Kinetics of the Gas-phase Unimolecular Thermal Isomerisation and Decomposition of 1,1-Dichloro-2,3-dimethylcyclopropane. Part II.[1] *trans*-1,1-Dichloro-2,3-dimethylcyclopropane

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At temperatures between 268·6 and 364·0 °C, *trans*-1,1-dichloro-2,3-dimethylcyclopropane undergoes isomerisation to *trans*-3,4-dichloropent-2-ene and also decomposition to produce *trans*-3-chloropenta-1,3-diene and hydrogen chloride. In this temperature range the decomposition is the more important reaction, unlike the case of *cis*-1,1-dichloro-2,3-dimethylcyclopropane which undergoes mainly isomerisation. It is shown that the *trans*-3-chloropenta-1,3-diene is a primary product from the *trans*-starting material. The decomposition reaction in a seasoned reaction vessel is first order up to *ca.* 35% decomposition and the rate constants are independent of pressure from 4 to 55 Torr, and unaffected by added propene or by change in the surface: volume ratio. The rate constants fit the Arrhenius expression $\log_{10} k_{\text{diene}}/\text{s}^{-1} = (14{\cdot}11 \pm 0{\cdot}34) - (47{,}726 \pm 888)/4{\cdot}576T$.

THERE have been many studies of the thermal isomerisations of cyclopropane derivatives in the gas-phase. It is thought that cyclopropane[2] itself, methylcyclopropane,[3] and *trans*- and *cis*-1,2-dimethylcyclopropane[4] probably isomerise *via* biradical intermediates. The isomerisations of 1,1-dichlorocyclopropane[5] to 2,3-dichloropropene, and of *cis*-1,1-dichloro-2,3-dimethylcyclopropane to *trans*-3,4-dichloropent-2-ene[1] have been reported and mechanisms have been suggested which involve chlorine atom migration. We now report a study of the thermal isomerisation and decomposition of *trans*-1,1-dichloro-2,3-dimethylcyclopropane.

EXPERIMENTAL

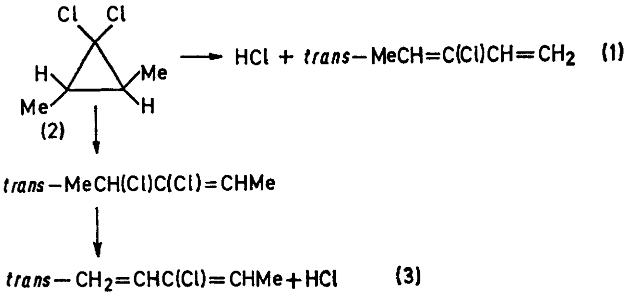
Apparatus.—The apparatus and experimental procedure were similar to that described previously.[6] Two cylindrical Pyrex reaction vessels were used: vessel A ($V = 1064$ cm^3, $S/V = 1{\cdot}66$ cm^{-1}) was unpacked while vessel B ($V = 882{\cdot}6$ cm^3, $S/V = 8{\cdot}02$ cm^{-1}) was packed with Pyrex tubes. Analyses were carried out on a Pye 104 chromatograph using a 12 ft column of 15% di-isodecyl phthalate on 80—100 mesh Celite at 100 °C.

Materials.—*trans*-1,1-Dichloro-2,3-dimethylcyclopropane was prepared by the addition of dichlorocarbene to *trans*-but-2-ene.[7] Dichlorocarbene was prepared *in situ* from the action of potassium t-butoxide on chloroform. The product was purified by distillation through a 1 m Nester-Faust spinning band column. The compound obtained was chromatographically pure on the following columns: 12 ft di-isodecyl phthalate on Celite, and 15 ft squalane on Celite. The i.r. and ^{1}H n.m.r. spectra have been described elsewhere.[1]

RESULTS

The decomposition and isomerisation of *trans*-1,1-dichloro-2,3-dimethylcyclopropane was investigated from 268·6 to 364 °C and from 4 to 55 Torr. Above 300 °C reproducible results were obtained after about 20 high pressure runs. Below 300 °C results were less reproducible. The major organic product is *trans*-3-chloropenta-1,3-diene (97% at 364 °C; 60% at 268·6 °C) and a minor product is *trans*-3,4-dichloropent-2-ene (3% at 364 °C; 40% at 268·6 °C). Pure samples of these products were obtained by flowing *trans*-1,1-dichloro-2,3-dimethylcyclopropane through a reaction vessel, packed with Pyrex helices, at 530 °C. Preparative g.l.c. was then used to obtain pure samples of *trans*-3-chloropenta-1,3-diene and *trans*-3,4-dichloropent-2-ene. The ^{1}H n.m.r. spectra of both compounds were in agreement with previously published data.[8]

The formation of *trans*-3-chloropenta-1,3-diene may occur in two ways, either as a primary decomposition product by reaction (1) or as a secondary product involving isomerisation to the monoene [reaction (2)] and its subsequent decomposition [reaction (3)].



From the appearance curve for the minor product (Figure 1) it is clear that the isomerisation reaction (2) occurs producing the monoene as a primary product. Within the temperature range of this study *trans*-3,4-dichloropent-2-ene undergoes slow decomposition to *trans*-3-chloropenta-1,3-diene. However this can only account for *ca.* 20% of the *trans*-3-chloropenta-1,3-diene produced in the middle of the temperature range. The major reaction producing the diene, particularly in the early stages, is therefore reaction (1). In agreement with this a pressure change occurs which is proportional to the amount of diene produced measured from the g.l.c. peak area (Figure 2). In addition, the shape of the pressure–time curve (Figure 3) and the

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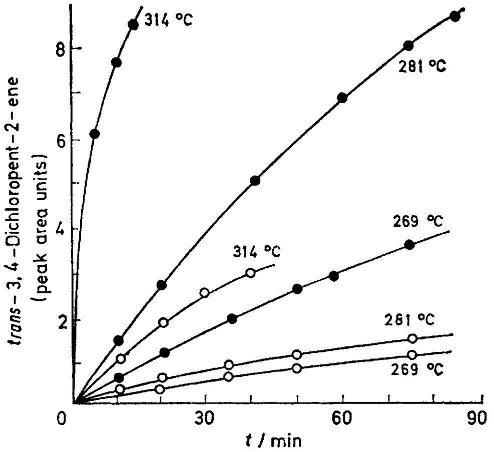


FIGURE 1 Plot of *trans*-3,4-dichloropent-2-ene against time for the isomerisations of *trans*- and *cis*-1,1-dichloro-2,3-dimethylcyclopropane at different temperatures: ●, *cis*-isomer; ○, *trans*-isomer

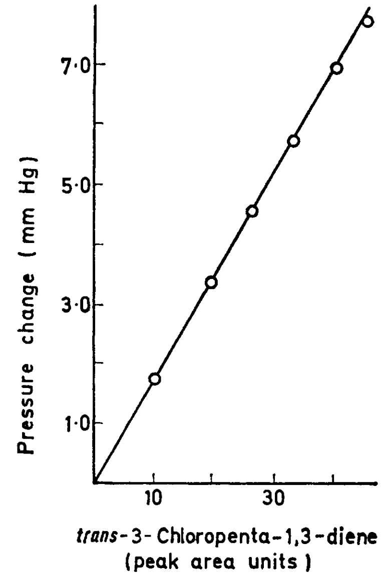


FIGURE 2 Plot of *trans*-3-chloropenta-1,3-diene against the pressure change observed in the pyrolysis of *trans*-1,1-dichloro-2,3-dimethylcyclopropane

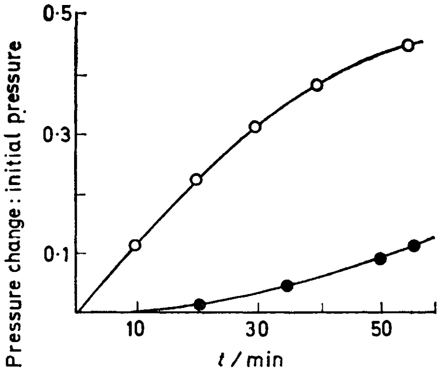


FIGURE 3 Pressure changes observed in the pyrolyses of *trans*- and *cis*-1,1-dichloro-2,3-dimethylcyclopropane at 314 °C: ●, *cis*-isomer; ○, *trans*-isomer

diene–time curve (Figure 4) show that the diene is mainly a primary product. The pressure change for *trans*-1,1-dichloro-2,3-dimethylcyclopropane follows a first-order relationship up to *ca.* 35% decomposition and the calculated first-order rate constants (Table 1) fit the Arrhenius equation $\log_{10} k_{\text{diene}}/\text{s}^{-1} = (14{\cdot}11 \pm 0{\cdot}34) - (47{,}726 \pm 888)/4{\cdot}576T$.

From chromatographic measurements of the disappearance of starting material, the rate is first order in *trans*-1,1-dichloro-2,3-dimethylcyclopropane up to *ca.* 35% decomposition, although the first-order rate constants show a wide scatter. This irreproducibility is unaffected by surface : volume ratio since the calculated first-order rate constants are similar in both packed and unpacked vessels.

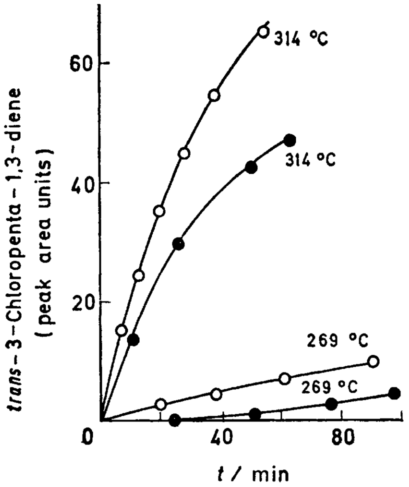


FIGURE 4 *trans*-3-Chloropenta-1,3-diene produced from the pyrolysis of *trans*- and *cis*-1,1-dichloro-2,3-dimethylcyclopropane: ●, *cis*-isomer; ○, *trans*-isomer

The decomposition was studied in the presence of propene; the added propene varied from 15 to 50% of the total reaction mixture. The decomposition was first order, and the rate constants calculated from pressure change were similar to those obtained in the absence of propene (Table 2).

TABLE 1

Mean first-order rate constants (k_{diene})

T/°C	No. of runs	$10^5 k_{\text{diene}}/\text{s}^{-1}$
268·6	5	0·74 ± 0·06
290·0	4	3·89 ± 0·11
302·1	4	6·48 ± 0·13
315·0	5	18·6 ± 0·62
340·0	6	116 ± 9·3
364·0	6	609 ± 15

TABLE 2

Effect of propene on the decomposition of *trans*-1,1-dichloro-2,3-dimethylcyclopropane at 304 °C

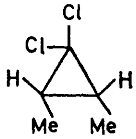
Propene (%)	$10^4 k_{\text{diene}}/\text{s}^{-1}$
0	1·11
15·0	1·13
18·0	1·08
31·3	1·13
46·3	1·09

We have briefly re-investigated the isomerisation of *cis*-1,1-dichloro-2,3-dimethylcyclopropane. The pressure changes observed in the pyrolyses of *trans*- and of *cis*-1,1-dichloro-2,3-dimethylcyclopropane as a function of time are compared in Figure 3, while Figure 4 is a plot of the formation of *trans*-3-chloropenta-1,3-diene as a function of time for the two isomers.

We consider that, in the pyrolysis of *cis*-1,1-dichloro-2,3-dimethylcyclopropane, *trans*-3-chloropenta-1,3-diene is both a primary and a secondary minor product.

DISCUSSION

There are considerable differences in the pyrolyses of *trans*- and of *cis*-1,1-dichloro-2,3-dimethylcyclopropane. It was postulated[1] that *cis*-1,1-dichloro-2,3-dimethylcyclopropane undergoes a unimolecular process in which migration of the chlorine atom *trans* to the methyl groups occurs, with simultaneous, outward rotation of the methyl groups in a disrotatory manner, to give *trans*-3,4-dichloropent-2-ene [reaction (4)].

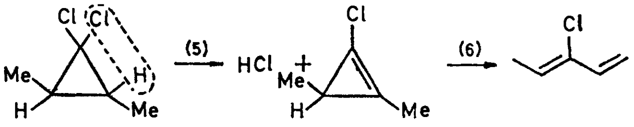


$\longrightarrow$ *trans*—MeCH(Cl)C(Cl)=CHMe (4)

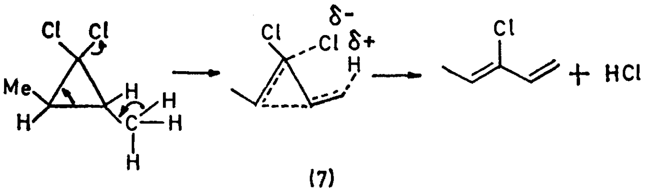
The minor product *trans*-3-chloropenta-1,3-diene was thought to be formed by the subsequent elimination of hydrogen chloride from *trans*-3,4-dichloropent-2-ene [reaction (3)]. Such a scheme implies that *trans*-3-chloropenta-1,3-diene is a secondary product. On re-examination of the pyrolysis of *cis*-1,1 dichloro-2,3-dimethylcyclopropane, it appears that, while at low temperatures *trans*-3-chloropenta-1,3-diene is a secondary product arising from reaction (3), at higher temperatures it is a primary, as well as a secondary product.

Our present study of the pyrolysis of *trans*-1,1-dichloro-2,3-dimethylcyclopropane indicates that both the major organic product, *trans*-3-chloropenta-1,3-diene, and the minor product, *trans*-3,4-dichloropent-2-ene, are formed by primary reaction steps. *trans*-3,4-Dichloropent-2-ene is probably formed in the pyrolysis of *trans*-1,1-dichloro-2,3-dimethylcyclopropane by a similar mechanism to its formation in the pyrolysis of *cis*-1,1-dichloro-2,3-dimethylcyclopropane. The corresponding reaction (2) however is slower than reaction (4). The isomerisation of a *trans*-*gem*-dihalogenocyclopropane is often slower than that of a *cis*-isomer. Parham and Yong[9] observed that the solvolysis of 1,1-dichloro-2,3-dipropylcyclopropane at 80 °C in the presence of ethanolic silver nitrate was 24 times faster for the *cis*-isomer than for the *trans*-isomer. Similarly Sandler[10] observed that *cis*-1,1-dibromo-2,3-dimethylcyclopropane rearranged at a faster rate during solvolysis, than the *trans*-isomer. It was also observed that both the *cis*- and *trans*-isomers gave the *trans*-rearrangement products.

trans-3-Chloropenta-1,3-diene is the major product in the pyrolysis of *trans*-1,1-dichloro-2,3-dimethylcyclopropane. Two possible mechanisms may be considered for its formation, involving elimination of hydrogen either from the cyclopropane ring or from a methyl group. Since *cis*-1,1-dichloro-2,3-dimethylcyclopropane has two ring hydrogens *cis* to the same chlorine atom, whereas the *trans*-isomer has two ring hydrogens *cis* to two different chlorine atoms, this substitution may favour the *cis*-elimination of hydrogen chloride from the ring in the case of the *trans*-isomer. This elimination could produce a substituted cyclopropene intermediate which could ring open followed by hydrogen migration to give the diene [reaction (5)/(6)]. This reaction mechanism is open to several objections. Step (5) involves the concerted *cis*-elimination of hydrogen chloride which is strictly an orbital-symmetry forbidden process.[11] In addition step (6) involves both ring opening and hydrogen migration and is unlikely to be a simple process although similar steps have been proposed to account for diene formation from methylcyclopropene[12] at lower temperatures.



An alternative mechanism which we favour involves the elimination of hydrogen from a methyl group rather than from the ring. Again, reaction-path degeneracy would favour the reaction from the *trans*- rather than the *cis*-isomer of the starting material, as is observed. A concerted mechanism (7) may be written which appears to be consistent with the Woodward–Hoffmann rules.



(7)

We do not consider that the present evidence enables a clear distinction between these alternative mechanisms and it is hoped to study suitably labelled compounds which should enable such a distinction to be made.

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