

749. *The Thermal Decomposition of cyclopentyl Bromide.*

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The thermal decomposition of *cyclopentyl bromide* into *cyclopentene* and hydrogen bromide has been studied in a static system at temperatures between 300° and 360° c. The decomposition is homogeneous and obeys first-order kinetics in its early stages; the rate constant is given by

$$k = 10^{11.9} \exp(-41,400/RT) \text{ sec.}^{-1}$$

The elimination of hydrogen bromide is probably a molecular process, as the addition of *cyclohexene* has no effect upon the rate.

DURING the past few years the thermal decomposition of many aliphatic bromides has been investigated, chiefly by Maccoll and his collaborators.^{1,2} The majority of these bromides, in the presence of an inhibitor, decompose by a four-centre molecular elimination mechanism into hydrogen bromide and an olefin. One of the compounds which has been found to react in this way is *cyclohexyl bromide*.³ The rate constant for its decomposition is given by the Arrhenius equation

$$k = 10^{13.5} \exp(-46,100/RT) \text{ sec.}^{-1}$$

The investigation of the decomposition of *cyclopentyl bromide* was undertaken in the hope that a knowledge of the rate factors, *A* and *E* in the Arrhenius equation, would throw light on the features of molecules which determine the rates of molecular elimination reactions. In particular, it was thought that the different degrees of flexibility of the carbon rings might influence the rates.

EXPERIMENTAL

Materials.—The *cyclopentyl bromide* was a gift from the Michigan Chemical Company. It was degassed and purified by bulb-to-bulb distillation. No significant quantities of impurity could be detected by vapour-phase chromatography. The *cyclohexene*, which was similarly degassed, was freed from peroxides by shaking with acid ferrous sulphate solution.

Apparatus.—The decomposition was studied in a bulb of 385 c.c. capacity attached to a conventional vacuum-system by tubing with a total dead space of approx. 13 c.c. The bulb was contained in a mercury-vapour jacket, whose temperature could be readily controlled by varying the pressure under which the mercury boiled. The temperature of the jacket was determined by reference to standard tables of the vapour pressure of mercury. The reaction was studied by following the change in pressure in the reaction vessel on a mercury manometer. It was found that the hydrogen bromide formed did not appreciably attack the mercury during a run, for the reaction vessel was separated from the manometer by about 30 cm. of 2-mm. capillary tubing.

Procedure.—Runs were started by admitting a suitable quantity of the bromide to the reaction vessel from a storage bulb; in some runs a quantity of *cyclohexene* was also added. Readings of the pressure in the vessel were then recorded at convenient intervals. At the end of some of the runs the quantity of hydrogen bromide formed was determined analytically. It was found that inexplicably erratic and high results were usually obtained when the unseparated products were titrated with alkali, so the following procedure was adopted. First, the products were condensed in a side bulb, and the hydrogen bromide was separated by low-temperature distillation. Its amount was then determined by pressure measurements and by dissolving the gas in water and titrating the solution for hydrogen and halide ions. The results of the three determinations were always in excellent agreement. When a proper correction was made for the dead space it was found that the analytical results agreed well with degrees of decomposition deduced from the pressure measurements.

Rate constants were determined in the usual way from first-order plots of the logarithms of

¹ Harden and Maccoll, *J.*, 1955, 2454, and ref. 4.

² For similar reactions, see Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955.

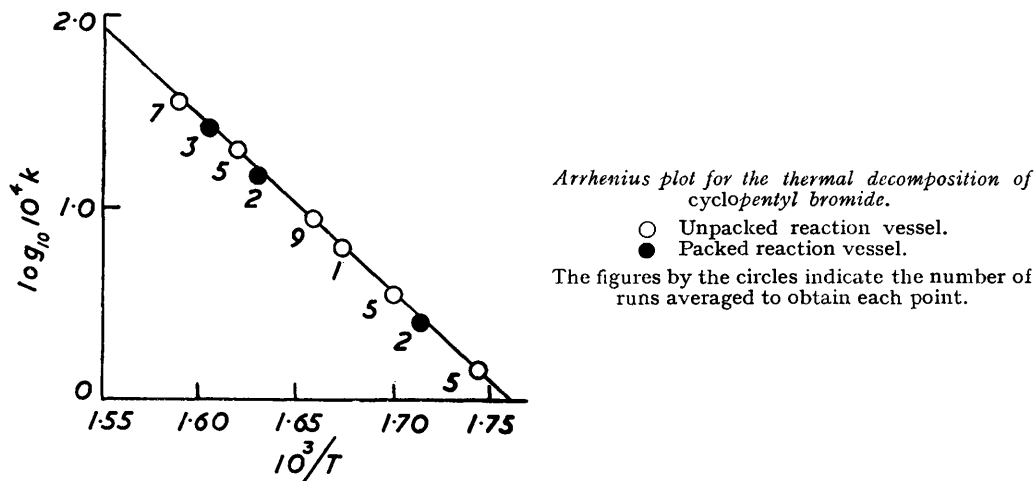
³ Green and Maccoll, *J.*, 1955, 2449.

the pressure changes against time. The logarithmic plots were strictly linear for the first third of the reaction but thereafter tended to curve. The curvature was probably caused by the increasing importance of the back reaction. The rate constants for a few runs were calculated from the full expression for a first-order reaction opposed by a second-order reaction. The rate constants obtained in this way differed by only about 10% from those calculated by applying the equation for a simple first-order reaction to the observations made during the first third of the decomposition. All the rate constants reported here were determined by the less tedious procedure.

All runs showed short induction periods. Their lengths corresponded roughly to the time needed for 2–3% of the bromide to decompose. The presence of *cyclohexene* appeared to shorten the induction periods slightly.

RESULTS and DISCUSSION

Preliminary runs in a clean-walled reaction vessel gave first-order rate constants which decreased slowly but steadily from run to run. Maccoll and his collaborators observed similar behaviour with other bromides and attributed the effect to heterogeneous processes. They therefore seasoned their reaction vessels by decomposing allyl bromide in them. This



remedy proved effective for *cyclopentyl* bromide also. It was used after any occasion on which air had been admitted to the reaction vessel. Incidentally, Maccoll's rate constant ⁴ for the decomposition of allyl bromide was confirmed.

The first-order nature of the decomposition was demonstrated by studying it with various initial pressures of *cyclopentyl* bromide. The results obtained for a typical series of runs, all corrected to 356.5°, were as follows:

Initial pressure (mm.)	38.0	49.6	59.6	79.5	94.0	105.0	107.5
$10^3 k$ (sec. ⁻¹)	3.48	3.48	3.39	3.66	3.53	3.80	3.78

The very small effect on the rate constant of the addition of *cyclohexene* can be seen from the following Table, in which the observed rate constants are compared with those calculated from the Arrhenius equation. The variations in the rates are of the same order as the experimental error.

<i>cycloHexene</i> (mm.)	20.0	30.0	10.0	9.0	40.0
<i>cycloPentyl</i> bromide (mm.)	60.0	72.5	64.0	48.2	38.0
Temp.	300.7°	315.2°	331.3°	344.5°	365.5°
k (obs.)/ k (calc.)	1.05	0.95	1.02	0.98	0.91

Seven runs were carried out with the reaction vessel packed with Pyrex tubing so that the surface/volume ratio was increased from 0.9 to 2.0 cm.⁻¹. The results of these runs are distinctively plotted alongside the other results in the Figure. It can be seen that there is no evidence for any heterogeneous contribution to the reaction in an aged vessel.

⁴ Maccoll, *J.*, 1955, 965.

The results of all the runs are shown on an Arrhenius plot in the Figure. The Arrhenius equation was derived by a least-squares treatment of the results for all the individual runs. The results are best expressed by the equation :

$$k = 10^{11.9} \exp (-41,400/RT) \text{ sec.}^{-1}$$

Our experiments indicate that this is the rate constant for the homogeneous gas-phase molecular elimination of hydrogen bromide from *cyclopentyl* bromide.

The rate constant for this decomposition at 380° (0.010 sec.⁻¹) is very slightly greater than that (0.008 sec.⁻¹) for the similar decomposition of *cyclohexyl* bromide. This conclusion is of interest in view of a recent important suggestion⁵ that the rate constants for the molecular elimination of hydrogen bromide from aliphatic bromides should run parallel to the rate constants for the elimination of bromide ions from the bromides by the S_N1 mechanism. No measurements on the rates of the S_N1 reactions of *cyclopentyl* and *cyclohexyl* bromide have been reported. It has been found,⁶ however, that the S_N1 reaction of 1-methyl*cyclopentyl* chloride in 80% aqueous ethanol at 25° is 125 times more rapid than the corresponding reaction of 1-methyl*cyclohexyl* chloride. Evidently the parallelism between the rates of the S_N1 reactions and the molecular eliminations breaks down in this instance. Probably the cause is the different natures of the strains in the two types of transition states.

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⁵ Maccoll and Thomas, *Nature*, 1955, **176**, 392.

⁶ Brown and Borkowski, *J. Amer. Chem. Soc.*, 1952, **74**, 1894.
