791. *The Thermal Unimolecular Isomerisation of 1-Isopropenyl-1-methylcyclopropane*

By C. S. ELLIOTT and H. M. FREY

The thermal isomerisation of 1-isopropenyl-1-methylcyclopropane has been investigated in the range 325—368°. In this range, in an "aged" reaction vessel, the compound isomerises to give 1,2-dimethylcyclopentene by a homogeneous first-order process, which is probably unimolecular. The rate constants for the isomerisation were independent of pressure down to 0·5 mm. and fit the Arrhenius equation,

$$k = 10^{14\cdot14} \exp(-50{,}500/\boldsymbol{R}T)\text{sec.}^{-1}$$

Some difficulties encountered in the use of a flame-ionisation detector for precise quantitative work are discussed.

THE work reported in this Paper is part of a continuing study on the gas-phase thermal decompositions of a number of substituted cyclopropanes. To date, five distinct types of isomerisation reaction have been studied in the gas phase, and evidence produced that they are probably all true unimolecular transformations. Cyclopropane and alkylcyclopropanes isomerise to yield olefins.[1a] Appropriately substituted dialkylcyclopropanes, and also deuterocyclopropanes, undergo geometrical isomerisation.[1c] Vinylcyclopropane and some substituted vinylcyclopropanes undergo a ring expansion to yield cyclopentenes.[1b] Ethylidenecyclopropane undergoes a reversible isomerisation to yield 1-methyl-2-vinylcyclopropane, and this is almost certainly a general reaction for substituted methylenecyclopropanes.[1d] Finally *cis*-1-methyl-2-vinylcyclopropane has been found to isomerise to *cis*-hexa-1,4-diene (by a 1–5-hydrogen shift with ring rupture); this is almost certainly a general reaction for substituted vinylcyclopropanes of the correct stereochemical configuration.[1e] In the present study, 1-isopropenyl-1-methylcyclopropane has been found to isomerise to 1,2-dimethylcyclopentene (a reaction analogous to the third type mentioned above), and the rate parameters have been found to have the values expected for this type of reaction.

EXPERIMENTAL

Materials.—1-*Isopropenyl*-1-*methylcyclopropane*. This was prepared by the action of diazomethane on 2,3-dimethylbuta-1,3-diene in the presence of cuprous chloride.[2] The diene was present in large excess, since the cyclopropane initially formed reacts more rapidly with the diazomethane (to give a bicyclopropyl compound) than does the diene. Fractional distillation yielded the crude cyclopropane, which was further purified by preparative gas chromatography. Gas-chromatographic analysis of the final product showed it to be more than 99·5% pure.

1,2-*Dimethylcyclopentene*. 2-Methylcyclopentanone was converted into 1,2-dimethylcyclopentan-1-ol by treatment with methylmagnesium iodide. The alcohol was dehydrated with a drop of concentrated sulphuric acid to yield mainly 1,2-dimethylcyclopentene, together with a small quantity of 2,3-dimethylcyclopentene. The 1,2-dimethylcyclopentene was obtained in high purity by preparative gas chromatography.

Kinetic Apparatus.—This was essentially the same as described previously.[3]

Procedure.—The cyclopropane was introduced into the reaction vessel from a storage vessel at a known pressure. After the completion of the pyrolysis, the contents of the reaction vessel were shared with a 250-ml. evacuated gas pipette (at room temperature). Five seconds were

---

[1] (*a*) T. S. Chambers and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **50**, 399; J. P. Chesick, *ibid.*, 1960, **82**, 3277; (*b*) B. S. Rabinovitch, E. W. Schlag, and K. Wiberg, *J. Chem. Phys.*, 1958, **28**, 504; M. C. Flowers and H. M. Frey, *Proc. Roy. Soc.*, 1960, *A*, **257**, 122; (*c*) M. C. Flowers and H. M. Frey, *J.*, 1961, 3547; (*d*) J. P. Chesick, *J. Amer. Chem. Soc.*, 1963, **85**, 2720; (*e*) R. J. Ellis and H. M. Frey, *Proc. Chem. Soc.*, 1964, 221.

[2] W. von E. Doering and W. R. Roth, *Tetrahedron*, 1963, **19**, 715.

[3] C. S. Elliott and H. M. Frey, *J.*, 1964, 900.

allowed for the transfer. Nitrogen was then added to the pipette until the total pressure was 100 mm.

Analysis.—Analysis was by gas chromatography with a 12 ft. × 0·125 in. (o.d.) coiled stainless steel column filled with 60—80 mesh Chromosorb P containing 30% w/w di-2-cyanoethyl ether and heated to 43°. Nitrogen was used as the carrier gas. Samples were introduced into the chromatograph by means of an Aerograph 6-way stainless steel greaseless valve. The sample space was a 25-ml. copper tube heated to 60°. An Aerograph flame-ionisation detector was employed, and signals from it were amplified with a Perkin-Elmer F11 ionisation amplifier. Signals from the amplifier were fed to a Sunvic recorder and integrated as described previously.[4]

Previous work reported from this laboratory on thermal decomposition involved the use of katharometers as detectors in the analytical systems. In the present work, flame-ionisation detectors were used for the first time; considerable difficulties were experienced in obtaining reproducible and accurate results with this detector. In the earlier work, the entire contents of the reaction vessel were removed after a run by freezing them into a cooled, evacuated, gas pipette, followed by "flash" evaporation, but this method was found to lead to very poor reproducibility in the present work. Since only about 10% of the mixture in the gas pipette was removed for each analysis, it is probable that this lack of reproducibility was due to poor mixing, resulting from differences in volatility of the components of the reaction mixtures. (Similar difficulties were not found with less sensitive detectors since, in such cases, a much larger fraction of the contents of the gas pipette were taken for analysis). To avoid these difficulties, the reaction mixture at the end of a run was shared between the reaction vessel and the previously evacuated gas pipette; this removed more than half the contents of the reaction vessel.

The reaction mixture was admitted to the gas chromatograph by first sharing the contents of the gas pipette with the evacuated sample space. Provided that the pressure in the evacuated sample volume is very much smaller than that in the pipette, the fraction of gas transferred from the pipette to the sample volume depends only on the ratio of these volumes. However, with the low pressures used in the reaction vessel, and with the difficulty experienced in preventing some leakage in the 6-way Aerograph valve, this inequality of pressures could not be maintained. Accordingly, after the contents of the reaction vessel had been shared with the gas pipette, nitrogen was added to the pipette to bring the total pressure up to 100 mm.

As a result of a series of experiments, it was found that the best results were obtained by using as the sample space a coiled copper tube heated to 60°. After injection into the chromatograph column, only a negligible fraction of the sample mixture remained in the sample space. Provided that the procedure described was employed, analyses were reproducible within ±0·5%.

Finally, the response of the detector was determined for various sizes of sample. The flame-ionisation detector has been frequently reported to have an enormous dynamic range, and to have a linear response to sample size, also over a very large range of sample sizes. We have found that this is not true above a certain sample size; for the compounds employed in this work, this is about 10^{-6} moles. Analysis of sample mixtures at total sample sizes above 10^{-6} moles gave results indicating that the calibration factors were varying with the sample size. In the range from 10^{-6} to 10^{-5} moles, the calibration factors may vary by as much as 10%. Below 10^{-6} mole, the calibration factors remained constant (within experimental error) over the range of sample sizes investigated. In the remainder of the work, care was taken to ensure that the analytical samples were always of such a size as to be within the linear range of the detector.

A further complication arises when chromatographic columns are used at temperatures where there is appreciable bleeding of the liquid phase. Even though it is possible to offset this effect by using a backing-off current, the range of sample sizes which fall in the linear region is affected. Thus, if there is appreciable bleeding, it is to be expected that the sample size must be reduced to fall within the linear range; this has been confirmed experimentally.

RESULTS AND DISCUSSION

In the temperature range 325—358° in an "aged" reaction vessel, 1-isopropenyl-1-methylcyclopropane undergoes a structural isomerisation reaction to yield 1,2-dimethylcyclopentene. The retention time of the product and its mass-spectrographic cracking

---

[4] H. M. Frey and D. C. Marshall, *J.*, 1962, 3052.

pattern were identical with those of an authentic sample of the cyclopentene. At the highest temperatures used, another product was also formed, almost certainly a diene, but as its yield never exceeded 1·5% of the total product, no attempts at further identification were made. Runs were carried out with an initial reactant pressure of 2 mm. and at nine different temperatures. At each temperature, at least 10 runs were analysed, each in duplicate, the decomposition varying from 10 to 80%. Plots of the logarithm of undecomposed cyclopropane *vs.* time were straight lines, and the overall rate was evaluated at each temperature by the method of least squares. The results obtained are shown in Table 1.

TABLE 1

Overall rate constants for the decomposition of 1-isopropenyl-1-cyclopropane

Temp. (°K)	598·6	603·6	608·1	614·9	620·3	626·8	630·9	635·8	641·6
$10^5 k$ (sec.$^{-1}$)	5·137	7·293	9·844	15·94	22·25	34·54	44·56	61·70	88·83

From the Arrhenius plot of the values in Table 1 the Arrhenius parameters were evaluated by the method of least squares, whence

$$k_{\text{overall}} = 10^{14\cdot16} \exp(-50{,}500/\boldsymbol{R}T)\text{sec.}^{-1}$$

Random errors in the determination of these parameters are negligible (95% confidence limits), and the maximum error in the energy of activation, which is due to uncertainties about the temperature measurements, is almost certainly less than ±500 cal.

One series of runs was carried out at 623·3°K in a reaction vessel packed with lengths of glass tubing to increase the surface to volume ratio by a factor of nine. After the reaction vessel had been " aged " at 670°K, reproducible kinetic results were obtained, and the rate constant for the decomposition in the packed vessel found to be $29\cdot17 \times 10^{-5}$ sec.$^{-1}$. This lies, within experimental error, on the Arrhenius plot, and indicates that there can be no appreciable heterogeneous component of the reaction. (Value calculated from Arrhenius equation is $28\cdot8 \times 10^{-5}$ sec.$^{-1}$.)

The decomposition is thus homogeneous and kinetically first-order. In addition, the fact that both the reactant and product are likely to be excellent radical-chain inhibitors makes the occurrence of such a process in the present system highly improbable. The evidence therefore indicates that the isomerisation is a true unimolecular process.

A series of runs was carried out in the pressure range 3·2—0·5 mm. In this range the rate constant was found to be independent of presure. The results are shown in Table 2. The reaction is thus being studied in the high-pressure region. For a molecule of the complexity of this cyclopropane, appreciable fall-off of the first-order rate constant is not to be expected until pressures well below 1 mm. are reached.

TABLE 2

Rate constants as a function of pressure at 637·6°K

Pressure (mm.)	0·7	1·0	1·4	1·8	2·7	3·2
$10^5 k$ (sec.$^{-1}$)	68·3	69·0	68·5	69·0	69·3	69·5

Value calculated from Arrhenius equation, $68\cdot7 \times 10^{-5}$ sec.$^{-1}$

As has been mentioned earlier, another minor product was detected, as well as the dimethylcyclopentene. As the relative amounts of this product increased with increasing temperature, it must arise from a process with a higher energy of activation than the isomerisation to the cyclopentene. It is almost certainly formed by the " normal " type of cyclopropane rearrangement (which, with cyclopropane, yields propene, and is responsible for the occurrence of small amounts of dienes [5] in the isomerisation of vinylcyclopropane). If this minor product is assumed to be primary, and all the evidence

---

[5] C. A. Wellington, *J. Phys. Chem.*, 1962, **66**, 1671.

is consistent with this, an analysis of the data taking account of the minor product, yields the Arrhenius equation for the isomerisation to the 1,2-dimethylcyclopentene

$$k_{\text{cyclopentane}} = 10^{14\cdot14} \exp(-50{,}500/\boldsymbol{R}T)\text{sec.}^{-1}$$

The Arrhenius parameters obtained for this isomerisation can be compared with those obtained in the studies on the isomerisations of related vinylcyclopropanes to cyclopentenes. Some of the data are shown in Table **3**.

TABLE 3

Arrhenius parameters for the isomerisation of some vinylcyclopropanes

Substituents	$\log_{10} A$	E (k. cal. mole^{-1})	Ref.
1-Vinyl	13·5	49·6	(1*c*)
1-But-1-enyl	13·79	49·98	(6)
1-Isopropenyl	13·89	50·9	(7)
1-Methyl-1-vinyl	14·11	49·35	(8)
1-Isopropenyl-1-methyl	14·14	50·5	This work

The closely similar values for all these isomerisations is a clear indication that they all proceed through essentially the same transition state. Closer inspection of the results shows that, on going from vinyl- to isopropenyl-cyclopropane, there is a small increase in the energy of activation of the reaction. Similarly, 1,1-disubstituted cyclopropanes isomerise with somewhat lower energies of activation than the singly substituted molecules (the same effect is also observed in the isomerisation of alkylcyclopropanes to olefins). The combination of these two factors results in the energy of activation of 1-isopropenyl-1-methylcyclopropane being between the values obtained for isopropenylcyclopropane and 1-methyl-1-vinylcyclopropane.

One of us (C. S. E.) thanks the D.S.I.R. for a research studentship.

CHEMISTRY DEPARTMENT, THE UNIVERSITY, SOUTHAMPTON. [*Received, February 8th*, 1965.]

---

[6] R. J. Ellis and H. M. Frey, *J.*, 1964, 4188.
[7] H. M. Frey and D. C. Marshall, *J.*, 1962, 3981.
[8] R. J. Ellis and H. M. Frey, *J.*, 1964, 959.