

The Gas-phase Unimolecular Thermal Isomerization of Pentachlorocyclopropane

By J. C. Ferrero, J. J. Cosa, and E. H. Staricco,* Departamento de Físico-Química, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, Córdoba, Argentina

The gas-phase thermal isomerization of pentachlorocyclopropane to 1,1,3,3,3-pentachloropropene has been studied in the temperature range 440–490 K at pressures between 10 and 50 Torr. The reaction is of the first order and was unaffected by changes in surface:volume ratio or by the addition of cyclohexene. The rate constants

$$\log_{10} k/s^{-1} = (14.16 \pm 0.23) - (39,963 \pm 500)/4.5767 \quad (i)$$

fit the Arrhenius equation (i). The reaction is interpreted as a unimolecular process taking place with chlorine-atom migration through a concerted transition state.

In spite of the substantial effect that chlorine substitution has on the Arrhenius parameters of the isomerization of cyclopropanes few kinetic studies have been reported. Only monochloro-,¹ 1,1-dichloro-,² and *cis*-1,1-dichloro-2,3-dimethylcyclopropane³ have been the subject of kinetic investigations. In every case the reactions were interpreted in terms of a mechanism involving chlorine-atom migration without ring opening to form a diradical. This is in contrast with the pyrolysis of cyclopropane and its alkyl derivatives⁴ which proceed mainly through a diradical intermediate.^{4,5} The pyrolysis of a number of *gem*-dichlorocyclopropanes have also been reported.⁶ A concerted mechanism with chlorine migration was postulated in order to explain the products obtained. Further support for this mechanism arises from the pyrolysis of *cis*-1,1,2,3-tetrachlorocyclopropane⁶ which is characterized by the absence of *cis-trans*-isomerization of the reactant. However, it has been suggested that the isomerizations of monochloro- and 1,1-dichlorocyclopropane could proceed through other mechanisms than concerted.⁷ Thus, for the former a radical-chain process was suggested and for the latter a diradical intermediate.

We now report a kinetic study of the thermal isomerization of pentachlorocyclopropane to 1,1,3,3,3-pentachloropropene. The migration of a chlorine atom is required to explain the product of the reaction independently of whether it takes place through a diradical intermediate or a concerted process. However we believe that the kinetic data here reported agree better with a mechanism involving chlorine-atom migration through a concerted process and provide further evidence against a diradical intermediate for the isomerization of chlorinated cyclopropanes.

EXPERIMENTAL

Apparatus.—A conventional high-vacuum system was employed. Greaseless stopcocks were used throughout to

¹ R. C. S. Grant and E. S. Swinbourne, *Chem. Comm.*, 1966, 620.

² K. A. W. Parry and P. J. Robinson, *J. Chem. Soc. (B)*, 1969, 49.

³ K. A. Holbrook and K. A. W. Parry, *J. Chem. Soc. (B)*, 1970, 1019.

⁴ H. M. Frey, *Adv. Phys. Org. Chem.*, 1966, **4**, 147; D. W. Setser and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, 1964, **86**, 564; L. B. Sims and P. E. Yankwich, *J. Phys. Chem.*, 1967, **3459**, and references therein.

avoid absorption. Most runs were carried out in a cylindrical Pyrex vessel of 280 cm³ volume, provided with a small side-tube. Some runs were carried out in a similar vessel packed with Pyrex tubes, with a surface:volume ratio 9 times larger. Both reactions vessels were mounted in a high-temperature oil-bath. The temperature of the bath was controlled to better than ± 0.1 °C by a Lauda Electronic regulator type PTR 50 and was measured with a calibrated chromel–alumel thermocouple.

The dead-space was smaller than 1% and electrically heated to avoid condensation. To eliminate a possible initial irreproducibility the vessels were aged by heating a large sample of reactant for several half-lives at 300 °C.

Procedure.—Runs were carried out by introducing a weighed amount of pentachlorocyclopropane into the high-vacuum system where it was exhaustively degassed. Before the vessel was heated to the desired temperature the reactant was transferred to the side-tube by freezing with liquid nitrogen. The sample was then expanded into the heated reaction vessel by rapid electrical heating. At the end of a run the entire mixture was frozen into a previously evacuated U-tube cooled in liquid nitrogen, from which it was then transferred to a small tube equipped with a septum. After this the tube was sealed off and samples were taken from it for analysis. Between runs the reaction vessel was evacuated below 10⁻⁴ Torr.

Analysis.—Quantitative analysis was by g.l.c. with a Varian Aerograph Model 202 chromatograph equipped with a Gow-Mac gas density detector. The reaction mixture was resolved with a 3 m stainless steel column packed with Chromosorb P containing 10% (w/w) of dinonyl phthalate and operated at 125 °C. The carrier gas was nitrogen. Flows through the column and the detector were 38 and 120 ml s⁻¹ respectively. Retention time was 15 min for pentachlorocyclopropane and 17 min for 1,1,3,3,3-pentachloropropene. Signals from the detector were registered on a Speedomax W recorder. All runs were analysed at least in triplicate.

Materials.—Pentachlorocyclopropane was synthesized by the addition of dichlorocarbene to trichloroethylene in dimethoxyethane.⁸ The product obtained by reduced-pressure distillation was then distilled *in vacuo* between room temperature and that of liquid nitrogen. The penta-

⁵ H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 1968, **72**, 1866.

⁶ R. Fields, R. N. Haszeldine, and D. Peter, *J. Chem. Soc. (C)*, 1969, 165.

⁷ S. N. Benson and H. E. O'Neal, 'Kinetic Data on Gas Phase Unimolecular Reactions,' NSRDS-NBS 21, U.S. Government Printing Office, Washington, 1970.

⁸ S. W. Tobey and R. West, *J. Amer. Chem. Soc.*, 1966, **88**, 2478; *Tetrahedron Letters*, 1963, 1179.

chlorocyclopropane recovered was 99.8% pure as shown by g.l.c. on the following columns: Silicone SE-30 on Chromosorb W, Silicone QF-1 on firebrick and dinonyl phthalate on Chromosorb P. The i.r. spectrum agreed well with that reported.⁸

1,1,3,3,3-Pentachloropropene⁸ was prepared by distillation of pentachlorocyclopropane under nitrogen (740 Torr). It was used for g.l.c. and spectroscopic references.

RESULTS

In the temperature range 170–220 °C pentachlorocyclopropane undergoes a first-order isomerization to 1,1,3,3,3-pentachloropropene. This was the sole identified product of the reaction as was confirmed by i.r. spectroscopy and by g.l.c. comparison with an authentic sample. However at 220 °C and above 60% isomerization a new unidentified product began to appear.

The isomerization of pentachlorocyclopropane during distillation above 100 °C has been reported.⁸ This made it

TABLE 1
Rate constants for the isomerization of pentachlorocyclopropane

<i>t</i> /°C	Initial pressure/Torr	10 ⁵ <i>k</i> /s ⁻¹
167.1	15–45	0.212
177.0	20–50	0.592
187.4	10–50	1.536
197.3	10–50	3.655
207.2	15–40	9.473
217.1	15–50	23.14

necessary to confirm whether decomposition occurred during the treatment of the reactant before a run. A test was made by introducing a sample of reactant into the vessel at 180 °C during 1 min as described above; the sample was recovered unchanged.

TABLE 2

Reactant	Product	log ₁₀ <i>A</i> /s ⁻¹	<i>E</i> /kcal mol ⁻¹	Ref.
Cyclopropane	Propene	15.45	65.600	4
Chlorocyclopropane	3-Chloropropene	14.8	56.200	1
1,1-Dichlorocyclopropane	2,3-Dichloropropene	15.13	57.810	2
<i>cis</i> -1,1-Dichloro-2,3-dimethylcyclopropane	<i>trans</i> -3,4-Dichloropent-2-ene	13.65	44.568	3
Pentachlorocyclopropane	1,1,3,3,3-Pentachloropropene	14.16	39.963	Present work

At each of the temperatures at which the reaction was studied, at least eight runs were carried out. The rate constants were calculated from a plot of log (*C₀/C_t*) against time by the method of least squares. The rate constants were accurately of the first order in the range of isomerization studied which was between 15 and 60%.

The rate constants were also independent of the pressure in the range 10–50 Torr of reactant. The results obtained are shown in Table 1. An Arrhenius plot of the rate constants gave a good straight line, which corresponds to equation (1) calculated by the method of least squares; the error limits are standard deviations.

$$\log_{10} k/s^{-1} = (14.16 \pm 0.23) - (39,963 \pm 500)/4.576T \quad (1)$$

A series of runs were carried out at 187.4 and 197.3 °C in the packed vessel. A light increase in the reaction rate was observed when the clean packed vessel was used. However, when it was aged as described above the rate constants agreed with those of the unpacked vessel within experi-

mental error. The average rate constant at 187.4 °C was $1.634 \times 10^{-5} \text{ s}^{-1}$ and at 197.3 °C was $3.487 \times 10^{-5} \text{ s}^{-1}$. From these data we conclude that the reaction is homogeneous.

The reaction was also studied in the presence of 10–100 Torr of added cyclohexene. Runs were carried out at 192.3 and 197.3 °C. The rate constants were 2.616×10^{-5} and $3.996 \times 10^{-5} \text{ s}^{-1}$ respectively and fit well on the Arrhenius plot. Thus any radical-chain mechanism can be ruled out.

DISCUSSION

The isomerization of pentachlorocyclopropane to 1,1,3,3,3-pentachloropropene is accurately of the first order. The reaction is homogeneous and a radical-chain process can be ruled out. We conclude that the reaction is unimolecular.

Irrespective of whether the reaction takes place through a diradical intermediate or through a concerted process, a chlorine-atom migration is required to explain the product formed by the reaction. The migration of a chlorine instead of a hydrogen atom can be understood by the relative weakness of the C–Cl bond compared with the C–H bond.⁹ However this fact on its own cannot explain the low activation energy observed, as 1,1-dichlorocyclopropane isomerization also requires chlorine migration, having an activation energy 17.8 kcal mol⁻¹ higher than pentachlorocyclopropane.²

The Arrhenius parameters for isomerization of chlorinated cyclopropanes do not show a clear correlation among them (Table 2) and different reaction mechanisms have been suggested.

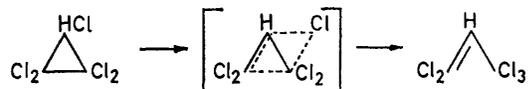
Although a concerted process has been postulated,²

Benson and O'Neal have suggested that the isomerization of 1,1-dichlorocyclopropane could take place through a diradical intermediate.⁷ They considered that if the activation energy for chlorine migration is sufficiently low, ring-opening to form the diradical should be the rate-determining step. If that is the case for pentachlorocyclopropane the lowering in activation energy with respect to cyclopropane must be attributed to an increase in the strain energy of the ring or to large stabilization of the diradical by chlorine substitution. These do not seem the only factors to be taken into account, as qualitative results show that 1,1,2,3-tetrachlorocyclopropane⁶ isomerizes at a lower temperature than pentachlorocyclopropane. Moreover, the lower *A* factor is unexpected on the basis of a diradical mechanism. The large moment of inertia of the CCl₂ rotating

⁹ T. L. Cottrell, 'The Strength of Chemical Bonds,' Butterworths, London, 2nd edn., 1958.

groups would contribute significantly to an increase in the activation entropy of the reaction, although a large barrier to internal rotation would be imposed.

The normal A factor would come from a relative tightening of the transition state, mainly associated with the loss of entropy of the internal rotations as compared with the cyclopropane transition state. We believe it arises from a structure involving a chlorine bridge of the same type postulated for 1,1-dichlorocyclopropane² and shown in the Scheme. The decrease



in the activation energy could be attributed to the low energy required for chlorine migration, an increase of the

strain energy,¹⁰ and the effect of the CCl_2 group in stabilizing the incipient double bond.⁶ The weakness of the C-C bond α to the CClH group compared with the hydrogenated C-C bond in cyclopropane will also contribute.

We believe that although a diradical mechanism does not seem to operate for this reaction the surprising effect of chlorine substitution on cyclopropane needs further kinetic studies in order to explain fully the reactions of chlorinated cyclopropanes.

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¹⁰ H. H. Bent, *Chem. Rev.*, 1961, **61**, 275.