795. *The Thermal Isomerization of* 1,1-*Dimethylcyclopropane.*

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The thermal isomerization of 1,1-dimethylcyclopropane has been investigated between 447° and 511° c. In this range, in an " aged " reaction vessel, the isomerization is homogeneous and unimolecular. The main products of the isomerization are 3-methylbut-1-ene and 2-methylbut-2-ene which are formed in nearly equal amounts. The first-order rate constant begins to decrease at a pressure of about 4 mm., and at 0·1 mm. it has fallen to 70% of the high-pressure value. A mechanism similar to that suggested for the isomerization of cyclopropane is consistent with the products formed and with the *A* factor for this reaction.

Experimental

Preparation of 1,1-*Dimethylcyclopropane.*—(*a*) 1,3-Dibromo-2,2-dimethylpropane was prepared from 2,2-dimethylpropane-1,3-diol in a manner similar to that of Shortridge *et al.*[1] A purer final product could be obtained by extraction of the crude product with concentrated sulphuric acid, followed by washing with aqueous sodium carbonate and water, before drying and fractional distillation. The overall yield was 42%.

(*b*) 1,3-Dibromo-2,2-dimethylpropane was cyclised by the method of Shortridge *et al.*[1] The 1,1-dimethylcyclopropane was freed from olefins (the major impurities) by prolonged contact at 0° with a 1% solution of potassium permanganate in saturated sodium hydrogen carbonate. The dimethylcyclopropane was distilled from this mixture into a trap cooled to $-78°$. Distillation at $-78°$ into a trap cooled in liquid oxygen removed water, and the final product, obtained by fractional distillation under reduced pressure at $-24°$ in a 13 in. Podbielniack column, contained $<1\%$ of total impurity.

Nitric oxide, prepared from " AnalaR " concentrated sulphuric acid and saturated sodium nitrate solution in presence of mercury, was condensed and stored in a liquid-oxygen trap.

Carbon dioxide, from the commercial solid was subjected to two trap-to-trap distillations ($-78°$ to $-186°$) to remove water and non-condensable gases.

Apparatus.—A conventional " static " apparatus was used. Most isomerizations were carried out in a cylindrical silica reaction vessel (volume 205 ml.) fitted with a thermocouple well. In a few runs a reaction vessel packed with silica tubes (volume 139 ml.) was employed. The temperature was measured by use of a platinum/platinum–rhodium thermocouple calibrated against a standard platinum resistance thermometer. By using a furnace with a graded winding tapped at two points for external shunts the temperature gradient over the entire reaction vessel was kept to less than 0·5°. The temperature of the furnace, controlled by a Sunvic RT2 regulator, could be maintained indefinitely to within 0·2°.

Procedure.—1,1-Dimethylcyclopropane was admitted to the reaction vessel from a series of graduated gas pipettes. After each run the reaction vessel was opened to a 100 ml. evacuated bulb cooled in liquid oxygen. Between runs the reaction vessel was pumped down to 10^{-5} mm. Before any series of runs the vessel was " aged " by the addition of 100 mm. of the cyclopropane and allowing this to remain in the vessel for 36 hr. With a reaction vessel not so " aged " the rates were faster and not reproducible.

Analysis.—Reaction products were analysed by gas chromatography in a 30 ft. × 0·17 in. (i.d.) coiled copper column packed with hexane-2,5-dione on firebrick (30—60 mesh) with an additional 4 ft. (0·17 in. diam.) glass column packed with silver nitrate in ethylene glycol on a similar support. Both columns were at 0°. Hydrogen was the carrier gas. For the analysis of the runs at 100 mm. pressure and those in the packed reaction vessel, a Pye platinum-filament katharometer was used. All the other runs were analysed with a Gow-Mac (tungsten filament) katharometer. The silver nitrate–ethylene glycol column was necessary to separate the 1,1-dimethylcyclopropane and 3-methylbut-1-ene which are otherwise eluted at the same time.[2] The column was calibrated with synthetic mixtures of the products and reactant, equivalent to varying percentage decompositions. Determination of the percentage decomposition could be

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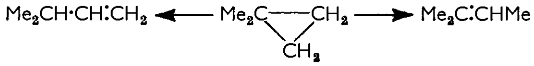
[1] Shortridge, Craig, Greenlee, Derfer, and Boord, *J. Amer. Chem. Soc.*, 1948, **70**, 946.

[2] Frey, *Nature*, 1959, **183**, 743.

estimated to ±2% but the determination of the ratio of the products was less accurate (5%). Corrections were made throughout for " dead space " in capillaries and for impurities.

RESULTS AND DISCUSSION

In the temperature range investigated (447—511°) 1,1-dimethylcyclopropane undergoes a first-order isomerization to give principally 3-methylbut-1-ene and 2-methylbut-2-ene in nearly equal amounts. In addition small amounts (approximately 1%) of 2-methylbut-1-ene were formed. Simultaneously with the isomerization there was a small amount of thermal " cracking " which increased relative to the isomerization at the higher temperatures and higher percentage deompositions. The main products of the " cracking " reaction were ethane, ethylene, propane, and propene, and the total of the " cracking " compounds was less than 1% of the products of isomerization. Later experiments showed that these products could be accounted for almost entirely by the secondary decompositions of the primary isomerization products.



Preliminary runs at 490° with various pressures of dimethylcyclopropane in the range 550—6 mm. showed that in this pressure region the rate constant for the isomerization was independent of the pressure. Detailed studies were therefore carried out at 100 mm. pressure at 7 temperatures between 447° and 511°. At each, at least 8 runs were carried out in which the decomposition varied between 10 and 60%. Plots of the logarithm of the percentage of 1,1-dimethylcyclopropane against time were linear. No pressure change was observable on a simple mercury manometer during the reaction, in agreement with the small amount of cracking products formed.

The first-order rate constants are shown in Table 1. An Arrhenius plot gave a good straight line, and the frequency factor and energy of activation were calculated by the method of least squares, whence

TABLE 1. *Rate constants for the isomerization of* 1,1-*dimethylcyclopropane.*

Temp.	447·3°	455·2°	463·0°	477·6°	485·8°	501·1°	511·3°
10^4k (sec.$^{-1}$)	1·14	1·82	2·94	6·56	10·1	24·2	40·4

$$k = 10^{15\cdot05} \exp(-62{,}600/\mathbf{R}T) \text{ sec.}^{-1}$$

The statistical probable error was only a few calories which merely indicates that the results are highly reproducible. The greatest uncertainty arises over the mean temperature of the reaction vessel, which can safely be assumed to be less than ±0·3° from the measured temperature. This would introduce a maximum uncertainty in the energy of activation of ±600 cal.

The thermal isomerizations of 3-methylbut-1-ene, 2-methylbut-2-ene, and 2-methylbut-1-ene (the initial products of the isomerization of dimethylcyclopropane) were briefly investigated so that the initial ratio of the products of the isomerization could be calculated with allowance for their own reactions. These compounds all isomerized more rapidly than they underwent thermal " cracking," though the " cracking " products were present in sufficient quantities to suggest that almost none were formed from the dimethylcyclopropane directly. Unlike the isomerization of 1,1-dimethylcyclopropane, the rates of isomerization of these compounds were strongly pressure-dependent in the range 12—100 mm. The corrections to be applied as a result of these experiments were small under all conditions. The corrected values are shown in Table 2.

The accuracy with which these ratios could be determined was not sufficient to decide definitely whether there is a difference in the energy of activation for the isomerization of dimethylcyclopropane to 3-methylbut-1-ene and 2-methylbut-2-ene. If there is a difference it is not greater than 500 cal. mole^{-1}. In the case of the formation of 2-methylbut-1-ene, the quantities formed are so small that very large percentage errors are possible in the experimental value of the energy of activation and a value of as high as 68,000 cal. mole^{-1} is not inconsistent with the experimental data.

TABLE 2. *Primary ratios of isomerization products.*

Temp.	3-Methyl-but-1-ene	2-Methyl-but-2-ene	2-Methyl-but-1-ene	Temp.	3-Methyl-but-1-ene	2-Methyl-but-2-ene	2-Methyl-but-1-ene
447·3°	1	0·95	0·013	477·6°	1	0·95	0·015
455·2	1	0·93	0·013	485·8	1	0·96	†
463·0	1	0·94	0·018	501·1	1	0·98	†
477 *	1	0·96	0·023	511·3	1	0·98	0·018

* Packed reaction vessel.

† A very large scatter in these experimental values makes the average value unreliable.

All rate data refer to reaction vessels that had been "aged." If a clean reaction vessel was used the rate of isomerization of dimethylcyclopropane for the first run was at least twice that for an "aged" vessel. This increase in rate could be accounted for almost entirely by the additional production of 3-methylbut-1-ene. It thus appears that on a clean silica surface there is a heterogeneous reaction leading to this. To ensure that the rate constants obtained for the "aged" reaction vessels were for the homogeneous reaction only, a series of runs were carried out at 477° in a packed reaction vessel whose surface: volume ratio was 9·7 times that of the unpacked vessel. The rate plot obtained is shown in Fig. 1. The rate constant in the packed vessel is slightly *less* than that for the unpacked vessel and this can be accounted for by a drop of slightly less than 1° in the temperature. Since no thermocouple well was provided in the packed reaction vessel this temperature difference could not be checked. The packed vessel had a somewhat different geometry from the unpacked one, and this temperature difference is within the possible experimental errors.

FIG. 1.

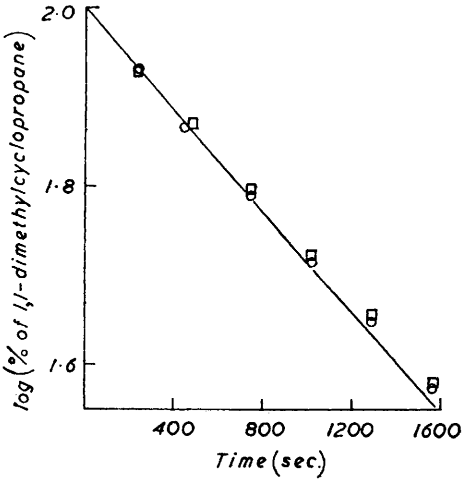
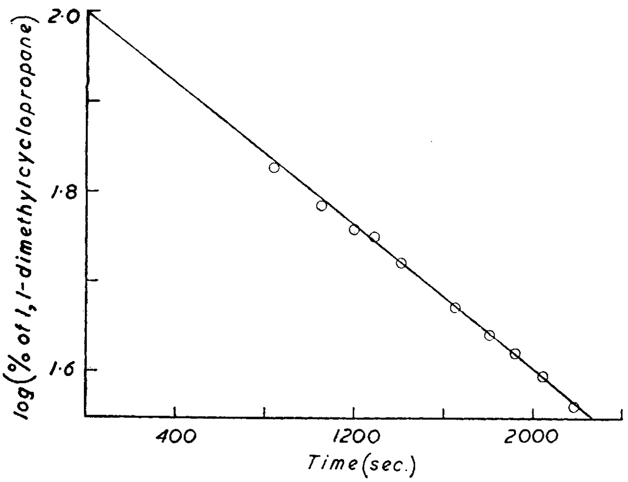


FIG. 2.



Solid curve, unpacked reaction vessel.
○, Packed reaction vessel.
☐, Packed reaction vessel, with 10% of nitric oxide.

Several runs were carried out at 477° in the packed reaction vessel with 100 mm. of 1,1-dimethylcyclopropane and about 11 mm. of nitric oxide (Fig. 1). Nitric oxide had no inhibitory effect; indeed it caused a small increase in the rate.

Since the isomerization in an "aged" reaction vessel appeared to be homogeneous, was of first order over a large pressure range, and was not retarded by nitric oxide, it was considered probable that the reaction was a true unimolecular transformation. The rate of such transformations must show a pressure-dependence if the pressure is lowered sufficiently. By analogy with the pressure at which the first-order rate constant of the thermal isomerization of cyclopropane begins to decrease, as compared with the pressure at which excited cyclopropane, formed by the addition of methylene to ethylene, begins to isomerize, it is possible to estimate crudely the pressure at which the first-order rate constant for the thermal isomerization of dimethylcyclopropane should commence to fall, from the data on the excited molecule formed by the addition of methylene to isobutene,[3-6] to be *ca.* 3 mm. Accordingly runs were carried out below 6 mm. down to 0·1 mm. The values of the rate constants obtained are shown in Table 3. From a plot of the logarithm of the rate constant against the logarithm of the pressure it appears that the rate constant begins to decrease at approximately 4 mm.

TABLE 3. *Rate constants of isomerization at* 477·6°.

Pressure (mm.)	100	7·4	0·9	0·48	0·2	0·1
10^4k (sec.$^{-1}$)	6·56	6·56	6·09	5·73	5·18	4·66

At the very lowest pressures it was necessary to allow a reasonable percentage of the dimethylcyclopropane to isomerize before even the first point on the rate curve could be obtained, in order that sufficient products were present for accurate analysis. Thus, at 0·1 mm. the isomerization was only followed from 23 to 54% completion; however, the results (Fig. 2) were sufficiently precise to enable a reasonably accurate rate constant to be computed.

The ratio of the products did not appear to change significantly as the pressure was lowered. 2-Methylbut-1-ene was not detected in the runs at 0·1 mm. because the peak height would be of the same order as the " noise " of the katharometer. A *precise* ratio of the products could not be obtained for the low-pressure runs as the rates of isomerization of the primary products were not determined at low pressures (and these rates were highly pressure-dependent).

The apparatus was not designed for use with small amounts of dimethylcyclopropane in the presence of a large excess of non-condensable gas, and even at 0·1 mm. the fall-off of the rate constant compared with the high-pressure value is still small, so only one series of runs was carried out on the low-pressure isomerization in the presence of inert gas, carbon dioxide. Runs were carried out at 477° with 0·2 mm. of 1,1-dimethylcyclopropane and 3 mm. of carbon dioxide. The rate constant was $5{\cdot}84 \times 10^{-4}$ sec.$^{-1}$. In the absence of carbon dioxide it is $5{\cdot}07 \times 10^{-4}$ sec.$^{-1}$ at 0·2 mm. Thus the presence of carbon dioxide helps towards maintaining the Maxwell–Boltzmann distribution of energy. On a pressure-to-pressure basis carbon dioxide is approximately 0·13 times as effective as the dimethylcyclopropane itself. On a collision-to-collision basis, the ratio of the collision diameters of the dimethylcyclopropane to carbon dioxide being assumed to be 2 : 1, carbon dioxide is 0·26 times as effective.

From these results it appears most probable that the thermal isomerization of 1,1-dimethylcyclopropane is a true unimolecular reaction. In the Slater treatment of the isomerization of cyclopropane [7] the critical co-ordinate in the transition state is taken to be the distance between any hydrogen atom and any carbon atom to which it is not bound. The dimethylcyclopropane isomerization may be treated similarly. Thus rearrangement would be expected to take place when the distance between any of the four hydrogen atoms directly attached to the cyclopropane ring and a carbon atom in the ring to which they were not bonded became smaller than a critical value. Shifts of hydrogen atoms on

[3] Frey, *J. Amer. Chem. Soc.*, 1957, **79**, 1259.

[4] Prichard, Sowden, and Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, *A*, **217**, 563.

[5] Knox, Trotman-Dickenson, and Wells, *J.*, 1958, 2897.

[6] Frey, *Proc. Roy. Soc.*, 1959, *A*, **250**, 409.

[7] Slater, *Proc. Roy. Soc.*, 1953, *A*, **218**, 224.

carbon atom 2 to carbon atom 3 or *vice versa* will result in the isomerization to 2-methylbut-2-ene. Shifts of these hydrogen atoms to carbon atom 1 will result in the transformation to 3-methylbut-1-ene. The closely similar yields of these two products makes it clear that these shifts must have closely similar probabilities. In the Slater treatment the most important factors governing the magnitude of the " *A* " factor for the cyclopropane isomerization are the high symmetry of the molecule (leading to twelve equivalent critical co-ordinates) and the values of the vibration frequencies of the carbon–hydrogen bonds. While no vibrational analysis for the dimethylcyclopropane molecule is available it seems likely that the carbon–hydrogen frequencies of the methylene groups in this molecule cannot differ appreciably from their values in cyclopropane. Accordingly one would expect that the " *A* " factor for the isomerization of the cyclopropane would be 1·5 (12/8) times as great as the " *A* " factor for this reaction. The actual experimental ratio is 1·3 which (the probable errors being considered) is in excellent agreement with this value.

The formation of the small quantities of 2-methylbut-1-ene is thought to proceed through a transition state whose critical co-ordinate is the distance between a hydrogen atom on either of the methyl groups and either carbon 2 or carbon 3. Since in the normal equilibrium configuration of the molecule this length is greater than the corresponding length in the transition states leading to the other isomerization products it is perhaps not surprising that little of the reaction proceeds *via* this path.

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