1057. *Fluorinated Cyclopropanes. Part IV.*[1] *The Thermal Isomerisation of* 1,1-*Difluoro-*, 1,1,2-*Trifluoro-*, *and* 1,1,2,2-*Tetrafluorocyclopropane*

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The thermal decompositions of three fluorinated cyclopropanes have been studied in static systems over a wide range of pressures. The reactions are apparently unimolecular, and can be described as follows:

	log A (sec.$^{-1}$)	E (cal. mole^{-1})	s
1,1-Difluorocyclopropane	14·09	56,350	17
1,1,2-Trifluorocyclopropane	14·43	50,520	18
1,1,2,2-Tetrafluorocyclopropane	15·27	48,480	21

where s is the number of Kassel oscillators required to described the decline of the first-order rate constant at low pressures. The results are correlated with results on the thermal isomerisation of cyclopropane and monofluorocyclopropane and on the isomerisation of the fluorocyclopropanes produced by the addition of methylene to ethylenes.

Part III [1] described the investigation of the rate of addition of methylene to fluorinated ethylenes and the rates of isomerisation of the activated cyclopropanes so formed. It was found that the logarithms of the relative rate constants of isomerisation (k_E sec.$^{-1}$) of the cyclopropanes produced from methylene generated by the photolysis of keten at 3130 Å were: cyclopropane,[2] 10·08; monofluorocyclopropane,[1] 9·82; 1,1-difluorocyclopropane, 9·44; 1,1,2-trifluorocyclopropane, 9·69; 1,1,2,2-tetrafluorocyclopropane, 10·56. Four factors have to be taken into account when seeking to interpret these observations. These are: the activation energy and A factor of the thermal isomerisation of the cyclopropane, the number of effective Kassel oscillators in the cyclopropane, and the exothermicity of the addition reaction. Information on the first two points can be obtained from the study of the thermal isomerisation of the cyclopropanes at high pressure. Information on the third can be obtained by studies of the isomerisations in the low-pressure region where the first-order rate constant is a function of pressure. The fourth point can only be settled by determinations of the heats of formation of the ethylenes and the cyclopropanes; a set of these is not yet available. A further point should not be wholly overlooked. The rates of isomerisation are derived from the assumption that the rates of deactivation of all the activated cyclopropanes are identical and equal to the rate of collision, which has, following previous workers, been taken as 10^{10} sec.$^{-1}$ atm.$^{-1}$. It is unlikely that this assumption is incorrect by as much as a factor of 2, but it would be valuable to have positive information.

Results and Discussion

The results obtained for runs with each cyclopropane in unpacked reaction vessels are listed in Tables 1—6. In addition, runs were carried out for each cyclopropane in a packed

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[1] Part III, F. Casas, J. A. Kerr, and A. F. Trotman-Dickenson, *J.*, 1965, 1141.

[2] H. M. Frey and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, 1957, **79**, 6373.

TABLE 1

The thermal isomerisation of 1,1-difluorocyclopropane

Temp. (°K)	Time (sec.)	Initial concn. (10^{-6} mole cm.$^{-3}$)	% Isom.	10^4k (sec.$^{-1}$)	Temp. (°K)	Time (sec.)	Initial concn. (10^{-6} mole cm.$^{-3}$)	% Isom.	10^4k (sec.$^{-1}$)
674·3	5310	48·90	30·10	0·675	722·7	703	46·80	59·70	11·7
676·9	5040	48·54	34·34	0·831	732·5	550	46·80	59·10	16·0
679·5	4500	49·60	34·16	0·931	734·5	762	46·80	76·15	18·8
697·3	1560	46·10	35·40	2·80	739·1	268	46·70	41·70	20·1
703·5	2520	46·90	63·45	3·99	739·1	397	47·10	59·75	23·3
707·3	1800	47·30	56·10	4·57	740·1	542	46·80	71·20	22·9
707·4	1350	47·40	45·14	4·46	757·4	226	46·80	81·00	73·6
718·6	604	47·90	43·82	6·49	768·1	164	47·20	83·50	110·0
719·4	758	44·30	52·25	9·72					

TABLE 2

The thermal isomerisation of 1,1-difluorocyclopropane at low pressure

Temp. (°K)	Pressure (cm.)	10^3k at 738·2°K (sec.$^{-1}$)	Temp. (°K)	— Pressure (cm.)	10^3k at 738·2°K (sec.$^{-1}$)	Temp. (°K)	Pressure (cm.)	10^3k at 738·2°K (sec.$^{-1}$)
738·7	4·10	2·42	739·7	0·1776	1·97	740·0	0·0199	1·33
738·6	2·25	2·36	738·8	0·1632	2·01	740·0	0·0132	1·32
737·3	1·05	2·33	739·6	0·0596	1·73	736·8	0·0116	1·60
734·2	0·65	2·22	737·5	0·0320	1·71	732·8	0·0070	1·29
736·3	0·65	2·22	739·9	0·0212	1·36	738·6	0·0068	1·11

TABLE 3

The thermal isomerisation of 1,1,2-trifluorocyclopropane

Temp. (°K)	Time (sec.)	Initial concn. (10^{-6} mole cm.$^{-3}$)	% Isom.	10^4k (sec.$^{-1}$)	Temp. (°K)	Time (sec.)	Initial concn. (10^{-6} mole cm.$^{-3}$)	% Isom.	10^4k (sec.$^{-1}$)
590·2	3915	34·70	19·20	0·568	613·8	4740	34·20	74·80	2·90
590·1	5760	35·60	26·82	0·543	613·6	795	35·30	18·38	2·54
598·1	3990	35·50	32·95	1·00	627·3	1320	33·70	57·25	6·43
600·1	6300	35·70	44·40	0·933	627·3	1980	34·30	73·90	6·78
600·9	11,847	35·60	77·40	1·25	634·0	780	34·50	54·25	10·05
604·9	3600	35·10	40·10	1·42	633·6	450	34·50	39·10	10·99
614·1	1800	34·50	41·50	2·98	641·7	443	33·95	54·75	17·93
614·7	2310	34·55	47·20	2·77	641·8	560	33·65	61·10	16·84

TABLE 4

The thermal isomerisation of 1,1,2-trifluorocyclopropane at low pressure

Temp. (°K)	Pressure (cm.)	10^3k at 628·2°K (sec.$^{-1}$)	Temp. (°K)	Pressure (cm.)	10^3k at 628·2°K (sec.$^{-1}$)	Temp. (°K)	Pressure (cm.)	10^3k at 628·2°K (sec.$^{-1}$)
630·9	15·60	2·50	631·8	4·05	2·30	633·5	0·0525	1·62
629·6	7·55	2·37	628·2	1·05	2·31	633·5	0·0438	1·58
628·2	7·00	2·47	628·2	0·97	2·24	622·8	0·0301	1·58
629·1	5·37	2·47	632·1	0·1932	1·78	631·7	0·0271	1·60
629·2	4·85	2·39	632·8	0·1131	1·90	630·8	0·0069	1·25

TABLE 5

The thermal isomerisation of 1,1,2,2-tetrafluorocyclopropane

Temp. (°K)	Time (sec.)	Initial concn. (10^{-6} mole cm.$^{-3}$)	% Isom.	10^4k (sec.$^{-1}$)	Temp. (°K)	Time (sec.)	Initial concn. (10^{-6} mole cm.$^{-3}$)	% Isom.	10^4k (sec.$^{-1}$)
525·3	9740	46·90	12·70	0·138	559·9	3600	45·30	52·50	2·07
525·9	14,760	47,60	22·00	0·169	560·1	1800	45·80	29·90	1·97
532·7	8895	47·00	17·60	0·217	561·4	2430	45·15	46·60	2·58
537·4	9040	45·40	27·00	0·343	568·4	1276	45·30	40·10	4·0
538·4	7820	45·50	24·80	0·365	568·5	960	45·30	33·10	4·18
551·9	1800	46·70	17·70	1·08	580·1	540	44·40	41·10	9·77
551·8	2760	46·20	26·80	1·13	580·2	310	45·55	27·70	10·43
553·1	4500	46·30	37·50	1·04	596·1	180	46·50	49·40	37·87
555·5	7200	45·20	61·80	1·34	596·3	162	44·10	44·70	36·56

TABLE 6

The thermal isomerisation of 1,1,2,2-tetrafluorocyclopropane at low pressures

Temp. (°K)	580·4	579·4	580·5	576·8	573·3	577·3	575·0
Pressure (cm.)	20·60	13·55	5·85	0·90	0·0922	0·0138	0·0048
10^4k at 578·2°K (sec.$^{-1}$)	8·93	8·96	8·84	8·52	7·11	5·59	4·21

reaction vessel for which the surface : volume ratio was 10 cm.$^{-1}$, *i.e.*, five times the ratio for the vessel normally used at the higher pressures. When the packed vessel had been conditioned by the decomposition products of allyl bromide for two days, rate constants were obtained that were in excellent agreement with those found with the normal vessel. Because the reactions could only be followed by the disappearance of the reactant, errors in the rate constant were large when the percentage decomposition was either great or small. The first-order nature of the reactions, indicated by runs in which the percentage decomposition at constant temperature and pressure was varied, was confirmed by runs in which the percentage decomposition was roughly constant, and the initial pressure varied as shown below.

1,1-Difluorocyclopropane at 700°K and 280 mm., $10^4k(\text{sec.}^{-1}) = 3{\cdot}30$ for 35%, and 3·28 for 64% decomposition. At 738°K, $10^3k(\text{sec.}^{-1}) = 2{\cdot}51$ (28 cm.), 2·42 (4·10 cm.), 2·36 (2·25 cm.), 2·33 (1·05 cm.).

1,1,2-Trifluorocyclopropane at 614°K, $10^4k(\text{sec.}^{-1}) = 2{\cdot}74$ for 18%, 2·98 for 42%, 2·64 for 47%, and 2·97 for 75%. At 628°K, $10^3k(\text{sec.}^{-1}) = 2{\cdot}50$ (15·6 cm.), 2·47 (7·0 cm.), 2·39 (4·9 cm.).

1,1,2,2-Tetrafluorocyclopropane at 553°K, $10^4k(\text{sec.}^{-1}) = 1{\cdot}15$ for 18%, 1·04 for 38%, and 1·10 for 62%. At 578°K $10^4k(\text{sec.}^{-1}) = 8{\cdot}93$ (20·6 cm.), 8·96 (13·6 cm.), and 8·84 (5·9 cm.). There is therefore strong evidence that the reactions are homogeneous and first-order; they are probably unimolecular.

Table 7 summarises the findings for all the fluorinated cyclopropanes. It can be seen from the errors derived for the Arrhenius parameters by a least-squares treatment that the reproducibility was satisfactory. The values of *s*, the number of Kassel oscillators for each molecule, were found by fitting the results for the fall-off with pressure to the curves shown in Figures 1—3. These curves were obtained by interpolation of the calculations of Schlag, Rabinovitch, and Schneider.[5] The collision diameters were taken as cyclopropane, 5·00 Å, mono- and di-fluorocyclopropane, 5·21 Å, and tri- and tetra-fluorocyclopropane, 5·42 Å.

TABLE 7

The thermal isomerisation of fluorinated cyclopropanes

Molecule	A (sec.$^{-1}$)	s	E_0 (kcal. mole^{-1})	E (kcal. mole^{-1})	Ref.
Cyclopropane	15·2	13	65·0	104	4
Monofluorocyclopropane	14·6	15	61·0	112	3
1,1-Difluorocyclopropane	14·09 ± 0·10	17	56·35 ± 0·30	115	This work
1,1,2-Trifluorocyclopropane	14·43 ± 0·14	18	50·52 ± 0·43	107	This work
1,1,2,2-Tetrafluorocyclopropane	15·27 ± 0·18	21	48·48 ± 0·51	116	This work

The specific rate constant for molecules containing energy E distributed throughout the different modes of vibration is given approximately by

$$k_E = A([E - E_0]/E)^{s-1}$$

where E_0 is the minimum energy required for isomerisation which can be identified with the activation energy at high pressures. If the values of A, E_0, and s listed in Table 7 are combined with the values of k_E found from the experiments with methylene, the mean

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[3] F. Casas, J. A. Kerr, and A. F. Trotman-Dickenson, *J.*, 1964, 3655.

[4] H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, *A*, **217**, 563; W. E. Falconer, T. F. Hunter, and A. F. Trotman-Dickenson, *J.*, 1961, 609.

[5] E. W. Schlag, B. S. Rabinovitch, and F. W. Schneider, *J. Chem. Phys.*, 1960, **32**, 1599.

energy constant, E, of the molecules formed by addition of methylene can be calculated. The values of E obtained in this way are listed in Table 7. The energy content of the molecules depends upon the heat of formation and vibrational excitation of the methylene, which should be the same in each case, on the energy content of the reactant ethylene, and on the exothermicity of the addition reactions. The energy content of the ethylenes will not vary by more than about 1 kcal. mole^{-1} between ethylene and tetrafluoroethylene, because the temperature of the reactions was low and the vibrational frequencies are high. The variations in the values of E found could, therefore, be attributed to variations in the exothermicity of the addition reactions. In fact it seems unlikely that the variations in exothermicity are more than a few kcal. mole^{-1}; certainly the variation in exothermicity would be expected to be regular. The variations must largely be ascribed to experimental error. s is particularly difficult to determine precisely, and a change of one in the number of oscillators corresponds to a change of 5 kcal. mole^{-1} in E. E is very sensitive to errors in the determination of A and E_0. A change of 1 kcal. mole^{-1} in the activation energy changes E by 7 kcal. mole^{-1}. It seems safest to conclude that the exothermicities of the additions do not differ greatly, but that additions to more fluorinated ethylenes are slightly more exothermic.

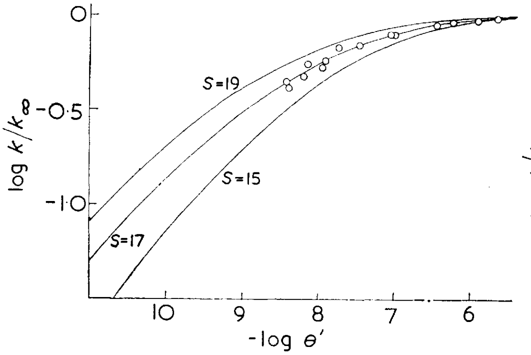

FIGURE 1

1,1-Difluorocyclopropane

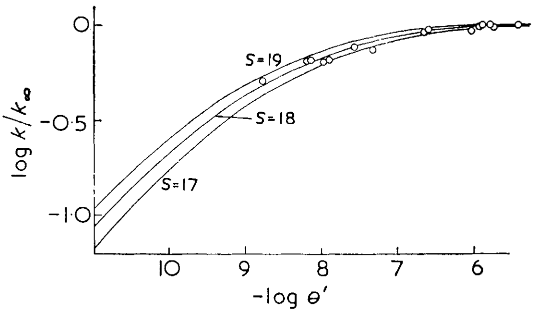

FIGURE 2

1,1,2-Trifluorocyclopropane

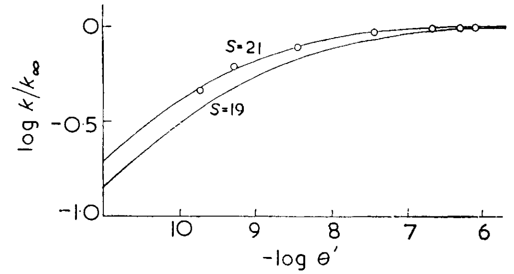

FIGURE 3

1,1,2,2-Tetrafluorocyclopropane

The dependence of rate constant of thermal isomerisation of fluorocyclopropanes on pressure

$\theta' = A/\omega$, where $\omega = ZC$,
$Z = 4N\sigma^2(\pi \mathbf{R}T/M)^{\frac{1}{2}}$,
$C = 1{\cdot}603 \times 10^{-5}p/T$,
M = molecular weight,
p = pressure in mm. Hg, and
σ = collision diameter

It is interesting to note that although the number of oscillators present is 21 for each of the cyclopropane molecules, the number of Kassel oscillators increases from a value of about half the possible to close to the theoretical maximum with increasing fluorine substitution. A value near to one half the possible seems to be common for molecules containing a high proportion of hydrogen atoms, whereas molecules which consist largely of heavy atoms, which are mechanically more significant, have s values close to the maximum.

EXPERIMENTAL

Materials.—Keten and the fluorinated ethylenes were obtained as previously.[1] The cyclopropanes were produced by the photolysis for 5—8 hr. of keten mixed with the appropriate ethylene in the proportion of about 1 : 5 and at a total pressure of 5 atm. in a 500-c.c. Pyrex reaction vessel, cooled by tap water. The products were passed through a mixture of potassium hydroxide and ethylene glycol on firebrick to absorb the keten, and the cyclopropane was separated by gas–liquid chromatography (g.l.c.). It was about 98% pure.

Apparatus.—Pyrex reactions vessels of 6·99, 50·0, and 500 ml. were used for runs at pressures above 20 mm., at intermediate pressures, and at pressures below 1 mm., respectively. The cells were connected to the apparatus through stainless steel valves with Fluon seats. They were immersed in a molten-salt bath contained in a stainless-steel beaker. Temperature control was by a Sunvic R.T.2 controller, with the platinum resistance thermometer in the annular space around the beaker. Temperatures were measured by a thermocouple in a well immersed in the salt bath.

Procedure.—The propenes formed by isomerisation polymerised, and it was therefore necessary to measure the rate constants by determining the amounts of cyclopropanes remaining after convenient times. Analysis was by g.l.c. with 6-m. columns of 30% dibutyl phthalate on firebrick. The detector was a katharometer at high pressures and a hydrogen-flame detector at low pressures.

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[*Received, January 22nd*, 1965.]