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Pyrolysis of Fluorocarbons¹

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The pyrolytic decomposition of several gaseous fluorocarbons held in contact with a heated platinum filament has been studied at various temperatures and pressures. Apparently the filament acts as a catalyst. Under the conditions used the rate of decomposition increases in the order: C_2F_6 , cyclo- F_6F_{10} , C_3F_8 , $n-C_4F_{10}$, $n-C_6F_{12}$. The observed decomposition of octafluoropropane is a first-order reaction having an experimental activation energy of about 84 kcal. per mole. In the case of hexafluoroethane the experimental evidence does not lead to a clear interpretation; however, it strongly suggests that the reaction is first order with an activation energy close to 51 kcal. per mole. Pyrolysis of each of the compounds listed above gives rise to a gaseous product, a high polymer and a trace of carbon. Two unsaturated fluorocarbons, hexafluoropropene and octafluoro-2-methylpropene found in the products have a high degree of thermal stability. While the experiments do not establish reaction mechanisms, they do indicate that the primary rupture in the molecule occurs at a carbon-carbon bond and that resulting unsaturated molecules or free radicals combine to form polymers.

In spite of the fact that saturated fluorocarbons have been known for some time to be much more stable than the corresponding hydrocarbons, little quantitative information regarding their pyrolysis is available. The first qualitative work in the field was that of Swarts² who found that perfluoroethane decomposed slowly in the presence of a glowing platinum filament forming both a white solid and a gas made up principally of carbon tetrafluoride. Swarts held the opinion that the gas probably also contained hexafluorobenzene and perfluorocyclohexane. Much later, Lewis and Naylor³ reported that the thermal decomposition of polytetrafluoroethylene, an essentially saturated polymer, occurred at 600 to 700° and yielded the monomer, tetrafluoroethylene, together with relatively small amounts of octafluorocyclobutane and the compound now known to be hexafluoropropene. The pyrolysis of tetrafluoroethylene in the presence of a platinum filament at 1340° has been found by Harmon⁴ to produce C_3F_6 (hexafluoropropene). At temperatures between 125 and 500° he observed that the dimer, octafluorocyclobutane, was produced but that contact of this substance with a hot platinum filament resulted in its decomposition to form tetrafluoroethylene and C_3F_6 (hexafluoropropene). The dimerization reaction has been studied by Lacher, Tompkin and Park⁵ who found the change to be homogeneous and of the second order.

Rogers,⁶ in this Laboratory, studied the thermal decomposition of dodecafluoro-*n*-pentane. The complex nature of the products obtained indicated that the reaction was not simple. It was felt, therefore, that a systematic study of the pyrolysis of fluorocarbons should commence with the most simple of these substances. The present paper is the direct result of this opinion.

Experimental

Apparatus.—The apparatus consisted of an assemblage of the following units: (1) a pyrolysis vessel, (2) a manometer for measuring gas pressure, (3) a gas density balance, (4) a

Toepler pump for moving the gas from one part of the system to another, (5) a system for drying fluorocarbons and for purifying them by removal of atmospheric gases, (6) a fractionating column suitable for analyzing the gaseous products, (7) pumps for evacuating the system, (8) other equipment used to prepare and handle the materials, to measure temperatures, etc.

The pyrolysis vessel was constructed from a 31-cm. length of copper tubing having an inner diameter of 7.6 cm. All of the metal parts were copper, bronze or brass and they were silver-soldered in place. In order that the inner surface might be clean and free from oxide it was gold-plated. The total volume was 1480 cc. An electrically heated filament, a 30-gage platinum wire 25.7 cm. long, extended horizontally along the axis of the vessel. It was supported at one end by a tungsten spring which partially compensated for thermal expansion and at the other end by a copper tube which also acted as an electrical ground. The temperature of the wire when heated was uniform, except at the ends. A fitting at one end of the vessel allowed the filament and its supports to be removed as a unit. The fitting was made gas-tight by Apiezon M stopcock lubricant, some of which was unavoidably in contact with gas in the system. A constant voltage transformer was used as the source of power for the filament. The side of the chamber was provided with a Kel-F (polychlorotrifluoroethylene), plastic window through which the filament temperature was measured with a Leeds and Northrup optical pyrometer. Corrections for the emissivity of platinum,⁷ taken as 0.33 varied from 73 to 120° over the temperature range observed. The optical absorption of the window also required a correction of 14 to 25° which was determined by observing how much the presence of the window lowered the apparent temperature of the filament. The accuracy of the pyrometer was checked by focusing it on a chromel-alumel thermocouple held at various temperatures in a furnace. It was found to be correct within the experimental error involved in taking the readings. While temperature measurements could be reproduced to within $\pm 5^\circ$ it is possible that the observed values did not have this degree of accuracy. Changes occurring in the nature of the platinum surface may have changed the emissivity factor.

The pyrolysis vessel was cooled externally by jets of water to prevent softening of the lubricant on the fitting.

A Kovar metal-glass seal joined copper tubing leading from the pyrolysis vessel to the remainder of the system, which was made of Pyrex glass.

Procedure.—The reaction vessel was cleaned, assembled and left evacuated for a few hours to test for leaks. For a period of about an hour the filament was held at approximately 1300°, then it was cooled. A sample of pure dry fluorocarbon was then admitted to the evacuated vessel and the filament was heated to the desired temperature. As the reaction progressed it was followed by observing the pressure of the gas and by occasionally measuring its density. While the density was being determined the filament was cold. The filament was heated only when all of the gas was present in the pyrolysis vessel and the manometer to which it was connected. A new filament was used for each run.

(1) Presented in part at the New York Meeting of the American Chemical Society, Sept. 3, 1951. This paper is based upon the Ph.D. thesis of R. K. Steunenberg, 1951.

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

(3) E. E. Lewis and H. A. Naylor, *THIS JOURNAL*, **69**, 1968 (1947).

(4) J. Harmon, U. S. Patent 2,404,374 (1946).

(5) J. R. Lacher, G. E. Tompkin and J. D. Park, *THIS JOURNAL*, **74**, 1693 (1952).

(6) G. C. Rogers and G. H. Cady, *THIS JOURNAL*, **73**, 3513 (1951).

(7) American Inst. of Mining and Met. Engineers, "Pyrometry" p. 337 (1920).

Analyses of the products were made as follows: (1) The small amount of carbon which deposited on the filament was determined at the end of a run by heating the wire in air. The loss in weight corresponded to the amount of carbon. (2) The weight of polymer deposited on the walls was taken to be equal to the loss in weight of the gas, less the weight of carbon on the filament. (3) The loss in weight of the gas during reaction was found from pressure and density measurements. (4) Polymer from the walls was analyzed for fluorine by treating it with an excess of sodium and then titrating the fluoride ion by the method of Hoskins and Ferris.⁸ (5) Carbon monoxide was determined by condensing the gaseous product in a trap cooled by liquid oxygen. The pressure of uncondensed gas was taken to be that of carbon monoxide. This material had the density of carbon monoxide and it was capable of absorption in a solution of cuprous chloride in hydrochloric acid. (6) Silicon tetrafluoride in the product obtained from hexafluoroethane was absorbed in 1 *N* sodium hydroxide solution and the resulting fluoride ion was later titrated. Silicic acid could be precipitated from the solution. (7) Mixtures of gaseous fluorocarbons from the runs were analyzed by fractional distillation using an unpacked column of 2 mm. inside diameter and 60 cm. length. Insulation was provided by a silvered jacket. The column had a total reflux type head which was equipped with a fine capillary probe through which the distillate was removed. For each distillation, a plot of head temperature *vs.* volume of distillate was made. This together with vapor densities of the various cuts served to measure and identify CF_4 , C_2F_6 and C_3F_8 . The unsaturated compounds, hexafluoropropene and octafluoro-2-methylpropene, were characterized further by preparation of their chlorinated derivatives. The gas was placed in a bulb with an excess of chlorine and was exposed to sunlight for several hours. Unreacted chlorine was then removed by soda lime and the gas was dried over phosphorus pentoxide. The boiling points, vapor densities and amounts of these substances were then measured.

Materials.—Hexafluoroethane of commercial grade was passed through a copper vessel containing 36 moles of cobalt trifluoride at about 270°. It was then kept for three hours in a bottle containing a platinum wire heated to 1300°. The product was distilled in a fractionating column and the best of the hexafluoroethane fraction was collected for use in the pyrolysis studies.

Octafluoropropane of commercial grade was refined in the same manner as that described for hexafluoroethane, except that the gas was not exposed to the platinum filament. The product boiled at -38° and had a density at 25° of 188 g. per gram molecular volume.

Decafluoro-*n*-butane, dodecafluoro-*n*-pentane and decafluorocyclopentane of high purity were available as the result of other research in this Laboratory.

Tetrafluoroethylene was prepared by the pyrolysis of its polymer, Teflon.⁹ An iron pipe containing chips of the polymer was held in a muffle furnace at 750° and the products were pumped off through a trap cooled by liquid oxygen. Since the gas pressure remained less than 1 mm., a high yield of tetrafluoroethylene resulted. The product was purified by a bulb to bulb distillation, after which it had a density of 101 g. per gram molecular volume (theoretical = 100).

Results

Hexafluoroethane.—This was the first compound studied and it presented the greatest difficulties. At first, a glass reaction vessel was employed with the result that pyrolysis of the fluorocarbon yielded not only carbon tetrafluoride and a solid white polymer but also much carbon monoxide and silicon tetrafluoride. Cooling the glass vessel and the support for the filament did not stop the attack upon the glass. When the copper reaction vessel, gold-plated on the inner surface, was used in place of glass, the production of carbon monoxide and silicon tetrafluoride was greatly reduced but not eliminated.

Some early runs made both in glass and in the metal vessel had induction periods, lasting as much as four hours. With the filament held at temperatures as high as 1250° substantially no reaction took place; then the reaction started and proceeded smoothly. After making two

changes, the induction period was no longer encountered. One change was to pretreat the gas with a hot filament as described in the section on procedure; the other was the use of a different supply of platinum wire, the old stock being exhausted.

Prolonged use of a platinum filament resulted at first in pitting of its surface and finally in breakage. The surface also became blackened by the deposition of a small amount of carbon.

In spite of the experimental difficulties involved, studies were made to determine the influence of both temperature and pressure upon the reaction.

At temperatures above 1200° the principal products were carbon tetrafluoride and a white polymer which collected upon the walls of the vessel, the greatest amount of the latter collecting just above the filament. Reducing the pressure caused an increase in the relative proportions of both carbon monoxide and silicon tetrafluoride in the product. The polymer resembled Teflon (polytetrafluoroethylene) and was found by analysis to contain 75 ± 1% fluorine (theoretical for $(CF_2)_n$ is 76.0%). In a number of the runs the solid was formed in an amount corresponding to about 40 g., or 0.8 mole, of $-CF_2-$ per mole of CF_4 produced. The relative proportions of carbon monoxide and silicon tetrafluoride seemed also to be about constant at one mole of CO to 1.4 moles of SiF_4 . A fractional distillation of one reaction product indicated the presence of no gaseous fluorocarbons other than carbon tetrafluoride and hexafluoroethane. In other runs which had been carried to completion, the density of the fluorocarbon gas remaining after removal of CO and SiF_4 was identical to that of CF_4 . If higher fluorocarbons were present, the amounts were very small. The above observations make it appear that the principal net reaction was $nC_2F_6 = nCF_4 + (CF_2)_n$ but that a side reaction involving glass was also important.

A detailed table of data for the various runs is available on microfilm.⁹ A summary is presented in Table I. To obtain part of the data, partial pressures of C_2F_6 were calculated from the observed total pressures of gas, the densities and the observed pressures of CO. It was assumed that the only gases present were CF_4 , C_2F_6 , CO and SiF_4 and that the volume ratio of CO to SiF_4 in all cases was 1 to 1.4. Column 6 gives the calculated ratio of moles of CO per mole of CF_4 in the gas. This ratio may be regarded as an indication of the relative importance of the two competing processes.

When the natural logarithm of the pressure of hexafluoroethane is plotted *vs.* time, the data for most of the runs yield substantially straight lines indicative of a first order reaction. The slopes of these lines give the values of the rate constant listed in Table I.

TABLE I
PYROLYSIS OF HEXAFLUOROETHANE

Initial pressure C_2F_6 , mm.	Filament temp., °C.	<i>k</i> , fraction of C_2F_6 consumed per hour	Duration of run, hours	Fraction of C_2F_6 consumed, %	Product ratio CO/ CF_4
115	1050	0.0039	15	6	1.1
108	1150	.0071	16	10	2.1
116	1200	.017	16	23	1.2
116	1225	.030	15	38	0.50
57	1250	.060	15	60	.50
111	1250	.036	14	39	.13
226	1250	.031	14	41	.11
550	1250	.015	15	21	.16
113	1300	.050	11	49	.35
118	1400	.17	6	63	.11
230	1400	.15	9	66	.13
232	1450	.20	10	85	.08

Some of the graphs indicate a relatively rapid reaction for the first hour followed by a slower change for the remainder

(9) For detailed table order Document 3608 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or \$1.00 for photocopies (6 × 8 inches) readable without optical aid.

(8) W. M. Hoskins and C. A. Ferris, *Ind. Eng. Chem., Anal. Ed.*, **8**, 6 (1936).

of the run. In these cases the values of k given in the table correspond to the reactions occurring after the first hour.

A plot of $\log k$ vs. the reciprocal of the absolute temperature gives points lying close to a straight line having a slope corresponding to an experimental energy of activation for the reaction of 51 kcal. per mole. Because of the experimental difficulties involved, this figure may differ widely from the correct value.

Octafluoropropane.—The pyrolysis of this substance was much easier to study than that of hexafluoroethane. Decomposition occurred at lower temperatures, the platinum wire was attacked only a little and no evidence was found for a reaction involving glass. Carbon monoxide and silicon tetrafluoride were not found among the reaction products. No induction period was encountered and the reaction took place smoothly with no initial period of abnormally rapid change. Products of the pyrolysis were: hexafluoroethane, hexafluoropropene, octafluoro-2-methylpropene, a solid polymer resembling Teflon, and a trace of carbon. Table II indicates the proportions of these products found under various conditions. They are substantially constant. In the case of runs made at initial pressures of 50 mm. and 100 mm. (measured with the filament cool) the gaseous products were too small in volume to allow one to make a good analytical distillation. It is probable, however, that these runs also gave the same products and in the same proportions, for the final gas densities after these runs were nearly the same as those for the products of other completed reactions.

The two unsaturated compounds formed by the reaction were identified by their physical properties and by the properties of their dichloro derivatives. Hexafluoropropene from these reactions distilled at a column head temperature of about -32 to -30° and it had a density of 152 g. per G.M.V. (should be -29.4° and 150 g. per G.M.V.). Its dichloro derivative boiled at about 34° and had a density of 216 g. per G.M.V. (should be: 34.7° and 221 g. per G.M.V.). Octafluoro-2-methylpropene from these reactions distilled at 6 to 7° , froze at about -130° and had a density of 203 g. per G.M.V. Its dichloro derivative boiled at 63.4° and had a density of 273 g. per G.M.V. The boiling point of the fluorocarbon is that reported by Brice, *et al.*,¹⁰ for octafluoro-2-methylpropene.

TABLE II

PYROLYSIS PRODUCTS OF OCTAFLUOROPROPANE

The data are given in terms of moles of product per mole of C_3F_8 reacted. Initial pressures are those observed with the system at room temperature and with the filament not heated.

t , $^\circ\text{C}$.	Initial pressure, mm.	C_2F_6	C_3F_6	C_4F_8	$-(CF_2)-$ (as polymer)
1000	500	1.1	0.24
1050	500	0.96	0.10	0.11	.26
1100	500	0.99	.09	.12	.32
1150	500	1.01	.07	.12	.36
1200	500	1.05	.05	.10	.33
1150	200	0.94	.11	.10	.36

If one takes into account the fact that one mole of C_3F_8 gives rise to the quantities of C_2F_6 , C_3F_6 and C_4F_8 indicated in Table II, he reaches the conclusion that the polymer contains about two atoms of fluorine per atom of carbon. The number of "moles" of polymer given in the table has been obtained by dividing its weight in grams (calculated from the loss in weight of the gas) by 50.

In order that the partial pressure of octafluoropropane could be calculated from the observed pressures and gas densities it was assumed that the gas was composed of octafluoropropane and a mixture of other fluorocarbons. The relative proportions of these other fluorocarbons was assumed to be the same throughout the run as at the end of the run. In all runs the relative numbers of moles of these compounds were close to 12.8 moles of C_2F_6 to 1.38 moles

(10) T. J. Brice, J. D. LaZerte, L. J. Hals and W. H. Pearson, Paper No. 39 Section 14, Twelfth International Congress of Pure and Applied Chemistry, Sept. 10, 1951, New York. These authors give the following boiling points: $CF_2=CF_2-CF=CF_2$, 1° ; $CF_2=CF=CF-CF_2$, 0° ; $CF_2-CF=CF_2$, 6.5° .



of C_4F_8 to one mole of C_3F_6 . One incomplete run gave nearly the same relative proportions of these products as were found in a completed run under the same conditions.

For each run, a plot of the logarithm of the partial pressure of octafluoropropane vs. time gives a straight line indicative of a first order reaction. Rate constants obtained from these graphs appear in Table III. Detailed experimental data are available on microfilm.⁹

TABLE III

PYROLYSIS OF OCTAFLUOROPROPANE

Filament temp., $^\circ\text{C}$.	Initial pressure of C_3F_8 filament cool	k , fraction of C_3F_8 decomposed per hour	Half-time for reaction hours
1000	500	0.010	69
1050	500	.038	18
1100	500	.11	6.4
1150	50	.39	1.8
1150	100	.36	1.9
1150	200	.36	1.9
1150	500	.33	2.1
1200	500	.95	0.73

Logarithms of the rate constants, when plotted against the reciprocal of the absolute temperature, fall close to a straight line having a slope corresponding to an experimental activation energy of 84 kcal. per mole.

Other Fluorocarbons.—Single pyrolysis runs were made using tetrafluoroethylene, decafluoro-*n*-butane, dodecafluoro-*n*-pentane and decafluorocyclopentane. With the exception of the last of these, the reaction was run substantially to completion, as indicated by no further change in pressure and density of the product. Decafluorocyclopentane had such a high degree of stability that only 30% of it decomposed in 24 hours with the filament at 1250° . The run was discontinued at this point. At 1000° this substance appeared not to decompose at all and at 1200° the rate was very slow.

Grayish-white solid polymers were obtained from tetrafluoroethylene and decafluoro-*n*-butane. Dodecafluoro-*n*-pentane yielded a polymeric product containing an appreciable amount of a straw-colored tar-like material. Most of the polymer from decafluorocyclopentane was also a straw-colored tar-like material which was soluble in liquid tetradecafluoromethylcyclohexane, C_7F_{14} . A material balance indicates that this polymer contained only about one atom of fluorine per atom of carbon.

Yields of products from these runs are given in Table IV. As far as is known, the product listed as C_4F_8 was in each case composed only of octafluoro-2-methylpropene. There is a possibility, however, that a small part of this material might have been octafluorocyclobutane, even though evidence for the presence of this substance was not found. It is also possible that traces of other compounds not listed in the table might have been present. Data regarding the progress of the reactions are available on microfilm.⁹

TABLE IV

PYROLYSIS PRODUCTS

Product yield, moles of product per mole of reactant consumed	Fluorocarbon pyrolyzed			
	<i>n</i> - C_4F_{10}	<i>n</i> - C_5F_{12}	C_2F_4	Cyclo- C_5F_{10}
CF_4	0.00	0.00	0.00	0.18
C_2F_6	.65	.49	.00	.68
C_3F_8	.38	.48	.00	.00
C_3F_6	.16	.31	.28	.43
C_4F_8	.18	.19	.04	.18
C	.01	.01	Trace	.25
CO	.00	.00	0.00	.14
$-(CF_2)-$ polymer	.21	.92	.94	1.20 ^a

^a A material balance indicates this product to contain about one atom of F per atom of C.

Table V gives the reaction conditions and compares the rates of decomposition of the different fluorocarbons studied in this research. The position of tetrafluoroethylene in this

table is based upon its behavior in the presence of a hot platinum filament. Since the compound is known to polymerize at low temperatures, it is actually the most easily pyrolyzed substance of those listed.

TABLE V
COMPARATIVE THERMAL STABILITIES OF SOME FLUOROCARBONS

Compound (in order of decreasing stability)	Pressure, mm.	Temp., °C.	Reaction half-time, hr.
CF ₄	...	Carbon arc	...
C ₂ F ₆	500	1250	46
Cyclo-C ₃ F ₈	500	1250	40
C ₃ F ₈	500	1100	6.4
<i>n</i> -C ₄ F ₁₀	500	1000	6.5
C ₂ F ₄	500	1000	1.8
<i>n</i> -C ₅ F ₁₂	500	1000	0.7

Discussion

Experimental evidence strongly supports the following conclusions: (1) Pyrolysis of a fluorocarbon on a hot platinum filament is a catalytic reaction (evidence: induction periods sometimes found for C₂F₆). (2) Rupture of a fluorocarbon molecule occurs at a C-C bond (evidence: (a) products obtained, (b) slower corrosion of platinum filament than would be expected if F atoms were formed by rupture of a C-F bond). (3) Fluorocarbons of the normal paraffin series decompose more easily as the chain length in-

creases. (4) Among the most stable of the fluorocarbons are the substances: carbon tetrafluoride, hexafluoroethane, decafluorocyclopentane, hexafluoropropene and octafluoro-2-methylpropene. (5) Fluorocarbons which have been tested are more stable than the corresponding hydrocarbons. (6) Pyrolysis of a fluorocarbon gives rise to unsaturated molecules or free radicals which combine to form polymers.

The fifth of these conclusions is strikingly illustrated in Fig. 1 in which the decomposition temperatures (temperature at which decomposition is easy to observe) of analogous compounds are plotted against the heats of formation from atoms. Data, except those for hexafluoroethane and octafluoropropane, have been taken from the literature.

While evidence regarding detailed reaction mechanisms is not conclusive, a few comments are appropriate. The decomposition of octafluoropropane may be considered to involve a rupture of the molecule to form a molecule of C₂F₆ and a CF₂ free radical. This may be a process involving several steps. The products C₃F₈, C₄F₈ and -(CF₂)_{*n*} may be formed from CF₂ radicals. Similar processes for the pyrolysis of other paraffinic fluorocarbons may be proposed to account for the formation of lower paraffin fluorocarbons and substances of the general formula C_{*n*}F_{2*n*}. In the case of dodecafluoro-*n*-pentane it appears that the rupture occurs at the middle of the molecule rather than at the end, because no C₄F₁₀ is found in the gases produced. It is of interest and perhaps significant that one mole of each of the paraffin fluorocarbons tested in this study, with the exception perhaps of C₂F₆, gives rise to a total of practically one mole of paraffinic products. When one tries to explain all of the reactions on the basis of the splitting off of CF₂ free radicals, he is left wondering why C₂F₆ fails to give rise to C₃F₈ and C₄F₈ and why *n*-C₅F₁₂ fails to yield *n*-C₄F₁₀.

Free radicals of the formula CF₂ are known to be capable of formation and to have a half-life of a second or more.¹¹

The side reaction accompanying the decomposition of hexafluoroethane is not adequately explained. Perhaps an active substance formed at the filament reacts with stopcock grease used to make the pyrolysis vessel tight. If hydrogen fluoride is produced, it will later react with glass parts of the apparatus to give silicon tetrafluoride and water. The latter would react with fluorocarbon at the hot filament.

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(11) R. K. Laird, E. B. Andrews and R. F. Barrow, *Trans. Faraday Soc.*, **46**, 803 (1950).

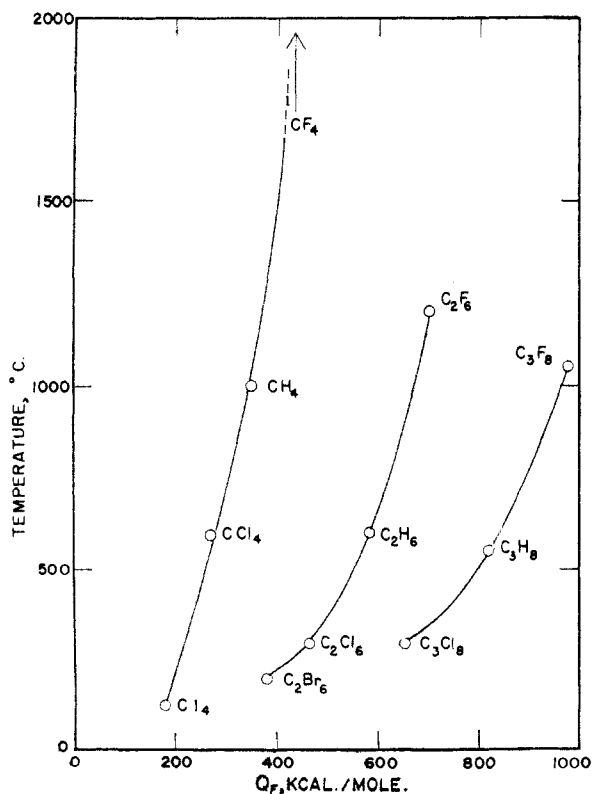


Fig. 1.—Comparison of thermal stabilities.