride of *cis*-1,2-cyclobutanedicarboxylic acid. <sup>c</sup> 0.11 mm. nitric oxide added. <sup>d</sup> In packed vessel C. <sup>e</sup> In unpacked vessel B, other experiments in vessel A. <sup>f</sup> 0.52 mm. nitric oxide added.

Experiments were performed to ascertain whether the *cis* or *trans*-2-butene reacts further after its formation. It was found that a pure sample of *cis*- or *trans*-2-butene undergoes less than 0.1% conversion to the other isomer under the conditions of the usual kinetic experiment. These observations are in good agreement with the data obtained by Anderson, Bell, Diamond and Wilson<sup>10</sup> and by Rabinovitch and Michel<sup>11</sup> on the thermal isomerization of *cis*-2-butene. It was observed that a mixture of ethylene, propylene, *trans*-2-butene and *cis*-2-butene reacts to a negligible extent for the conditions to which the reaction products would be subjected in the rate studies.

Prior to a study of the kinetics it was necessary to find out whether pressure-time measurements could be used to evaluate the over-all rate of decomposition of *cis*-1,2-dimethylcyclobutane. If reactions 1 and 2 were the only processes occurring, then in a constant volume system  $\Delta P = \frac{1}{2} P_{C_4H_8} + P_{C_2H_4} = \frac{1}{2} (P_{C_4H_8} + P_{C_4H_8} + P_{C_2H_4})$ . Examination of the results in Table I shows that these relationships are obeyed reasonably well for experiments at  $420^\circ$ . In Fig. 1 the quantity  $\Delta P / (\frac{1}{2} P_{C_4H_8} + P_{C_2H_4})$  is given for experiments covering most of the conditions used in the kinetic studies. This plot gives evidence that the experimental ratios usually are within 2% of the value 1.00, and thus the pressure increase seems to be a reliable measure of the extent of reaction 1 plus 2. The data in Table I also indicate that a satisfactory material balance has been obtained for various conditions. The sum of the pressure of the undecomposed dimethylcyclobutanes (column 7) and one-half the total pressure of ethylene, propylene and butenes is very nearly equal to the initial pressure of *cis*-1,2-dimethylcyclobutane (column 1). In a preliminary experiment it had been found that when a sample of *cis*-1,2-dimethylcyclobutane was decomposed for a period of 13 half-lives, the pressure attained a value 1.98 times the initial pressure.

As indicated above, accompanying the decomposition by reactions 1 and 2 is a small amount of isomerization by reaction 3. To minimize the effect of this geometric isomerization only the data obtained during the first 12.5% decomposition were used for calculation of the rate con-

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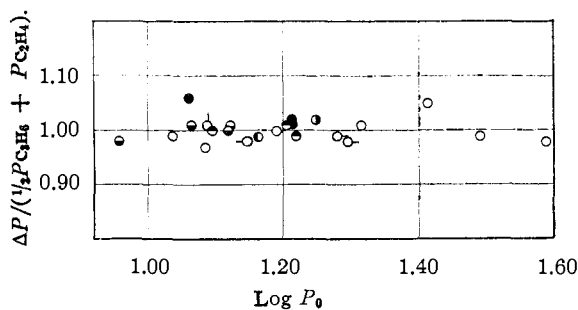


Fig. 1.—Value of  $\Delta P / (\frac{1}{2} P_{C_3H_6} + P_{C_4H_8})$  for the decomposition of *cis*-1,2-dimethylcyclobutane under various conditions:  $\ominus$ , 430°;  $\circ$ , 420°;  $\bullet$ , 410°;  $\odot$ , 400°;  $\oplus$ , 390°;  $\ominus$ , 380°;  $\circ$ , 0.11 mm. NO added;  $\circ$ , packed vessel;  $\diamond$ , sample prepared from 2-methylcyclobutanecarboxylic acid.

starts. Careful analysis of the undecomposed dimethylcyclobutanes (fraction III) after about 15% decomposition has shown that fraction III is 96–97% *cis* isomer. Consequently, the average composition of the dimethylcyclobutane is at least 98% *cis* isomer over the initial 12.5% decomposition. Studies<sup>6</sup> which will be reported later have shown that the rates of decomposition and isomerization of the *trans*-1,2-dimethylcyclobutane are considerably less than those for the *cis* isomer. In view of these findings it was apparent that only a small fraction of the *trans*-1,2-dimethylcyclobutane formed in reaction 3 will undergo subsequent reaction. Since the undecomposed dimethylcyclobutane is nearly 100% *cis* isomer in the initial stages, the time for 12.5% pressure increase has been used to calculate the first order constant and a small correction, amounting to about 1.2 parts per hundred, has been applied to the rate constant to compensate for the effect of the geometric isomerization.

## Results

**Pressure-Time Curve and Order of the Reaction.**—The observed correspondence between the pressure increase and the amount of decomposition made it possible to use pressure measurements for following the over-all rate of decomposition. The shape of the pressure-time curve gave no indication of an induction period and remained the same in the presence of nitric oxide or propylene and in the packed vessel. Rate constants for the decomposition (with the small correction for the isomerization) were calculated for a series of experiments at 420° for pure *cis*-1,2-dimethylcyclobutane with initial pressures from 5.8 to 393 mm. The data, most of which are given in Fig. 2, show that the first order rate constant  $k$  for the over-all decomposition (reaction 1 plus 2) is essentially unaltered over a 67-fold variation in initial pressure. Plots of  $\log [P_0 / (2P_0 - P_t)]$  vs. time were linear up to 15% pressure increase; the slight curvature observed at higher percentages of reaction was understandable on the basis of the gradual formation of the *trans* isomer which decomposes at a slower rate. The rate constants calculated from the slopes of the lines of such plots agreed within 0.5% with the rate constants calculated from the time for 12.5% pressure increase.

Since in the majority of the experiments the products after about one-eighth decomposition were analyzed by gas chromatography, it was possible to calculate the rate constants  $k_1$  and  $k_2$  for the individual reactions 1 and 2. The amounts of propylene and ethylene, which were more reliable than those for the 2-butenes, were the

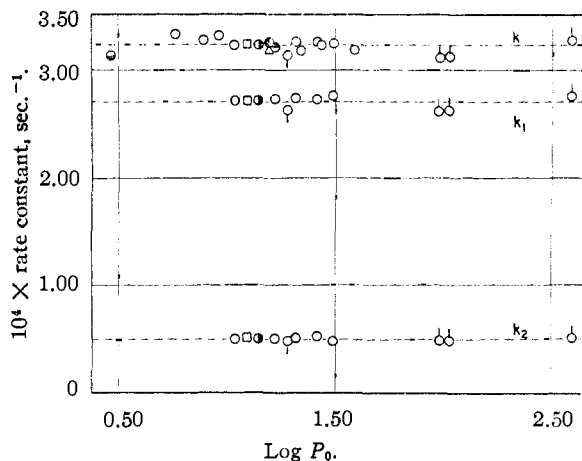


Fig. 2.—First order rate constants for the decomposition of *cis*-1,2-dimethylcyclobutane at 420°. Dashed lines denote average values of the points shown for pure sample A:  $\ominus$ , 3.42 mm. propylene added;  $\square$ , sample prepared from 2-methylcyclobutanecarboxylic acid;  $\bullet$ , 0.11 mm. NO added;  $\Delta$ , purified, pre-pyrolyzed sample;  $\odot$ , 0.52 mm. NO added;  $\oplus$ , 5.94 mm. propylene added;  $\circ$ , packed vessel;  $\diamond$ , vessel B.

important quantities in the evaluation of the rate constants by the use of the following relationships:  $k_1 = [P_{C_3H_6} / (P_{C_3H_6} + P_{C_2H_4} + P_{C_2H_2})]k$  and  $k_2 = [2 P_{C_2H_4} / (P_{C_3H_6} + P_{C_2H_4} + P_{C_2H_2})]k$  where  $k$  represents the over-all first order rate constant obtained from pressure measurements. The values of the rate constants for reactions 1 and 2, which are shown in Fig. 2, are independent of pressure over a 36-fold change and are not affected by changes in surface to volume ratio or addition of free radical chain inhibitors.

**Effect of Temperature.**—The first order rate constant,  $k$ , for the over-all decomposition of *cis*-1,2-dimethylcyclobutane has been determined over the temperature range 380–430°. In Fig. 3 the

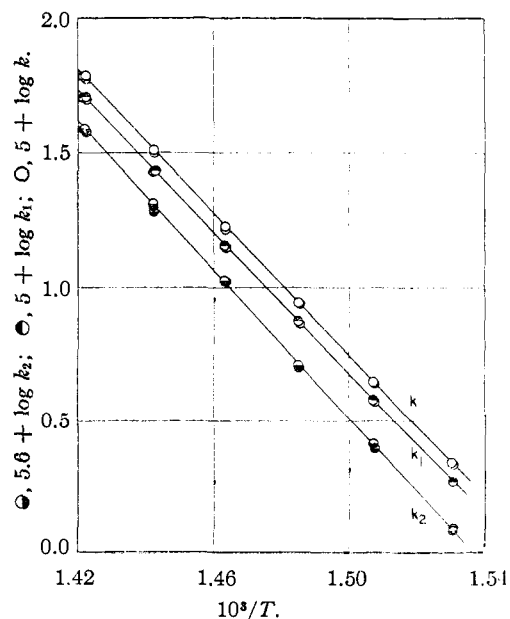


Fig. 3.—Dependence of the first order rate constants upon the temperature.

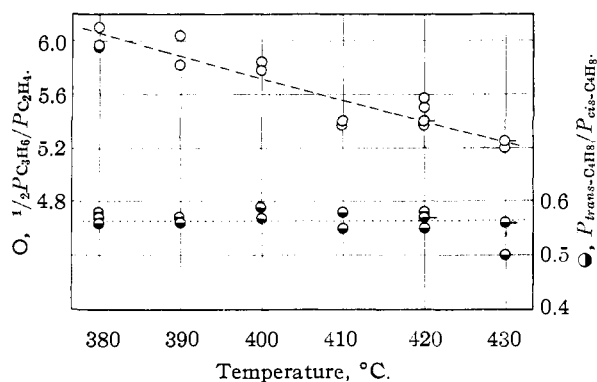


Fig. 4.—Effect of temperature on the ring cleavage products from *cis*-1,2-dimethylcyclobutane at 10–20 mm. initial pressure. For  $P_{\text{trans-C}_4\text{H}_8}/P_{\text{cis-C}_4\text{H}_8}$  the dotted line represents the average value at temperatures from 380 to 430°. Circles with horizontal lines indicate that two or more points coincide.

highest line is a plot of  $\log k$  vs.  $1/T$ . The activation energy calculated from the slope of this line is 60.8 kcal./mole which was the value obtained also from a least squares calculation of the data. The rate of the decomposition may be expressed as  $k = 4.8 \times 10^{15} \exp(-60800/RT)$  sec.<sup>-1</sup>. This activation energy will not correspond exactly to the activation energy of reaction 1 or 2 unless each of the individual reactions has the same activation energy. That reactions 1 and 2 do not have the same temperature coefficient was indicated by the analyses of the products at temperatures from 380 to 430°. The data have been plotted in Fig. 4 in terms of the ratio  $1/2 P_{\text{C}_3\text{H}_6}/P_{\text{C}_2\text{H}_4}$  at various temperatures. This ratio decreases from a value of 6.0 at 380° to about 5.2 at 430°. The slightly curved dashed line indicates the way in which the ratio would vary if reaction 2 had an activation energy 2.6 kcal./mole greater than reaction 1. To ascertain the activation energies for reactions 1 and 2, the rate constants  $k_1$  and  $k_2$  have been obtained at the different temperatures on the basis of the product analyses using the method outlined above. These data have been plotted in Fig. 3 with the curve designated as ( $k_1$ ) representing  $\log k_1$  vs.  $1/T$  and curve ( $k_2$ ) representing  $\log k_2$  vs.  $1/T$ . The steeper slope of curve ( $k_2$ ) gives evidence for a higher activation energy for reaction 2. Activation energies have been calculated both from the slopes of these graphs and by the method of least squares. The rate expressions are

$$k_1 = 3.0 \times 10^{15} \exp(-60400/RT) \text{ sec.}^{-1}$$

$$k_2 = 3.7 \times 10^{15} \exp(-63000/RT) \text{ sec.}^{-1}$$

A difference in activation energy of about 2.6 to 2.7 kcal./mole between reactions 1 and 2 also was indicated from the slope of a plot of  $\log (1/2 P_{\text{C}_3\text{H}_6}/P_{\text{C}_2\text{H}_4})$  vs.  $1/T$  (not shown).

With respect to the effect of temperature on the composition of the products, it is of interest that the ratio of *trans*-2-butene to *cis*-2-butene did not vary significantly from a value of 0.57 as the temperature was increased from 380 to 430° (see Fig. 4). This ratio, however, is not at the equilibrium value

which has been reported in one publication to be 1.12 at 417°<sup>10</sup> and in another paper to be 1.31 and 1.40 at 427° and 327°, respectively.<sup>12</sup>

### Discussion

The results of this investigation show that the main type of thermal reaction of *cis*-1,2-dimethylcyclobutane is decomposition into two molecules of propylene or into a molecule of ethylene and a molecule of 2-butene (*cis* or *trans*). These results are similar to the simple ring cleavages observed for other cyclobutane compounds. It was found that a slower geometric isomerization to *trans*-1,2-dimethylcyclobutane also occurs. Non-catalytic *cis-trans* isomerization has been observed for 1,2-dideuteriocyclopropane<sup>13</sup> and 1,2-dimethylcyclopropane,<sup>14</sup> but in these cases the geometric isomerization is faster than the structural isomerization. Both of the ring cleavages involved in the decomposition of *cis*-1,2-dimethylcyclobutane seem to be homogeneous first order reactions free from free radical chain processes. The frequency factors which are slightly higher than many unimolecular reactions can be interpreted in terms of the transition state theory as indicating positive entropies of activation. Values of the entropy of activation  $\Delta S^*$  have been calculated by equating each experimental frequency factor at 430° to  $\kappa(kT/h) \exp(\Delta S^*/R)$  and assuming  $\kappa$ , the transmission coefficient, to be unity. The entropies of activation for reactions 1 and 2 were computed to be + 8.6 e.u. and + 9.0 e.u., respectively. The positive values are in accord with processes involving ring opening. That the first order constant does not fall off at an initial pressure of 5.8 mm. seems reasonable for a unimolecular reaction of a molecule of the complexity of *cis*-1,2-dimethylcyclobutane.

The activation energy for the over-all decomposition of *cis*-1,2-dimethylcyclobutane (60.8 kcal./mole) is in about the same range as those observed for cyclobutane and the monoalkylsubstituted cyclobutanes (61.2–62.5 kcal./mole). In the methyl substituted series of cyclobutane derivatives the relative rate constants of the decomposition reactions<sup>15</sup> at 430° for cyclobutane, methylcyclobutane and *cis*-1,2-dimethylcyclobutane are 1.0, 1.5 and 4.0. The larger change in going from the methyl to the *cis*-dimethyl derivative indicates that a steric effect plays a significant role. This has been confirmed by the observation that the rate of ring cleavage of *trans*-1,2-dimethylcyclobutane is slower than that of the *cis* compound.<sup>5</sup> Another aspect of the kinetic findings is that the rate of decomposition to produce propylene is 5 to 6 times faster than the decomposition to form ethylene and 2-butene. This preference of ring cleavage presumably results from the combined effects of alkyl substitution on the ring and steric repulsion of the *cis* methyl groups.

It is significant that the 2-butene formed during the decomposition is about 64% *cis* and 36% *trans*.

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Since the product is not 100% *cis*-2-butene, the ring cleavage into two olefins does not occur without some disturbance of the geometrical features of the *cis*-oriented methyl groups. On the other hand the distribution of the 2-butenes differs from the equilibrium composition (literature values, 43 to 47% *cis*-2-butene near 417°). It appears that if a biradical exists momentarily as an intermediate, it decomposes before the original geom-

etry is completely converted to the equilibrium distribution.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, NEW YORK]

## Studies in Non-Stoichiometry. Electrical Conductivity and Carrier Mobility in Lithium Tungsten Bronzes<sup>1</sup>

BY M. J. SIENKO AND THU BA NGUYEN TRUONG

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Single crystal resistivity measurements, X-ray spacings and densities are reported for three lithium tungsten bronzes:  $\text{Li}_{.394}\text{WO}_3$ ,  $\text{Li}_{.377}\text{WO}_3$ , and  $\text{Li}_{.365}\text{WO}_3$ . In the range  $-150$  to  $90^\circ$ , conduction is metallic, in contradiction to previous reports. The electron mobility increases with lithium content and decreases with temperature. Arguments are given for believing there should be a transition from localization of electrons to delocalization at approximately  $\text{Li}_{.25}\text{WO}_3$ . Reexamination of previously reported magnetic results suggest a maximum in the effective mass of the carriers at  $\text{M}_{.30}\text{WO}_3$ . The change in effective mass and mobility is attributed mainly to the effect of cationic point charge defects on the  $5d$  conduction band.

The non-stoichiometric alkali metal tungsten bronzes,  $\text{M}_x\text{WO}_3$  ( $0 < x < 1$ ), also written  $x\text{MW}^{\text{VO}}_3 \cdot (1-x)\text{W}^{\text{VI}}\text{O}_3$ , can be considered to be derived from a host  $\text{WO}_3$  lattice doped with alkali metal M. The sodium tungsten bronzes, for which the data are most extensive, are metallic—they have a positive thermal coefficient of resistivity,<sup>2</sup> a small temperature-independent paramagnetism<sup>3</sup> and a negative Hall coefficient<sup>4</sup> that corresponds to one free carrier per sodium atom. A possible model<sup>5</sup> for the tungsten bronzes is one in which metal M is viewed as an interstitial donor in a  $\text{WO}_3$  lattice, with the donated electrons being accepted into the  $5d_x$  conduction band levels of the  $\text{WO}_3$  host. On this basis there should be little difference between sodium tungsten bronze and lithium tungsten bronze, inasmuch as both have perovskite-type structures and both alkali atoms have nearly the same ionization energy. If, as seems reasonable, a deep lithium trap is excluded, then the semiconductivity reported<sup>6</sup> for  $\text{Li}_x\text{WO}_3$  would have to be attributed to contact resistances or to grain boundary effects. Furthermore, the finding in  $\text{Li}_x\text{WO}_3$  of small, temperature-independent paramagnetic moments,<sup>7</sup> nearly constant with varying lithium content, strongly suggests a metallic origin of the susceptibility and hence of the conductivity. To this end, we have undertaken in this work the preparation of single crystals of

$\text{Li}_x\text{WO}_3$  and the measurement of their electrical resistivities as a function of temperature. By using a potential probe method, we avoid the interpretation complications inherent with contact resistances and measurements on powders.

**Preparation.**—Crystals of  $\text{Li}_x\text{WO}_3$  were prepared by electrodeposition from fused mixtures of  $\text{Li}_2\text{CO}_3$  and  $\text{WO}_3$ . The electrolysis cell consisted of a nest of three porcelain crucibles with a Pt or W cathode in the center crucible and a Pt anode in the outer. Slits cut on opposite sides of the two inner crucibles served to increase the effective electrode separation. The best crystals were obtained (on the cathode) under the following conditions: molar ratio  $\text{Li}_2\text{CO}_3/\text{WO}_3$ , 1/1.75; temperature, 780–850°; cathode current density, 0.35 amp./cm.<sup>2</sup>; time of electrolysis, 20–25 hr. Under these conditions, with argon flow through the furnace and with electrode geometry arranged so as to minimize migration of the anode-product oxygen into the cathode compartment, well-shaped, blue-black crystals 3 to 4 mm. long and 1.5 to 2 mm. wide usually could be obtained.

It is assumed that on fusion the  $\text{Li}_2\text{CO}_3\text{-WO}_3$  mix evolved carbon dioxide with formation of  $\text{Li}_2\text{WO}_4$ , which then equilibrated with the  $\text{WO}_3$ . There seemed to be considerable time lag in this equilibration of the  $\text{Li}_2\text{WO}_4\text{-WO}_3$  melt. Separate studies of "current vs. applied voltage" decomposition curves gave, on extrapolation to zero current, "decomposition potentials" which normally fell in the range 0.9–1.0 volt, but a reproducible decomposition potential was obtainable only after 1 hr. or so of equilibration at the approximate final electrolysis temperature. Such behavior was noted independent of whether the initial charge put in the cell was  $\text{Li}_2\text{CO}_3$  and  $\text{WO}_3$  or, as was used occasionally,  $\text{Li}_2\text{WO}_4$  and  $\text{WO}_3$ . The time lag may be due to poly-anion formation that is slow or to slow clustering of oxytungstate structures

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