706. Fluorinated Cyclopropanes. Part II.[1] The Thermal Isomerization of Monofluorocyclopropane.

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At 25 cm. pressure, between 412 and 503° the overall unimolecular rate constant for the isomerization of monofluorocyclopropane to the four possible monofluoropropenes is given by

$$\log k\ (\text{sec.}^{-1}) = (14{\cdot}58 \pm 0{\cdot}20) - (61010 \pm 680)/2{\cdot}303RT.$$

The rate constant has been measured down to a pressure of 0·17 mm., where the rate is one-fifth of that at high pressures. The fall-off corresponds to the behaviour expected for a molecule with 12—14 effective oscillators according to the Rice–Ramsperger–Kassel treatment.

THE interpretation of results obtained on the rates of isomerization of fluorinated cyclopropanes formed in an activated state by the addition of methylene to fluorinated ethylenes [1,2] depends upon a knowledge of the rates of thermal isomerization of, and number of, effective oscillators in the cyclopropanes. These can be found by measuring the rates of isomerization over a suitable range of temperature and pressure. Monofluorocylopropane was selected for an initial investigation because it is readily prepared and is most likely to resemble unsubstituted cyclopropane in its behaviour.[3-6]

EXPERIMENTAL

Monofluorocyclopropane was prepared by the addition of methylene (from the photolysis of keten) to monofluoroethylene in a 500-c.c. Pyrex reaction vessel at 4 atm. The products were transferred to a gas-chromatographic system through a tube packed with a solution of potassium hydroxide in polyethylene glycol on firebrick to remove the keten. 3-Fluoropropene was prepared from allyl bromide and anhydrous potassium fluoride.[7] 2-Fluoropropene was prepared from 1,2-dichloro-2-fluoropropane.[8] All three products were purified by gas chromatography.

Thermal isomerizations were largely carried out in a 4·3-c.c. Pyrex reaction vessel. Runs at low pressures were done in vessels of 50 and 300 c.c. The consequent change in the surface : volume ratio did not alter the rate of reaction, which was therefore homogeneous. In each case the relatively small dead-space was determined, and a correction made. The vessels were placed in a stainless steel beaker containing molten salts. An air space of about 1·5 cm. separated the walls of the beaker from the sides of an electric furnace. A thermometer controller was placed in the gap. The temperature, measured by a thermocouple placed in a well

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[1] The paper by Grzybowska, Knox, and Trotman-Dickenson, *J.*, 1963, 746, is considered as Part I.
[2] Casas, Kerr, and Trotman-Dickenson, unpublished work.
[3] Chambers and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 399.
[4] Pritchard, Sowden, and Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, *A*, **217**, 562.
[5] Falconer, Hunter, and Trotman-Dickenson, *J.*, 1961, 609.
[6] Kennedy and Pritchard, *J. Phys. Chem.*, 1963, **67**, 161.
[7] Hoffman, *J. Org. Chem.*, 1949, **14**, 105.
[8] Austin, Coffman, Hoehn, and Raasch, *J. Amer. Chem. Soc.*, 1953, **75**, 4834.

in the salt-bath, was constant to ±0·2° during a run. Before a series of runs the reaction vessel was aged with cyclopropane and then with one run with monofluorocyclopropane. Analysis was by gas chromatography, with a thermal conductivity detector for high-pressure work and a hydrogen-flame ionization detector for low pressures. The column was 6 m. of 30% dibutyl phthalate on firebrick (60—80 mesh) at 0°. Equal quantities of the three monofluoro-isomers produced equal signals from both detectors.

RESULTS AND DISCUSSION

The rate constants for thermal isomerization were measured at 25·0 ± 0·2 cm. between 411·7 and 503·1°. The percentage conversions were varied between 40 and 95%. The constants were obtained by measurement of the disappearance of the cyclopropane, as only about 95% of the cyclopropane removed could be accounted for as propenes. Presumably some polymerization occurred. In addition, some ethylenes, amounting to about 2%, were formed at the highest temperatures and in runs that lasted more than 10 hours. The results of 13 consecutive runs are shown in Fig. 1 from which a least-squares treatment yields

$$\log k\ (\text{sec.}^{-1}) = (14{\cdot}58 \pm 0{\cdot}20) - (61010 \pm 680)/2{\cdot}303\boldsymbol{R}T.$$

Apart from the small quantities of ethylenes, only four products were formed, as was expected, for there are four isomeric monofluoropropenes, namely, *cis*- and *trans*-1-fluoropropene and 2- and 3-fluoropropene. The retention times of the four peaks on the chromatogram were 25, 30, 35, and 63 min. (monofluorocyclopropane 71 min.). The first and fourth peaks were shown by the retention times and infrared spectra to be 2- and 3-fluoropropene, respectively. Because of polymerization it could only roughly be estimated that the activation energy for the formation of 2-fluoropropene is about 4 and of 3-fluoropropene about 1 kcal./mole higher than for the formation of 1-fluoropropene. It is worth noting that the activation energy for the formation of but-2-ene from methylcyclopropane is 2·3 kcal./mole higher than for the other butenes.[9] No physical constants for *cis*- and *trans*-fluoropropene that would permit positive identification have been published. The compound with an elution time of 30 min. will hereinafter be called " *trans*- " because it is frequently found that the retention volumes for *trans*-compounds on phthalate columns are less than those for *cis*-compounds even when the *trans*-compound has the higher boiling point (cf. the but-2-enes). At 453° the distribution of products is then: 2-fluoropropene, 9·1%; *trans*-1-fluoropropene, 60·9%; *cis*-1-fluoropropene, 18·5%; 3-fluoropropene, 11·4%. The distribution is determined by kinetic factors and does not correspond to thermodynamic equilibrium.

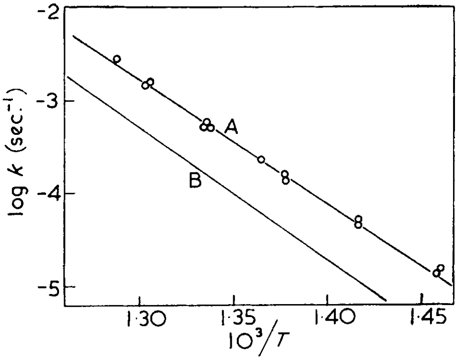

FIG. 1. Arrhenius plot for the isomerization of monofluorocyclopropane (A) compared with that for cyclopropane (B).

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[9] Chesick, *J. Amer. Chem. Soc.*, 1960, **82**, 3277.

Pressure-dependence of the rate of thermal isomerization of monofluorocyclopropane.

Temp. (°c)	Pressure (cm.)	Decomp. (%)	Parts/100 parts of products *				10^4k (sec.$^{-1}$)
			2-FP	*t*-1-FP	*c*-1-FP	3-FP	
474·4°	46·44	60·3	7·9	54·8	17·6	19·6	5·64
474·7	25·00	57·2	8·5	52·2	20·0	19·2	5·69
474·7	15·40	78·1	7·7	60·2	20·2	11·8	5·41
474·9	15·22	46·4	8·8	55·6	22·6	12·9	5·60
475·6	9·55	51·2	7·1	65·2	20·9	6·8	5·89
474·5	9·48	68·8	7·2	63·2	19·8	9·9	5·26
475·8	4·20	99·5	6·7	58·3	19·7	15·2	5·42
475·1	2·15	67·0	5·3	66·9	18·6	9·2	4·49
475·6	1·32	48·4	5·5	64·9	23·0	6·7	4·42
475·3	0·53	63·6	4·5	65·6	24·1	5·8	4·01
475·1	0·50	60·8	5·0	61·5	23·6	8·9	3·90
475·3	0·20	55·5	3·4	65·3	26·4	4·0	2·99
475·5	0·16	56·6	4·1	54·5	37·1	5·3	2·68
475·8	0·10	59·7	2·7	63·8	29·4	4·0	2·48
475·8	0·0712	63·2	2·4	62·5	30·0	5·1	2·08
475·8	0·0566	62·4	1·9	64·7	30·9	2·5	2·09
474·4	0·0267	62·8	1·7	60·0	34·3	4·1	1·56
475·9	0·0167	58·05	2·5	55·2	37·1	5·2	1·16

* 2-FP, 2-fluoropropene; *t*-1-FP, *trans*-1-fluoropropene; *c*-1-FP, *cis*-1-fluoropropene; 3-FP, 3-fluoropropene.

The Table lists results obtained for the isomerization over a wide range of pressures. The material balance fell at low pressures presumably because of polymerization, particularly of 2- and 3-fluoropropene, which would account for the reduction in yield of these isomers. In Fig. 2 the dependence of the rate constant on pressure for monofluorocyclopropane is compared with that for cyclopropane and methylcyclopropane, together with curves obtained by the evaluation of the classical Rice–Ramsperger–Kassel integral. The evaluation was obtained by interpolation of the results of Schlag, Rabinovitch, and Schneider.[10] k_∞ was taken from the Arrhenius equation at 25 cm. as $5{\cdot}68 \times 10^{-4}$ sec.$^{-1}$ and σ, the collision diameter of monofluorocyclopropane, as $5{\cdot}20 \times 10^{-8}$ cm. The results indicate that the number of effective oscillators lies between 12 and 14; a similar treatment for cyclopropane yields between 11 and 13. The precise values are, however, very sensitive to the values adopted for k_∞, the A factor, and above all the collision diameter.

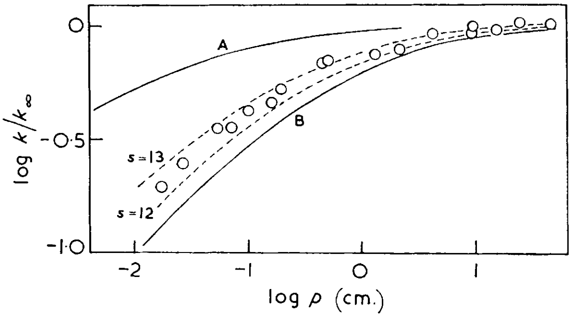

FIG. 2. The pressure-dependence of the rate constant for the isomerization of monofluorocyclopropane (circles) at 475·1°. Solid lines show the pressure-dependence of the isomerization of cyclopropane (B) and methylcyclopropane (A). Broken lines for monofluorocyclopropane show Rice–Ramsperger–Kassel plots for 12 and 13 effective oscillators.

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[10] Schlag, Rabinovitch, and Schneider, *J. Chem. Phys.*, 1960, **32**, 1599.