Prepared for
J. Phys. Chem.
January, 1962

N62 12550

12550

THERMAL DECOMPOSITION OF SOME LINEAR PERFLUOROALKANES IN AN INCONEL TUBE

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ABSTRACT

The products of the pyrolysis reactions of perfluoropropane, perfluoroethane, and carbon tetrafluoride in an Inconel bomb are described. The values for the energy of activation and frequency factor for the first-order pyrolysis reactions are, respectively: (1) 80 kcal. per mole and 2×10^{14} sec.$^{-1}$ for perfluoropropane; (2) 53 kcal. per mole and 3×10^{7} sec.$^{-1}$ for perfluoroethane; and (3) 96 kcal. per mole and 4×10^{13} sec.$^{-1}$ for carbon tetrafluoride.

INTRODUCTION

The saturated perfluorocarbons are well known for their chemical stability relative to their hydrocarbon equivalents. But, while many investigations have been made as to the products and the kinetics of the pyrolysis of the hydrocarbons, less information is available for the perfluorocarbons.

"Teflon" has been heated at 500° to 700° C. to produce tetrafluoroethylene, perfluoropropene, and perfluoroisobutene in varying proportions, depending on the conditions involved.[1] Perfluoropropane and perfluoroethane have been pyrolyzed between 1000° and 1400° C. by means of a hot-filament technique.[2]

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(1) E. E. Lewis and M. A. Naylor, J. Am. Chem. Soc., 69, 1968-70 (1947).

(2) R. K. Steuneberg and G. H. Cady, J. Am. Chem. Soc., 74, 4165-8 (1952).

The present investigation was concerned with the pyrolysis reactions of three linear perfluoroalkanes: (1) carbon tetrafluoride; (2) perfluoroethane; and (3) perfluoropropane. The procedure involved heating the gas in an Inconel bomb between 660° and 1090° C. The results should lead to a better understanding of the pyrolysis of perfluorocarbons in general.

EXPERIMENTAL

Materials

(a) Perfluoropropane and Carbon Tetrafluoride. - Both gaseous perfluoropropane (b.p. - 36.7° C., obtained as Genetron-218 from General Chemical Division) and carbon tetrafluoride (obtained as Freon-14 from DuPont) were used without purification, since their infrared spectra indicated better than 99 mole percent purity.

(b) Perfluoroethane. - Gaseous perfluoroethane was prepared by pyrolyzing perfluoropropane (250-300 mm. Hg) at about 800° C. in an Inconel bomb for about 20 min. The gaseous materials were passed through a trap at -195° C. and were distilled subsequently at -110° C. The crude perfluoroethane so produced was then resubmitted to this pyrolysis and purification process. Infrared spectra indicated the presence in the final product of only C_2F_6, 2.45 mole percent CF_4, 0.54 mole percent C_3F_8, and 0.23 mole percent SiF_4. Molecular weight determinations agreed with the value of 96.8 mole percent C_2F_6 by difference.

Pyrolysis of the Perfluorocarbons

(a) Apparatus. - All pyrolysis reactions were run by the static method in an Inconel bomb (646 ml.) heated in a wire-wound 210-volt furnace. The furnace temperature was held constant to an estimated ±3° C.

The bomb was connected to a vacuum train for the usual gas manipulations by means of a small entry line (estimated volume was 10 ml.) with a metal-to-glass connector.

(b) Procedure. - Several perfluoropropane pyrolysis runs at about 800° C. were made initially in an attempt to condition the bomb surface. In addition, prior to each pyrolysis run, the bomb was heated at about 900° C. in vacuo for at least 15 min. and then at the desired pyrolysis temperature for 15 min. at a pressure of about 10^{-3} mm. Hg. The perfluorocarbon gas (calculated to give a pressure of 100 mm. Hg at the desired pyrolysis temperature) was then introduced into the evacuated bomb. Since it was found (with gaseous nitrogen) that a 30-sec. interval was more than sufficient for the heating of the gas within the bomb to the desired temperature, the bomb was opened briefly after 30 sec. to equalize the pressure within the bomb and within the manometer system. After the gas pressure within the bomb had been measured, the bomb valve was closed. Then, all gaseous materials remaining in the manometer system was evacuated.

The molar quantities of the perfluorocarbon gas contained initially in the vacuum train system and after expansion into the bomb were calculated. Therefore the molar quantity of the gaseous perfluorocarbon introduced into the bomb was readily determined by difference.

After the desired time interval, the pyrolysis reaction was quenched rapidly by trapping all the residual gaseous materials at -195° C. Analyses were made by determining the total moles of the residual gaseous materials and by determining the percentage of each gas from quantitative comparisons with known standardized infrared spectra.

For an investigation of possible heterogeneous effects on the pyrolysis of these perfluorocarbon molecules, the surface-volume ratio was almost doubled by the addition of fine nickel wire (about 0.02 in. diameter).

RESULTS AND DISCUSSION OF RESULTS

Perfluoropropane

Several 15-min. pyrolysis runs of perfluoropropane were made between 660° and 1035° C. The molar quantities of the gaseous materials obtained per mole of initial perfluoropropane are shown in Fig. 1. It was found that the gaseous products, up to about 750° C., were perfluoroethane, perfluoroisobutene, a trace of perfluoropropene, and unreacted perfluoropropane. A pyrolysis run at 713° C., in which the gaseous materials are expressed in millimoles serves as an illustration:

$$0.885\ C_3F_8 \rightarrow 0.617\ C_3F_8 + 0.257\ C_2F_6 + 0.016\ \text{iso-}C_4F_8$$

The carbon that remained unaccounted for by these gaseous products was assumed to exist as a nonvolatile polymeric fluorocarbon, $(CF_2)_x$. A material balance at 713° C. after the 15-min. interval indicated that essentially 1 mole of perfluoroethane was obtained per mole of perfluoropropane decomposed:

$$C_3F_8 \rightarrow 0.96\ C_2F_6 + 0.060\ \text{iso-}C_4F_8 + 0.84(CF_2)_x + 0.08F\ (\text{Metal Fluoride})$$

Starting at about 750° C., the perfluorethane and perfluoroisobutene gases produced from perfluoropropane were being pyrolyzed subsequently to produce carbon tetrafluoride as the only gaseous fluorocarbon product. This is illustrated by perfluoropropane pyrolysis run at 861° C., in which the gaseous materials are expressed in millimoles:

$$0.787\ C_3F_8 \rightarrow 0.027\ C_3F_8 + 0.225\ C_2F_6 + 0.0044\ \text{iso-}C_4F_8 + 0.075\ CF_4 + 0.0099\ SiF_4$$

Again, the carbon that remained unaccounted for was assumed to exist as a polymeric fluorocarbon, $(CF_2)_x$. The difference in the molar quantity of fluorine, between the total and that accounted for by the gaseous products and by the assumed polymer, was assumed to exist as a metal fluoride. Therefore, a material balance at 861° C. after the 15-min. interval indicated that the major products were a polymeric fluorocarbon and a metal fluoride:

$$C_3F_8 \rightarrow 0.30\ C_2F_6 + 0.006\ \text{iso-}C_4F_8 + 0.099\ CF_4 + 0.012\ SiF_4 + 2.28(CF_2)_x + 1.15\ F\ \text{(Metal Fluoride)}$$

Finally, starting at about 930° C., the carbon tetrafluoride, produced as a side product in the subsequent pyrolysis of the perfluoroethane product, was in turn decomposed to nongaseous products.

The kinetics of the pyrolysis reaction of perfluoropropane (100 mm. Hg) in the Inconel bomb was investigated between 670° and 720° C. Essentially, a first-order reaction was obtained as indicated by a plot of the log of the partial pressure of perfluoropropane remaining versus time. The calculated specific reaction rate values (k) of the first-order equations are shown in Table I. A plot of these rate values against the reciprocal of the absolute temperature, as suggested by the Arrhenius equation, gave a value of 80 ± 3 kcal. per mole for the energy of activation of the reaction. Finally, the corresponding frequency factor was calculated to be 2×10^{14} sec.$^{-1}$.

TABLE I

SPECIFIC REACTION RATES FOR THE PYROLYSIS

OF PERFLUOROPROPANE

Temperature, °K.	Average k values $\times 10^{-4}$, sec.$^{-1}$
943	0.709
959	1.52
970	1.97
981	3.51
992	6.26

A value of 84 kcal. per mole for the activation energy of the pyrolysis of perfluoropropane by means of a hot-filament technique was reported by Steunenberg.[2] However, this hot-filament technique should inherently result in a slower reaction rate because of the difficulty of maintaining a uniform temperature throughout the gas phase. Apparently, this slower reactivity was observed by Steunenberg, who suggested that a much higher temperature range of about 1000° to 1200° C. was necessary for the pyrolysis reaction.

The calculated frequency factor of 2×10^{14} sec.$^{-1}$ for the pyrolysis of perfluoropropane suggests that the reaction may have been predominantly a unimolecular homogeneous one.[3]

The bond dissociation energy values for the carbon-carbon bond in perfluoroethane and the carbon-fluorine bond in carbon tetrafluoride have been determined as 64 and 117.5 kcal. respectively.[4] Therefore, the observed activation energy value (80 kcal.) for a first order homogeneous reaction suggests that the rate controlling step in the pyrolysis

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(3) S. W. Benson, "The Foundation of Chemical Kinetics", McGraw-Hill Co., N. Y. p. 264, 1960.

(4) J. F. Reed and B. S. Rabinovitch, J. Phys. Chem., <u>61</u>, 598-605 (1957).

of perfluoropropane may involve the homolytic scission of a carbon-carbon bond.

Perfluoroethane

Several 15-min. pyrolysis runs of perfluoroethane in the Inconel bomb were made between 745° and 990° C. The molar quantities of the gaseous materials obtained per mole of initial perfluoroethane are shown in Fig. 2. The formation of carbon tetrafluoride was found to be a relatively unimportant side reaction up to about 830° C., as shown by a pyrolysis run at 824° C. in which the gaseous materials were expressed in millimoles:

$$0.739\ C_2F_6 \rightarrow 0.130\ C_2F_6 + 0.029\ CF_4 + 0.0042\ SiF_4$$

It was assumed that the carbon and fluorine which remained unaccounted for by these gaseous products existed as a nonvolatile polymeric fluorocarbon, $(CF_2)_x$, and a metal fluoride. A material balance at 824° C. after the 15-min. interval indicated that essentially two moles of polymeric $(CF_2)_x$ and two moles of fluorine, as metal fluoride, were obtained per mole of perfluoroethane decomposed:

$$C_2F_6 + \text{Metal (Inconel)} \rightarrow 1.95\ (CF_2)_x + 1.98\ F\ \text{(Metal Fluoride)}$$
$$+ 0.047\ CF_4 + 0.007\ SiF_4$$

A somewhat different course for the perfluoroethane pyrolysis was suggested by Steunenberg[2] for the hot-filament technique in which 1 mole of carbon tetrafluoride was obtained per mole of perfluoroethane pyrolyzed. Although the present investigation (as shown in Fig. 2) did indicate that the quantity of carbon tetrafluoride increased somewhat with increasing temperature, nothing approaching a 1:1 molar conversion was ever obtained.

For example, at 870° C., where essentially all of the perfluoroethane had decomposed within the 15-min. interval, only about 11 percent of the perfluoroethane had decomposed to produce carbon tetrafluoride.

Finally, starting at about 930° C., the gaseous carbon tetrafluoride was subsequently pyrolyzed to the polymer and metal fluoride.

Essentially, a first-order reaction was obtained for the pyrolysis of perfluoroethane (100 mm. Hg) in the bomb between 745° and 805° C. The specific reaction rates (k) calculated from the first-order equations are shown in Table II. The activation energy for the pyrolysis reaction was determined to be 53 ± 3 kcal. per mole from the Arrhenius plot. Finally, the corresponding frequency factor was calculated to be 3×10^7 $sec.^{-1}$.

TABLE II

SPECIFIC REACTION RATES FOR THE PYROLYSIS OF PERFLUOROETHANE

Temperature, °K.	Average k values $\times 10^{-4}$, $sec.^{-1}$
1020	1.29
1036	2.12
1047	2.49
1058	3.05
1080	6.11

The observed values of 53 kcal. per mole for the activation energy and 3×10^7 $sec.^{-1}$ for the frequency factor compare reasonably well with those of Mercer,[5] who obtained values of 50 kcal. per mole and 10^8 $sec.^{-1}$, respectively, in a flowing toluene system. However, Mercer stated that

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(5) P. D. Mercer and H. O. Pritchard, J. Chem. Soc., 1957, 2843-4.

these values cannot be considered as a measure of the dissociation energy of perfluoroethane. Steunenberg[2] reported a value of 51 kcal. per mole for the energy of activation but suggested that the value may differ widely from the correct value because of experimental difficulties.

Values ranging from 64 kcal. per mole[4] to 124 kcal. per mole[6] have been suggested for the dissociation energy of the carbon-carbon bond in perfluoroethane. Therefore, the observed values of 53 kcal. per mole and 3×10^7 sec.$^{-1}$ for the pyrolysis of perfluoroethane were too low for the usual homogeneous unimolecular reaction. In order that the reaction may continue to proceed in a first-order heterogeneous manner, the metal fluoride, obtained as a product in the pyrolysis, should be removed or loosened continuously so that new metal surface would be exposed. Indeed, as anticipated, it was found that metal fluoride did volatilize and condense into the cold zone. This condensate was shown to contain nickel fluoride and iron by means of spot tests and X-ray diffraction. Thus, it seems quite possible that the pyrolysis of perfluoroethane may proceed in a heterogeneous manner.

If the mechanism is assumed to be the heterogeneous dissociation of perfluoroethane, then the rate of the perfluoroethane disappearance should be essentially first order to the surface as well as to the perfluoroethane. However, no increase in the reaction rate was observed at 770° C. with a twofold increase in surface. It has been suggested that a system involving surface initiation to produce radicals which diffuse out into the homogeneous phase for a chain reaction may be nearly

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(6) N. Luft, J. Chem. Phys. 23, 973-4 (1955).

independent of the surface/volume ratio.[7] Therefore the observed values for the activation energy (53 kcal.) and the frequency factor (3×10^{7} sec.$^{-1}$) for a first-order reaction suggests that the rate controlling step in the pyrolysis of perfluoroethane in an Inconel bomb may involve a homolytic scission of the carbon-carbon bond at the metal surface and that the subsequent reaction mechanism may involve a complex sequence of reactions.

Although sufficient data were not available for a more positive identification, it is believed that the major course of the perfluoroethane pyrolysis to produce the polymer and metal fluoride may proceed with different kinetics at higher temperatures. Approximate values of 85 kcal. per mole and 10^{14} sec.$^{-1}$ were suggested for the activation energy and frequency factor, respectively, at temperatures greater than about 800° C. The similarity of these values to reported values for ethane (ranging from 70 kcal. per mole[8] with a frequency factor of about 10^{14} sec.$^{-1}$, to 77 kcal. per mole[9] with a frequency factor of about 10^{16} sec.$^{-1}$) suggested the possibility that perfluoroethane was being pyrolyzed homogeneously at the higher temperatures.

Carbon Tetrafluoride

Several 15-min. pyrolysis runs of carbon tetrafluoride were made in the bomb between 935° and 1090° C. The molar quantities of the unreacted carbon tetrafluoride are shown in Fig. 3. Since the only gaseous fluorocarbon obtained was unreacted carbon tetrafluoride, the products

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(7) Reference 3, p. 619, 1960.
(8) E. W. Steacie and G. Shane, Can. J. Res., B18, 203 (1940).
(9) R. E. Paul and L. F. Marek, Ind. Eng. Chem., 26, 454 (1934).

were assumed to be a nonvolatile polymeric fluorocarbon, $(CF_2)_x$, and a metal fluoride as follows:

$$CF_4 + \text{Metal (Inconel)} \longrightarrow (CF_2)_x + \text{Metal Fluoride}$$

The specific reaction rate values (k), which were calculated from the observed first-order equations for the pyrolysis of carbon tetrafluoride between 930° and 990° C., are shown in Table III. Values of 96 ± 3 kcal. per mole and 4×10^{13} sec.^{-1} were obtained for the energy of activation and frequency factor, respectively.

TABLE III

SPECIFIC REACTION RATES FOR THE PYROLYSIS

OF CARBON TETRAFLUORIDE

Temperature, °K.	Average k values $\times 10^{-4}$, sec.^{-1}
1203	1.37
1209	2.09
1223	2.34
1231	3.90
1241	4.77
1263	9.33

Values ranging from 118 kcal. per mole[4] to 138 kcal. per mole[6] have been reported for the dissociation energy of the carbon-fluorine bond in carbon tetrafluoride. Therefore, the observed energy of activation of 96 kcal. per mole was too low for the usual homogeneous unimolecular reaction. However, no increase in reaction rates was observed at 990° C. with a twofold increase in surface. Therefore, as was suggested for perfluoroethane, it is believed that the rate controlling step in the pyrolysis of carbon tetrafluoride in an Inconel bomb may involve a homolytic scission of the carbon-fluorine bond at the metal surface and that the subsequent reaction mechanism may involve a complex sequence of reactions.

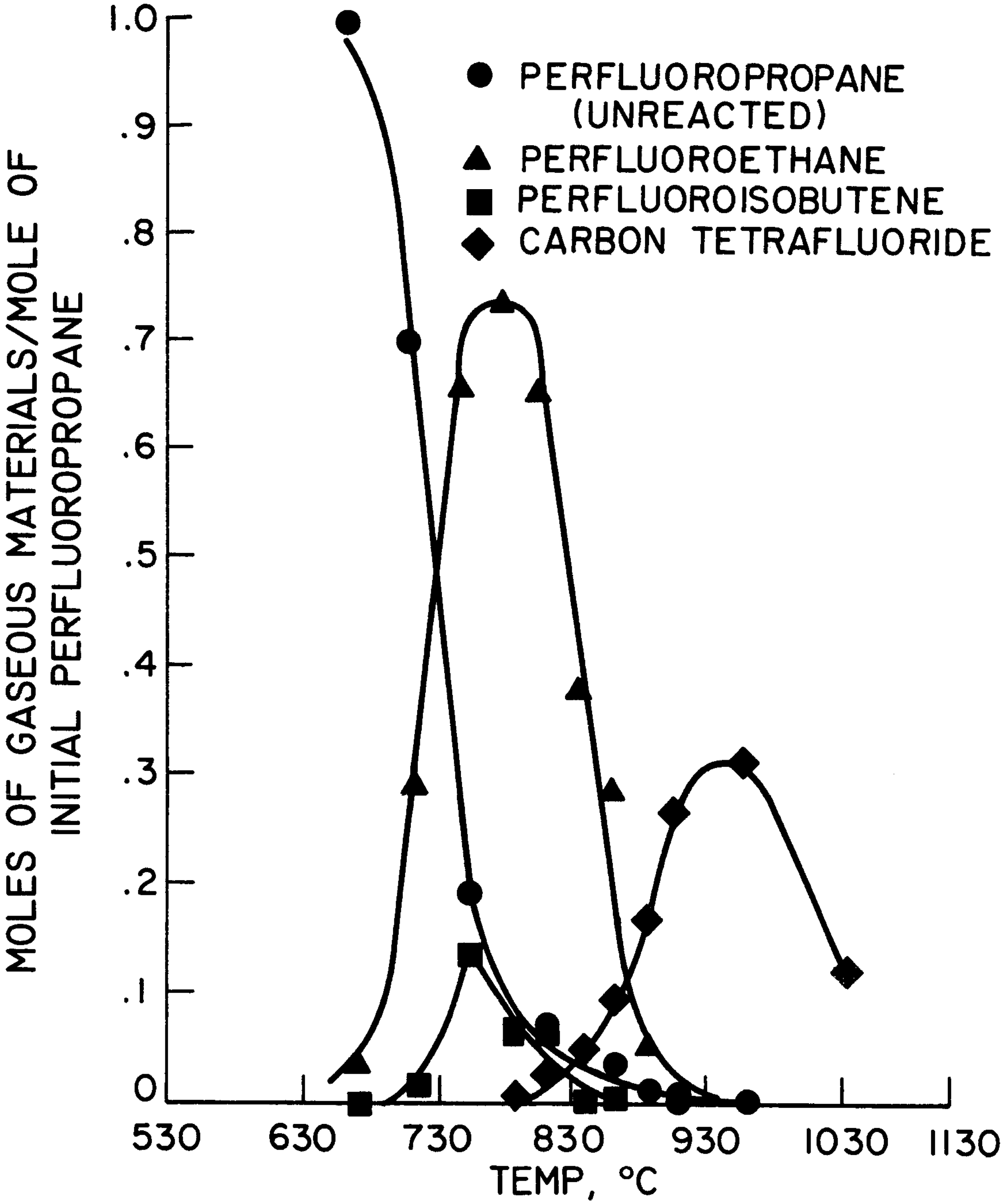

Fig. 1. - Composition of the gas after pyrolysis of perfluoropropane. Time, 15 min.; initial pressure, 100 mm.

E-1330

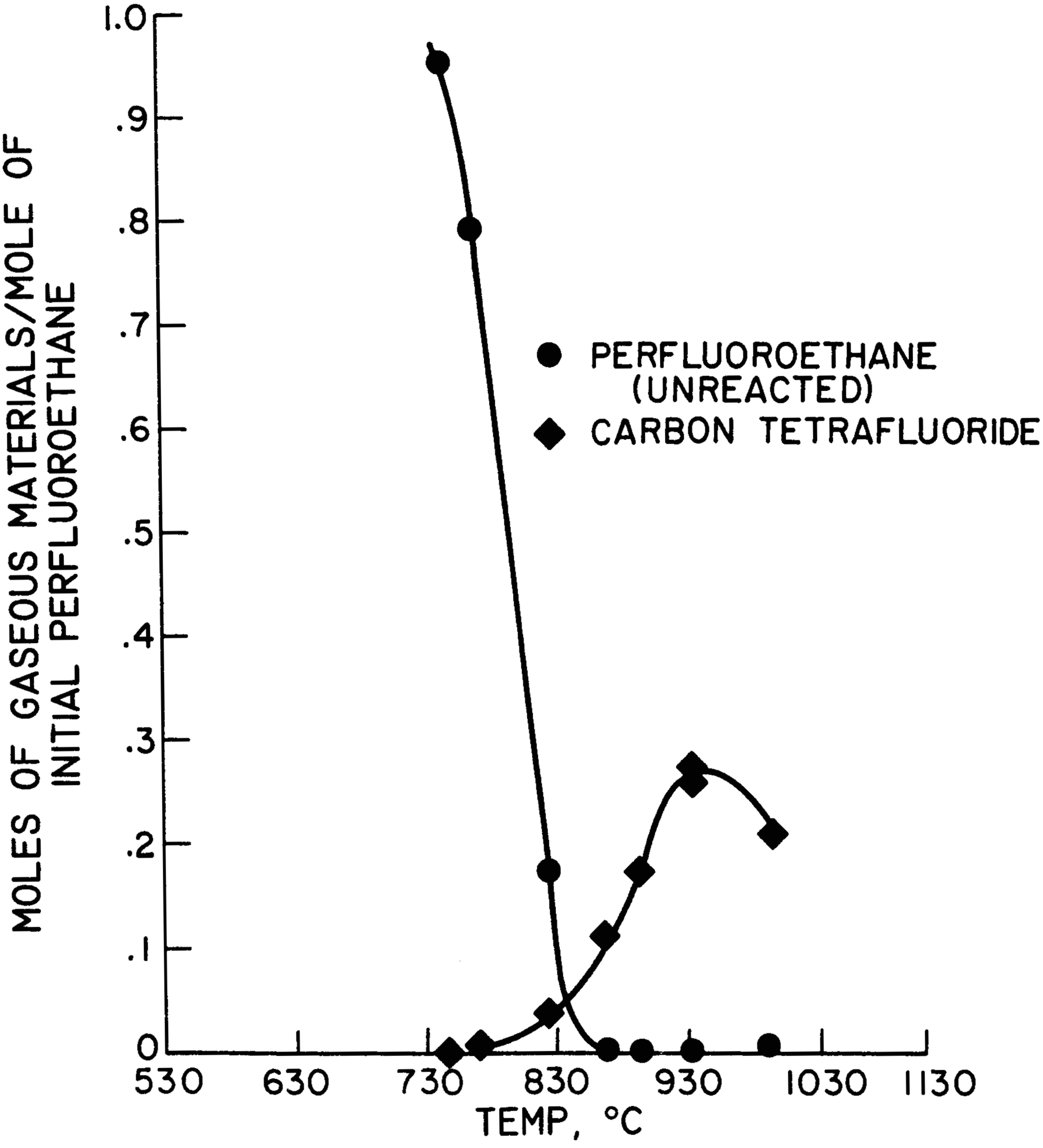

Fig. 2. - Composition of the gas after pyrolysis of perfluoroethane. Time, 15 min.; initial pressure, 100 mm.

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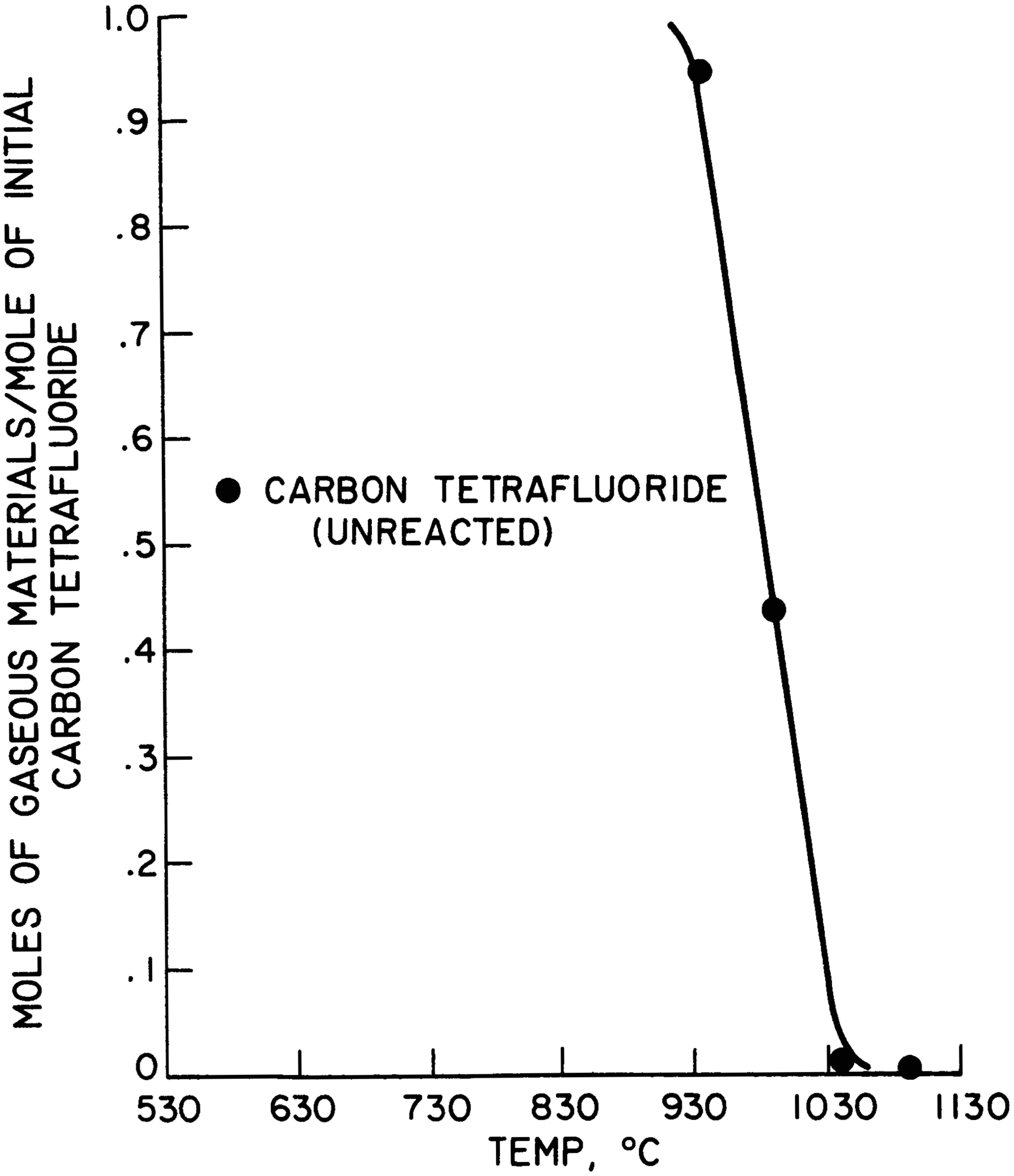

Fig. 3. - Composition of the gas after pyrolysis of carbon tetrafluoride. Time, 15 min.; initial pressure, 100 mm.