

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Thermal Reaction of Hexafluoroethane with Quartz

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That the introduction of many fluorine atoms into organic molecules tends to impart a high degree of stability is well known. Midgley and Henne² have indicated the increase in general stability and in resistance to hydrolysis when two fluorine atoms are introduced upon the same carbon atom, this stabilizing influence extending to bonds of other carbon atoms. Brockway³ has correlated their results with measurements, showing reduction of bond distances in cases of stabilization. In itself, the carbon to fluorine bond has an extremely high dissociation energy.⁴ In order to gain insight into the extent of this stabilizing tendency in the case of the saturated hydrocarbons, it seemed advisable to undertake the thermal decomposition of hexafluoroethane. Comparison with results obtained under similar conditions with much-studied ethane might be expected to yield significant information. Use of the completely fluorinated compound would eliminate possible anomalies due to the presence of a third atomic species, and would presumably simplify the experimental problems by removing the possibility of encountering hydrogen fluoride among the products.

According to Swarts,⁵ a platinum wire heated to redness in an atmosphere of rigorously dry hexafluoroethane caused a slow increase of pressure, but his data were not capable of kinetic interpretation.

Experimental

Apparatus and Materials.—The apparatus consisted essentially of a 200-cc. quartz reaction cell attached through a Pyrex-quartz seal and a stopcock to a 2-liter storage flask. Both these flasks were provided with manometers, and in addition the reaction flask was connected to a mercury reservoir in which the mercury level could be raised or lowered to stir the gas in the reaction system; the latter was provided with a ground-glass mercury float cut-off placed just above the reservoir, to prevent overflow of mercury into the reaction cell and to give a positive boundary for the reaction system. Since early experiments indicated that no free fluorine was formed, the use of stopcocks elsewhere was safe. The whole system could be evacuated. In order to hold the volume of the reaction system external to the furnace to a minimum, and thereby to reduce the magnitude of the "dead-space" correction in subsequent calculations, as much as possible of the connecting tubing in the reaction system was made of 2 mm. capillary.

Preliminary experiments had indicated an extremely small temperature coefficient of reaction, so that hand control of the heating was considered adequate. Fluctua-

tions were kept within about $\pm 1/2^\circ$, and since it was not necessary to know the temperature with great precision, it was measured with an uncalibrated chromel-alumel thermocouple.

For analysis of the products, the device described by Haden and Luttrupp⁶ was used. This consists essentially of a McLeod gage with a 500-cc. bulb, having a small chamber of about 2 cc. connected above the capillary through a stopcock. This chamber could be separately evacuated, and was closed with a ground glass joint having a cup for the introduction of analytical reagents. It was also possible to use this apparatus as a Töpler pump to collect material from the reaction system.

Hexafluoroethane of about 99.4% purity was supplied by du Pont through the Naval Research Laboratory. The principal impurity was believed by them to be tetrafluoroethylene. At one stage of the experiments a crack in the apparatus admitted the atmosphere into the storage flask. For repurification, the condensable gas was several times condensed in a liquid air trap, the non-condensed gas being pumped off each time. Also an appreciable part of the condensed residue was discarded toward the end of the re-evaporation, in order to remove water and carbon dioxide. In addition, a Dry Ice-acetone cooling bath was placed around a trap of the reservoir system, through which the sample would have to pass, and left there for about half an hour before a sample was taken for a run. Passage of the sample through the cold trap ensured complete absence of water vapor.

Procedure.—The experimental procedure was to introduce the hexafluoroethane into the reaction cell at a known temperature and to read the pressure as a function of time.

The introduction of cold starting material into the reaction system resulted in pressure increase, due only to heating, before reaction had set in. This necessitated a certain degree of arbitrariness as to what pressure corresponded to the actual initial conditions, and as to what time after the introduction of the sample was the true starting point. That the choice made was not too seriously in error is indicated by the fairly consistent values of $\Delta P/\Delta t$ during the early stages of the runs. The uniform curves during any one run indicate adequate accuracy in the measurement of the pressure increments. The reproducibility from run to run was not as good, but this must be attributed to the character of the reaction and not to experimental error.

When the reaction was allowed to go to completion to allow analysis of the products, the gas in the reaction system was stirred toward the end of the run by lowering and raising the mercury in the reservoir, so that the gas in the connecting tubing was eventually forced into the hot reaction cell and decomposed also; after this the final pressure was read.

In cases of complete reaction, the products were separated into fractions condensable and non-condensable with liquid air. The non-condensable fraction was pumped off, and the condensable fraction allowed to evaporate into the reaction bulb, its pressure being then measured; the pressure of the condensable fraction may be obtained by difference. The molecular weight of each fraction was determined by the Dumas method of direct weighing. The bulbs used for the weighings were designed primarily for storage purposes and so were heavier than would have been best for the molecular weight determinations. The pressures were sufficiently low so that use of the perfect gas law introduced no appreciable error. The results are estimated to be correct within one per cent.

The Haden-Luttrupp modified McLeod gage was used

(6) Haden and Luttrupp, *Ind. Eng. Chem., Anal. Ed.*, **13**, 571 (1941).

(1) Present address: Southern Research Institute, Birmingham, Ala. This work was performed as part of a contract between the Naval Research Laboratory and the University of North Carolina.

(2) Midgley and Henne, *THIS JOURNAL*, **47**, 882 (1936).

(3) Brockway, *J. Phys. Chem.*, **41**, 185 (1937).

(4) See Rice, "Electronic Structure and Chemical Binding," McGraw-Hill Book Co., New York, N. Y., 1940, p. 190.

(5) Swarts, *Bull. soc. chim. Belg.*, **42**, 114 (1933).

for the subsequent analyses. Silver oxide was used to absorb carbon monoxide from the non-condensable gas, after the method of Blacet, MacDonald and Leighton.⁷ Some of the oxide oxidizes the monoxide to dioxide, which reacts with residual silver oxide to form the carbonate. Absorptive speed of different samples of silver oxide varied widely, and it was found that complete absorption could be depended upon only when a lengthy additional exposure to reagent produced no pressure change. In all cases tested it seemed that the oxidation to carbon dioxide proceeded much faster than the subsequent absorption; therefore, in the later tests, exposure to silver oxide for oxidation were alternated with exposures to potassium hydroxide, which was a much more effective agent for absorption. The optimum conditions for the analysis were not obtained in the time available, but, within a very few per cent., the entire non-condensable fraction was absorbed by these reagents.

The condensable fraction was essentially entirely soluble in a volume of water several times its own volume, giving in the process of solution a flocculent white precipitate. The solution etched the glass of the flask in which it stood for several days. After filtration, the precipitate was ignited to incandescence without apparent change. After completion of the runs, the interior of the quartz reaction flask in the furnace was observed to have been very uniformly etched. (The outside of the flask had apparently suffered much the worse attack; it was coated with a white scale which seemed to be devitrified quartz.) These observations indicated that a large part of the condensable fraction was silicon tetrafluoride, hydrolyzing to silicon dioxide upon contact with water. The remainder seemed to be carbon dioxide. At -114° with an uncalibrated pentane thermometer, the condensed mixture had a vapor pressure of 139 mm., in reasonably satisfactory agreement with the sum of the pressures of silicon tetrafluoride and carbon dioxide, in view of the rapidity with which the vapor pressure of silicon tetrafluoride changes with the temperature. Reagents used in the attempt to analyze this fraction were dilute hydrochloric acid solution (for

this micro procedure, placed on a small cotton plug in the top cell of the Haden-Luttrupp apparatus) and potassium hydroxide. The hydrochloric acid solution decomposed the silicon tetrafluoride and presumably absorbed almost all of the hydrofluoric acid produced. The acid present prevented very much absorption of carbon dioxide. Subsequent exposure to potassium hydroxide then removed the carbon dioxide. The analysis made on this basis gives a molecular weight which agrees very well with that determined for the mixture.

Results

The experimental results are recorded in Fig. 1 and Tables I and II.

Figure 1 shows the time-pressure data for the significant runs made, omitting earlier runs with greater dead space. It is obvious from this figure that the rate of reaction depends very little on temperature and very strongly on pressure. While it appears fairly obvious that it will not be possible to get any correlation of order with mechanism in this case, nevertheless, on account of the appreciable dead space, even in the runs reported, it appeared desirable to apply the method of Allen⁸ to determine the apparent order. The conclusion of his attack is that

$$\log \frac{dP}{dt} - \log T = \text{constant} - n \log R$$

in which P is pressure, t is time, T is the absolute temperature, n is the order, and R is the number of moles of reactant left unreacted at time t (R must be calculated from the experimental results by the procedure given by Allen). These quantities are plotted in Fig. 2, with R' signifying the mean value of R during the time interval covered

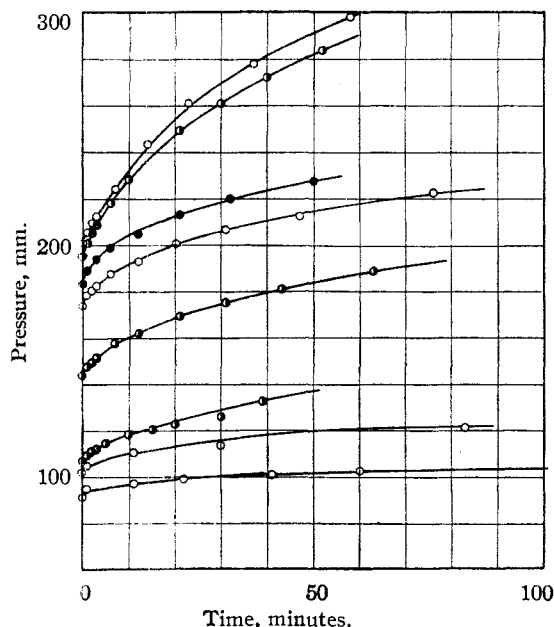


Fig. 1.—Reaction velocity measurements: hot volume, 207 cc.; cold volume, 24 cc. + 0.063 pressure in cm.; furnace temperatures: \circ , 1073 to 1074 $^{\circ}$ K.; \bullet , 1084 $^{\circ}$ K.; \blacksquare , 1114 to 1115 $^{\circ}$ K.; external temperatures 303 to 305 $^{\circ}$ K.

(7) Blacet, MacDonald and Leighton, *Ind. Eng. Chem., Anal. Ed.*, **5**, 272 (1933).

TABLE I
MOLECULAR WEIGHTS AND PRESSURE RATIOS

Run	Init. press., mm.	Temp., $^{\circ}$ K.	Molecular weights		Pressure ratios	
			Con-densed	Non-con-densed	Final init.	Cond. init.
2	110	1000	81	..	3.24	..
3	143	1069	..	31.9	3.26	..
4	125	1112	80	30.8	3.23	2.20
5	121	1102	81	30.2	3.19	2.21
10	183.5	1084	3.18	2.23
13	144	1114	3.37	..
		Av.	81	31.0	3.25	2.21

TABLE II
ANALYSIS OF CONDENSED FRACTION

Pressure of sample, mm.	339	257
Pressure after H ₂ O-HCl	168	...
Temperature, $^{\circ}$ C.	31	30
Pressure above H ₂ O vapor	135	...
Pressure after KOH	37	31
Pressure above H ₂ O vapor	4	0
Apparent percentage of CO ₂ , %	39.8	...
Apparent percentage of SiF ₄ , %	60.2	...
Molecular weight of mixtures using apparent percentages	80.1	

(8) Allen, *THIS JOURNAL*, **56**, 2053 (1934). In making these calculations q was taken equal to 3.20 (see Table I below). Calculations were also made with $q = 3.50$, but this produced no significant changes.

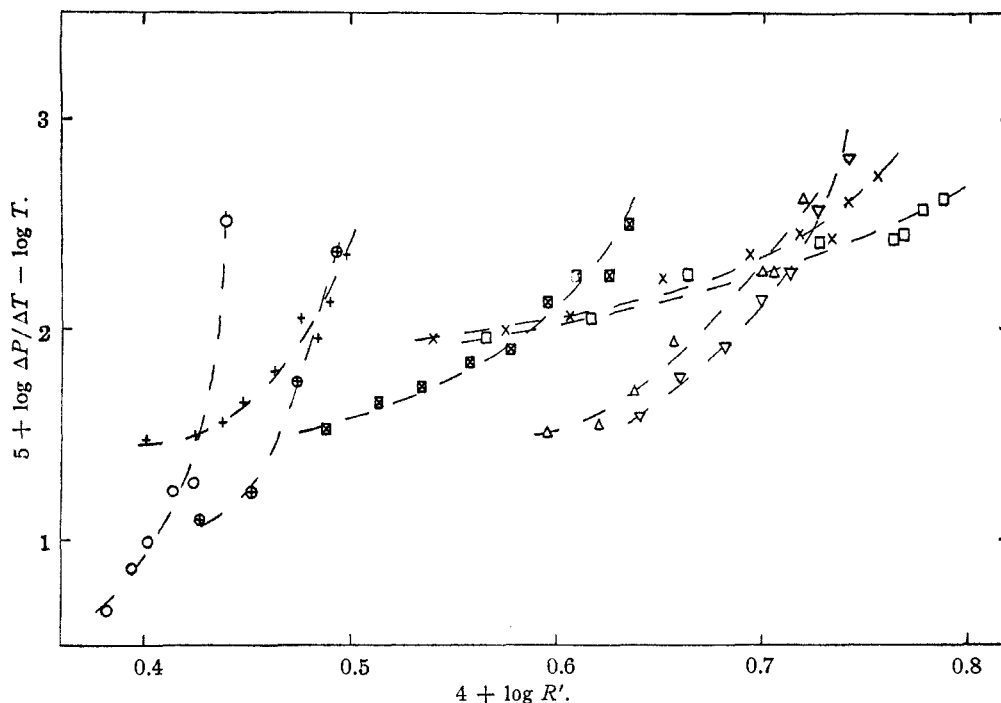


Fig. 2.—Analysis of reaction-rate data: run numbers, temperature in °K., and initial pressure in mm.: O, 6, 1073, 91.5; ⊕, 7, 1074, 102.0; □, 8, 1074, 201.0; Δ, 9, 1073, 174; ▽, 10, 1084, 183.5; ×, 11, 1115, 195.0; +, 12, 1115, 107.0; square with cross inside, 13, 1114, 144.0.

by each point and with additive constants being introduced to keep the numerical values convenient in magnitude. The slopes of the curves should give the reaction orders.

The apparent order of the reaction is seen to vary widely and the mechanism must be quite complex.

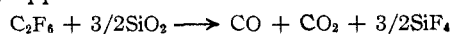
The temperature coefficient of the reaction is extremely low. A later test at 589°C. gave no measurable pressure increase in forty minutes, while 710°C. produced barely perceptible reaction.

The product analyses indicate that some part of the over-all reaction is heterogeneous. However, these two characteristics of the rate measurements, variable order and low temperature coefficient, show specifically that the rate-determining step is heterogeneous. It seems quite definite that homogeneous decomposition is not yet appreciable at 842°C., so low is the temperature coefficient.

Tables I and II are self explanatory: molecular weights of condensed and non-condensed fractions; ratios of final to initial pressures and of condensable product to initial pressures; and analysis of the condensable fraction.

Discussion

A survey of all these data indicates that the over-all reaction, by however complex a mechanism, approximates



From Table I it is seen readily that the ratio of the pressure of non-condensed gases to initial pressure is approximately unity, as required by this equation, and, as noted above, the gas appears to be carbon monoxide; it must be mixed, however, with a small amount of other gas which, from the average measured molecular weight, must be a gas of high molecular weight, possibly in part, unreacted C_2F_6 . Two per cent. of C_2F_6 would give a molecular weight of 30.6. Such a percentage of C_2F_6 would in runs 3, 4 and 5 require a final pressure of approximately 2.5 mm. of C_2F_6 in the reaction flask at the end of the run. It might be expected that this would appear with the condensable rather than the non-condensable fraction, since this pressure is considerably higher than the vapor pressure of C_2F_6 at liquid air temperatures, about 90°K., which is estimated by a long extrapolation from data of Ruff⁹ (using Ruff's equation) to be about 0.004 mm. However, in pumping off the non-condensable from the condensable gases, the pumping was done into a volume nearly three times the volume of the reaction flask at an absolute temperature only about one-fourth as great. This would effectively multiply the pressure by about ten-fold, and with six or eight pumpings the effective multiplication factor could be sixty- or eighty-fold. This still would not bring the estimated pressure to 2.5 mm.; we can only say that it seems likely that part of the discrepancy of the

(9) Ruff, *Z. anorg. allgem. Chem.*, **210**, 173 (1933).

molecular weight arises from the presence of unreacted C_2F_6 . There may be some other heavy gas present in small quantities, arising either from impurity or side-reaction.

The condensed fraction has, as nearly as may be judged, the composition, molecular weight, and vapor pressure (at -114°) to be expected from the proposed equation. The ratio of pressure of condensed gas to initial pressure is, however, low, so that it appears that not all of the original material is accounted for. In this connection it may be mentioned that small amounts of a gray-white solid product were deposited in the reaction system outside the furnace. A similar phenomenon was recorded by Swarts.⁵ In our case this effect was more noticeable in some preliminary runs with slightly contaminated gas. During the rest of the runs the deposition was much less noticeable, but it apparently continued to some extent. Whether it was sufficient to account for the missing material is difficult to decide.

In the introduction it was indicated that a comparison with the measured decomposition of ethane might be significant. Schumacher's¹⁰

(10) Schumacher, "Chemische Gasreaktionen," Verlag Theodor Steinkopf, Dresden, 1938, p. 154.

summary of the studies of ethane indicate that homogeneous decomposition becomes appreciable at around $850^\circ K$. The fact that homogeneous decomposition of the hexafluoroethane is inappreciable nearly 250° higher indicates a degree of stability out of the class of the hydrocarbons.

Summary

On the basis of measurements in the range, $800-842^\circ C$., the thermal decomposition of hexafluoroethane in quartz has been demonstrated to be a complex heterogeneous reaction. Minimum temperature for reaction is about 600° , but it seems highly probable that homogeneous decomposition does not occur even at 842° . This places hexafluoroethane among the most stable of known organic compounds. In a quartz vessel the predominant reaction seems to be



with, however, some loss of material, which possibly is contained in a gray-white solid which distills out of the reaction flask.

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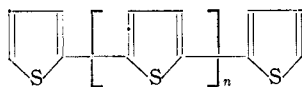
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Chromatographic and Spectral Characteristics of Some Polythienyls

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During an investigation of certain plant materials we became interested in some representatives of the α -polythienyl series, which is characterized by the following formula



While 2,2'-bithienyl ($n = 0$) has been known for some time,^{1a} the compounds with $n = 1$ to 4 have been prepared only recently by Steinkopf and his collaborators.² They found that a mixture of several members of this series is formed by the interaction of 2-iodothiophene and copper bronze, and that the mixture can be separated by distillation and crystallization procedures. We wish to report that such a resolution can be advantageously carried out by chromatographing on alumina from petroleum ether or carbon bisulfide solution. The adsorption affinity decreases markedly with n , so that terthienyl, quaterthienyl, and quinquethienyl ($n = 1$ to 3) form well-separated zones whose migration

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(1a) Cf. the monograph, W. Steinkopf, "Die Chemie des Thiophens," Th. Steinkopff, Dresden, 1941.

(2) W. Steinkopf, R. Leitsmann and K. H. Hofmann, *Ann.*, **546**, 180 (1941).

can best be followed during development by their fluorescence in ultraviolet light. Bithienyl is rapidly washed into the filtrate. Furthermore, the Tswett column allows a homogeneity test by which traces of higher or lower members of the series may be easily detected in a given sample.

So far as we know the spectral curves of the polythienyls have not yet been reported. As expected, an increase of the number of thienyl residues in the molecule shifts the position of the main maximum toward longer wave lengths (Figs. 1-2; Table I). In hexane solution a secondary peak, whose position is independent (within 5

TABLE I
MOLECULAR EXTINCTION COEFFICIENTS (MAXIMA) FOR
SOME α -POLYTHIENYLS

	In hexane		In benzene	
	$m\mu$	$E_{mol.}^{1 cm.} \times 10^{-4}$	$m\mu$	$E_{mol.}^{1 cm.} \times 10^{-4}$
Thiophene	231	0.56
Bithienyl	301	1.23	305	1.21
Terthienyl	350	2.31	355	2.19
Quaterthienyl	385	3.45	391	3.20
Quinquethienyl	418	3.81
1-Methyl-terthienyl	355	2.41
1,8-Dimethyl-terthienyl	359	2.61