

THE THERMAL DECOMPOSITION OF
PERFLUOROPROPENE

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ABSTRACT

The thermal decomposition of perfluoropropene in the temperature and initial pressure ranges 550 to 675°C and 50 to 200 torr is discussed. The rate of decomposition of perfluoropropene is shown to be first order with respect to the perfluoropropene concentration. The first order rate constant (k_4) is given by:

$$k_4 = 2.58 \times 10^7 \exp(-44,580/RT) \text{ sec}^{-1}.$$

INTRODUCTION

The thermal decomposition of a few of the low molecular weight fluorocarbons have been studied. The pyrolysis of tetrafluoroethylene has been investigated in the temperature range 300° to 800°C by Miller¹, Lacher, Tompkin and Park², Atkinson and Trenwith³ and Atkinson and Atkinson⁴. It has been shown that this reaction system can be divided into three phases. At low temperatures ($T < 550^\circ\text{C}$) octafluorocyclobutane is the main product; at medium temperatures ($550 < T < 700^\circ\text{C}$) perfluoropropene and a perfluorobutene are produced; and at high temperatures ($T > 700^\circ\text{C}$) perfluoroethane and non-volatiles are produced. In the temperature range 300-550° it has been shown that the pyrolysis of tetrafluoroethylene can be represented by:

$$\frac{d[\text{C}_2\text{F}_4]}{dt} = -k_1 [\text{C}_2\text{F}_4]^2 + k_2 [\text{C-C}_4\text{F}_8] \quad (1)$$

The second order rate constant k_1 as given in References (2) and (3) are respectively

$$k_1 = 16.5 \times 10^{10} \exp(-26,299/RT) \text{ cc/mole-sec}^{-1} \quad (2)$$

and

$$k_1 = 10.3 \times 10^7 \exp(-25,400/RT) \text{ cc/mole-sec}^{-1} \quad (3)$$

These two second order rate constants are consistent to within approximately twenty percent. Both Lacher, Tompkin and Park² and Atkinson and Trenwith³ determined their rate constants by measuring the system pressure as a function of reaction time.

Recently Drennan and Matula⁵ have determined k_1 based on simultaneous measurements of total pressure, tetrafluoroethylene, and octafluorocyclobutane concentrations as a function of reaction time. These three simultaneous measurements allowed three independent evaluations of k_1 to be made. In general the numerical values of k_1 based on the tetrafluoroethylene and total pressure data were consistent and in good agreement with the results of Atkinson and Trenwith³. However, the numerical value of k_1 based on the measured octafluorocyclobutane concentration as a function of time were consistently lower than the other two values.

A number of investigators have studied the thermal decomposition of octafluorocyclobutane^{3,4,6,7,8}. Butler⁷ has shown that in the temperature range 360 to 560°C the numerical value of the first order constant k_2 can be represented by

$$k_2 = 10^{16.0} \exp(-74,300/RT) \text{ sec}^{-1} \quad (4)$$

Using a single-pulse shock tube, Lifshitz, Carroll and Bauer⁸ have evaluated k_2 in the temperature range 770 to 930°C.

$$k_2 = 2.1 \times 10^{16} \exp(-74,300/RT) \text{ sec}^{-1} \quad (5)$$

Atkinson and Atkinson⁴ have also studied the pyrolysis of perfluoropropene and perfluoroisobutene in the temperature ranges 600 to 675 and 700 to 750°C respectively. They concluded that above 700°C that the perfluoroisobutene disproportionates giving perfluoroethane and non volatile products by a first-order mechanism. When perfluoropropene was pyrolysed in nickel

vessels in the temperature range 600-675°C the major gas phase reaction product was found to be perfluoroisobutene, and the rate of loss of perfluoropropene was represented by the rate equation:

$$\frac{d[C_3F_6]}{dt} = -1.5 \sqrt{2} k_3 [C_3F_6]^{1.5} \quad (6)$$

where

$$k_3 = 3.4 \times 10^{10} \exp(-53,500/RT) \text{ (1/mole)}^{1/2} \text{-sec}^{-1} \quad (7)$$

The purpose of the present investigation is to study the thermal decomposition of perfluoropropene in the temperature range 550-675°C.

EXPERIMENTAL

All of the pyrolyses were conducted in a static reaction system. The reactants were introduced into a cylindrical (250mm long by 6 cm I.D.), Vycor reactor vessel which was enclosed in a horizontal wire-wound furnace. Power was supplied to the furnace through a commercially available temperature controller which was capable of maintaining temperature control to within $\pm 0.5^\circ\text{C}$ over a period of several hours. In order to insure that temperature gradients along the furnace cavity were negligible, a manually controlled guard heater was placed at each end of the furnace cavity.

The temperature of the reactor vessel was monitored by four chromel-alumel thermocouples which were placed in contact with the reactor wall and equally spaced along the longitudinal axis of the vessel. The sampling tube which extended to the geometric center of the vessel and the pump tube which was sealed flush with the reactor wall were both made of 6mm Vycor tubing. Both the sampling and pump tubes were terminated outside of the furnace by 2 mm greaseless Vacuum stopcocks. The cool volume between the furnace and the stopcocks was made as small as possible.

An Aerograph model 202-B dual column, hot wire, thermal conductivity gas chromatograph and a Beckman IR-10 infrared spectrophotometer with a spectral range $300-4000\text{cm}^{-1}$ were used to identify and quantitatively determine the gaseous products as a function of reaction time. It was found that a 5 ft. column of 50/80 mesh Poropak (Waters Associate, Inc.) type N separated all of the reaction products. The column temperature was 135°C , and a helium carrier gas flow rate of 60 cc/min was maintained. The products were characterized by both their IR spectra and their gas chromatographic retention times. The concentrations of the various products were determined by comparing the electrical output of the chromatograph from the unknown sample to the output from a calibration mixture of known component concentrations.

The perfluoropropene used in these experiments was purchased from Air Products and Chemicals, Inc. The manufacturer suggested that the minimum purity of this gas was 99 percent. Subsequent gas chromatographic analysis of the gas indicated that it was well within the manufacturer's specifications. Trace impurities of octafluorocyclobutane (approx. 0.04%) and perfluorobutene-2 (approx. 0.02%) were detected. For all practical purposes the gas was free of air and other low molecular weight fluorocarbons. In all experiments the perfluoropropene was used directly from the cylinder without further purification.

Reactants and calibration mixtures were introduced into the reactor and gas chromatograph through a glass manifold equipped with greaseless vacuum stopcocks. An Aerograph 2-position, 6-way linear gas sampling valve was used in conjunction with a 2 ml sample volume to inject samples into the gas chromatograph. All pressure measurements were made with a Wallace and Tiernam Type 145 Precision Dial Manometer which has a range of 0 to 30 in of Hg. vacuum and a least count of 0.05 in of Hg. A mechanical vacuum pump, vented through a standard laboratory fume hood, was capable of evacuating the system to a pressure of approximately 10^{-3} torr.

The actual experimental data have been obtained by applying standard experimental procedures. The reactants were introduced into the reactor, which was maintained at a controlled temperature. The time dependence of the concentration of both reactants and

products was determined by withdrawing a sample from the reactor at various reaction times and analyzing the sample with the aid of the gas chromatograph and the IR spectrophotometer. These data which were obtained with temperature, initial pressure and reactant composition as independent variables were used for the evaluation of the necessary rate equations and the appropriate Arrhenius parameters.

RESULTS

The pyrolysis of perfluoropropene was studied over the temperature and initial pressure ranges 552-676°C and 50-200 torr respectively. The order of the reaction with respect to perfluoropropene was determined by measuring the half-life of perfluoropropene as a function of initial perfluoropropene concentration at 599°C. The half-lives for initial perfluoropropene pressures of 51, 102 and 204 torr were 70, 64 and 58 minutes respectively. Based on these data the reaction order was calculated to be 1.01. Therefore for all practical purposes the rate equation for the pyrolysis of perfluoropropene can be represented by the first order expression

$$\frac{d[C_3F_6]}{dt} = -k_4[C_3F_6] \quad (8)$$

The average values of the rate constant k_4 calculated from the integrated form of Eq. (8) as a function of initial

pressure and temperature are given in Table 1. An Arrhenius plot of the first order rate constant (k_4) as determined from the data is given in Figure 1. A least mean squares fit to the experimental data yields

$$k_4 = 2.58 \times 10^7 \exp(-44,580/RT) \text{ sec}^{-1} \quad (9)$$

Gas chromatographic and infrared analysis of the reaction products indicated that perfluorobutene-2 and perfluoroisobutene were the major fluorocarbon reaction products. The perfluorobutene-2 was identified by its gas chromatographic retention time. Since pure perfluoroisobutene was not available for calibration of the gas chromatograph, the perfluoroisobutene in the reaction products was identified by its uniquely characteristic infrared absorption line at 10.05 microns⁴. In addition to the above mentioned fluorocarbons traces of perfluorobutene-1 were detected under certain operating conditions. The perfluorobutene-1 was detected by both its characteristic retention time and its IR spectra. The concentration of perfluorobutene-2 as a function of reaction time for initial perfluoropropene pressures of 204 torr and various temperatures is shown in Figure 2. At 676°C the perfluorobutene-2 had leveled off at a concentration of approximately 2.0×10^{-7} m/cc by a reaction time of ten minutes. In all cases the rate of perfluorobutene-2 production increased as the initial perfluoropropene concentration was increased. The order of the production of perfluorobutene-2 with respect to perfluoropropene was between one and two.

The concentration of perfluoroisobutene as a function of reaction time for initial perfluoropropene pressures of 204 torr and various temperatures is shown in Figure 3. Since pure perfluoroisobutene was not available for calibration of the gas chromatograph, the quantitative results for this compound are based on the assumption that the chromatograph has the same sensitivity to perfluoroisobutene as the average of the perfluorobutene-2 and octafluorocyclobutane sensitivities. The rate of production of perfluoroisobutene increases as the initial perfluoropropene concentration is increased, and the rate of production of perfluoroisobutene with respect to perfluoropropene also has an order between one and two.

In addition to the fluorocarbons mentioned above, the gas phase reaction products contained carbon monoxide, carbon dioxide and silicon tetrafluoride. Butler⁷ also noticed side reactions with the wall when he studied the pyrolysis of octafluorocyclobutane in a Pyrex vessel in the temperature range 360-560°C. In all cases these three compounds were significant products. A mass balance on the carbon, including all of the gaseous carbon containing compounds, at 650°C indicated that a small carbon mass loss of 10 to 25 percent occurred. This mass loss is attributed to the small flakes of white dust that condensed in the cooler parts of the system.

DISCUSSION

The experimental results indicate that the pyrolysis of perfluoropropene in the temperature and initial pressure ranges 550-675°C and 50 to 400 torr can be represented by a first order reaction. The first order rate constant has an activation energy of 44.6 Kcal/mole and is given by Eq. 9. When the pyrolysis of perfluoropropene was carried out in nickel vessels in the same temperature range, Atkinson and Atkinson⁴ reported that their data could be represented by a reaction of order 1.5. Perfluoroisobutene and octafluorocyclobutane were the only products reported by these investigators, and in all cases only small quantities of octafluorocyclobutane were produced. They also noted small material losses which they suggested were associated with a white dust that settled in the cooler parts of their system.

The discrepancy between the order of reaction as reported in Reference 4 and the results of the present investigation bears further consideration. In their paper Atkinson and Atkinson⁴ do not specify what range of initial perfluoropropene pressures were considered. However, one Figure showing the time dependence of the concentrations of the various products and reactants at 600°C is given in their paper. In this case the initial perfluoropropene pressure was approximately 400 torr. The half-life of the reaction, as measured by Atkinson and Atkinson⁴, at these conditions is approximately 60 minutes. As discussed earlier, the half-life of the perfluoropropene

pyrolysis at 599°C determined in the present investigation varied between 58 and 70 minutes when the initial perfluoropropene pressure was varied from approximately 50 to 200 torr. It should be noted that a reaction of order 1.5 requires that the half-life be approximately doubled when the initial reactant concentration is decreased by a factor of four. Considering these comments and the fact that the half-life as measured by Atkinson and Atkinson⁴ is approximately the same as determined in this investigation it is reasonable to suggest that the pyrolyses of perfluoropropene is a first order reaction.

In order to assess the possible effects of heterogeneous reactions on the rate of the pyrolysis of perfluoropropene, the initial rate of consumption of perfluoropropene based on the present results in a Vycor vessel and the results of Reference 4 in a nickel vessel were calculated as a function of initial reactant pressure over the experimental temperature range. The numerical results of these calculations at 600°C are listed in Table II. Over the entire temperature range of this investigation the experimentally determined initial rate of reaction in a Vycor vessel is within a factor of two higher or lower than the corresponding rate in a nickel vessel as predicted by Atkinson and Atkinson⁴. Butler⁷ has previously shown that the first order rate constants for the production of tetrafluoroethylene and perfluoropropene from octafluorocyclobutane were not strongly influenced by heterogeneous effects in a Pyrex reactor even though carbon monoxide, carbon dioxide, and silicon tetrafluoride were produced during the course of the reaction.

Therefore it is concluded that the first order kinetics determined in this investigation are primarily homogeneous in nature.

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TABLE I

AVERAGE VALUES OF THE FIRST-ORDER
RATE CONSTANT, k_4

T	Initial Pressure	Number of Points	$k_4 \times 10^5$
(°C)	(torr)		(sec ⁻¹)
676	204	7	141
676	102	9	149
650	204	11	73.5
650	102	6	71.2
650	51	6	73.2
599	204	6	20.5
599	102	7	18.7
599	51	10	18.5
552	408	10	3.73
552	204	9	2.67

TABLE II

Comparison of Initial Rate of Consumption
of Perfluoropropene in Nickel and Vycor
Reactors

$$T = 600^{\circ}\text{C}$$

$$R_o = -\left(\frac{d[\text{C}_3\text{F}_6]}{dt}\right)_{t=0}$$

P_o	$(R_o)^a \times 10^8$ Nickel	$(R_o)^b \times 10^8$ Vycor
(torr)	(m/l-sec ⁻¹)	(m/l-sec ⁻¹)
51	9.7	17
102	27	35
204	77	61
408	218	140

^aData from Reference (4)

^bPresent experimental results

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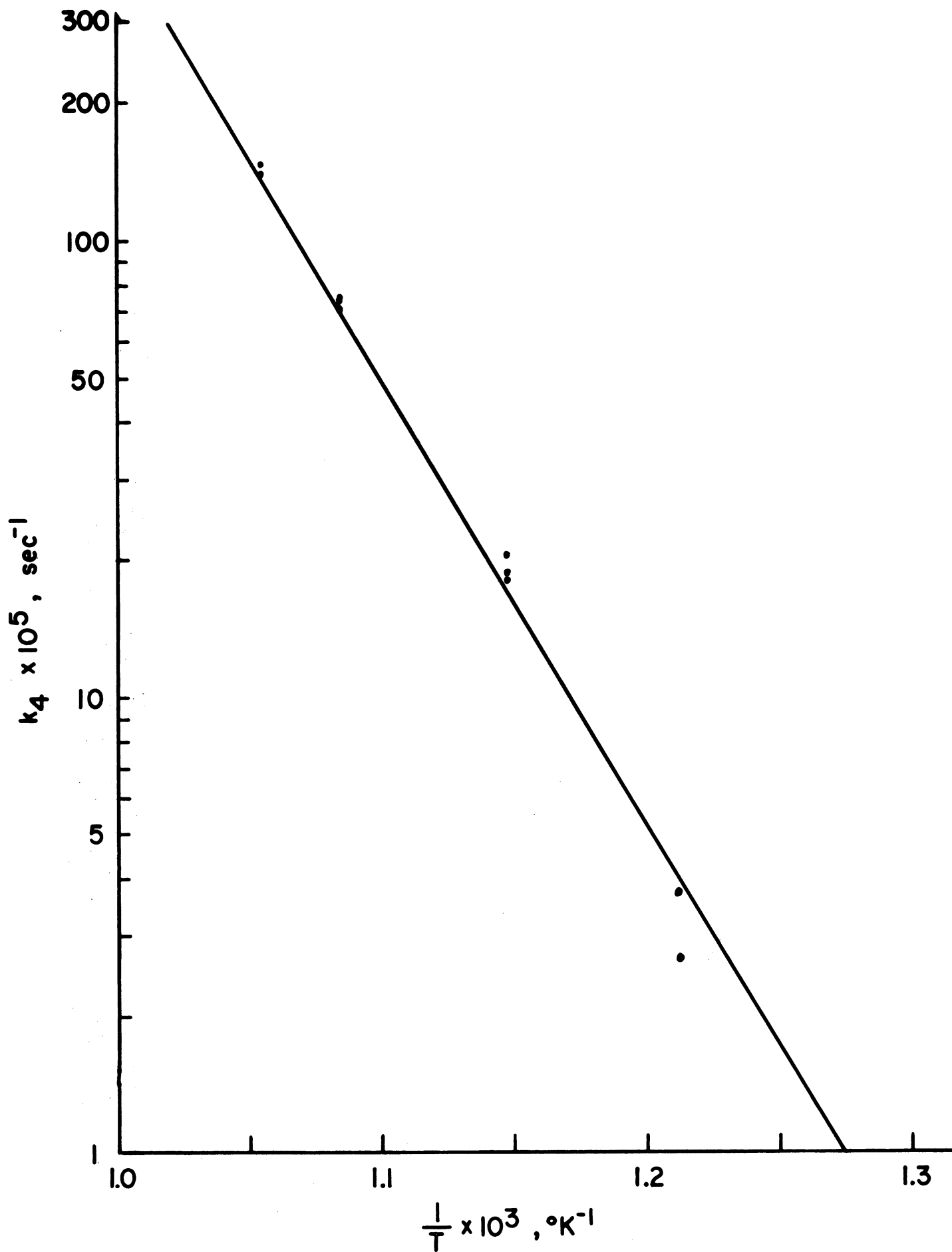


FIG 1
ARRHENIUS PLOT OF k_4 VS $1/T$

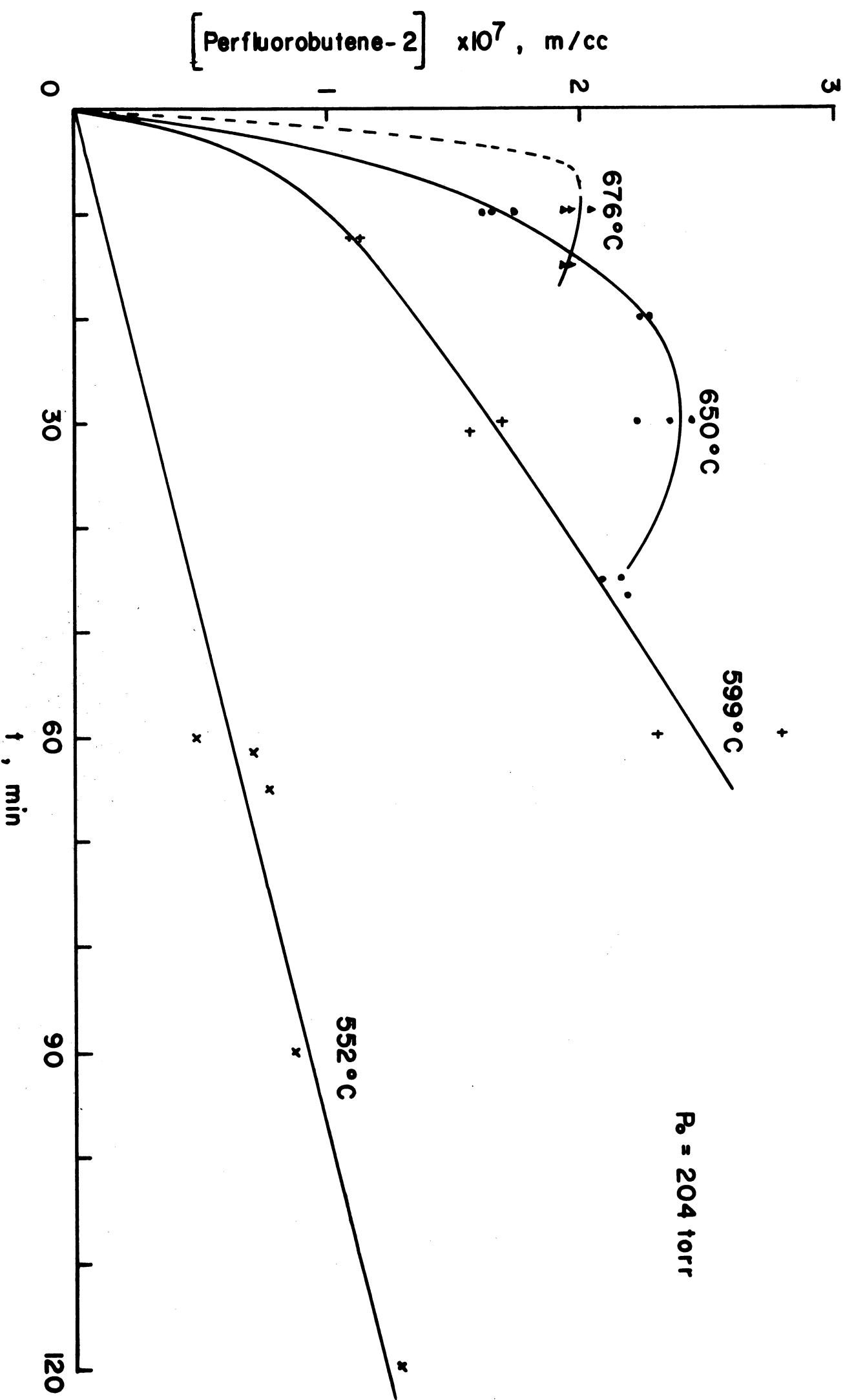
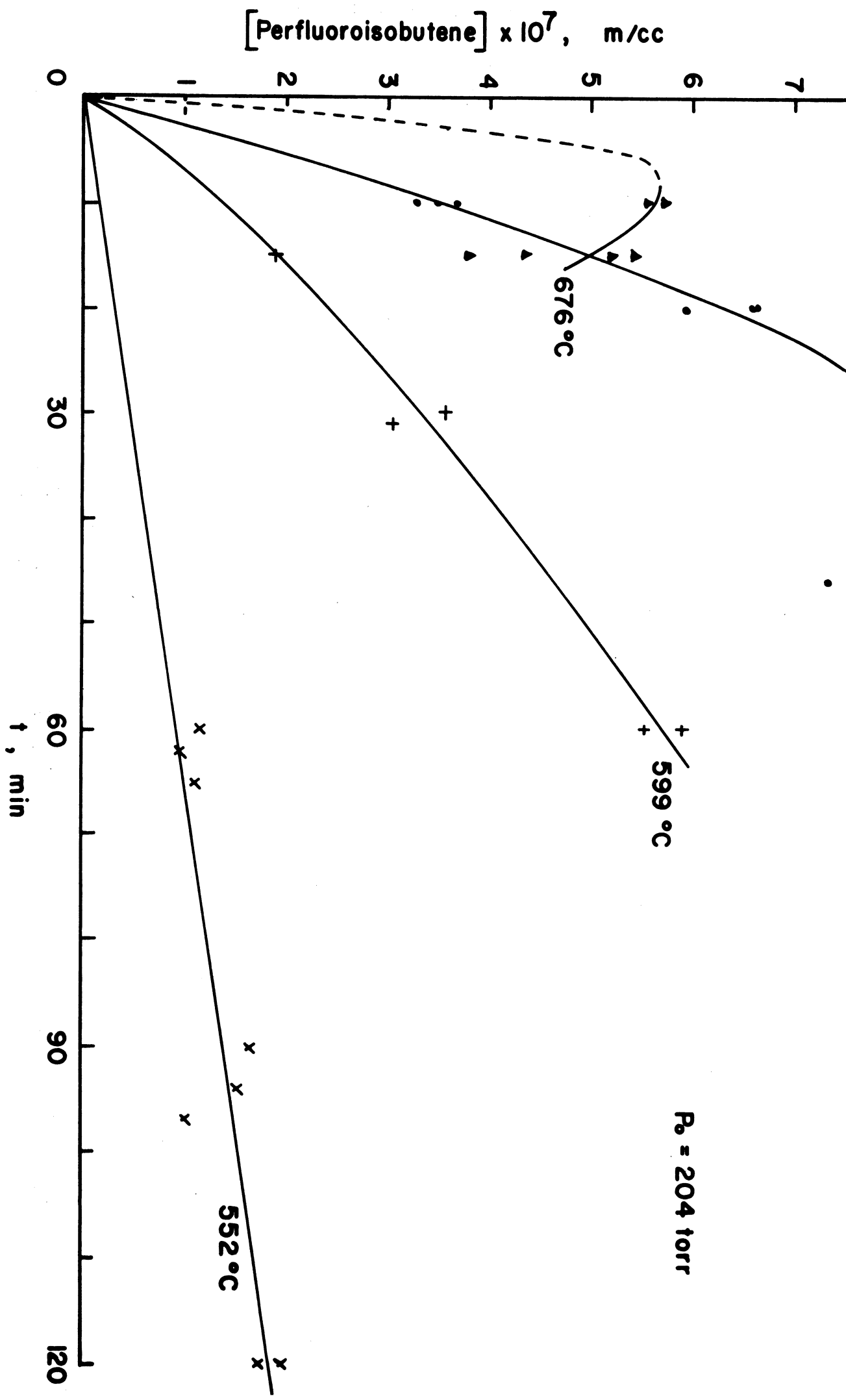


FIG 2

PERFLUOROBUTENE - 2 PRODUCTION IN PERFLUOROPROPENE



PERFLUOROISOBUTENE PRODUCTION IN PERFLUOROPROPENE PYROLYSIS

FIG 3

DOCUMENT CONTROL DATA - R & D

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