Thermal Unimolecular Isomerization of Cyclobutenes

Part 5.—The Isomerization of 3-Methylcyclobutene at Low Pressures

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The thermal isomerization of 3-methylcyclobutene has been investigated at 123.5 and 148.5° and over a pressure range from 45 to 0.01 mm. In this range the rate constant decreases with decreasing pressure. The experimental results are compared with the theoretical curves obtained by evaluating the Kassel integral and the results are most closely fitted by a value of S = 15, indicating 15 effective oscillators out of a total number of 33 vibrational modes. Consistency tests on the experimental data indicate that over most of the pressure range there is no departure from unimolecular behaviour. The relative efficiencies of carbon dioxide, normal, iso- and neo-pentane compared with the reactant itself in maintaining the Maxwell-Boltzmann distribution of energies have been determined. Some values of the Kassel integral obtained by quadrature are listed in an appendix.

An essential feature of the Lindemann mechanism of a unimolecular reaction is that, below a certain pressure, the first-order rate constant should decrease with decreasing pressure. While this prediction has been verified,¹ the simple theory does not yield a relationship which is in quantitative agreement with the experimental results. The more elaborate Kassel theory does fit the results quantitatively fairly well, but at the expense of introducing an adjustable parameter S. There is, as yet, no satisfactory way for arriving at the value of this parameter by any independent method. Since the Kassel curves may be calculated readily once the Arrhenius parameters of the reaction are known and the particular S value selected, if for no other reason it does provide a good method for comparing and systematising the experimental results of the various investigations. Despite the effort that has been applied to the study of unimolecular reactions, there are still relatively few reliable data in the "fall-off" region. One of the purposes of the present investigation was to obtain such data for 3-methylcyclobutene.

Another feature of all theories of unimolecular reactions is the assumption of unit collisional deactivation efficiency of the activated molecules by non-activated ones. The experimental justification for this assumption rests on the observation that the efficiency of various added (non-reacting) molecules for this process is always less than that of an equivalent quantity of the reactant, and further the range of relative efficiencies is quite small, (about 20:1). This is in contrast to the results obtained in studies on vibrational relaxation for the lowest vibrational levels, where the collisional deactivational efficiencies are very low. This justification may not be as convincing as it appears on first sight. Since most unimolecular reactions only occur at relatively elevated temperatures, the number of different molecules that are sufficiently stable at the reaction temperatures to be employed as inert gases is restricted, and in particular has meant that a molecule of greater complexity (and hence having the possibility of a greater range of vibrational frequencies) might have a collisional deactivating efficiency greater than that of the reactant. Since 3-methylcyclobutene isomerizes at a convenient rate below 150° this system did seem to offer the possibility of employing complex molecules as inert gases.

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The Marcus 2 extension of the Kassel theory is probably the best model available for discussing unimolecular reactions. Its quantitative use does, however, require a detailed knowledge of the transition complex. Failure to obtain an exact fit of the theoretical and experimental curves using this theory may result if an incorrect vibrational description of the activated complex is used. It may also result if the assumption of deactivation on every collision of the excited molecule is in error.

The work reported in this paper is discussed in terms of the Kassel theory. In a later paper we will extend the treatment to cover the Kassel-Marcus theory.

EXPERIMENTAL

3-METHYLCYCLOBUTENE.—A sample of this compound had been prepared previously.³ After degassing, an analysis showed it to contain less than 0.4 % total impurity.

Carbon dioxide was obtained from the commercial solid (Drikold). It was subjected to three trap-to-trap distillations $(-78 \text{ to } -186^\circ)$ to remove water and non-condensable gases.

Normal and iso-pentane were Philips pure grade samples of stated purity of at least 99 mole %. They were degassed before use. The neo-pentane used was a sample of Matheson C.P. grade and was repeated frozen and melted, with pumping, before use.

APPARATUS

A conventional high vacuum apparatus was used, as described in earlier work.⁴ The reaction vessel for runs with sample pressures above 1 mm was a 150 ml spherical Pyrex bulb, and this was immersed in a high temperature oil thermostat. 4 mm int. diam. tubing was used for the connections to the vacuum line. The reaction vessel was closed with a Springhams greaseless stopcock (Viton A diaphragm) mounted close to the oil surface, which reduced the dead space to 0.2 %.

In the pressure range 1.0-0.01 mm a 11. Pyrex cylindrical reaction vessel was used. It was mounted in the thermostat with its axis horizontal. At the outlet was a 10 mm bore greaseless stopcock connected via 12 mm bore tubing to a 200 ml bulb into which samples were frozen after reaction. The use of wide bore tubing ensured that the time of removal of the reaction mixture was short compared to the reaction time even at the lowest pressures. Subsequently, the sample was transferred from this bulb to the gas pipette for analysis.

Two McLeod gauges were connected to the system for measuring sample pressures. One had a direct-reading scale which covered the range 0.1-0.01 mm. The second gauge was used between 5.0 and 0.1 mm. Above 5 mm pressures were measured directly using a cathetometer and a small bore manometer.

Gaseous mixtures were prepared in a vacuum apparatus containing no greased stopcocks. It consisted of a bulb of fixed volume, closed at both ends by diaphragm valves, and maintained by a liquid thermostatted jacket at a constant temperature to within 0.2° . The bulb was connected to three storage vessels and a large-bore mercury manometer. After expanding gas from a storage vessel into the fixed volume (when its pressure was measured) the sample was then frozen into a 500 ml bulb containing a magnetically operated paddle stirrer. After freezing all the components into this bulb, they were then flash evaporated and the mixture stirred for at least 48 h before use.

ANALYTICAL APPARATUS

One modification was made to the apparatus described previously.⁴ A Solartron transistor unit type no. AS 1200 was used as a power supply for the katharometer. Under normal analytical conditions the katharometer current was set at 200 mA and the output fed to a 5 mV recorder. For small samples the current was increased to 300 mA and the signal fed to a 1 mV recorder. The chromatographic column was a 30 ft. by 0.17 in. int. diam. coiled copper spiral filled with 40-60 mesh Chromasorb P containing 20 % w/w di-2-cyanoethyl ether as the liquid phase and operated at room temperature. Hydrogen

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was used as the carrier gas, inlet pressure 7.5 lb. in.² flow rate 20 ml/min. With these conditions the retention times of 3-methylcyclobutene and trans-penta-1,3-diene were 10 and 26 min respectively.

RESULTS AND DISCUSSION

An earlier study of the thermal isomerization of 3-methylcyclobutene showed that it was a unimolecular reaction and yielded the Arrhenius equation $k_{\infty} = 10^{13,53} \exp(-31,550/RT) \sec^{-1}$ for the high-pressure rate constant. Preliminary results had indicated that the rate constant commenced to "fall off" at about 7 mm. In the present work a detailed investigation was carried out at two temperatures 123.5 and

TABLE	1RATE	CONSTANTS	FOR	THE	ISOMERIZATION	OF	3-METHYLCYCLOBUTENE
				AT	123·5°C		

pressure (mm)	104 ksec ⁻¹	pressure (mm)	10 ⁴ ksec ⁻¹	pressure (mm)	104 ksec-1
	1.39 *	2.09	1.34	0.092	0.889
45 ∙0	1.39	1.31	1.30	0.087	0.876
27.4	1.40	1.15	1.25	0.078	0.841
21.5	1.39	1.07	1.25	0.010	0.817
17.9	1.39	0.972	1.24	0.067	0.809
12.9	1.38	0.797	1.21	0.059	0.804
9.71	1.37	0.624	1.21	0.054	0.787
7.00	1.38	0.204	1.17	0.046	0.747
5.48	1.37	0.353	1.14	0.038	0.692
4.66	1.37	0.261	1.10	0.029	0.660
3.94	1.38	0.225	1.07	0.025	0.633
3.29	1.35	0.195	1.03	0.020	0.574
3.06	1.35	0.151	0.993	0.012	0.485
2.78	1.35	0.130	0.958	0.010	0.476
2.53	1.34	0.102	0.921		2 110

Table 2.—Rate constants for the isomerization of 3-methylcyclobutene at $148.5^{\circ}C$

essure (mm)	10 ³ ksec ⁻¹	pressure (mm)	103 ksec-1	pressure (mm)	103 ksec-1
	1.49 *	2.04	1.37	0.114	0.915
32.3	1.50	1.64	1.34	0.111	0.895
20.7	1.49	1.13	1.32	0.097	0.880
16.7	1.49	1.10	1.30	0.091	0.858
15.1	1.47	0.934	1.28	0.086	0.841
12.2	1.49	0.860	1.27	0.080	0 ·827
11.0	1.47	0.675	1.24	0.078	0.824
9.25	1.46	0.634	1.22	0.071	0.802
8.86	1.46	0.613	1.21	0.068	0.790
8·18	1-47	0.540	1.20	0.061	0.762
7.59	1.47	0.503	1.20	0.057	0.740
6.49	1.46	0.437	1.17	0.053	0.727
5.61	1.46	0.365	1.14	0.045	0.693
4.90	1.44	0.281	1.09	0.036	0.653
4 ·16	1.43	0.214	1.04	0.029	0.594
3.85	1.42	0.211	1.02	0.023	0.559
3.42	1.43	0.156	0 ·978	0.017	0.487
2.92	1.41	0.148	0.969	0.012	0.429
2.43	1.40				
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* obtained from extrapolation of the graph of 1/k against 1/p.

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148.5° and at pressures from 45.0 to 0.01 mm. To avoid errors resulting from the finite times of transfer of the reaction mixture no run was carried out for a time of less than 14 min. The results obtained are listed in tables 1 and 2.

The values at infinite pressure were obtained by extrapolation of the graphs of 1/k against 1/p over a small range, using results near the high-pressure limit. These values were in close agreement with those of 1.38×10^{-4} sec⁻¹ and 1.48×10^{-3} sec⁻¹ calculated directly from the Arrhenius equation. This method of estimating k_{∞} was preferred to that of extrapolating a plot of 1/k against $1/p^{\frac{1}{2}}$. This latter method ⁵ is useful when data are only available in the region where considerable "fall-off" of the rate constant has occurred, but does give an over-estimate of the high-pressure value.

Using the high-pressure values of the rate constants together with those obtained at low pressures the values of $\log (k/k_{\infty})$ were obtained for various pressures. These are shown in fig. 1 and 2 where they are plotted against the logarithm of the pressure. Fall-off commences at about 12 mm at 148.5° and 7 mm at 123.5°. This is in agreement with theoretical predictons that fall-off occurs at a higher pressure at higher temperatures.

The internal consistency of the results in terms of a generalized Lindemann mechanism was examined using the tests derived by Johnston and White.⁶ They derived certain inequality relationships which should be obeyed. Using the terms defined in their paper these are

$$v_2/v_1^2 \ge 1$$

and

$$v_1 v_3 / v_2^2 \ge 1$$

The three moments v_1 , v_2 and v_3 and their derived quantities are shown in the appendix for the results obtained at 148.5°. v_2/v_1^2 is greater than 1 over the entire pressure range considered. In a few cases the value of v_1v_3/v_2^2 falls below unity. This failure of v_1v_3/v_2^2 always to be greater than unity may be due to a very small error in the value of k_{∞} and the accumulated errors in the moments. It may also be due to real experimental errors at the lowest pressures.

The Kassel integral equation for a unimolecular reaction may be put in the form,

$$\frac{k}{k_{\infty}} = \frac{1}{(s-1)!} \int_{0}^{\infty} \frac{\exp(-x)x^{s-1}dx}{1 + (A/\lambda Zp)(x/x+b)^{s-1}}$$

where $b = E_0/RT$, A the Arrhenius frequency factor, Z the collision frequency and λ the fraction of activated molecules deactivated by a single collision. The integral was evaluated for the two reaction temperatures for values of S from 12 to 15. The diameter of the 3-methylcyclobutene was taken as 7 Å for purposes of evaluating Z. The value of λ was assumed to be unity. The integral was converted into a summation using the Gauss-Laguerre quadrature formula and evaluated on a Pegasus computor. At the start of the work tables were only available for, at the most, 15 values of the zeros of the Laguerre polynomial and the corresponding weighting factors.⁷ During the course of the work 32 values became available but the use of these gave identical results, within the limits of accuracy required. The results are given in the appendix.

Some of the experimental results together with the Kassel curves are shown in fig. 1 and 2.

Over most of the pressure region studied the experimental values fall between the theoretical curves for S = 14 and S = 15. However at the lowest pressures the experimental values decrease more rapidly with pressure than the theoretical curve. It is in this region that v_1v_3/v_2^2 is not always greater than one. It is possible that in

this region a small systematic error is responsible for this deviation. The most probable cause is a slow surface-catalysed polymerization of the initially formed trans penta-1,3-diene. While no evidence for the reaction was found in the high-pressure runs the occurrence of such a reaction even though insignificant at higher pressures could become important at the lowest pressures and would lead to apparently low values of the rate constants. The value of the parameter S which describes the



FIG. 2.—Isomerization of 3-methylcyclobutene at 148.5°.

experimental data most precisely is between 14 and 15. However, the choice of these values is also dependent on the value chosen for the molecular diameter. The chosen value of 7 Å may be a little high, and if it is then the value of S = 15 is to be preferred to S = 14.

It has been established that inert gases, present in a reaction mixture, can participate in intermolecular energy transfer processes, thereby assisting to maintain the Maxwell-Boltzman energy distribution. For a compound undergoing a unimolecular reaction in the "fall-off" region, the addition of an inert gas increases the rate constant towards the high-pressure limit. A series of mixtures of 3-methylcyclobutene with carbon dioxide normal, iso and neo-pentane were prepared. These mixtures were **ISOMERIZATION OF CYCLOBUTENES**

then decomposed at a series of pressures in the fall off region. (Runs were carried out at between 7 and 13 different pressures in each case). From these results the relative efficiencies of these gases for collisional deactivation compared with the reactant itself were obtained and these are shown in table 3.

TABLE 3.--RELATIVE EFFICIENCIES OF INERT GASES IN TRANSFERRING ENERGY

compound	molecular diameter (Å)	E_{p}	Ec
3-methylcyclobutene	7.0	1	1
carbon dioxide	4 ·1	0.32	0.48
n-pentane	5.8	1.09	1.32
iso-pentane	5.3	0.96	1.25
neo-pentane	5.2	0·85	1.12

 E_p = relative efficiency of inert gas pressure for pressure.

 $E_c = ,, ,, ,,$ collision for collision.

Values of molecular diameters of the pentanes are taken from the work of McGrath and Ubbelohde. 8

TABLE 4.—CONSISTENCY	TESTSISOMERIZATION	AT	148·5°	\mathbf{C}
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108 M (m/cm ³)	103 k (sec ⁻¹)	$10^{8} v_{1}$	10 ¹⁶ v ₂	ν_2/ν_1	$10^{24}\nu_{3}$	v_1v_3/v_2^2
8	1.487	0.690	0.970	2.04		
35-2	1.459	0.676	0.695	2.11	0.821	0.58
33.7	1.458	0.671	1.11	2.47	·	
18.7	1.437	0.649	1.21	2.87		
15.8	1.432	0.608	1.71	4.63		
14.6	1.423	0.658	0.925	2.14	1.30	1.00
13·0	1.428	0.538	2.35	8.12		
11.1	1.406	0∙640	0.996	2.43	3.32	2.14
9.24	1.403	0.553	1.65	5.40		
7.75	1.372	0.650	0.757	1.79	2.28	2.59
6.22	1.343	0.667	0.602	1.35	2.94	5.41
4·29	1.319	0.547	0.993	3.32	0.43	0.24
4·17	1.296	0 ∙614	0.740	1.96	1.55	1.74
3.56	1.284	0.562	0.842	2.67	1.00	0.80
3.27	1.268	0.565	0.800	2.51	1.10	0.97
2.41	1.218	0.532	0 ·748	2.64	1.05	1.00
2.06	1.197	0.498	0.739	2.98	0.96	0.87
1.66	1.166	0.458	0.702	3.35	0.890	0 ·83
1.39	1.140	0.422	0.664	3.73	0.834	0.80
1.07	1.089	0.391	0.590	3.86	0 ·786	0.88
0.816	1.036	0.355	0 ·518	4.11	0.713	0 ∙94
0.592	0.978	0.308	0.439	4.63	0 ·787	1.26
0.564	0.969	0.302	0.427	4.68	0 .598	0.99
0.434	0.915	0.271	0.369	5.02	0.523	1.04
0.421	0.895	0.278	0.366	4.74	0.524	1.09
0·344	0.858	0.252	0.325	5.11	0 ·467	1.11

 $v_1 = M(k_{\infty} - k)/k,$ $v_n + 1 = M(kv_n^{\infty} - kv_n)/k.$

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	Pressure (mm)	S = 12	13	14	15
b = 37.7	121.6	0.987	0.992	0.995	0.997
	38.30	0.965	0.979	0.987	0.992
	12.16	0.918	0.947	0.966	0.978
	3.83	0.836	0.887	0.922	0.946
	1.216	0.716	0.789	0.845	0.886
	0.383	0.569	0.658	0.731	0.792
	0.1216	0.418	0.208	0.592	0.664
	0.0383	0.281	0.364	0.443	0.521
	0.0122	0.177	0.240	0.309	0.379
b = 40.0	121.6	0.991	0.995	0 ·997	0.998
	38.30	0·9 76	0.986	0.992	0.995
	12.16	0.943	0.965	0.978	0.986
	3.83	0.878	0.919	0.947	0.965
	1.216	0.776	0.840	0.888	0.922
	0.383	0.639	0.725	0.793	0.847
	0.1216	0.490	0.584	0.667	0.738
	0.0383	0.345	0.435	0.523	0.601
	0.0122	0.224	0.302	0.379	0.460

molecular diameter 7 Å; Arrhenius A factor 1013-58

The value obtained for carbon dioxide compares well with that obtained in other systems.⁹ The values obtained for the pentanes are very high. The values of their efficiency based on collision for collision are all greater than one. If this is accepted unconditionally then it implies that the assumption of unit collisional deactivational efficiency by the reactant molecule itself is incorrect. We do not, however, believe that the evidence obtained is sufficient to warrant this conclusion. The values of E_c depend on the values assumed for the collision diameters of the pentanes and for the 3-methylcyclobutene. We have already indicated that the chosen value for 3-methylcyclobutene may be somewhat high and if a smaller value is chosen then the calculated values for E_c will also be smaller. Nevertheless, it is clear that the pentanes must be highly efficient at removing energy from the activated molecules. It is possible that the high efficiency of n-pentane is to be associated with the very low frequency torsional oscillations that must occur in such a molecule.

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