97. *The Thermal Reactions of Chlorotrifluoroethylene.*

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The thermal reactions of chlorotrifluoroethylene at 300—500°/<1 atm. are described. Dimerization to *cis*- and *trans*-1,2-dichlorohexafluorocyclobutane is measurably reversible above 425°; *cis*–*trans*-isomerization of the dimers occurs. Near 500°, 1,4-dichlorohexafluorobut-2-ene is formed slowly by a secondary reaction. The nuclear magnetic resonance spectra of the products are reported, and vapour pressures and infrared spectra are given for the butene.

The rates of the main reactions have been measured, and the rate constants are summarized by the following equations: for loss of C_2F_3Cl by $2C_2F_3Cl \longrightarrow C_4F_6Cl_2$, $k = 4{\cdot}3 \times 10^7 \exp(-26{,}600/\boldsymbol{R}T)$ l. mole^{-1} sec.$^{-1}$; for $C_4F_6Cl_2 \longrightarrow 2C_2F_3Cl$, $k = 2{\cdot}5 \times 10^{15} \exp(-65{,}300/\boldsymbol{R}T)$ sec.$^{-1}$; for *cis*-$C_4F_6Cl_2 \longrightarrow$ *trans*-$C_4F_6Cl_2$, $k = 1{\cdot}25 \times 10^{15} \exp(-60{,}200/\boldsymbol{R}T)$ sec.$^{-1}$; and for *trans*-$C_4F_6Cl_2 \longrightarrow$ *cis*-$C_4F_6Cl_2$, $k = 7{\cdot}5 \times 10^{14} \exp(-60{,}200/\boldsymbol{R}T)$ sec.$^{-1}$.

The *trans*- and the *cis*-dimer are formed at equal rates from chlorotrifluoroethylene, but have an equilibrium ratio of 1·67; the ratio does not vary with temperature. Heat and entropy changes for the dimerization and the isomerization are deduced, and the activated complexes involved in the reactions are discussed.

In a previous paper,[1] the thermal dimerization of tetrafluoroethylene to perfluorocyclobutane was shown to be reversible at 520° and above, and measurements of the activation energies for both forward and back reactions were reported. We have found that the thermal dimerization of chlorotrifluorethylene to 1,2-dichlorohexafluorocyclobutane is also reversible. Exclusive formation of the 1,2-dichloro-isomer in this dimerization has been observed both by Henne and Ruh,[2] for the high-pressure reaction at 200°, and by Lacher, Tompkin, and Park [3] for reaction at 300—500° under pressures below atmospheric. Lacher *et al.* measured the rate of the dimerization and found, for $-d[C_2F_3Cl]/dt = k[C_2F_3Cl]^2$, $k = 3{\cdot}53 \times 10^7 \exp(-26{,}320/\boldsymbol{R}T)$ l. mole^{-1} sec.$^{-1}$. We have determined rate constants for the reverse reaction, and also substantially confirmed the figures of Lacher *et al.* for the dimerization. Together, these measurements yield values for the heat and entropy of dimerization. The 1,2-dichlorohexafluorocyclobutane formed by dimerization is shown to be a non-equilibrium mixture of *cis*- and *trans*-isomers. Isomerization, which

[1] Atkinson and Trenwith, *J.*, 1953, 2082.

[2] Henne and Ruh, *J. Amer. Chem. Soc.*, 1947, **69**, 279.

[3] Lacher, Tompkin, and Park, *J. Amer. Chem. Soc.*, 1952, **74**, 1693.

is faster than dissociation, was investigated, and both kinetic constants and equilibrium constants for the interconversion of *cis*- and *trans*-1,2-dichlorohexafluorocyclobutane have been determined.

EXPERIMENTAL

Materials.—*Chlorotrifluoroethylene.* This was purified by fractional distillation in a Podbielniak column, and purity was checked by infrared spectroscopy and gas chromatography.

1,2-*Dichlorohexafluorocyclobutane.* The material was prepared by pyrolyzing chlorotrifluoroethylene, and was separated and purified by fractional distillation and gas chromatography. Samples enriched in the *cis*- and the *trans*-isomers severally were prepared by gas chromatography, columns of dibutyl phthalate and dinonyl phthalate on Celite being used in series.

Pyrolyses.—*Apparatus.* Pyrolyses were performed in Pyrex or nickel cylindrical vessels, 5 cm. in diameter and 12—24 cm. long, housed in a tubular electric furnace thermostat-controlled to $\pm\frac{1}{2}^\circ$. The temperature of the vessel was measured with a calibrated Chromel–Alumel thermocouple in an axial well. The capillary inlet to the vessel was connected to a capillary mercury manometer and an inlet stopcock. Seams in the nickel vesel were welded by the argon-arc process to minimize the formation of oxide, and all of the vessels were seasoned before use by prolonged pyrolysis of chlorotrifluoroethylene.

Procedure. Pyrolyses were performed by static methods. Reactions involving a pressure change were followed by reading the manometer against a scale or with a cathetometer. Reactions followed analytically were performed as series of runs of varying durations and at common initial pressures; each run was terminated by condensing the contents of the reaction vessel into a trap and analyzing them by gas chromatography.

Analyses.—Quantitative analyses were carried out by gas chromatography under standardized conditions. Portions of the vaporized sample were injected into the nitrogen stream.

Analyses for chlorotrifluoroethylene and 1,2-dichlorohexafluorocyclobutane were made on a column (166 cm. × 5 mm.) of dioctyl sebacate (20% on 30—60 mesh Celite). Standard operating conditions were used, and analyses were effected by measuring the peak areas and using calibrations performed with pure materials.

Analyses for *cis*- and *trans*-1,2-dichlorohexafluorocyclobutane were made on three 5-mm. columns in series: 325 cm. of dibutyl phthalate (20% on 52—72 mesh Celite), 166 cm. of dibutyl phthalate (20% on 30—60 mesh Celite), and 166 cm. of dinonyl phthalate (20% on 60—80 mesh Celite). The isomers were not completely resolved with these columns, but the peak produced showed either two maxima or one maximum and a shoulder. The peak shape was characterized by the ratio $H_t = h_t/(h_t + h_c)$, where h_t and h_c are the heights above the base line of the maxima or shoulders corresponding to the *trans*- and *cis*-isomers. The ratio was only slightly dependent on operating conditions, but a small correction was applied for sample size. The pure isomers were not available to make standard mixtures, so a series of mixtures was analyzed by nuclear magnetic resonance spectroscopy. The CFCl peaks of the isomers were well separated at 56·4 Mc./sec., and their areas were measured in the spectra of each mixture for both increasing and decreasing field. The mole fraction, N_t, of the *trans*-isomer was calculated as $A_t/(A_t + A_c)$, where A_t and A_c are the areas of the *trans*- and the *cis*-peak. A calibration curve of H_t against N_t was drawn for values of N_t between 0·19 and 0·87, and was closely linear.

Infrared Spectra.—Infrared spectra were measured by using a Perkin-Elmer spectrophotometer model 21B and a 10-cm. gas cell. Nitrogen was added to the gas cell to make the total pressure one atmosphere.

Nuclear Magnetic Resonance Spectra.—^{19}F resnoance spectra were measured at 56·4 Mc./sec. with a Varian Associates spectrometer. Spectra were internally referenced to either perfluorocyclobutane or benzotrifluoride, and were calibrated in c./sec. by the usual side-band technique. Chemical shifts are given in p.p.m., and a positive value means that resonance occurs at a higher field. Peak areas for quantitative work were measured by using a planimeter.

RESULTS

Properties and Identification of the Products.—(a) 1,2-*Dichlorohexafluorocyclobutane.* The initial products of dimerization were the *cis*- and *trans*-isomers of 1,2-dichlorohexafluorocyclobutane.[2,3] Complete separation of the isomers was never achieved, but certain individual properties were derived from observations on mixtures of known composition. Differences in the infrared spectra of the isomers were revealed by the relative intensities of bands at 1047 and 1027 cm.$^{-1}$, and at 893 and 862 cm.$^{-1}$ in different mixtures. We shall label the isomers by the frequencies of the characteristic bands at 1047 and 1027 cm.$^{-1}$. Comparison of our spectra with those obtained by Lacher, Büchler, and Park [4] shows that these authors did not achieve the separation of the isomers to 99% purity which they claimed. Whilst their *trans*-isomer was probably over 95% pure, the shoulder at 1027 cm.$^{-1}$ and the relative intensities of the 862 and the 893 cm.$^{-1}$ band show that their *cis*-isomer was less than 80% pure. Thus, the physical properties given by Lacher and his co-workers do not refer to the pure *cis*-isomer. These authors estimated the dipole moment of the *cis*-isomer as 0·1 D. That of the *trans*-isomer is probably about half the *cis*-value (we doubt whether it is zero, as was assumed by Lacher *et al.*[4]). The difference in the dielectric constant of benzene solutions of the isomers due to the very small difference in their dipole moments led Lacher *et al.* to assign the *cis*-configuration to the 1047-isomer.

The ^{19}F magnetic resonance spectra of the isomers are distinct, and each consists of a single line plus a symmetrical AB quartet. The single lines at 2·8 and $-6{\cdot}8$ p.p.m. (perfluorocyclobutane = 0) are due to the CFCl fluorine nuclei of the 1047- and 1027-isomers respectively. The quartets can be analyzed as AB spectra [5,6] and are due to CF_2 resonances with chemical shifts of $-16{\cdot}2$ and $-4{\cdot}0$ p.p.m., and $-12{\cdot}2$ and $-8{\cdot}1$ p.p.m. in the respective isomers, with a coupling constant of 218 c./sec. in both cases. This agrees with the coupling constants found in polyfluorocyclobutanes by Phillips [5] and Shoolery.[7] The chemical shift between the two fluorine nuclei in the CF_2 groups is 12·2 p.p.m. in the 1047-isomer but only 4·1 p.p.m. in the 1027-isomer. Taking this as a measure of the asymmetry of the CF_2 groups, we believe this favours the assignment to the 1047-isomer of the *cis*-configuration, in which both chlorine atoms are on the same side of the ring.

(b) 1,3-*Dichlorohexafluorocyclobutane*. Careful purification of the cyclic dimers failed to remove two impurity peaks in their nuclear magnetic resonance spectra. These were a triplet at $-13{\cdot}1$ p.p.m. and a quintuplet at $+1{\cdot}6$ p.p.m., always in the ratio 2 : 1 in total intensity, and both with splittings of 4·8 c./sec. We believe that these lines are due to *trans*-1,3-dichlorohexafluorocyclobutane. This molecule has two sets of equivalent ^{19}F nuclei (A_2X_4 system) whereas the other three cyclic dimers have three sets. The observed fine structure of the lines suggests that the *cis*- and *trans*-AX coupling constants are very similar.

(c) 1,4-*Dichlorohexafluorobut*-2-*ene*. This material was produced in small amounts during the pyrolysis of chlorotrifluoroethylene and its cyclic dimers, and was separated and purified by gas chromatography. The molecular weight (from the vapour density) was 231·4 (Calc. for $C_4F_6Cl_2$: *M*, 233·0); the vapour pressure (isoteniscope, 6—57°) was given by $\log_{10} P(\text{mm.}) = 8{\cdot}233 - 1774/T$, and the b. p. (760 mm.) was 58·2°. The presence of unsaturation was shown by the immediate decoloration of potassium permanganate in acetone. The infrared spectrum in the sodium chloride range has strong bands at *ca.* 1256, 1213, 1178, 1121, 1030, 949, and 765 cm.$^{-1}$, and a weak band at *ca.* 1715 cm.$^{-1}$. The nuclear magnetic resonance spectrum of the material in carbon tetrachloride consists of lines at $-4{\cdot}9$ and 90·4 p.p.m. (benzotrifluoride = 0) with intensities in the ratio 2 : 1. Both lines show fine structure and are symmetrical about their centres. The low-field line consists of a doublet with a separation of 17·0 c./sec. and a weaker doublet with a separation of 7·0 c./sec.; the high-field line consists of a strong central component with weaker components at $\pm 5{\cdot}0$, $\pm 12{\cdot}0$, and $\pm 17{\cdot}0$ c./sec.

The molecular weight, b. p., and presence of unsaturation show that the material is a dichlorohexafluorobutene. The absence of strong C=C stretching absorption in the infrared spectrum shows that the material is not a but-1-ene or an isobutene. Of the but-2-enes only 1,4-dichlorohexafluorobut-2-ene explains the observed nuclear magnetic resonance spectrum, which also shows that only one stereoisomer is present. Infrared absorption in the C=C stretching region (*ca.* 1700 cm.$^{-1}$) is very weak, and probably indicates a *trans*-structure for the material; the C=C absorption band is considerably weaker than in the spectrum of *cis–trans*-perfluorobut-2-ene.[8] Our present analysis of the nuclear magnetic resonance spectrum as an

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[4] Lacher, Büchler, and Park, *J. Chem. Phys.*, 1952, **20**, 1014.

[5] Phillips, *J. Chem. Phys.*, 1956, **25**, 949.

[6] Pople, Schneider, and Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959.

[7] Shoolery, *Discuss. Faraday Soc.*, 1955, **19**, 215.

[8] Brice, LaZerte, Hals, and Pearlson, *J. Amer. Chem. Soc.*, 1953, **75**, 2698.

A_2X_4 system favours the *trans*-structure, but without examining the spectra of the other stereoisomer we cannot make a definite structural assignment.

Miller[9] obtained as a product of the pyrolysis of chlorotrifluoroethylene a dichlorohexafluorobutene to which he assigned the structure $CF_2{=}CF{\cdot}CFCl{\cdot}CF_2Cl$. However, the infrared spectrum[10] of a sample of the material does not show the expected intense C=C absorption at about 1800 cm.$^{-1}$, but does show all the absorptions of our but-2-ene. We conclude that Miller's product contained our but-2-ene as a major component, together with other components which gave rise to absorption at *ca.* 1780 and 1710 cm.$^{-1}$.

Qualitative Features of the System.—In the range 300—500° pyrolysis of chlorotrifluoroethylene leads to the cyclic dimer 1,2-dichlorohexafluorocyclobutane, and an equilibrium in which the dimer predominates is approached. The equilibrium can likewise be approached by pyrolysis of the pure dimer, which dissociates into the monomer. The *cis*- and the *trans*-isomer of the dimer are initially formed at similar rates from the monomer, but at equilibrium the *trans*-form predominates. Pyrolyses of *cis*- and of *trans*-enriched samples of the dimer showed that *cis–trans*-isomerization occurs.

The nuclear magnetic resonance spectra of the dimers showed that about 1% of 1,3-dichlorohexafluorocyclobutane was formed in some pyrolyses. Asymmetric cleavage of the 1,2-dimers was shown to be negligible below 500°. Dichlorohexafluorobut-2-ene was formed at the higher temperatures of the range by slow secondary reactions involving no pressure change and not interfering with the kinetic measurements. The formation of non-condensable gas by heterogeneous attack on the glass was also negligible.

Symbols. Chlorotrifluoroethylene (monomer), M, m; 1,2-dichlorohexafluorocyclobutane (dimer), D, d; *cis*-D, D_c, c; *trans*-D, D_t, t; the lower-case letters are used as subscripts. P, total pressure; C, concentration; N, mole fraction; N_t^d, mole fraction of D_t in D, *i.e.*, $N_t^d = C_t/(C_c + C_t)$. The subscripts o and e refer to initial and equilibrium states. k and K are the rate and equilibrium constants (concentration units mole l.$^{-1}$); the reaction referred to is indicated by a pair of subscripts, showing in order the reactant and product. Thus, k_{mc} refers to $2M \longrightarrow D_c$.

Cyclic Dimerization of Chlorotrifluoroethylene.—The main reaction of chlorotrifluoroethylene below 500° is the formation of 1,2-dichlorohexafluorocyclobutane, which is the only product formed in the early stages of reaction. The reaction could thus be followed by observing pressure changes at constant volume. For each run the second-order rate constant was obtained from the slope of a plot of $1/(2P - P_0)$ against time, a correction for dead space being

TABLE 1.

Rate constants for the dimerization of chlorotrifluoroethylene.

Temp.	P_0 (mm.)	$3 + \log_{10} k_{md}$ *	Temp.	P_0 (mm.)	$3 + \log_{10} k_{md}$ *	Temp.	P_0 (mm.)	$3 + \log_{10} k_{md}$ *
	Pyrex vessel			Pyrex vessel			Packed Pyrex vessel	
350·2°	326	1·300	301·7°	180·5	0·598	310·1°	227·0	0·724
350·5	116	1·230	310·5	235·2	0·709	319·2	217·0	0·887
350·5	186	1·220	350·0	158·8	1·314	396·1	196·5	1·972
396·0	283	1·951	369·0	249·0	1·542	435·2	204·5	2·422
402·3	125	1·950	388·8	219·5	1·811	472·6	212·0	2·883
402·5	210	1·952	403·1	200·0	1·992			
402·8	348	2·027	417·1	163·0	2·171		Nickel vessel	
450·2	369	2·625	433·7	152·0	2·326	448·8	356	2·629
450·3	202	2·546	445·2	153·4	2·481	449·7	235	2·640
450·4	142	2·559	457·5	140·0	2·614	520·9	290	3·413
450·4	158	2·588	466·3	406·0	2·775	550·0	240	3·563
496·3	308	3·104	466·4	174·0	2·751			
496·5	195	3·102	478·9	170·0	2·896			
496·5	330	3·101	497·4	160·2	3·094			
496·7	104	3·121						

* k_{md} in l. mole^{-1} sec.$^{-1}$.

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[9] Miller, "The Preparation, Properties, and Technology of Fluorine and Organic Fluorine Compounds," ed. Slesser and Schram, National Nuclear Energy Series, Div. VII, 1, McGraw-Hill, New York, 1951, pp. 567—685.

[10] Smith, Alpert, Saunders, Brown, and Moran, Naval Research Laboratory (Washington, D.C.), Report No. 3924 (1952).

applied. Such plots were initially linear with an intercept equal to $1/P_0$. Runs were made in Pyrex vessels (including a packed vessel with a ten-fold increase of area–volume ratio) over the range 302—497°, and up to 550° in a nickel vessel, and at pressures between 100 and 400 mm. The rate constants, given in Table 1, are independent of pressure and vessel. They can be expressed by the following Arrhenius equation, derived by the method of least squares; the errors shown are the probable errors.[11]

$$dC_m/dt = -k_{md}C_m^2; \quad \log_{10}k_{md}\ (\text{l. mole}^{-1}\ \text{sec.}^{-1}) = 7{\cdot}63 \pm 0{\cdot}06 - (5{\cdot}82 \pm 0{\cdot}04)10^3/T.$$

To determine the relative rates of formation of the *cis*- and *trans*-isomers, the *trans*/*cis* ratio was determined for series of runs of short durations. The initial ratio was always close to unity, and it can be shown [12] that for the formation of the dimers in the system $2M \longrightarrow D_c \rightleftharpoons D_t \longleftarrow 2M$, in which $k_{mt} \approx k_{mc}$, the initial slope of plots of $\log_{10}(C_t/C_c)$ against time is $(k_{ct} - k_{tc})/2{\cdot}303$. Independently determined values of k_{ct} and k_{tc} were used to predict initial slopes, and extrapolations to zero time were then made. The intercepts obtained are:

Temp.	301·5°	350·0°	357·2°	397·1°	448·8°	461·2°	499·1°
$\log_{10}(C_t/C_c)_0$	−0·012	−0·010	0·015	0·002	0·010	0·000	0·005

No definite trend with temperature is apparent. The mean value of $\log_{10}(C_t/C_c)_0$ is 0·001, and the probable error of the mean is 0·002. We conclude that $k_{mt} = k_{mc}$ within experimental error.

Dissociation of the Dimers into Chlorotrifluoroethylene.—Dissociation was studied in a Pyrex vessel over the ranges 426—514°, and 30—140 mm. The only side reactions under these conditions were the fast *cis–trans*-isomerization and the slow formation of dichlorohexafluorobut-2-ene at the higher temperatures. None of the side reactions involves a pressure change, so the dissociation could be studied in the early stages of reaction by observing pressure changes. First-order rate constants were derived from the slopes of plots of $\log_{10}(2P_0 - P)$ against time, a correction being made for dead space. Despite the back reaction, the plots were initially linear with an intercept of $\log_{10} P_0$. Rate constants derived from runs carried out with two samples of different isomer composition (26% and 68% *trans*) did not differ significantly. This is not surprising since the *cis–trans*-isomerization is fast; the measured rate constants are listed in Table 2, and yield the following least squares line: $dC_d/dt = -k_{dm}C_d$; $\log_{10}k_{dm}\ (\text{sec.}^{-1}) = 15{\cdot}40 \pm 0{\cdot}18 - (14{\cdot}28 \pm 0{\cdot}13)10^3/T$.

cis–trans-*Isomerization of the Dimers.*—A series of runs was carried out in a Pyrex vessel at about 60 mm. pressure between 425° and 469°. At each temperature two sets of runs were made, approaching the equilibrium from either side, with dimer samples containing 19% and 89% of the *trans*-isomer. The *trans*/*cis*-ratio in the products of each run was determined by the gas-chromatographic method described above. For opposing first-order reactions such

TABLE 2.

Rate constants for the dissociation of 1,2-dichlorohexafluorocyclobutane into chlorotrifluoroethylene.

Temp.	P_0 (mm.)	$6 + \log_{10} k_{dm}$ *	Temp.	P_0 (mm.)	$6 + \log_{10} k_{dm}$ *	Temp.	P_0 (mm.)	$6 + \log_{10} k_{dm}$ *
Initial dimer compn. $N^d_{t,0} = 0{\cdot}68$			Initial dimer compn. $N^d_{t,0} = 0{\cdot}68$			Initial dimer compn. $N^d_{t,0} = 0{\cdot}26$		
425·5°	94·6	0·942	479·0°	81·0	2·341	439·3°	69·6	1·400
426·0	78·3	1·038	479·0	81·6	2·399	449·5	60·2	1·636
448·5	72·8	1·613	489·0	60·5	2·616	460·0	106·6	1·879
448·7	120·2	1·640	490·2	93·9	2·666	470·3	70·0	2·219
449·2	46·1	1·574	499·3	83·7	2·901	488·1	53·8	2·645
449·2	92·5	1·540	499·3	91·1	2·892	488·1	54·7	2·623
449·8	137·3	1·636	513·1	29·9	3·288	501·9	53·8	2·922
459·3	76·9	2·005	513·1	62·9	3·271			
460·0	81·4	1·988	513·6	91·3	3·313			
468·8	46·5	2·128						

* k_{dm} in sec.$^{-1}$.

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[11] Margenau and Murphy, " The Mathematics of Physics and Chemistry," Van Nostrand, New York, 1956, 519.

[12] Stedman. Ph.D. Thesis, London, 1960.

as $D_t \rightleftharpoons D_c$ plots of $\log_{10}|C_t - C_{t,e}|$ against time are linear with a slope of $-(k_{ct} + k_{tc})/2{\cdot}303$. It can be shown [12] that for the system $2M \leftarrow D_c \rightleftharpoons D_t \rightarrow 2M$ plots of $\log_{10}|N_t^d - K_{ct}/(1 + K_{ct})|$ against time are initially linear with a slope of $-(k_{ct} + k_{tc})/2{\cdot}303 + (k_{cm} - k_{tm})N_t^d N_c^d/2{\cdot}303 (N_t^d - K_{ct}/[1 + K_{ct}])$; where $N_t^d = C_t/(C_c + C_t)$, and $K_{ct}/(1 + K_{ct})$ is the value N_t^d would have at equilibrium. Such plots, where the observed value of K_{ct} (1·667) was used, were closely linear (see Figure), and the slope correction-term for dissociation was shown to be small. The mean slope of the two lines at each temperature was used to obtain $(k_{ct} + k_{tc})$, and the individual rate constants found by using the value of K_{ct} ($= k_{ct}/k_{ct}$) are as listed.

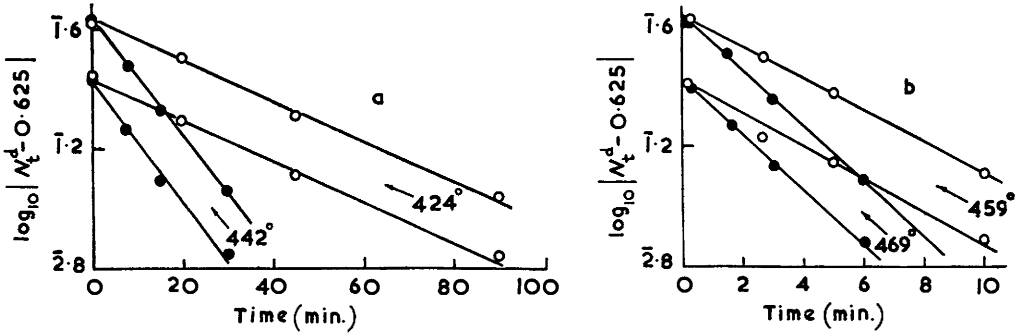

FIG. 1. Isomerization of *cis-* and *trans-*1,2-dichlorohexafluorocyclobutane.
a, ○ 424°, ● 442°; b, ○ 459°, ● 469°. At each temperature; $N_{t,0}^d = 0{\cdot}19$, upper line; $N_{t,0}^d = 0{\cdot}89$, lower line.

Temp.	424·3°	441·9°	459·1°	468·8°
$5 + \log_{10} (k_{ct} + k_{tc})$ (sec.$^{-1}$)	$1{\cdot}420_5$	$1{\cdot}885_5$	$2{\cdot}318_5$	$2{\cdot}551_7$
$5 + \log_{10} k_{ct}$ (sec.$^{-1}$)	1·216	1·681	2·114	2·348
$5 + \log_{10} k_{tc}$ (sec.$^{-1}$)	0·994	1·459	1·892	2·126

A run at 30 mm. pressure yielded the same rate constant as did the 60 mm. runs.

The Arrhenius equations, derived by the method of least squares, for the rate constants are:

$$dC_t/dt = -k_{tc}C_t;\ \log_{10} k_{tc}(\text{sec.}^{-1}) = 14{\cdot}87 - 13{\cdot}17 \times 10^3/T$$
$$dC_c/dt = -k_{ct}C_c;\ \log_{10} k_{ct}(\text{sec.}^{-1}) = 15{\cdot}10 - 13{\cdot}17 \times 10^3/T$$

cis–trans-*Equilibrium in the Dimer.*—It was not possible to observe a true monomer/*cis*–*trans*-dimer equilibrium, owing to the slow formation of dichlorohexafluorobut-2-ene and other products. However, by pyrolyzing mixtures of near-equilibrium composition and measuring the *trans*/*cis*-ratio in the product, it was possible to obtain fairly accurate values of the equilibrium constant for the isomerization. Runs were made at a total pressure of about 80 mm. and over the range 374—510°. The measured values of the equilibrium constant are listed in Table 3. The rather large scatter is probably associated with the adverse conditions for observing equilibrium, but no trend with temperature is apparent. The mean value of $\log_{10}K_{ct}$ is 0·218, and the probable error of the mean is 0·002. Values for the extremes of the temperature range are probably less reliable, and a weighted mean of 0·222 was adopted. Displacement of the equilibrium by the formation of the butene was shown not to exceed 0·009 at 470° and would be much less at lower temperatures.

Application of Reaction Rate Theories to Results.—Activation energies and *A*-factors can be derived directly from the Arrhenius rate equations. The usual collision-theory treatment of

TABLE 3.

Equilibrium *trans*/*cis*-Ratio for 1,2-Dichlorohexafluorocyclobutane.

Temp.	373·8°	374·5°	378·3°	388·3°	399·1°	404·4°	409·0°	418·6°	429·7°
$\log_{10} (C_t/C_c)_e$	0·194	0·211	0·219	$0{\cdot}213_5$	0·234	0·216	0·225	0·224	0·225
Temp.	446·2°	454·7°	460·9°	468·3°	479·4°	491·0°	501·3°	510·3°	
$\log_{10} (C_t/C_c)_e$	0·223	0·237	0·201	0·238	$0{\cdot}219_5$	0·209	0·210	0·211	

the dimerization results yields a steric factor of $3{\cdot}3 \times 10^{-4}$ for the formation of dimer, a value $5{\cdot}73 \times 10^{-8}$ cm. being assumed for the molecular diameter of chlorotrifluoroethylene.

The transition-state theory of reaction rates [13] predicts that the rate constant is given by the expression,

$$\log_{10}(k/T^{1-\Delta n^{\ddagger}}) = \log_{10}(\kappa \boldsymbol{k}\boldsymbol{R}^{-\Delta n^{\ddagger}}/\boldsymbol{h}) + \Delta S^{\ddagger}/2{\cdot}303\boldsymbol{R} - \Delta H^{\ddagger}/2{\cdot}303\boldsymbol{R}T \quad . \quad . \quad . \quad (1)$$

By tabulating pairs of values of $\log_{10}(k/T^{1-\Delta n^{\ddagger}})$ and $1/T$ and performing least-squares calculations, all the rate constants were summarized in equations of the form of (1). Heats and entropies of reaction could then be derived directly. In the case of dissociation of the dimer it was assumed that the rate constants k_{dm} were for an equilibrium *cis-trans* mixture. The transition-state equation then becomes, by taking $\kappa = 1$ and $\Delta n^{\ddagger} = 0$:

$$\log_{10}(k_{\text{dm}}/T) = \log_{10}(\boldsymbol{k}/\boldsymbol{h}) + \log_{10}(2/[1 + K_{\text{ct}}]) + \Delta S_{\text{cm}}^{\ddagger}/2{\cdot}303\boldsymbol{R} - \Delta H_{\text{cm}}^{\ddagger}/2{\cdot}303\boldsymbol{R}T,$$

and $\Delta S_{\text{cm}}^{\ddagger}$ and $\Delta H_{\text{cm}}^{\ddagger}$ can be derived as before. From the *cis–trans*-equilibrium constant the heat and entropy of isomerization are obtained directly. The results of these calculations are summarized in Table 4.

TABLE 4.

Reaction	*A*	*E* (kcal. mole⁻¹)	ΔH° (kcal. mole⁻¹)	ΔS° (cal. deg.⁻¹ mole⁻¹)	$\Delta H^{\ddagger}$ [a] (kcal. mole⁻¹)	$\Delta S^{\ddagger}$ [a] (cal. deg.⁻¹ mole⁻¹)
$2M \rightarrow D$	$4{\cdot}3 \times 10^{7}$ l. mole⁻¹ sec.⁻¹	26·6				
$2M \rightarrow D_c$			−40·0	−47·3	23·9	−38·6
$2M \rightarrow D_t$			−40·0	−46·3	23·9	−38·6
$D \rightarrow 2M$	$2{\cdot}5 \times 10^{15}$ sec.⁻¹	65·3				
$D_c \rightarrow 2M$					63·9	8·7
$D_t \rightarrow 2M$					63·9	7·7
$D_c \rightarrow D_t$	$1{\cdot}25 \times 10^{15}$ sec.⁻¹	60·2	0	1·0	58·8	6·7
$D_t \rightarrow D_c$	$7{\cdot}5 \times 10^{14}$ sec.⁻¹	60·2			58·8	5·7
$2C_2F_4 \rightarrow C_4F_8$ [b]	$10{\cdot}3 \times 10^{7}$ l. mole⁻¹ sec.⁻¹	25·4	−50·4	−48·1	22·2	−37·5
$C_4F_8 \rightarrow 2C_2F_4$ [b]	$8{\cdot}9 \times 10^{15}$ sec.⁻¹	74·1			72·6	10·6

Standard State: 1 atmosphere pressure.

[a] For $\kappa = 1$. [b] From Atkinson and Trenwith;[1] the thermodynamic constants are recalculated and differ slightly from those originally given.

DISCUSSION

Our rate equation for the dimerization of chlorotrifluoroethylene is in excellent agreement with that of Lacher, Tompkin, and Park.[3] These authors predicted that the *cis*/*trans*-ratio in the product would be determined essentially by the symmetry numbers in the rotational partition functions in the Eyring rate equation. By assuming that the activated complexes were rigid and had the same symmetry numbers as the products (*i.e.*, $\sigma_t = 2$, $\sigma_c = 1$), a *cis*/*trans*-ratio of 2 was predicted, and they compared this with their experimental figure of 5. In a recent paper from the same laboratory, Park, Holler, and Lacher [14] report an experimental ratio of 1, and cite this as evidence in favour of an open-chain activated state with free rotation as opposed to a rigid activated state. In fact, the existence of (+)- and (−)-forms of the *trans*-isomer was not taken into account by Lacher, Tompkin, and Park.[3] With this correction we find that a total *cis*/*trans*-ratio of 1 is predicted for both rigid and non-rigid activated states. Our experimental ratio agrees with that reported by Park, Holler, and Lacher, but the *cis*/*trans*-ratio alone provides little useful information about the activated complex.

We believe that a better approach is through the calculation of entropies of activation. The fact that the *cis*- and *trans*-isomers are formed at equal rates at all temperatures shows that they are formed through the same activated complex. The high positive entropies of activation for dissociation are associated with the high *A*-factors of the reaction, and this is commonly found in ring-opening reactions.[15] We find that the observed entropy of activation can be explained by an open-chain activated complex in which the CFCl–CFCl

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[13] Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, 1941.

[14] Park, Holler, and Lacher, *J. Org. Chem.*, 1960, **25**, 990.

[15] Gowenlock, *Quart. Rev.*, 1960, **14**, 133.

bond of the dimer is essentially broken, and which has a limited freedom for internal rotation about the CF_2–CFCl bonds.

The heat and entropy of activation for isomerization of the dimer are both smaller than for dissociation. This is consistent with the activated complex's being less open and more rigid for isomerization. For isomerization to occur the CFCl groups need separate only sufficiently to allow one of them to rotate.

The heat and entropy of activation for dissociation of 1,2-dichlorohexafluorocyclobutane are both smaller than for dissociation of perfluorocyclobutane, for which $\Delta H^{\ddagger} =$ 72·6 kcal. mole^{-1} and $\Delta S^{\ddagger} =$ 10·6 cal. deg.$^{-1}$ mole^{-1}. Dissociation of perfluorocyclobutane, which has the higher activation energy, also has the higher change in heat content. Substitution of two fluorine atoms by chlorine has distinctly lowered the stability of the ring. In the range of observation there is no difference in heat content between *cis*- and *trans*-substitution, but this does not rule out the existence of a small difference at 0° K.

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