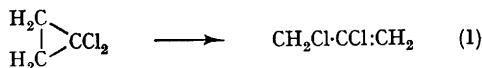


Kinetics of the Gas-phase Thermal Isomerisation of 1,1-Dichlorocyclopropane

By K. A. W. PARRY and P. J. ROBINSON*

(Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester, 1)

A RECENT kinetic investigation¹ of the pyrolysis of cyclopropyl chloride and bromide led to the suggestion that isomerisation occurred by intramolecular migration of a halogen rather than a hydrogen atom, although the nature of the product (3-chloropropene from the chloride) neither proved nor disproved this hypothesis. A similar conclusion was reached from a study of the isomerisation of 1,1-dibromo-2,3-dimethylcyclopropane to 3,4-dibromopent-2-ene in kerosene solution,² the main evidence in this case being the separation of the originally geminal bromine atoms during the reaction. Other workers in our own department have found³ that 1,1-dichlorocyclopropane reacts in a flow system at 650° (residence time *ca.* 0.2 sec.) to give 2,3-dichloropropene as the major product:



and this reaction is interpreted in terms of an intramolecular chlorine migration. The identity of the product precludes any possibility of intramolecular hydrogen atom migration, but radical chain mechanisms were not conclusively ruled out.

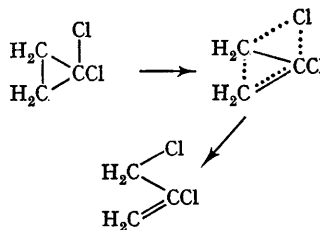
We now report a kinetic study of the pyrolysis of 1,1-dichlorocyclopropane at 342–441° and 20–120 torr pressure in a static Pyrex system, using g.l.c. analysis to follow the course of the reaction. After a small ageing effect the primary reaction proceeded cleanly according to equation (1), although there was slight secondary decomposition of the product olefin at the temperatures

involved (*e.g.*, 5% decomposition at 50% isomerisation). The isomerisation of the 1,1-dichlorocyclopropane was accurately first-order for at least 3 half-lives, and the first-order rate-constants were independent of initial pressure and fit the Arrhenius equation:

$$\log_{10} k \text{ (sec.}^{-1}\text{)} = (15.13 \pm 0.10) - \frac{(57,810 \pm 300)}{4.576T}$$

(the error limits being the statistical 95% confidence limits). The rate of isomerisation was completely unaffected by the presence of propene, 2,3-dichloropropene, or nitric oxide, or by increasing the surface-to-volume ratio 16 times.

We therefore conclude that the reaction (1) is unimolecular under the conditions employed, and this, together with the identity of the product, establishes beyond any reasonable doubt that the reaction involves intramolecular chlorine atom migration through a unimolecular transition-state of the type shown below:



The reaction cannot proceed through a trimethylene biradical intermediate since the more

stable, and therefore preferentially formed bi-radical $\dot{\text{C}}\text{Cl}_2\cdot\text{CH}_2\cdot\dot{\text{C}}\text{H}_2$ would not give rise to the observed product.

The Arrhenius parameters found here are very similar to those¹ for the isomerisation of cyclopropyl chloride to 3-chloropropene [$\log_{10}A$ (sec.⁻¹)

= 14.8, E = 56.2 kcal./mole], supporting the mechanism previously suggested for this compound.

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