gives 4 kcal. for $-\Delta F$, which is near the 5 kcal. per mole of silica, measured for the $-\Delta H$ of reaction as silica dissolves in an HSF acid.

PRINCETON, N. J. RECEIVED JUNE 27, 1951

[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

The Kinetics of the Vapor Phase Dimerization of Tetrafluoroethylene and Trifluorochloroethylene[1]

BY J. R. LACHER, G. W. TOMPKIN AND J. D. PARK

Using pressures of less than one atmosphere, the rates of dimerization of tetrafluoroethylene, chlorotrifluoroethylene and their interdimerization have been studied. The reactions are second order and homogeneous. The Arrhenius equations which will reproduce the experimental data are: $16.5 \times 10^{10}\ e^{-26,299/RT}$, $3.53 \times 10^{10}\ e^{-26320/RT}$ and $8.54 \times 10^{10}\ e^{-26300/RT}$ cc./mole sec.$^{-1}$, respectively. The significance of the symmetry numbers in determining the "A-factors" is discussed in terms of the structures of the molecules involved.

Introduction

The successful dimerization at high pressures of tetrafluoroethylene and chlorotrifluoroethylene has been carried out.[2,3] The interdimerization of the two olefins has also been reported.[4] In all cases a saturated cyclobutane was obtained. A kinetic study of the reactions was undertaken at pressures of less than one atmosphere and the results are reported here.

Experimental Details

The reaction flask consisted of a one-liter Pyrex vessel fitted with a thermocouple well and capillary entrance lines. In order to test for the homogeneity of the reaction, a flask packed with Pyrex tubing was used. A Bodenstein quartz spiral served to measure pressures to about 0.1 mm. The reaction flask was placed in an electric furnace consisting of an aluminum block suitably insulated. Temperatures could be controlled to 0.2° and there were no temperature gradients present in the furnace to this accuracy. The pressure change which accompanies the reaction was used to follow its rate, and infrared analysis of the product was used to test for side reactions. In case of the interdimerization of tetrafluoroethylene and chlorotrifluoroethylene the rate was followed by infrared absorption. Samples of tetrafluoroethylene and chlorotrifluoroethylene were kindly furnished by the "Kinetic" Chemicals Division of the du Pont Company and they were purified by methods previously described.[5,6]

The rate of dimerization of chlorotrifluoroethylene was studied at temperatures between 304.5 and 509.1° and at pressures of 100 and 600 mm. roughly. The reaction was found to be second order. Second order constants were obtained from the differential equation

$$\Delta P/\Delta t = -kP^2$$

Here ΔP is the change in the pressure in mm. of the monomer which occurs in the time interval Δt seconds. For P^2 the product of the pressure at the beginning of the time interval and that at the end were used. The constants so obtained are summarized in Table I. They are independent of the initial pressure as is shown in runs 1 through 6. No significant change occurs at 394° when the pressure varies from 105 to 623 mm. Run 16 shows that a packed cell is without effect. In run 18 a thermocouple was sealed into the reaction flask so that the gases came in contact with it. A very slight cooling (0.2°) of about five seconds duration was noted when the reactor was initially filled. No significant temperature rise was observed during the reaction.

TABLE I

DIMERIZATION OF CHLOROTRIFLUOROETHYLENE

Run	T°c	Initial pressure, mm.	$k \times 10^7$, mm.$^{-1}$ sec.$^{-1}$
13	304.5	619.1	1.0
18	346.7	502.9	4.7[a]
17	347.6	525.9	5.1
6	393.4	590.3	19
5	393.6	607.0	18
4	393.6	105.0	19
3	393.6	112.0	20
1	394.5	381.8	18
2	394.9	245.8	19
16	439.1	623.2	65[b]
15	439.8	615.8	65
14	440.4	619.5	66
8	507.5	257.3	300
9	507.6	256.7	300
10	507.6	190.0	310
11	508.7	143.5	310
12	508.7	104.3	320
7	509.1	347.9	310

[a] Seated in thermocouple. [b] Packed cell.

The rate constants were also independent of the extent of the reaction. This is shown in Fig. 1. The ratio of the rate constant for each increment to the rate constant for the initial increment is plotted as an ordinate and the per cent. completion of reaction is the abscissa. The logarithms of the rate constants so obtained when graphed as a function of

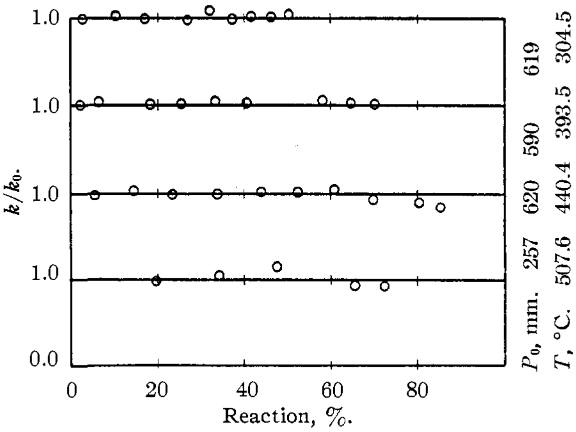

Fig. 1.—Ratio of second order rate constant at any time to initial rate constant, plotted as a function of per cent. reaction. Dimerization of chlorotrifluoroethylene.

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[1] This work was supported by Contract N6ONR-231, Task Order VI, with the Office of Naval Research, United States Navy. Presented before the Symposium on Fluorine Chemistry, 120th Meeting of the American Chemical Society, New York, N. Y., September, 1951.

[2] Jesse Harmon, U. S. Patent 2,404,374.

[3] A. L. Henne and R. P. Ruh, THIS JOURNAL, **69**, 279 (1947).

[4] Paul L. Barrick, U. S. Patent 2,427,116.

[5] J. R. Lacher, J. D. Park, *et al.*, THIS JOURNAL, **71**, 1330 (1949).

[6] J. R. Lacher, J. D. Park, *et al.*, *ibid.*, **71**, 1334 (1949).

the reciprocal of the absolute temperature gave a straight line.

The product of the reaction was determined by infrared analysis to be 1,2-dichlorohexafluorocyclobutane. No evidence for any side reaction could be obtained. It was also shown in this way that the product consisted of 80 to 90% of the *cis* dimer. This is interesting since both the photochemical and catalytic chlorination of hexafluorocyclobutane yield 80-90% of the *trans* isomer.[7]

The dimerization of tetrafluoroethylene was studied between temperatures of 288 and 466°. The reaction is complicated by two things. In the first place it is sufficiently exothermic so that a temperature rise is produced during the early part of the reaction. Using a reactor with a sealed-in thermocouple, it was found that the temperature rise varied from 0.8° at 290 to 3.5° at 460°. The magnitude of the rise was almost proportional to the rate of change of pressure with time. The results could be duplicated to within 0.2° in runs at similar temperatures and pressures. A plot of the temperature rise versus the per cent. reaction is shown in Fig. 2. A similar plot using values of the total time of reaction along the abscissa would show the maximum temperature rise in each case at about the same place. It was necessary to measure the average temperature during the runs. The second complicating factor is due to the fact that the velocity constants declined as the reaction progressed. This is shown in Fig. 3. This falling off of the constants could be due to the presence of a reversible reaction; however, experiments showed that octafluorocyclobutane was stable at the temperatures concerned. It was shown by experiment that octafluorocyclobutane inhibits the reaction. Although this aspect of the problem is being studied further, it is our feeling that the falling off of the rate constants is not due to the initial temperature rise and its subsequent decrease. The effect is not sufficiently large. The initial velocity constants were independent of the pressure and are reported in Table II. The rate constants at about 448° were independent of the initial pressure between 30 and 217 mm. The second order constants obeyed the Arrhenius equation and infrared analysis showed that no side reactions were taking place.

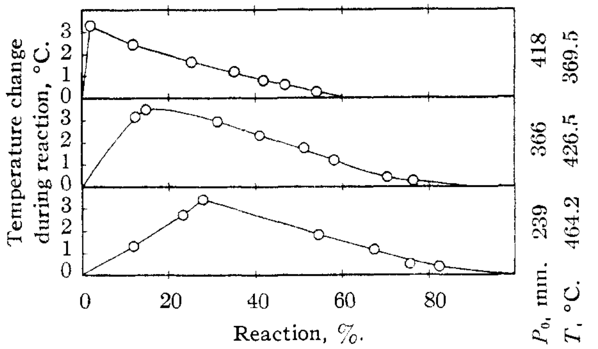

Fig. 2.—Variation of temperature during the dimerization of $CF_2{=}CF_2$.

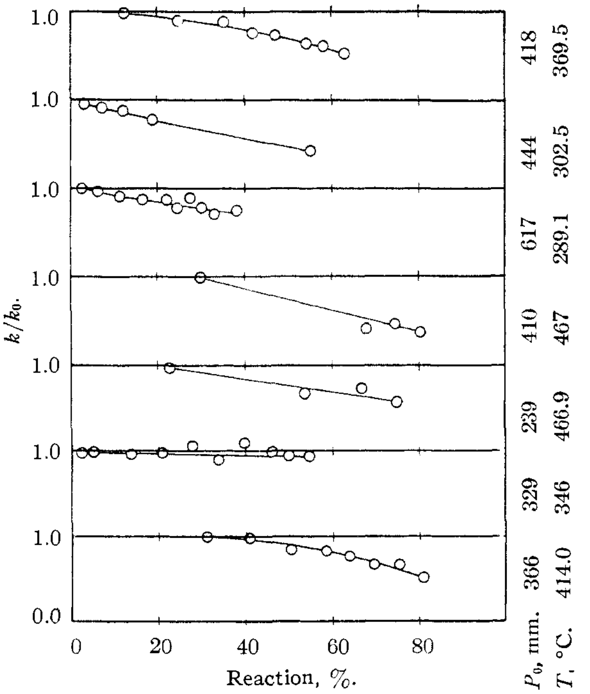

Fig. 3.—Ratio of second order rate constant at any time to initial rate constant, plotted as a function of per cent. reaction. Dimerization of tetrafluoroethylene.

Table II

Dimerization of Tetrafluoroethylene

T°c	Initial pressure, mm.	$k \times 10^7$, mm.$^{-1}$ sec.$^{-1}$
288.0	384.2	2.6[a]
290.2	617.0	2.7
291.5	376.0	4.1
302.9	443.8	4.5
318.4	276.2	9.6
346.5	392.2	24
341.6	518.5	25
348.4	430.9	26
372.8	418.3	39
413.1	366.2	170
414.4	322.6	150
448.2	157.8	410
448.3	30	420
448.3	55.6	420
449.0	217.3	430
461.8	277.0	520
466.4	410.2	620
466.4	238.7	660

[a] Packed cell.

The rate of interdimerization of tetrafluoro- and trifluorochloroethylene is complicated by the simultaneous occurrence of three reactions. Even though the rates of dimerization of the pure olefins are known, it is not practical to use the pressure change during a reaction to calculate the interdimerization velocity constant. Instead the two olefins were mixed at known initial pressures and allowed to react for a definite short period of time. The contents of the flask were then drawn into a 10-cm. gas cell and its composition determined by quantitative infrared analysis. Ordinarily the partial pressure of chlorotrifluoroethylene was obtained by measuring the optical density at 5.55 μ. The following equation was used to calculate the interdimerization constant, k_3

$$-\Delta p_1/\Delta t = k_1 p_1^2 + k_3 p_1 p_2$$

Here k_1 is the rate constant for the dimerization of trifluorochloroethylene, p_1 is its partial pressure and p_2 is the partial pressure of tetrafluoroethylene. Now the initial pressure of each olefin is known and after the time interval Δt, the partial pressure, p_1, of chlorotrifluoroethylene is measured by infrared analysis. Since twice the pressure drop noted during the reaction is the sum of the pressure drop for the two reactants, $p_1 + p_2$ is known at the end of the reaction increment. Thus, the final pressure of

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[7] Unpublished results of this Laboratory.

tetrafluoroethylene may be obtained. The rate constants obtained are given in Table III. They obey the Arrhenius equation. This method of calculation of the rate constant assumes that the rate of dimerization of trifluorochloroethylene is unaffected by the other reactants and products present and also that only three dimers are formed.

TABLE III

INTERDIMERIZATION OF $CF_2{=}CF_2$ AND $CF_2{=}CFCl$

T°c	Initial pressures, mm. $CF_2{=}CF_2$	Initial pressures, mm. $CF_2{=}CFCl$	$k \times 10^7$, mm.$^{-1}$ sec.$^{-1}$
305.1	156	272	2.5
343.1	119	223	9.8
371.6	77	144	30
396.9	134	234	64
437.5	190	324	142

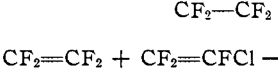
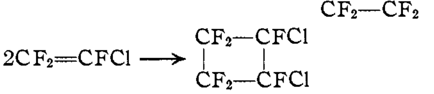
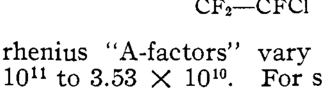
The latter was proven by allowing the two olefins to react for an extended period and then taking a complete infrared spectrum of the mixture. No evidence for any side reactions could be obtained in this way. In order to determine whether or not the rate of dimerization of trifluorochloroethylene was unchanged, the products of run 2 were analyzed also for 1,2-dichlorohexafluorocyclobutane. It was found that 37 mm. were present after 176 seconds. During this time the pressure of trifluorochloroethylene dropped from 324 to 219 mm. The second order rate constant, k_1, for the disappearance of monomer was calculated from these data to be 59×10^{-7} mm.$^{-1}$ sec.$^{-1}$. This agrees unexpectedly well with a value of 60×10^{-7} mm.$^{-1}$ sec.$^{-1}$ taken from the Arrhenius equation for this reaction.

Discussion

A summary of the experimental results for the three reactions studied is given in Table IV. The activation energies are identical within the experimental errors and have a value of 26,300 calories per mole. The heats of the three reactions are not known, but they probably are quite different, decreasing in the order given in the table. The Arrhenius "A-factors" vary fourfold from 16.5×10^{11} to 3.53×10^{10}. For simple bimolecular reactions the "A-factor" is equal to the number of collisions between reacting molecules at unit concentration. If we assume a molecular diameter of 5×10^{-8} cm. and a temperature of 700°K., this number is approximately 10^{14}. The experimental "A-factors" are smaller by about a factor of 10^3. This means that even if molecules collide[8] with sufficient energy, they seldom react. In order for the olefins to react they must not only collide with sufficient energy but they must be properly oriented with respect to each other.

TABLE IV

SECOND-ORDER VELOCITY CONSTANTS

Reaction	Rate constant cc./mole sec.$^{-1}$
	16.5×10^{10} $e^{-26,299/RT}$
	8.54×10^{10} $e^{-26,300/RT}$
	3.53×10^{10} $e^{-26,320/RT}$

The Eyring[9] rate equation is generally used for discussing this. The velocity constant is given by

$$k = \frac{kT}{h} \times \frac{F^{++}}{F^2} e \frac{-E^0}{RT}$$

Here kT/h is a frequency factor, E^0 the activation energy at absolute zero, and F^{++} and F the partition functions for the activated complex and the reacting olefin, respectively. It will be assumed that the activated complex has the same geometrical arrangement as the product. One can compute the translational and rotational partition functions with some certainty but such is not the case for the vibrational terms since the normal modes of vibration for all the molecules involved are not known. Nonetheless, fairly good agreement with experiment may be obtained if one assumes the activated complex is loosely bound, *i.e.*, has a number of low vibrational frequencies.

The effect of the symmetry number, which enters into the rotational partition function, on the reaction rate is interesting. A table of these numbers is:

Molecule	σ
Tetrafluoroethylene	4
Chlorotrifluoroethylene	1
Octafluorocyclobutane (planar)	8
Octafluorocyclobutane (puckered)	2
1,2-Dichlorohexafluorocyclobutane (*cis*)	1
1,2-Dichlorohexafluorocyclobutane (*trans*)	2
Monochloroheptafluorocyclobutane	1

In the dimerization of chlorotrifluoroethylene one finds experimentally about 5 parts *cis* to 1 of *trans* 1,2-dichlorohexafluorocyclobutane. If one computes the ratios of the "A-factors" leading to the *cis* and *trans* compound, one finds that the translational terms cancel and that the vibrational and rotational terms nearly do so except for the symmetry numbers. Hence, to this approximation

$$\frac{A\ cis}{A\ trans} = \frac{\sigma\ trans}{\sigma\ cis} = \frac{2}{1}$$

The symmetry numbers require that the *cis* isomer can be formed at twice the rate of the *trans*.

The infrared and raman spectra of octafluorocyclobutane have been interpreted both on the basis of a planar and non-planar ring[10-12] whereas electron diffraction indicates a non-planar structure.[13] The symmetry numbers will be significantly different in the two cases and this will affect the numeri-

TABLE V

RATIOS OF A-FACTORS

Ratio	Experimental	Planar	Puckered
A_1/A_3	4	2	8
A_2/A_3	2	4	4
A_3/A_3	1	1	1

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[8] G. B. Kistiakowsky and J. R. Lacher, THIS JOURNAL, **58**, 123 (1936).

[9] Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

[10] W. F. Edgell, THIS JOURNAL, **69**, 660 (1947).

[11] W. F. Edgell, *J. Chem. Phys.*, **18**, 571 (1950).

[12] H. H. Claassen, *ibid.*, **18**, 543 (1950).

[13] H. P. Lemaine and R. L. Livingston, *ibid.*, **18**, 569 (1950).

cal values of the "A-factors." The experimental ratios of the "A-factors" are given in column two of Table V.

A_1 refers to the dimerization of tetrafluoroethylene, A_3 to trifluorochloroethylene, and A_2 to the interdimerization. The experimental "A-factors" are in the ratio of 4/2/1. If one assumes that octafluorocyclobutane is planar, the symmetry numbers would require ratios of 2/4/1; on the other hand, a puckered ring gives 8/4/1. Although the rotational and vibrational partition functions do not cancel completely in this case, it is doubtful if they can bring about an inversion of the ratios as indicated in column three. The kinetic data, therefore, favor the puckered ring.

BOULDER, COLORADO RECEIVED OCTOBER 10, 1951

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Specific Heat and Degree of Crystallinity of Polychlorotrifluoroethylene

BY JOHN D. HOFFMAN

The specific heats of slow-cooled and air-quenched samples of polychlorotrifluoroethylene (m.p. 210–212°) have been measured between 0 and 250° in a differential calorimeter. The calorimeter is described. By comparison of the experimental heat of fusion with the heat of fusion of the pure crystalline polymer obtained from Flory's theory by Bueche, the degree of crystallinity at 0° was found to be 0.82 ± 0.07 for the slow-cooled sample and 0.35 ± 0.03 for the air-quenched sample. The enthalpies of the pure crystals and supercooled liquid polymer were obtained as functions of temperature by a simple interpolation procedure. Comparison of these enthalpies with the observed enthalpies permitted the degree of crystallinity of both the air-quenched and slow-cooled polymer to be calculated as a function of temperature. The results for the slow-cooled sample were in good agreement with those obtained by Price by a volume method. The quenched sample showed a distinct tendency to crystallize on warming. Reasons were advanced for believing that the glass transformation temperature for this polymer is below −80°.

Introduction

The degree of crystallinity, X, of a polymeric system is usually defined by

$$X = (P_1 - P_x)/(P_1 - P_c) \qquad (1)$$

where P is an extensive property of the polymer, and the subscripts l, c, and x refer to the liquid, crystalline and mixed liquid + crystal polymer, respectively. In practice, P is most commonly the enthalpy, the volume, or an X-ray line intensity, all expressed on a per unit weight basis. The above definition of crystallinity obviously ignores surface energy and internal disorder effects in the crystals.

The principal difficulty in applying (1) to any practical case is to obtain P_c as a function of temperature. This was done for polyethylene[1] by extrapolating the enthalpies of the *n*-paraffins to infinite chain length for a series of temperatures, thus obtaining $H_c(T)$. In the case of polychlorotrifluoroethylene, such a scheme could not be used owing to a lack of suitable thermodynamic data on the shorter members of the series, so a somewhat different method was devised.

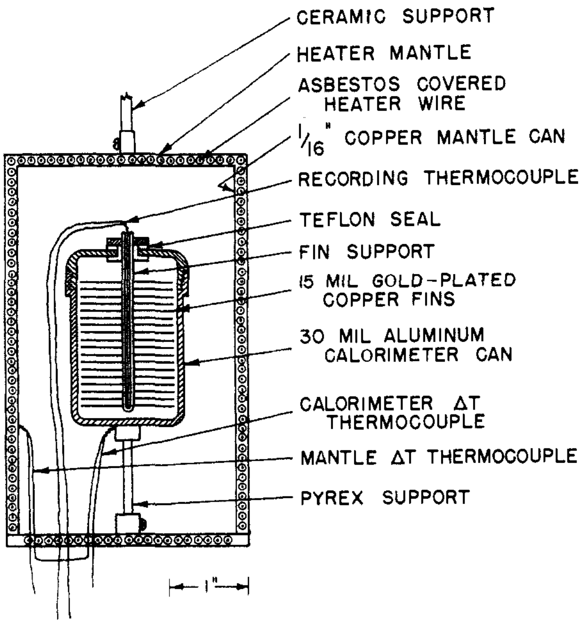

Fig. 1.—Cross-sectional view of differential calorimeter.

Price[2] has recently introduced a new method of obtaining the degree of crystallinity of polymers from volume–temperature plots provided that the glass transformation temperature, T_g, is known. The basis of this method is an ingenious way of fixing $V_c(T)$. If T_g is not known, the degree of crystallinity can still be bracketed. The bracketing procedure was used by Price to obtain the degree of crystallinity of slow-cooled polychlorotrifluoroethylene as a function of temperature, and it is one of the main objectives of this research to check his method with an independent determination of degree of crystallinity.

Apparatus.—The measurements were made in a differential calorimeter (Fig. 1) calibrated between 0° and 250° with diphenyl ether[3,4] and sapphire.[5] The assembly consisted of an outer heater mantle inside of which was supported an aluminum calorimeter. The shell of this calorimeter was made of aluminum instead of copper because polychlorotrifluoroethylene attacks copper at elevated temperatures. Special care was taken to design an efficient fin system so that fusion points and transition points would not be unduly smeared out, as is often the case with this type of calorimeter. It should be mentioned in this connection that the fusion of a purified sample of diphenyl ether occurred over less than 0.4°. The fins were made of 15 mil gold-plated oxygen-free copper spaced 1.6 mm. apart. Care was also taken to provide materials of high thermal

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(1) H. C. Raine, R. B. Richards and H. Ryder, *Trans. Faraday Soc.*, **41**, 56 (1945).

(2) F. P. Price, *J. Chem. Phys.*, **19**, 973 (1951).

(3) G. F. Furukawa, D. C. Ginnings, R. E. McCoskey and R. A. Nelson, *J. Res. Natl. Bur. Stds.*, **46**, 195 (1951).

(4) The author is indebted to Dr. Defoe C. Ginnings for use of these data prior to its publication.

(5) D. C. Ginnings and R. J. Corruccini, *J. Res. Natl. Bur. Stds.*, **38**, 593 (1947).