221. *The Thermal Unimolecular Isomerization of* 1,1-*Dimethyl-cyclopropane at Low Pressures.*

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The thermal unimolecular isomerization of 1,1-dimethylcyclopropane has been investigated in the pressure range from 35 to 0·0075 mm. and at five temperatures from 442° to 481°. The fall-off curves obtained are fitted by Kassel's equation, the molecule being assumed to contain 23 effective oscillators. Values for the energy of activation for the reaction have been obtained corresponding to the high-pressure limits, and intermediate pressures where fall-off has commenced. The relative efficiencies of nitrogen, argon, hydrogen, helium, methane, carbon dioxide, carbon tetrafluoride, sulphur hexafluoride, ethylene, and toluene in maintaining the Maxwell–Boltzmann distribution of energies have been measured. Application of some statistical consistency tests has shown that the data satisfy the general requirements of the Lindemann hypothesis to high accuracy. The Slater relation for the temperature dependence of fall-off behaviour, *viz.*, $\Delta \log p = (n/2)\log(T_2/T_1)$ is not consistent with the experimental results. Some values of the Kassel integral for $S = 20, 21, 22, 23$, and 24 which have been obtained by quadrature on a digital computer are given in the Appendix.

THE thermal isomerization of 1,1-dimethylcyclopropane to 2-methylbut-2-ene and 3-methylbut-1-ene has already been shown to be a homogeneous, unimolecular reaction.[1]

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[1] Flowers and Frey, *J.*, 1959, 3953.

The first-order rate constants are independent of pressure in the range 16—1600 mm., but below 4 mm. a decrease in the rate of reaction is observed.[2] Additional carbon dioxide increases the reaction rate in the fall-off region, proving that the decrease of reaction rate is due to the inability of the reactant to maintain the Maxwell–Boltzmann distribution of energies.

An investigation of this unimolecular reaction in the fall-off region was undertaken to obtain experimental data to test the validities of the various theories of unimolecular reactions.

It was pointed out in the previous investigation that, in the runs at low pressures, there may have been systematic errors in both the measurement of percentage decomposition and the measurement of pressure, due to absorption of the hydrocarbons in the stopcock greases. The apparatus used in this investigation has avoided the use of greased stopcocks to remove these uncertainties. The analytical technique has also been improved by using electrical integration of the peaks of the chromatograms.

<center>EXPERIMENTAL</center>

Preparation of 1,1-*Dimethylcyclopropane.*—1,1-Dimethylcyclopropane was prepared as described previously,[1] but was purified in a different way. The crude product was cooled to —78° and liquid bromine was added until the red colour persisted. With excess of bromine still present the mixture was allowed to warm slowly to 0°, and kept at 0° for 12 hr. Excess of bromine was then removed by washing with ice-cold sodium carbonate solution, followed by water. The product was then dried ($CaCl_2$) and roughly distilled. Finally the liquid was fractionally distilled under reduced pressure at —24° in a 13-in. Podbielniak column to give a product containing 0·1% of total impurity.

Inert Gases.—Nitrogen, argon, hydrogen, and helium (British Oxygen Co.) and methane (Matheson C.P. grade) were used straight from cylinders after passage over magnesium perchlorate to remove traces of water. No further purification was carried out. Their purity was checked by analysis with an MS 3 mass spectrometer. Oxygen was absent in all cases, except for the possibility of a trace in the hydrogen.

Ethylene and carbon tetrafluoride (Matheson C.P. grade) were condensed (liquid nitrogen), then allowed to warm to liquid-oxygen temperature, and any non-condensable gases were removed by pumping. Sulphur hexafluoride (Matheson C.P. grade) was condensed by liquid oxygen, and non-condensable gases removed by pumping.

" AnalaR " toluene was fractionally distilled and the middle fraction collected (5 ml. from an initial 250 ml.). Non-condensable gases were removed at —78°.

Apparatus.—A " static " apparatus was used, with mercury cut-offs, brass-bodied polyethylene diaphragm valves, and fluon–glass valves. This enabled the isomerization to be investigated without contact between the reaction mixtures and any greased stopcocks. The isomerizations were carried out in a cylindrical Pyrex vessel (volume 1406 ml.) fitted with a thermocouple well. A horizontal tube furnace (6 in. diam.) was used with the winding tapped at four points for external shunts. By suitable adjustment of the shunts the temperature gradient over the vessel was kept to 0·45°. Current to the furnace was supplied by a constant-voltage transformer. The temperature was controlled by a Sunvic RT 2 regulator and could be maintained to better than 0·1°. The temperatures were measured by use of a platinum–platinum–rhodium thermocouple calibrated against a standard platinum resistance thermometer.

Two McLeod gauges, connected to the vessel through a mercury cut-off, one covering the range 5—0·1 mm. and the other from 10^{-1} to 10^{-5} mm., were used for pressure measurement. For runs in the range 35—5 mm. the pressure was determined by measuring the depression of a column of mercury. It was not possible to use the apparatus above about 35 mm. pressure. All connecting tubing was of 12 mm. internal diameter.

Procedure.—1,1-Dimethylcyclopropane was admitted to the vessel and the two McLeod gauges through a mercury cut-off. After measurement of pressure, the McLeod gauges were isolated from the vessel. At the end of a run reaction mixtures were removed from the vessel by a two-stage process. The first step involved freezing out the entire mixture into a tube

[2] Flowers and Frey, *J. Phys. Chem.,* 1961, **65**, 373.

(*ca.* 130 ml.) cooled to −186°, which was connected to the reaction vessel *via* a mercury cut-off and a short length of 12 mm. tubing. The removal was complete in a very short time and errors due to the finite times of filling and emptying the vessel were small and tended to cancel one another. The reaction mixture was then transferred at leisure to a sample tube for later analysis. Between runs the vessel was pumped down to 10^{-5} mm. Subsequent runs were carried out by sharing the dimethylcyclopropane remaining in the McLeod gauges with the vessel. The range 35—0·0075 mm. pressure was normally investigated with two initial samples.

When inert gas was present the reaction mixture was removed from the furnace *via* a glass spiral (4 ft. × 7 mm. int. diam.) cooled to −186°, and pumping off any non-condensable gas.

Before any run the reaction vessel was " aged " by addition of approximately 10 mm. of dimethylcyclopropane and this was allowed to remain in the vessel for 24 hr. This process was repeated until reproducible reaction rates were obtained.

Analysis.—Reaction products were analysed by gas chromatography on a 30 ft. × 0·17 in. int. diam. coiled copper column packed with hexane-2,5-dione on Chromosorb (40—60 mesh) with an additional 2 ft. × 0·17 in. int. diam. stainless-steel column packed with silver nitrate in ethylene glycol also on Chromosorb. Both columns were maintained at 0°. Hydrogen was the carrier gas and a Gow-Mac (tungsten filament) katharometer was used as the detector. Calibrations were carried out with synthetic mixtures of the products and reactant. These were prepared in a specially designed vacuum system, consisting essentially of a calibration volume whose temperature was kept constant to within 0·2°, and a series of storage tubes. Brass-bodied polyethylene diaphragm valves were employed throughout. The pressure in the calibrated volume was measured by using a wide-bore mercury manometer and a cathetometer. Mixtures were made from gases which were always measured at the same (low) pressure in the calibrated volume, if necessary several portions being added. This made corrections for deviations from ideal-gas behaviour negligible.

This apparatus was also used to make up mixtures of inert gases with 1,1-dimethylcyclopropane: These mixtures were stored in large tubes, each containing a magnetic stirrer. Stirring was carried out for at least 24 hr. before the mixture was used.

The signals from the katharometer were fed *via* a variable attentuator to a Sunvic RSP 2, 0·5 mv recorder. The recorder was modified by fitting it with a 100-ohm retransmitting slidewire. Five accumulators were connected across this slidewire and the output from it (which was proportional to the katharometer signal) was used to drive a low-inertia integrating motor (Electro Methods), coupled to a revolution counter. At full-scale deflection on the recorder the motor gave 1500 counts/min. Determination of the percentage decomposition from the integrated areas of the peaks multiplied by the appropriate calibration factor could be estimated to better than ±0·5%. Corrections were made throughout for " dead space " (0·5% of the volume of the reaction vessel) and for impurities.

Glass stopcocks on the sample inlet system of the gas-chromatographic apparatus could not easily be replaced by greaseless valves. To minimize absorption problems a grease of sucrose in glycerol was used,[3] since hydrocarbons are almost insoluble in it. This was not suitable for use under high vacuum because of its appreciable vapour pressure, but was usable on the sample inlet system, and its lubricant properties were good.

RESULTS AND DISCUSSION

First-order rate constants for the isomerization of 1,1-dimethylcyclopropane were determined from single runs at pressures which covered the range 35—0·0075 mm. and at five temperatures between 442° and 481°. The extent of reaction varied between 20 and 35%. Duplicate analyses normally yielded rate constants which agreed to within 1%. The value of the limiting high-pressure rate constant, k_∞, was obtained by extrapolation of a plot of $1/k$ against $1/p$ to $1/p = 0$. The plot of $1/k$ against $1/p^{\frac{1}{2}}$, which has been suggested by Schlag and Rabinovitch [4] for use in determining values of k_∞, proves to overestimate the value of k_∞, if values of the rate constant are determined near the high-pressure limit. This is illustrated in Figs. 1 and 2 where the data refer to rate constants obtained at 469·8°. The curves of $\log k/k_\infty$ against $\log p$ obtained at 442·4° and 481·2°

[3] Puddington, *Ind. Eng. Chem. (Anal. Ed.),* 1944, **16,** 415.
[4] Schlag and Rabinovitch, *J. Amer. Chem. Soc.,* 1960, **82,** 5996.

are shown in Fig. 3. Similar curves were obtained for the three intermediate temperatures investigated. Onset of fall-off occurs at about 16 mm. at 442·4° and at 34 mm. at 481·2°. The value of 4 mm. found previously for the commencement of fall-off [1] is in error. The
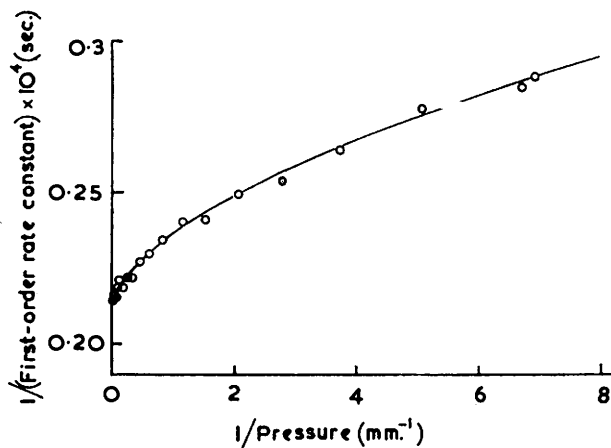

FIG. 1. Graph of reciprocal of rate constant against reciprocal of pressure for isomerization at 469·8°c.

FIG. 2. Graph of reciprocal of rate constant against reciprocal of the square root of the pressure.
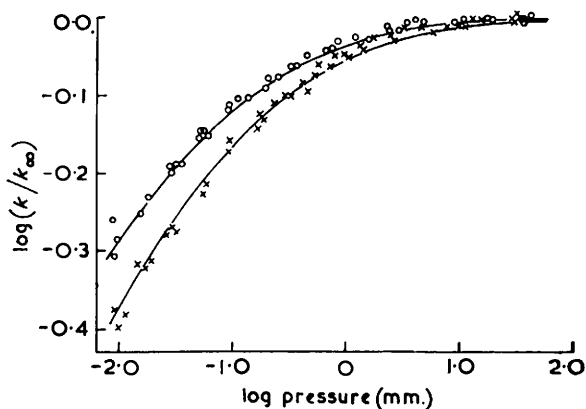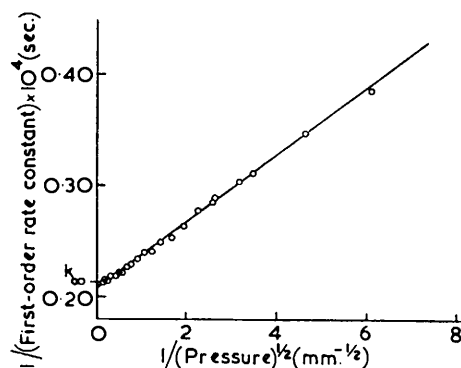

FIG. 3. Fall-off curves for the iso-merization at 442·4° and 481·2°c: o 442·4°; × 481·2°.

difference in rate constants observed between 100 and 7·4 mm. was ascribed to a small temperature difference in the reaction vessel since several changes in the apparatus had been made between the two series of runs. It now appears that the difference in rates

was due to the pressure change and the temperature of the reaction vessel had in fact remained constant. Activation energies and pre-exponential factors were calculated from the values of k_∞, and also from the values of the rate constants in the fall-off region, the method of least squares being used. The values of the rate constants in the fall-off region were obtained from the best smooth curves that could be drawn through the experimental points of the plots of log (k/k_∞) against pressure. The statistical probable error in the value of the activation energy determined from the k_∞ value is negligible but increases for the corresponding values obtained at lower pressures. The values are shown in Table 1 The mean temperature of the reaction vessel cannot differ by more than $0.5°$

TABLE 1.

" Least squares " Arrhenius parameters for the isomerization of
1,1-dimethylcyclopropane.

Pressure (mm.)	∞	∞	3·98	0·631	0·158	0·0398	0·01
E_a (kcal./mole)	62·6	63·6	63·2	62·25	60·8	59·1	57·0
$\log_{10} A$	15·05	15·37	15·23	14·92	14·44	13·83	13·09

from the measured value, which leads to a maximum uncertainty in the value of high-pressure energy of activation of ± 1000 cal. mole^{-1}. The value of this activation energy obtained in this work agrees with that obtained previously.[1]

It has been pointed out by Johnston and White [5] that if experimental data do not fit the requirements of the general Lindemann theory there is little point in using the data to test more detailed theories. They developed some useful consistency tests that can be applied to the experimental data. Values of the moments ν_1, ν_2, ν_3, and ν_4 have been calculated from the experimental fall-off curve at $449.6°$. (See ref. 5 for definitions of ν_1, etc.) Two values of k_∞ were employed (1.39 and 1.40×10^{-4} sec.$^{-1}$), either of which was obtainable by the extrapolation of the plot of $1/k$ against $1/p$. To satisfy the general Lindemann mechanism values of ν_2/ν_1^2, $\nu_1\nu_3/\nu_2^2$, $\nu_2\nu_4/\nu_3^2$, etc., must be equal to, or greater than, unity. As the experimental errors in the determination of ν_1, ν_2, etc., are cumulative, the tests very soon fail unless very precise data are used. With $k_\infty = 1.40 \times 10^{-4}$ sec.$^{-1}$ the inequalities were not satisfied over the higher half of the pressure range investigated with $\nu_1\nu_3/\nu_2^2$. The value $k_\infty = 1.39 \times 10^{-4}$ sec.$^{-1}$ however still gave values greater than unity for $\nu_2\nu_4/\nu_3^2$ (see Appendix). In this case the values for the four highest pressures could not be obtained because $k_\infty\nu^\infty_3 - k\nu_3$ became negative. The application of these consistency tests showed that the data satisfied the general Lindemann theory to a degree at least as good as that obtained for cyclopropane (see ref. 5). In addition it appears that the extrapolated values of k_∞ are correct to within 1%, for variation of less than 1% in k_∞ causes a failure of the consistency tests for different reasons.

The solid curves in the plots shown in Fig. 3 were obtained by integrating Kassel's [6] expression with $s = 23$, a molecular diameter of 5.5 Å, and the experimental high-pressure activation energy and pre-exponential factor. The curves have been shifted to lower pressure by 0.06 log units in order to obtain the best fit. This could have been accomplished by increasing the value of the molecular diameter, which is in any case only an estimate, by about 0.4 Å or by altering the experimental values of the activation energy or pre-exponential factor by amounts much smaller than the experimental error.

Kassel's integral was evaluated by using the Gauss–Laguerre quadrature formula.[7] The summation was carried out on a Ferranti Pegasus computer, and the values obtained are given in the Appendix. That the programme was correct, and also that the summation gave an accurate value of the integral, was checked by comparing the values obtained by using this method with those published for the same parameters.[8] It can be seen from

[5] Johnston and White, *J. Chem. Phys.*, 1954, **22**, 1969.
[6] Kassel, " Kinetics of Homogeneous Gas Reactions," Chemical Catalogue Co., New York, 1932.
[7] Kopal, " Numerical Analysis," Chapman and Hall, London, 1955, 371, 525.
[8] Schlag, Rabinovitch, and Schneider, *J. Chem. Phys.*, 1960, **32**, 1599.

Fig. 3 that the experimental and calculated shifts of the fall-off curves with temperature are in good agreement. A similar agreement is obtained for the three intermediate temperatures. It would have been possible to integrate Slater's [9] expression and determine the value of n which gave the same shaped curve as the experimental fall-off curve. However, because of approximations used to obtain the final value of Slater's expression, the accuracy of the integral decreases as n rises. In any case, from the work of Schlag et al.,[7] a value of $s = 23$ in Kassel's integral produces a similar shaped curve as $n = 19$ in Slater's integral. Calculation of n for Slater's classical model from the shift of the curves with temperature $[\Delta \log p = (1/2)n\log(T_2/T_1)]$ gives a value of $n = 29$. The difference between the two values is well outside the estimated experimental error. This suggests that the theoretical relationship is not valid. It seems probable that the discrepancy between theory and experiment would be even greater if the quantum model was used.

To compare the effect of additional degrees of freedom on the lifetimes of activated molecules the activation energies should be the same for all cases. This is satisfied for the isomerizations of cyclopropane and methylcyclopropane and, as expected, the onset of fall-off for methylcyclopropane occurs at lower pressures than for cyclopropane. The isomerization reactions of the dimethylcyclopropanes have slightly lower activation energies. The differences are much too small to account in themselves for the further lowering of onset of fall-off. With cyclopropane [10] fall-off has already begun at 1000 mm., for methylcyclopropane [11] it begins slightly below 100 mm., and for 1,1- and 1,2-dimethyl-cyclopropane [12] it begins at about 16 mm. The values of the effective number of vibrational modes calculated for Kassel's theory increase from 12 or 13 for cyclopropane, to 19 for methylcyclopropane, and 23 for 1,1-dimethylcyclopropane. Thus the ratio of effective number to total number of vibrational modes is constant, within experimental error (0·57—0·62 for cyclopropane, 0·63 for methylcyclopropane, and 0·59 for 1,1-dimethyl-cyclopropane).

As expected the average lifetime of activated molecules decreases with energy content. For " hot " 1,1-dimethylcyclopropane [13] the average lifetime is 3×10^{-8} sec. The average lifetime of thermally activated molecules at high pressures, calculated by Johnston and White's method,[5] is $1·0 \times 10^{-6}$ sec. Equating the collisional frequency to the reciprocal of the lifetime at the pressure for which $k/k_\infty = 0·5$ yields a value for the average lifetime of 8×10^{-6} sec.

It has already been shown that carbon dioxide increased the rate of the isomerization in the fall-off region, thus showing that the fall-off was due to the inability of the gas to maintain the Maxwell–Boltzmann distribution of energies. In an attempt to determine more about energy transfer in unimolecular reactions a study of the effect of a variety of inert gases on the rate of reaction when in the fall-off region was carried out at 459·4°.

The rates of reaction were increased in all cases. In no case was the first-order rate constant increased to a value greater than k_∞. As no curvature was observed in the plots of the logarithm of percentage of 1,1-dimethylcyclopropane against time when in the fall-off region,[1] the efficiencies of 3-methylbut-1-ene and 2-methylbut-2-ene with regard to energy transfer must be close to that of the parent. Fig. 4 shows the curves obtained with methane and with toluene as the gases added compared with the data obtained in the absence of inert gas. Similar plots were obtained with all the other gases employed. The relative efficiencies, pressure for pressure, were calculated as described by Trotman-Dickenson.[14] Values of the efficiencies can be obtained in this way if the relative

[9] Slater, " Theory of Unimolecular Reactions," Methuen, London, 1959.
[10] (a) Chambers and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 399; (b) Pritchard, Sowden, and Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, *A*, **217**, 563.
[11] Chesick, *J. Amer. Chem. Soc.*, 1960, **82**, 3277.
[12] Flowers and Frey, *Proc. Roy. Soc.*, 1960, *A*, **257**, 122.
[13] Frey, *Proc. Roy. Soc.*, 1959, *A*, **250**, 409.
[14] Trotman-Dickenson, " Gas Kinetics," Butterworths, London, 1955, p. 83.

probabilities for activation and deactivation for the various energy levels of the excited reactants do not depend strongly on the nature of the second body in the collision process.[15] The values for the relative efficiencies of the gases used expressed both on a pressure to pressure and a collision to collision basis are shown in Table 2. The same values for the

TABLE 2.

Relative efficiencies of inert gas based on pressure and collision for collision.

	pressure/pressure	collision/collision		pressure/pressure	collision/collision
Reactant	1	1	C_2H_4	0·47	0·43
He	0·10	0·07	CF_4	0·41	0·66
Ar	0·12	0·15	SF_6	0·45	0·65
H_2	0·1—0·5	—	CO_2	0·13	0·26
N_2	0·10	0·11	Toluene	1·20	0·85
$N_2 + 0.9\%$ O_2	0·20—0·3	—			
CH_4	0·37	0·30			

molecular diameters were employed as used by Pritchard *et al.*[16] For 1,1-dimethylcyclopropane, sulphur hexafluoride, and carbon tetrafluoride the values 5·5 Å, 5·5 Å, and 4·5 Å were used, respectively.

Within experimental error, the efficiencies were not dependent on pressure for nitrogen, helium, toluene, sulphur hexafluoride, and carbon tetrafluoride. The highest pressures

FIG. 4. Efficiency of inert gases in maintaining the Maxwell–Boltzmann distribution of energies: solid curve no inert gas; o methane added (10·2 : 1); × toluene added (1·03 : 1).
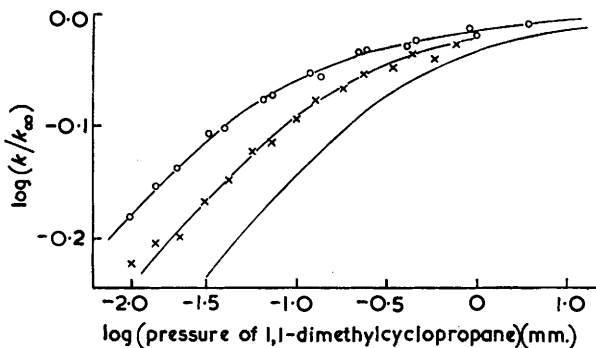
did in most cases give lower values for the efficiencies, but this was probably due to the fact that in this region small experimental errors in the determined rate constants would produce large errors in the values for the calculated efficiencies. A flattening on the fall-off curve obtained with added ethylene at higher pressures was due to a reaction product of ethylene itself contributing to the dimethylcyclopropane peak on the chromatogram. If a correction for the production of this compound was applied, the curves became similar to that of the parent alone. The efficiencies of methane, argon, and hydrogen appeared to increase continuously as the pressure was decreased. Only in the case of hydrogen was the effect very marked. The only explanation that can be offered in the case of hydrogen is that possibly a small amount of air entered the system during these runs. Mass spectral analysis of the mixture used, before attachment to the vacuum system, showed less than 0·1% of oxygen present. The effect of added nitrogen plus 0·9% of oxygen, compared with nitrogen alone, showed that the oxygen did increase the apparent efficiency of the inert gas, and also the efficiency increased as the total pressure was decreased, though the effect may not be sufficiently great to account completely for

[15] Volpe and Johnston, *J. Amer. Chem. Soc.*, 1956, **78**, 3903.
[16] Pritchard, Sowden, and Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, *A*, **218**, 416.

the results with hydrogen. This action of oxygen is probably due to a " de-aging " effect on the surface of the reaction vessel.

Within experimental error, the efficiencies of helium, ethylene, and methane in activating 1,1-dimethylcyclopropane are the same as for cyclobutane,[16] methylcyclopropane [11] and cyclopropane.[10b] For nitrogen, argon, and toluene the values obtained in this work fall between the values obtained for cyclopropane on the one hand, and methylcyclopropane and cyclobutane on the other. Although the differences appear to be outside the probable experimental errors, they may well be caused by systematic errors in the various investigations. This seems probable since there is no trend between cyclopropane and the dimethyl-substituted molecule.

The quantum version of Slater's theory predicts that the Arrhenius plot should be curved. A recent publication has shown that for the isomerization of cyclopropane no such curvature is observed within the quite small experimental error, and any deviations from a straight line are much smaller than those predicted.[17] In the present work no curvature of the Arrhenius plot was observed. This is shown in Table 3 where the

TABLE 3.

Deviations from " least squares " activation energies.

Temp. (°c)	442·4	449·6	459·4	469·8	481·2
Deviation (cal./mole)	−3	+7	−3	+2	+2
$10^3(\log k_{calc} - \log k_{exp})$	−0·9	+2·1	−0·9	+0·6	+0·6

greatest deviation from the Arrhenius expression corresponds to $\frac{1}{2}\%$ (0·002 log unit). Thus any curvature of the Arrhenius plot that may exist is considerably smaller than might be expected from the quantum harmonic oscillator model. In earlier work on 1,1-dimethylcyclopropane [1] and 1,2-dimethylcyclopropane [10] any deviations from the Arrhenius form were all within the small experimental errors.

The ratio of 3-methylbut-1-ene to 2-methylbut-2-ene observed in this investigation was not dependent on pressure or temperature and was equal to $1 : 1·12$ (the average of over 300 runs). It was observed in the previous investigation [1] that the rates of decomposition of 3-methylbut-1-ene and 2-methylbut-2-ene above about 16 mm. were dependent on pressure. A further investigation of these reactions has shown that the extent of the decomposition of 2-methylbut-2-ene at 459·4° during the time of the isomerization normally employed (20—25 minutes) was negligible at all pressures in the range 25—0·15 mm. Decomposition of 3-methylbut-1-ene during 22 minutes varied between 6·2% at 5 mm. and 2·8% at 0·09 mm. After a correction had been applied for this decomposition, the ratio of 3-methylbut-1-ene to 2-methylbut-2-ene could not be reduced to lower than $1 : 1·07$. Thus there appears to be a discrepancy between the ratio determined in this apparatus and that determined earlier which is outside the probable experimental error. The amount of 2-methylbut-1-ene formed decreased with pressure and below 0·1 mm. none was detected. It is possible that the number of effective oscillators contributing to the mode of decomposition giving rise to 2-methylbut-1-ene is smaller than for the major process thus causing the rate of decomposition to 2-methylbut-1-ene to start to decrease at higher pressures. A more probable explanation is that the 2-methylbut-1-ene is a secondary product, formed only from the decomposition of 3-methylbut-1-ene and 2-methylbut-2-ene and that, because the rate of these reactions decreases with pressure, below 0·1 mm. detectable quantities of 2-methylbut-1-ene are not formed. Lowering the pressure causes production of *cis*- and *trans*-pent-2-ene, products that were not detected above about 0·1 mm. The amounts were always small and less than about 0·5% of the total products of reaction.

[17] Falconer, Hunter, and Trotman-Dickenson, *J.*, 1961, 609.

APPENDIX

Application of consistency tests to data for isomerization at 449·6°.

[M] (10^8m/c.c.)	k (10^4sec.^{-1})	$10^8 \nu_1$	$10^{16} \nu_2$	ν_2/ν_1^2	$10^{25} \nu_3$	$\nu_1\nu_3/\nu_2^2$	$10^{33} \nu_4$	$\nu_2\nu_4/\nu_3^2$
∞	1·390	0·255	0·45		15			
55·7	1·384	0·242	0·806	13·7				
35·2	1·380	0·281						
22·2	1·375	0·242	0·355	6·1	21·9	4·2		
14·0	1·366	0·246	0·195	3·2	36·7	23·8		
8·83	1·356	0·221	0·357	7·3	9·16	1·59	53·9	2·29
5·57	1·341	0·203	0·303	7·4	9·10	2·03	35·2	1·29
3·52	1·318	0·192	0·272	7·4	7·10	1·84	39·8	2·14
2·22	1·288	0·176	0·220	7·1	5·89	2·15	22·6	1·43
1·40	1·252	0·154	0·181	7·6	4·45	2·09	16·9	1·54
0·883	1·208	0·133	0·142	8·0	3·31	2·18	12·2	1·57
0·557	1·158	0·108	0·107	9·1	2·34	2·21	8·41	1·64
0·352	1·102	0·0920	0·081	9·6	1·71	2·39	6·01	1·67
0·222	1·047	0·0727	0·059	11·2	1·19	2·49	3·90	1·62

Evaluation of Kassel's integral.

$$\frac{k}{k_\infty} = \frac{1}{(S-1)!} \int_0^\infty \frac{x^{s-1} \cdot e^{-x}\,dx}{1 + Ax^{s-1}/k_2[M](b+x)^{s-1}}$$

for $\log_{10} A = 15\cdot39$, and $\sigma = 5\cdot5$ Å.

b	P (mm.)	S=20	S=21	S=22	S=23	b	P (mm.)	S=20	S=21	S=22	S=23
42·5	276	0·994	0·996	0·997	0·998	44·3	264	0·996	0·998	0·998	0·999
	27·6	0·964	0·974	0·981	0·986		26·4	0·974	0·982	0·987	0·991
	2·76	0·853	0·885	0·909	0·928		2·64	0·886	0·913	0·932	0·948
	0·276	0·632	0·685	0·728	0·772		0·264	0·689	0·737	0·780	0·819
	0·0276	0·370	0·417	0·474	0·524		0·0264	0·425	0·479	0·539	0·585
43·1	272	0·995	0·997	0·998	0·998	44·8	262	0·997	0·998	0·999	
	27·2	0·967	0·976	0·983	0·988		26·2	0·976	0·983	0·988	
	2·72	0·864	0·894	0·917	0·934		2·62	0·893	0·919	0·937	
	0·272	0·650	0·701	0·744	0·787		0·262	0·703	0·749	0·792	
	0·0272	0·386	0·435	0·494	0·543		0·0262	0·439	0·495	0·555	
43·7	268	0·996	0·997	0·998	0·999						
	26·8	0·971	0·979	0·985	0·989						
	2·68	0·875	0·904	0·925	0·941						
	0·268	0·670	0·719	0·762	0·804						
	0·0268	0·406	0·457	0·517	0·564						

S	p (mm.)	b=42·4	43·1	43·7	44·3	44·7	S	p (mm.)	b=42·4	43·1	43·7	44·3	44·7
23	100·00	0·995	0·996	0·997	0·997	0·998	24	100·00	0·997	0·997	0·998	0·998	0·998
	31·60	0·988	0·990	0·991	0·992	0·993		31·60	0·991	0·992	0·994	0·995	0·995
	10·00	0·970	0·974	0·978	0·981	0·982		10·00	0·977	0·981	0·983	0·986	0·987
	3·16	0·934	0·942	0·949	0·955	0·959		3·16	0·949	0·956	0·961	0·966	0·969
	1·00	0·874	0·887	0·898	0·908	0·914		1·00	0·896	0·909	0·918	0·927	0·933
	0·316	0·785	0·805	0·821	0·837	0·846		0·316	0·818	0·836	0·850	0·863	0·872
	0·100	0·665	0·691	0·712	0·733	0·746		0·100	0·712	0·737	0·757	0·776	0·787
	0·0316	0·539	0·565	0·587	0·608	0·623		0·0316	0·581	0·609	0·633	0·657	0·672
	0·0100	0·411	0·439	0·462	0·485	0·500		0·0100	0·455	0·481	0·503	0·526	0·541

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