anthrene and tetraphenyl ethylene, through the behaviour of the latter could also be ascribed to a steric effect.

There is good reason to believe that the mechanism is also dependent on the vinyl monomer being initiated. This dependence was not shown up in the present study which was restricted to the polymerization of methyl methacrylate.

A further point of interest in the experimental results lies in the observation that mechanism appears to be more or less independent of cation. Presumably the environmental differences brought about by changing the alkali metal have an insignificant effect on the energetic factors which determine the mechanism.

The authors wish to thank Mr. C. W. Jefford and Dr. M. E. Bramwell for kindly determining the spectra of some of the polymers. They also wish to acknowledge support of the Air Force Office of Scientific Research during this project.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER 8, B. C., CANADA]

The Thermal Decomposition of Octafluorocyclobutane[1]

BY JAMES N. BUTLER

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Octafluorocyclobutane undergoes a reversible first-order thermal decomposition to tetrafluoroethylene in the temperature range from 360 to 560° with rate constant $k_1 = 10^{16.0}\ e^{-74,300\ \text{cal.}/RT}$ sec.$^{-1}$ and equilibrium constant $K_\text{o} = 10^{8.6}\ e^{-49,900\ \text{cal.}/RT}$ mole/l. A parallel decomposition forming hexafluoropropene occurs with first-order rate constant $K_3 = 10^{17.2}\ e^{-87,000\ \text{cal.}/RT}$ sec.$^{-1}$. The pressure dependence of k_1 and the decrease of activation energy at low pressures can be described by the classical theory of unimolecular reactions with approximately 20 of the 30 possible normal modes of vibration participating in the reaction. At pressures below 0.05 mm. the rate becomes pressure-independent, due to a slow heterogeneous reaction with the same activation energy as the homogeneous reaction. The rate of formation of C_3F_6 is primarily homogeneous under the conditions used. The rate of formation of C_2F_4 is enhanced by traces of oxygen, but the rate of formation of C_3F_6 is unaffected. No satisfactory results were obtained with inert gases, probably due to traces of oxygen. Side reactions with the walls of the pyrex vessel producing CO, CO_2, SiF_4, and possibly COF_2 were observed and corrected for in the calculations.

Introduction

The thermal decomposition of octafluorocyclobutane was briefly studied by Atkinson and coworkers in the course of their work on the thermal decomposition of tetrafluoroethylene.[2,3] At temperatures below 550°, the only fluorocarbons formed from octafluorocyclobutane are tetrafluoroethylene and hexafluoropropene. Gray and Pritchard[4] attempted to measure the rate of decomposition of octafluorocyclobutane by following the rise in pressure but found that the fluorocarbons attacked Pyrex producing silicon tetrafluoride and carbon monoxide. As a result, no useful data could be obtained by this method except at pressures of 300 mm. or greater.

The present work was undertaken to find out if the decomposition of octafluorocyclobutane was described by the theory of unimolecular reactions in spite of the complications occurring. Using gas chromatography for analysis, the rate of reaction can be followed by measuring the ratios of products after a definite length of time even though side reactions may occur. This method also allows the reaction to be studied at much lower temperatures and pressures than was heretofore possible.

Experimental

Furnace. Experiments were carried out in a one-liter spherical Pyrex flask kept at constant temperature by an electrically heated air bath. The temperature was controlled by operating the furnace from a variac and voltage regulating transformer and enclosing the furnace in an insulated copper drum which was cooled by circulating tap water at 8° through coils fastened to its outside. When a steady state had been established at 500°, the temperature of the flask varied less than 0.5° over a period of an hour. Temperature measurements were made using three chromel–alumel thermocouples. The one on the bottom of the flask consistently read about five degrees lower than the two at mid height, one of which read about half a degree higher than the other. The temperature of the gas in the flask was taken to be the average of the three readings. It is estimated that the absolute value of the temperature measurements may be in error by one or two degrees but that the relative values are consistent to less than 0.5 degrees. A 100 ml. reactor packed with glass wool was also used. Pressure measurements were made with a wide-bore manometer or McLeod gauge. The tubing connecting the 1-liter reactor to the vacuum system was 10 mm. or larger to minimize thermal transpiration effects.

Materials.—A sample of octafluorocyclobutane was donated by the Research Division of E. I. du Pont de Nemours and Co., Wilmington, Delaware. It was analyzed by gas chromatography, the only impurity being 0.005% tetrafluoroethylene. Tetrafluoroethylene and hexafluoropropene were prepared by pyrolysis of Teflon scraps in a quartz tube at a temperature of approximately 600° and a pressure of approximately 10^{-2} mm. The gas evolved was collected in a trap cooled with liquid nitrogen and consisted of 95% C_2F_4, 4% C_3F_6 and 1% C_4F_8, with traces of higher fluorocarbons. The components were separated and purified by gas chromatography on a two-meter silica gel column. The purified tetrafluoroethylene contained 0.1% C_3F_6 and less than 0.005% C_4F_8. It was stored as a gas at about 50 mm. pressure and showed no signs of polymerization or decomposition in a period of a year. Tetrafluoromethane, used as an inert gas, also was donated by the duPont Co. It contained 0.05% C_3F_8 and less than 0.1% C_2F_6. Prepurified nitrogen and Research Grade argon obtained from the Matheson Company also were used as inert gases.

Sampling and Analysis.—At the end of a run, the gas in the reactor was expanded into a dead space of about 20 ml. volume, this gas being discarded. The remainder of the gas was expanded into a one-liter bulb at room temperature. This bulb was detached and taken to the gas chromatograph. A Toepler pump was used to transfer the gas from the sample bulb to the 15 ml. sample loop through which the

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(1) Presented at the XVIIIth International Congress of Pure and Applied Chemistry, Montreal, Canada, 6–12 August, 1961.

(2) B. Atkinson and A. B. Trenwith, *J. Chem. Soc. (London)*, 2082 (1953).

(3) B. Atkinson and V. A. Atkinson, *ibid.*, 2086 (1957).

(4) B. F. Gray and H. O. Pritchard, *ibid.*, 1002 (1956).

carrier gas stream could be diverted. Analyses were made on a Perkin-Elmer model 154-C Vapor Fractometer, using a two-meter silica gel column and thermal conductivity detection. Carbon monoxide, tetrafluoroethylene, hexafluoropropene and octafluorocyclobutane could be separated at 100°. Carbon dioxide had the same retention time as tetrafluoroethylene at 100° but could be separated at room temperature. Carbonyl fluoride was hydrolyzed to carbon dioxide by the water which was always present on the column. Silicon tetrafluoride was irreversibly absorbed. Quantitative analysis was made using peak height ratios and calibration factors obtained by measuring gas mixtures of known composition under the same conditions. The measured composition of successive samples from the same reaction mixture varied by about 3%.

Side Reactions.—In addition to tetrafluoroethylene and hexafluoropropene, the reaction mixture contained carbon monoxide, silicon tetrafluoride,[4] carbon dioxide and possibly carbonyl fluoride.[5] These compounds resulted from the reaction of the fluorocarbons with the glass walls of the vessel, which were sufficiently etched after several months of service to appear frosted. Black flakes of solid, presumably carbon, also were found in the vessel. The over-all reactions which occur thus may be

$$2SiO_2 + C_4F_8 \longrightarrow 2SiF_4 + 4CO$$

$$2SiO_2 + C_4F_8 \longrightarrow 2SiF_4 + 2CO_2 + 2C$$

$$SiO_2 + C_4F_8 \longrightarrow SiF_4 + 2COF_2 + 2C$$

Silicon tetrafluoride was irreversibly adsorbed on the silica gel column, and carbonyl fluoride was hydrolyzed to carbon dioxide, so that the routine analysis only measured the amount of CO and the total amount of CO_2 and COF_2.

By knowing the initial pressure of C_4F_8 in the reactor and the final pressure of the reaction mixture, an approximate mass balance can be obtained. The principal uncertainty in such a calculation arises from being unable to separately measure the amounts of COF_2 and CO_2, and in the assumption of the simple stoichiometry above to calculate the amount of SiF_4.

If no COF_2 were formed and no material were lost, the initial pressure could be calculated from the final partial pressures

$$P_0 = P_{C_4F_8} + 1/2P_{C_2F_4} + 3/4P_{C_3F_6} + 1/4P_{CO} + 1/2P_{CO_2}$$

and the final total pressure, including SiF_4, calculated from the assumed stoichiometry, would be

$$P_f = P_{C_4F_8} + P_{C_2F_4} + P_{C_3F_6} + 3/2P_{CO} + 2P_{CO_2}$$

(If no carbon dioxide were formed and all the CO_2 measured came from the hydrolysis of COF_2, the above relation for P_0 would be the same, but the relation for P_f would then contain the term $3/2P_{CO_2}$ instead of $2P_{CO_2}$.) Since both initial and final pressures can be measured, as well as the relative amounts of the five compounds formed, the discrepancy between the measured and calculated initial pressures can be used to check if material is lost during the reaction.

The mass balance ratio is defined to be

$$R_m = \frac{P_0\,(\text{calculated}) - P_{C_4F_8}}{P_0\,(\text{measured}) - P_{C_4F_8}}$$

where the final partial pressure of C_4F_8 has been subtracted to make the ratio less dependent on the degree of decomposition. Mass balance ratios measured under a number of conditions of temperature and degree of decomposition are given in Table I. It will be noted that the mass balance ratio assuming only COF_2 is consistently lower than that calculated assuming only CO_2 but that neither shows any trend with temperature or per cent. decomposition. That the mass balance ratio assuming only CO_2 is closer to unity is not very strong evidence for the absence of COF_2. Polymerization could account for the lower mass balances even if only COF_2 were formed, although R_m might be expected to depend somewhat on the degree of decomposition in that case.

TABLE I

MASS BALANCE RATIOS

Temp., °C.	% decomp.	R_m assuming only CO_2	R_m assuming only COF_2
413.0	0.3	1.08	0.55
441.9	.7	1.07	.79
463.5	.4	1.04	.95
463.2	2.6	1.24	.88
482.5	5.7	1.61	1.56
512.7	4.8	1.02	0.58
513.1	11.7	1.03	.74
564.5	12.7	1.09	.67
564.2	75.6	1.02	.71

At the longest reaction times at 560°, a small peak following octafluorocyclobutane was observed and tentatively identified by its retention time to be octafluoroisobutene, since this compound was detected at higher temperatures by Atkinson.[3] The amount formed was too small for positive identification by infrared spectroscopy and too small to produce any observable effect on the mass balance ratio.

The formation of both CO and CO_2 was found to be approximately first order in tetrafluoroethylene. A rate constant for the formation of CO was calculated by the approximate relation

$$k_{CO} = \frac{1}{t}\,\frac{[CO]}{[C_2F_4]}$$

which does not allow for the increase of C_2F_4 from zero to the equilibrium value. As a result, constants calculated from short runs by this relation underestimate the true rate constant. In Table II are given a set of data obtained at 464° with wide variations in pressure and reaction time. Although the scatter is bad, it is apparent that the formation of CO is better described as first order in C_2F_4 than first order in C_4F_8.

The rate of formation of CO_2 (including COF_2 if present) appeared to vary with the age and history of the surface from 0.1 to 1.5 times the rate of formation of CO. The rate of formation of CO was more reproducible, and k_{CO} has an Arrhenius-type temperature dependence

$$k = 10^{7.5}\, e^{-43{,}000\ \text{cal.}/RT}\ \text{sec.}^{-1}$$

The rate of formation of CO was 20 to 200 times greater in a glass wool packed vessel.

Equilibrium Constants.—Since an accurate estimate of the rate constant for the formation of tetrafluoroethylene from octafluorocyclobutane re-

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(5) C. Willis, private communication, reports formation of COF_2 in many reactions of fluorine-containing compounds in glass vessels at high temperatures.

TABLE II

FORMATION OF CO AT 464°

Time, sec.	Press., mm.	$\frac{1}{t}\frac{[\mathrm{CO}]}{[\mathrm{C_2F_4}]} \times 10^6$	$\frac{1}{t}\frac{[\mathrm{CO}]}{[\mathrm{C_4F_8}]} \times 10^8$
2519	6.6	9.48	4.59
3610	76.6	5.37	3.94
3438	521.0	3.32	2.00
7517	1.15	7.88	11.6
12306	2.63	4.37	8.50
8985	30.5	5.24	8.57
21871	0.279	5.62	25.1
37695	0.524	4.64	32.8
17537	12.79	3.95	10.9
175920	177.8	8.46	11.5
171600	142.3	7.34	10.8
	Mean	5.97	11.85
	Std. dev.	2.01 = 30%	9.23 = 78%

quires an accurate knowledge of the equilibrium constant for this reaction, a study of the equilibrium was undertaken. Samples of octafluorocyclobutane and tetrafluoroethylene were pyrolyzed for varying lengths of time, the pressure being measured at the beginning and end of each run. The temperature range covered was from 413 to 565°, and the pressure range covered was from 20 to 700 mm. The partial pressures of C_2F_4 and C_4F_8 were calculated from the measured composition of the equilibrium mixture and the measured final pressure, assuming no COF_2 was formed. Because of the small amounts of side products, this could be done with greater accuracy than could an absolute calibration of the gas chromatograph. Neglecting COF_2 has negligible effect on the equilibrium constant. A least-squares straight line was fitted to a plot of log K *versus* $1/T$ for both the partial pressure and concentration equilibrium constant. Both K_p and K_c fitted a straight line equally well, as might be expected since the heat capacity change in the reaction is very small. The least-squares expressions obtained were (errors within 95% confidence limits)

$$K_p = \frac{P_{C_2F_4}{}^2}{P_{C_4F_8}} = 10^{13.7 \pm 0.5}\, e^{-51.400 \pm 1600 \text{ cal.}/RT} \text{ mm.}$$

$$K_c = \frac{[C_2F_4]^2}{[C_4F_8]} = 10^{8.6 \pm 0.5}\, e^{-49,900 \pm 1700 \text{ cal.}/RT} \text{ mole/l.}$$

K_c is consistent with the expression obtained from the ratio of the forward and reverse rate expressions given by Atkinson.[2]

Kinetics of Formation of Tetrafluoroethylene.—The kinetic expression for the reversible reaction of octafluorocyclobutane to form tetrafluoroethylene is

$$-\mathrm{d}[C_4F_8]/\mathrm{d}t = k_1[C_4F_8] - k_2[C_2F_4]^2$$

It can be directly integrated to give the following expression for k_1 in terms of measured quantities (the starting material is assumed to be pure C_4F_8)

$$k_1 = (2G/t)\,\{\tanh^{-1}[G(1 + 4P_0/MK_p)] - \tanh^{-1} G\}$$

where P_0 is the initial pressure; K_p is the partial pressure equilibrium constant

$$G = (1 + 16P_0/K_p)^{-1/2}$$

and

$$M = \frac{1}{2} + \frac{[C_4F_8]}{[C_2F_4]} + \frac{3}{4}\frac{[C_3F_6]}{[C_2F_4]} + \frac{1}{2}\frac{[CO_2]}{[C_2F_4]} + \frac{1}{4}\frac{[CO]}{[C_2F_4]}$$

In practice, the reaction could be allowed to proceed anywhere from 5 to 80% of the way to equilibrium without exceeding the error observed when the reaction was allowed to proceed just half-way to equilibrium. No trend of k_1 with degree of decomposition was observed.

The rate constant was measured over the temperature range from 360 to 560° and the pressure range from 0.003 to 600 mm. It was independent of pressure in the region above 10 mm. At high pressures, particularly at the higher temperatures where the reaction was fast, anomalously high rate constants were observed but were discarded in favor of those measured below 100 mm.

The rate constants measured as a function of temperature in the pressure region from 10 to 100 mm. fit the Arrhenius expression (errors are 95% confidence limits)

$$k_1 = 10^{16.0 \pm 0.2}\, e^{-74,300 \pm 800 \text{ cal.}/RT} \text{ sec.}^{-1}$$

These results are consistent with those of Atkinson.[2] No curvature of the Arrhenius line is detectable, but the large errors in the data at low temperatures (because the ratio $[C_4F_8]/[C_2F_4]$ was as large as 17,000 at 360°) do not preclude the possibility of a slight curvature.

Using the equilibrium constants measured, the rate of dimerization of tetrafluoroethylene can be calculated to obey the Arrhenius expression

$$k_2 = 10^{7.4 \pm 0.7}\, e^{-24,000 \pm 2500 \text{ cal.}/RT} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

This expression is consistent with that obtained by Atkinson[2] and Lacher, Tompkin and Park.[6]

Extensive measurements at lower pressures were carried out at 463, 510 and 560°, the rate constants being corrected to the standard temperature by using the above expression for k_1. At each temperature, the reciprocal of k_1 was plotted as a function of $P_0^{-1/2}$ and extrapolated to infinite pressure to obtain k_∞, as suggested by Rabinovitch.[7] The Arrhenius parameters for k_∞ are given in Table III.

TABLE III

ARRHENIUS PARAMETERS

$k_1 = Ae^{-E/RT}$

Pressure range, mm.	Average press., mm.	Number of points	Log A (Errors are 95%	E kcal. confidence)
Extrapolated	k_∞	3	15.79 ± 0.23	73.4 ± 0.8
10–300	....	62	16.03 ± .25	74.3 ± 0.8
5–10	7.3	11	15.92 ± .44	74.0 ± 1.6
2–5	3.0	7	16.23 ± .50	75.2 ± 1.8
1–2	1.5	9	15.36 ± .71	72.1 ± 2.5
0.5–1	0.70	8	14.93 ± .65	70.7 ± 2.3
.2–0.5	.31	11	15.46 ± .45	72.8 ± 1.6
.1– .5	.13	6	15.76 ± 2.96	74.0 ± 10.2
0.05– .1	.073	5	14.13 ± 2.24	68.2 ± 8.1
.01– .03	.021	6	15.36 ± 1.45	72.9 ± 5.2
0.003– .006	.0045	2	13.91	67.5

The ratios of the rate constants obtained at various pressures to the extrapolated infinite pressure rate constant at each temperature are plotted in Fig. 1. In spite of the bad scatter in the points, it is apparent that the rate constant does not fall

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(6) J. R. Lacher, G. W. Tompkin and J. D. Park, *J. Am. Chem. Soc.*, **74**, 1693 (1952).

(7) B. S. Rabinovitch and K. W. Michel, *ibid.*, **81**, 5065 (1959).

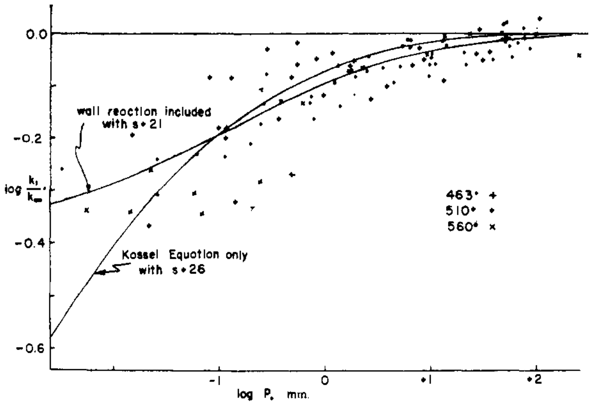

Fig. 1.—Pressure dependence of k_1 at three temperatures.

off indefinitely as the pressure is decreased, but approaches a limiting value about two-thirds of the infinite pressure rate. Two theoretical curves are drawn on the same diagram: one using the classical theory of unimolecular reactions without any modifications, the other with an additive pressure-independent term.

One form of the general rate expression for a homogeneous unimolecular reaction is[8,9]

$$\frac{k}{k_\infty} = I_s\left(\frac{\omega}{A}\right) = \frac{1}{(s-1)!}\int_0^\infty \frac{x^{s-1}\,e^{-x}\,dx}{1+\frac{A}{\omega}\left(\frac{x}{b+x}\right)^{s-1}}$$

where A is the pre-exponential factor in the Arrhenius expression for k_∞; s is a fall-off parameter, identified as the number of effective oscillators; E_0 is the activation energy for k_∞; $b = E_0/RT$; $\omega = \frac{4\pi\sigma^2 NP}{RT}\left(\frac{\pi RT}{M}\right)^{1/2}$ is the frequency of collisions at pressure P; σ is the collision diameter of the molecule.

To obtain the curves in Fig. 1, σ was chosen to be 5.5 Å., and b was chosen to be 44, corresponding to 565°. A table of the integral[10] was used to evaluate k/k_∞ as a function of pressure. For the simple curve, the best fit was obtained using s = 26. For the other curve, the rate was assumed to be compounded of a pressure-dependent rate k' and a pressure independent rate which was assumed to be two-thirds of the infinite pressure rate. The pressure dependence is then given by

$$k/k_\infty = 0.60I_s + 0.40$$

For this curve, the best fit was obtained using s = 21. By adjusting σ or b, the position of the curves on the pressure axis can be changed considerably, and an equally good fit could be obtained with different values of s.

The Kassel parameter s can be related to the Slater parameter n, the number of effective normal vibrational modes which contribute to the reaction.[10] For a comparable fit to the curves of Fig. 1 using the Slater expression, n would be 21 or 22, compared to the 30 possible modes of vibration of the octafluorocyclobutane molecule. Other molecules with 30 possible modes of vibration which have been investigated are *cis*-butene-2, with n = 28 giving the best fit to the pressure fall-off[7]; and methyl cyclopropane,[11] for which s = 19 or n = 19. Thus n = 21 is a reasonable value for octafluorocyclobutane.

The question arises as to whether the pressure-independent rate component observed at low pressures is due to activation of molecules by collision with the walls or to a concurrent heterogeneous reaction. At the lowest pressure (0.003 mm.) the mean free path of a C_4F_8 molecule is 2 cm., so that in going from the center of the reactor to the wall (a distance of 7 cm.), a molecule suffers three or four collisions. If activating collisions with the walls were just as effective as collisions with other molecules, one would expect that the pressure-independence would not become apparent until the mean free path became large compared with the radius of the vessel, perhaps at 5×10^{-4} mm. Thermal transpiration could cause the measured pressure to be lower than the pressure in the reactor, and hence produce at least part of the observed leveling off.

Thus it becomes important at low pressures to distinguish three different types of wall reaction: (1) Simple activation of molecules by collision with the walls, imparting energy to the molecules. (2) Reaction of molecules adsorbed on the walls leading to the same products as the homogeneous reaction. (3) Reaction of molecules with the material of the walls to produce other products.

Certainly a reaction of type 1 will occur at sufficiently low pressures. Reactions of type 3 are responsible for the formation of CO, CO_2 and SiF_4. If a reaction of type 2 occurs, it has an activation energy which is almost the same as the activation energy of the homogeneous reaction. The points obtained at various pressures were grouped into narrow ranges and each group was fitted to an Arrhenius temperature dependence. The results are given in Table III. The activation energy decreases slightly with decreasing pressure, being possibly three or four kilocalories below the high-pressure limit at the lowest pressures. This is consistent with the classical theory of unimolecular reactions[9] which would predict a decrease of about three kilocalories. The activation energy in a 100 ml. glass-wool-packed reactor having 50 times the surface/volume ratio of the 1-liter reactor is the same as in the 1-liter flask, although the rate at a given temperature is 30 times as large in the packed vessel.

On the other hand, heterogeneous reactions appear to be unimportant for the formation of tetrafluoroethylene at high pressures. Atkinson[2] showed that the same rate was obtained in a Pyrex vessel and an iron vessel at 550°. A 1-liter carbon-coated pyrex reactor (seasoned from the pyrolysis of hydrocarbons) gave rates that were the same as those obtained in a clean vessel. Exposing the surface to oxygen caused a temporary increase in the rate, but this is believed to be due to the catalytic effect of oxygen in the gas phase, discussed later. A clean 100 ml. reactor gave rates which

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[8] L. S. Kassel, "Kinetics of Homogeneous Gas Reactions, Reinhold Publishing Company, New York, N. Y., 1932.

[9] N. B. Slater, "Theory of Unimolecular Reactions," Cornell University Press, Ithaca, N. Y., 1959.

[10] E. W. Schlag, B. S. Rabinovitch and F. W. Schneidel, *J. Chem. Phys.*, **32**, 1599 (1960).

[11] J. P. Chesick, *J. Am. Chem. Soc.*, **82**, 3277 (1960).

were initially about 20% higher than those obtained with a 1-liter reactor at the same temperature but which decreased after a number of runs to approximately the same rate. These results are consistent with the interpretation of the pressure-independence as a reaction of type 2. In a sufficiently large reactor perhaps a more accurate pressure-fall off curve could be obtained.

Kinetics of Formation of Hexafluoropropene.—Hexafluoropropene is formed at a much slower rate than is tetrafluoroethylene, so that in practice the equilibrium between C_2F_4 and C_4F_8 was fully established by the time enough C_3F_6 had been formed to allow analysis. Under these conditions it is difficult to distinguish between a rate which is first order in C_4F_8 and a rate which is second order in C_2F_4. Atkinson,[3] on the basis of experiments where the contact time was very short, showed that C_3F_6 is initially formed more rapidly from C_4F_8 than from C_2F_4 and hence that the reaction is first order in C_4F_8. The results are thus best explained by the mechanism

$$C_4F_8 \xrightarrow{k_1} 2C_2F_4$$

$$C_4F_8 \xrightarrow{k_3} C_3F_6 + CF_2$$

$$2C_2F_4 \xrightarrow{k_2} C_4F_8$$

$$CF_2 + C_2F_4 \longrightarrow C_3F_6$$

Since in most of the experiments the amount of C_4F_8 was not seriously depleted during the course of the reaction, the mechanism above yields the approximate rate expression

$$k_3 = \frac{1}{2t}\frac{[C_3F_6]}{[C_4F_8]}$$

The rate of formation of C_3F_6 was measured at temperatures from 463 to 565° and at pressures from 20 to 600 mm. Within the experimental error no variation of k_3 with pressure could be detected. At the highest temperature, k_3 appeared to increase linearly with time, as shown in Fig. 2. This effect was not observed at lower temperatures.

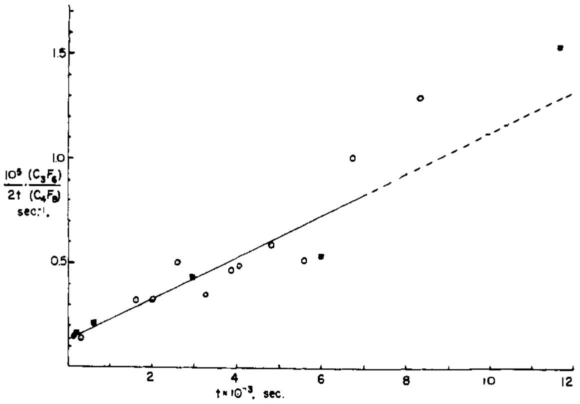

Fig. 2.—Apparent rate constant for the formation of hexafluoropropene as a function of reaction time at 560°: O, pure octafluorocyclobutane; ■, octafluorocyclobutane with one part in 10^5 of oxygen used.

When the products of reaction for 5000 sec. at 560° were removed from the reactor, distilled so that only C_2F_4, C_3F_6 and C_4F_8 remained, and then re-introduced to the reactor, the rate of formation of C_3F_6 was the same as if pure C_4F_8 were used as the starting material. This indicates that none of these three compounds catalyzes the reaction. A possible mechanism for catalysis involves the formation of some higher-boiling polymer of C_2F_4, perhaps C_6F_{12} or a surface film on the walls of the flask. It could not be too stable since it was removed by only a few minutes pumping on the reactor. If this compound decomposed slowly to give C_3F_6 among other things, at a rate which depended on the amount of compound, this could account for the increase in k_3 with time. If such steps are incorporated in the reaction scheme, the true k_3 is obtained by extrapolating the apparent k_3 to zero reaction time. Two arguments against this explanation are that it predicts a decrease of mass balance ratio at high temperatures and high degrees of conversion, an effect which is not observed (Table I) and that the extrapolated k_3 falls somewhat below the Arrhenius extrapolation of the lower temperature data.

In Fig. 3 are plotted the average values of k_3 obtained at each temperature, except for 560° where k_3 was obtained by extrapolation to zero reaction time. On the same figure are plotted the data obtained by Atkinson[3] using a flow system with a nickel pyrolysis tube. The rate obtained at 550° with the nickel tube is about 55 times as large as the rate obtained with a Pyrex vessel at the same temperature. A probable explanation is that the nickel surface catalyzes the decomposition. In a 100 ml. Pyrex reactor packed with glass wool having 50 times the surface-to-volume ratio of the one-liter Pyrex flask the rate of formation of C_3F_6 was about 10 times as large. This indicates that the rate measured in the one-liter vessel is principally the rate of the homogeneous decomposition.

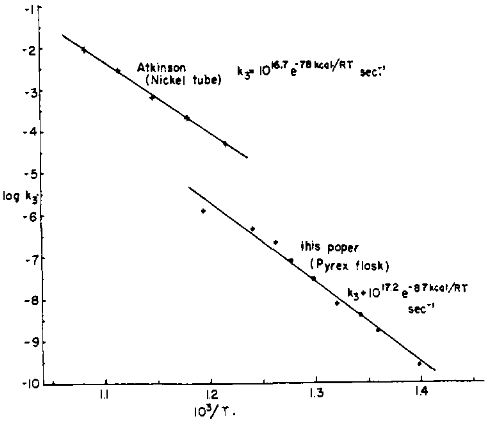

Fig. 3.—Comparison of k_3 obtained by Atkinson using a flow system with a nickel tube with the results of this paper using a one-liter Pyrex flask.

The Arrhenius expression for the rate constant obtained by a least-squares fit of the data is

$$k_3 = 10^{17.2 \pm 2.4} e^{-87,000 \pm 8000 \text{ cal.}/RT} \text{ sec.}^{-1}$$

If k_3 truly represents the rate constant for an elementary unimolecular reaction, its frequency

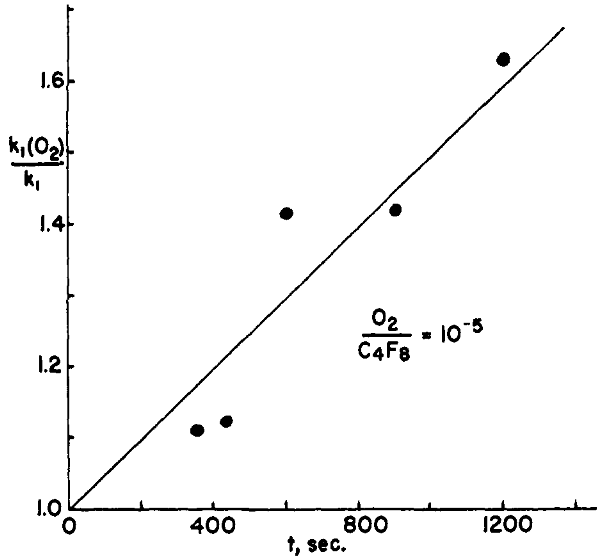

Fig. 4.—Ratio of k_1 obtained with octafluorocyclobutane containing one part in 10^5 of oxygen to k_1 obtained with pure octafluorocyclobutane, as a function of reaction time.

factor is among the highest directly measured.[12] In the case of the formation of C_3F_6 and CF_2 from C_4F_8, the transition state would be a distorted ring with two adjacent bonds longer than the other two. The entropy of activation calculated from the frequency factor of k_3 is 19 cal./deg. In the case of the formation of C_2F_4 from C_4F_8, the transition state would be a rectangular ring where two opposite bonds are simultaneously lengthened. The entropy of activation calculated from the frequency factor of k_1 is 14 cal./deg. It is not unreasonable that the first transition state, being of lower symmetry, should have the higher entropy.

Effect of Oxygen and Inert Gases.—Addition of one part in 10^5 of oxygen to octafluorocyclobutane caused the first-order rate constant for the decomposition to tetrafluoroethylene to increase as the reaction time increased, as is shown in Fig. 4. Addition of oxygen had no effect on the formation of C_3F_6, as can be seen from Fig. 2. Experiments to determine the efficiency of inert gases in activating C_4F_8 molecules were unsuccessful. Carbon tetrafluoride, argon and nitrogen all gave rather unreproducible rates, often as large as twice the high-pressure limiting rate in the absence of inert gas. Apparently small residual traces of oxygen in the inert gases were the cause of this difficulty. Only one part per million of oxygen in the inert gas would be necessary to produce this effect.

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[12] C. Steel and K. J. Laidler, *J. Chem. Phys.*, **34**, 1827 (1961).