122. *The Thermal Isomerization of Cyclopropane.*

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The thermal isomerization of cyclopropane to propene at 30 cm. pressure has been studied by gas-chromatographic analysis between 420° and 535°. The rate constant is given by

$$\log k_{30}\ (\text{sec.}^{-1}) = (15{\cdot}296 \pm 0{\cdot}007) - (65{,}084 \pm 26/2{\cdot}303\boldsymbol{R}T).$$

The Arrhenius equation represents the results within the limits of accuracy of the experiments.

Chambers and Kistiakowsky [1] first reliably determined the temperature-dependence of the isomerization of cyclopropane to propene. They found that their results for this rate constant at 469·6°, 499·5°, and 518·6° were best represented by

$$\log k\ (\text{sec.}^{-1}) = 15{\cdot}17 - (65{,}000/2{\cdot}303\boldsymbol{R}T)$$

They considered that the activation energy had been determined within ±2000 cal. mole^{-1}, but their results cannot readily be analysed statistically because they were rather few and because of the corrections that had to be applied to extrapolate them to infinite pressure. The isomerization of cyclopropane is of theoretical importance because it is one of the few clean unimolecular reactions whose rate constant varies over an experimentally accessible range of pressure. The interpretation of this dependence requires a knowledge of the Arrhenius equation and it was possible that the small divergence between theory and experiment arose because the A factor was not accurately known.[2,3] Slater's theoretical treatment [4] of the reaction based on a model with quantized oscillators predicts that the activation energy of the reaction should vary by 18% between 693° and 808° K. Although this variation seems large, the effect is that the theoretical curve for log k lies only 0·064 unit (16% for k) below the Arrhenius curve if the two curves are made to coincide at the extreme temperatures. The perfect fit of the rates at the extreme temperatures cannot be realised in practice; therefore the effect to be detected is a deviation of +0·032 log unit at the extreme temperatures and —0·032 log unit in the middle. The detection of such small trends calls for unusually self-consistent results.

Chambers and Kistiakowsky analysed the mixtures of propene and cyclopropane formed during the reaction by oxidation of the propene with potassium permanganate. This was cumbersome and accurate to only about ±2%. Pritchard, Sowden, and Trotman-Dickenson [5] later absorbed the propene with a mixture of mercuric acetate and mercuric nitrate. Much smaller samples could be analysed but the accuracy was not much better. Gas-chromatographic separation with a Janak nitrometer detector was used in this work because it is capable of an accuracy of a few parts in a thousand.

The rate constants for 30 cm. pressure are given by the expression

$$\log k_{30}\ (\text{sec.}^{-1}) = (15{\cdot}296 \pm 0{\cdot}007) - (65{,}084 \pm 26/2{\cdot}303\boldsymbol{R}T)$$

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[1] Chambers and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 399.

[2] Trotman-Dickenson, " Gas Kinetics," Butterworths, London, 1955.

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

[4] Slater, preceding paper.

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

The Table of deviations shows that few of the runs deviated from the Arrhenius expression by as much as 1% (0·004 log unit), and the mean deviation is less. This does not mean that the rate constants are known with that precision because the absolute temperature scale is known with much less certainty than the relative temperatures of the runs. For this reason the uncertainty in the Arrhenius parameters is considerably greater than that computed statistically. Fortunately it is the relative temperature scale that is of primary importance for testing the adequacy of the quantized oscillator model. The model predicts that if the experimental range is roughly divided into three parts with $10^3/T$ equal to 1·237—1·305, 1·305—1·373, and 1·373—1·442, then the mean deviation from the Arrhenius expression for each of the parts should be +0·011, —0·021, and +0·011. The mean deviations found are $+0{\cdot}002 \pm 0{\cdot}0028$, $-0{\cdot}0010 \pm 0{\cdot}0019$, and $0{\cdot}0010 \pm 0{\cdot}0031$. These figures show that the quantum theory differs from the observations by about five times the experimental error.

A more stringent test would depend either upon more accurate measurement of the rate constant or upon the extension of the temperature range. The accuracy of the measurements is limited by many factors, such as the measurement of the lengths of the runs, the estimation of reaction zone and the dead space, the timing of short runs, and the analysis of the products. Consideration of the probable sizes of the errors involved leads to an error fully equal to the reproducibility of the runs obtained here. The temperature range cannot be extended downwards because evidence was found that in runs three times as long as the longest recorded in the Table, about 1% of the propene disappeared, presumably by polymerization. Shorter runs require a flow system. Equally accurate relative measurements can be made with flow systems, but there is always some doubt about the continuity of the temperature scale with that of a static apparatus and of the effective reaction volume. These uncertainties cancel the advantages of shortening the reaction time.

Deviations of the experimental rate constants from the Arrhenius equation.

Temp. (° K)	10^3 (log $k_{\text{exp.}}$ — log $k_{\text{calc.}}$)	Temp. (° K)	10^3 (log $k_{\text{exp.}}$ — log $k_{\text{calc.}}$)	Temp. (° K)	10^3 (log $k_{\text{exp.}}$ — log $k_{\text{ealc.}}$)
808·34°	+2·5	773·48°	+4·3	732·85	−0·6
806·14	−0·6	773·57	−2·6	720·05	+2·0
806·38	−0·8	762·06	+1·8	720·04	+1·9
797·50	+5·5	761·95	−1·8	719·66	+3·9
797·29	+0·3	761·90	−1·8	710·60	−3·9
796·23	−0·9	761·87	−3·1	706·95	+1·0
784·81	−4·3	751·68	+1·7	706·93	+6·0
784·63	−3·2	751·83	−2·1	700·00	−4·1
784·79	−0·6	737·41	−4·0	693·87	−0·3
784·38	+2·2	737·56	−0·7	693·62	+2·0

The results obtained here can be corrected to infinite pressure with the aid of Slater's classical harmonic oscillator treatment which states that the position of the plot of log k/k_∞ against log p varies with temperature according to the expression

$$\Delta \log p = \tfrac{1}{2}n \log (T_2/T_1)$$

where n is the number of modes of vibration; in this instance $n = 14$. Hence at infinite pressure

$$\log k\ (\text{sec.}^{-1}) = 15{\cdot}45 - (65{,}600/2{\cdot}303\boldsymbol{R}T)$$

The result is in excellent agreement with Chambers and Kistiakowsky's [1] and with

$$\log k\ (\text{sec.}^{-1}) = 15{\cdot}2 - (65{,}500/2{\cdot}303\boldsymbol{R}T)$$

reported by Rabinovitch, Schlag, and Wiberg [6] after this work was begun. None of the discrepancy between the experimental and theoretical variations of k with pressure can, therefore, be ascribed to errors in the Arrhenius parameters.

[6] Rabinovitch, Schlag, and Wiberg, *J. Chem. Phys.*, 1958, **28**, 504.

The Arrhenius equation is similar to that for the structural isomerization of methylcyclopropane:[7]

$$\log k\ (\text{sec.}^{-1}) = 15{\cdot}45 - (65{,}000/2{\cdot}303\boldsymbol{R}T)$$

and of 1,1-dimethylcyclopropane:[8]

$$\log k\ (\text{sec.}^{-1}) = 15{\cdot}05 - (62{,}600/2{\cdot}303\boldsymbol{R}T)$$

The small changes in the rate constants with substitution are difficult to reconcile with the fission of a C–C bond as the rate-determining step.

Experimental.—*Apparatus.* The Pyrex reaction vessel (50 c.c.) was immersed in a lead bath placed in an electric furnace. The furnace-temperature was controlled by a Sunvic RT 2 resistance thermometer controller whose sensing element was in a copper tube brazed to a brass sheet which closely fitted the cylindrical former that carried the windings. The reaction temperature was measured by a double base-metal thermocouple in a well in the centre of the reaction vessel. The thermocouple was calibrated against a platinum/platinum–13% rhodium couple.

Materials. Cyclopropane (B.O.C.) was degassed and shown by analysis to contain no impurities.

Procedure. Runs were started by admitting 30 cm. pressure of cyclopropane to the reaction vessel. After a convenient time the mixture was frozen into a trap cooled by liquid oxygen. A few seconds later the trap was connected to the vacuum-line so that small quantities of non-condensable gases should not prevent the freezing-out of larger quantities of C_3 hydrocarbons. The mixture was analysed on a column of 1 ft. of activated alumina, followed by 3 ft. of firebrick with 20% of ethylene glycol saturated with silver nitrate, coupled to a Janak nitrometer detector. The amount of reaction always lay between 25% and 77%. The variation of rate constant with degree of conversion at one temperature was not systematically studied. The early work showed that the isomerization accurately obeys first-order kinetics. Results are in the Table.

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[7] Chesick, *J. Amer. Chem. Soc.*, 1960, **82**, 3277.

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