

Final Technical Report

COMBUSTION KINETICS OF TETRAFLUOROETHYLENE

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ABSTRACT

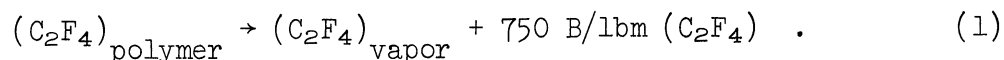
The pyrolysis of C_2F_4 , C_3F_8 , and CF_2O have been studied in the temperature and pressure ranges 300-455°C, 25-760 torr; 550-675°C, 50-410 torr; and 330-480°C, 25-600 torr, respectively. The rate equations and appropriate Arrhenius rate constants for these three reactions are reported. The oxidation kinetics of C_2F_4 are also being investigated and preliminary results in the temperature and pressure ranges 175-300°C and 25-200 torr are discussed. Finally the application of gas-solid chromatography techniques to the separation of low molecular weight fluorocarbons and the analysis of the C_2F_4 oxidation products are discussed.

I. INTRODUCTION

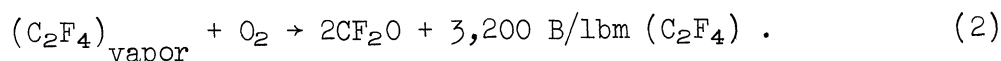
In many practical applications the detailed flow fields about reentry vehicles can only be calculated if the kinetics of the flow field are known. The flow field chemistry may be particularly important when combustion reactions are possible. Frequently, the ablation products of reentry vehicles may, undergo exothermic reactions in the boundary layer or the wake, and therefore, the combustion kinetics of ablation products are important in determining the state of the flow field including the wake electron densities.

Teflon $(C_2F_4)_n$ which is classified as a subliming ablator has been employed as an ablation material in a number of investigations.¹⁻⁴ Under the action of the aerodynamic heating, the Teflon surface begins to depolymerize into the monomer (C_2F_4) , that has a very high vapor pressure, after the surface reaches its ablation temperature. Under most conditions, the monomer flashes directly into the vapor phase without passing through the liquid state.

The Teflon ablation is given by



The C_2F_4 vapor may participate in the following combustion reaction in the boundary layer or vehicle wake



Comparing Eqs. (1) and (2) it is seen that the energy liberated by the combustion process is approximately four times the heat of ablation. Therefore, if the exothermic combustion reaction takes place to any extent in the boundary layer or wake, the flow field will be strongly influenced. The above discussion indicates that a general understanding of chemical kinetics of the C/F/O/N reaction system, including the oxidation of C_2F_4 and the pyrolysis and further reactions of the various oxidation products, is necessary before a complete understanding of the flow field in the region near a reentry vehicle using a Teflon ablation shield can be obtained.

The purpose of this continuing research project is to study the thermal oxidation of C_2F_4 and the thermal stability of the various fluorocarbons and oxygenated fluorocarbons that may be important in this reaction system. During the past year, the thermal stability of C_2F_4 and C_3F_6 have been studied. Since CF_2O is one of the primary oxygenated products of the C_2F_4 oxidation system,

its thermal stability has also been considered. The results of the preliminary C_2F_4 oxidation experiments are also reported.

II. ANALYTICAL DEVELOPMENTS

A. INTRODUCTION

During the course of these studies, gas chromatography techniques have been utilized as the primary analytical method for both the qualitative and quantitative determination of fluorocarbon mixtures. Therefore considerable effort has been expended to develop columns which can be employed to efficiently separate the various compounds of interest. The chromatographic separation of the major C_2F_4 oxidation products has been previously reported by Matula and co-workers.^{5,6} During the past year the relative retention times of a number of low molecular weight fluorocarbons on Poropak columns (Waters Associates, Inc.) have been determined and these results are reported below.

B. EXPERIMENTAL

An Aerograph model No. 202-B gas chromatograph employing a thermal conductivity detector was used for all of the separations. Mixtures were introduced into the gas chromatograph through a gas sampling valve used in conjunction with a 2 ml sample volume. The chromatograph was equipped with a linear temperature programmer which was capable of maintaining isothermal column operation in the temperature range 30 to 400°C.

The fluorocarbons utilized in this study were obtained from a number of sources. The perfluoromethane (CF_4), perfluoroethane (C_2F_6) and a mixture of cis- and trans- C_4F_8 -2 were purchased from the Matheson Company, East Rutherford, New Jersey. The 2-trifluoromethylpropene (C_4F_{10}), perfluorobutane (C_4F_{10}), perfluorobutadiene-1,2 (C_4F_6), perfluorobutyne-2 (C_4F_6), perfluorocyclobutene (c- C_4F_6), perfluorocyclobutane (c- C_4F_8), perfluoropropane (C_3F_8), and perfluoropropene (C_3F_6) were purchased from Penninsular Chem-Research Inc., Gainesville, Florida. The perfluoroethylene (C_2F_4) was purchased from Columbia Organic Chemicals, Inc., Columbia, South Carolina, and the iso- C_4F_8 was produced by pyrolysing perfluoropropene at 700°C for 15 min in a Vycor reactor vessel.

A number of variable length GSC columns were constructed by packing 1/4" O.D. copper tubing with 50/80 mesh Poropak (Waters Associate, Inc.). The separation capabilities of Types N, P, Q, R, S, and T Poropak were studied. Before final installation in the chromatgraph, each of the columns was heated to 200°C and purged with helium (60 ml/min) for 2 hr. The retention volumes of all compounds were determined from the analysis of both pure compounds and fluorocarbon mixtures that had been prepared in the laboratory. The separations were obtained by operating the columns isothermally in the temperature range 75 to 175°C while maintaining a constant helium carrier gas flow rate of 60 ml/min.

C. RESULTS AND DISCUSSION

The relative retention volumes of the various fluorocarbon compounds as a function of column material, length and temperature are listed in Tables 1-4. All of these results are based on a helium carrier gas flow rate of 60 ml/min. If the relative retention volume of a compound is not listed in the tables the retention time was greater than 25 min, and a notation of n.a. implies that a compound was not tested. Poropak Type P does not effectively separate the compounds of interest and hence results for this column are not listed. A 10 ft column of Poropak Type T maintained at 150°C was found to be the most effective for the separation of a mixture containing air and a large number of low molecular weight fluorocarbons. A GSC chromatogram of a complex, gaseous fluorocarbon mixture obtained with the aid of a 10 ft, Poropak Type T column is shown in Fig. 1. The column temperature was maintained at 150°C and the separation was completed in approximately 17 min. The perfluorocyclobutane and perfluorobutane were not resolved on this column.

TABLE 1

RELATIVE RETENTION VOLUMES OF SEVERAL FLUOROCARBONS ON PORAPAK TYPE T

 $(C_2F_6 = 1.00)$

Compound	6 ft at 100°C		6 ft at 150°C		6 ft at 175°C		10 ft at 150°C		10 ft at 175°C	
	t_m (a)	RRV(b)	t_m	RRV	t_m	RRV	t_m	RRV	t_m	RRV
Air	0.70	0.49	0.65	0.68	0.66	0.82	1.03	0.64	1.03	0.70
CF ₄	0.82	0.57	0.71	0.74	0.66	0.82	1.17	0.72	1.13	0.77
C ₂ F ₆	1.44	1.00	0.96	1.00	0.81	1.00	1.62	1.00	1.47	1.00
C ₂ F ₄	1.91	1.33	1.09	1.14	0.92	1.14	1.89	1.17	1.68	1.14
C ₃ F ₈	3.53	2.45	1.55	1.62	1.19	1.47	2.73	1.67	2.21	1.50
CF ₃ -C=C-CF ₃	5.91	4.10	1.92	2.00	1.39	1.72	3.51	2.17	2.75	1.87
C ₃ F ₆	6.61	4.59	2.10	2.19	1.47	1.82	3.84	2.37	2.96	2.01
c-C ₄ F ₈	10.6	7.36	2.90	3.02	1.94	2.39	5.40	3.33	3.90	2.65
CF ₃ -CF ₂ -CF ₂ -CF ₃	10.6	7.36	2.90	3.02	1.94	2.39	5.40	3.33	3.90	2.65
trans-C ₃ F ₈ -2	16.9	11.74	3.50	3.65	2.18	2.69	6.48	4.00	4.98	3.39
cis-C ₄ F ₈ -2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	7.30	4.51	n.a.	n.a.
c-C ₃ F ₆	18.0	12.50	3.95	4.12	2.44	3.01	7.45	4.60	5.02	3.42
CF ₂ =CF-CF=CF ₂	22.3	15.49	4.55	3.74	2.73	3.37	8.60	5.31	5.63	3.83
iso-C ₃ F ₈	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	10.4	6.42	n.a.	n.a.
CF ₃ -C=CF ₂ CF ₃	---	---	8.08	8.42	4.55	5.62	15.4	9.51	9.25	6.29

(a) t_m = retention time in minutes to peak.

(b) RRV = relative retention volume with respect to perfluoroethane.

Helium Carrier Gas Flow Rate: 60 ml/min

Column Material: 50/80 mesh

TABLE 2

RELATIVE RETENTION VOLUMES OF SEVERAL FLUOROCARBONS ON PORAPAK TYPE N

 $(C_2F_6 = 1.00)$

Compound	5 ft at 100°C		5 ft at 150°C		10 ft at 175°C	
	t_m (a)	RRV ^(b)	t_m	RRV	t_m	RRV
Air	0.60	0.49	0.58	0.76	1.17	0.81
CF ₄	0.71	0.58	0.58	0.76	1.17	0.81
C ₂ F ₆	1.22	1.00	0.76	1.00	1.44	1.00
C ₂ F ₄	1.56	1.27	0.86	1.12	1.62	1.12
C ₃ F ₈	2.87	2.35	1.19	1.57	2.03	1.41
CF ₃ -C=C-CF ₃	4.62	3.79	1.48	1.95	2.35	1.63
C ₃ F ₆	4.99	4.09	1.57	2.07	2.95	2.05
c-C ₄ F ₈	7.84	6.13	2.15	2.83	3.13	2.17
CF ₃ -CF ₂ -CF ₂ -CF ₃	8.44	6.92	2.24	2.93	3.13	2.17
trans-C ₄ D ₈ -2	12.53	10.27	2.56	3.37	3.46	2.40
cis-C ₄ F ₈ -2	n.a.	n.a.	n.a.	n.a.	3.70	2.57
c-C ₄ F ₆	12.53	10.27	2.83	3.72	3.90	2.71
CF ₂ =CF-CF=CF ₂	16.2	13.28	3.29	4.33	4.35	3.02
iso-C ₄ F ₈	n.a.	n.a.	n.a.	n.a.	4.65	3.23
CF ₃ -C=CF ₂ CF ₃	---	---	5.90	7.76	7.32	4.08

(a) t_m = retention time in minutes to peak.

(b) RRV = relative retention volume with respect to perfluoroethane.

Helium Carrier Gas Flow Rate: 60 ml/min

Column Material: 50/80 mesh

TABLE 3

RELATIVE RETENTION VOLUMES OF SEVERAL FLUOROCARBONS ON PORAPAK TYPES R AND S

(C₂F₆ = 1.00)

Compound	Type R		Type R		Type S		Type S	
	6 ft at 100°C		6 ft at 150°C		6 ft at 100°C		6 ft at 150°C	
	t _m (a)	RRV(b)	t _m	RRV	t _m	RRV	t _m	RRV
Air	0.85	0.57	0.86	0.80	0.80	0.57	0.75	0.75
CF ₄	0.95	0.64	0.86	0.80	0.90	0.64	0.80	0.80
C ₂ F ₆	1.48	1.00	1.07	1.00	1.41	1.00	1.00	1.00
C ₂ F ₄	1.86	1.26	1.17	1.10	1.71	1.21	1.10	1.12
C ₃ F ₈	3.00	2.03	1.54	1.44	2.98	2.11	1.42	1.42
CF ₃ -C=C-CF ₃	4.30	2.91	1.81	1.69	2.98	2.11	1.42	1.42
C ₃ F ₆	4.33	2.93	1.80	1.68	4.19	2.97	1.70	1.70
c-C ₄ F ₈	6.88	4.65	2.39	2.23	6.90	4.89	2.30	2.30
CF ₃ -CF ₂ -CF ₂ -CF ₃	7.56	5.11	2.57	2.40	7.63	5.41	2.45	2.45
trans-C ₄ F ₈ -2	8.80	5.95	2.57	2.40	8.80	6.24	2.45	2.45
c-C ₄ F ₆	9.62	6.50	2.87	2.68	9.98	7.08	2.70	2.70
CF ₂ =CF-CF=CF ₂	12.30	8.31	3.31	3.09	12.5	8.86	3.20	3.20
CF ₃ -C=CF ₂ CF ₃	---	---	6.10	5.70	---	---	5.69	5.69

(a) t_m = retention time in minutes to peak.(b) RRV = relative retention volume with respect to perfluoroethane. Helium Carrier gas flow rate: 60 ml/min
Column Material: 50/80 mesh

TABLE 4

RELATIVE RETENTION VOLUMES OF SEVERAL FLUOROCARBONS ON PROAPAK TYPE Q

 $(C_2F_6 = 1.00)$

Compound	6 ft at 100°C		6 ft at 150°C	
	t_m (a)	RRV(b)	t_m	RRV
Air	0.79	0.52	0.83	0.75
CF ₄	0.90	0.60	0.85	0.77
C ₂ F ₆	1.51	1.00	1.11	1.00
C ₂ F ₄	1.74	1.15	1.22	1.10
C ₃ F ₈	3.32	2.20	1.56	1.51
CF ₃ -C=C-CF ₃	4.55	3.01	1.80	1.73
C ₃ F ₆	4.20	2.78	1.95	1.76
c-C ₄ F ₈	7.49	4.96	2.81	2.53
CF ₃ -CF ₂ -CF ₂ -CF ₃	n.a.	n.a.	n.a.	n.a.
trans-C ₄ F ₈ -2	n.a.	n.a.	n.a.	n.a.
c-C ₄ F ₆	n.a.	n.a.	n.a.	n.a.
CF ₂ =CF-CF=CF ₂	n.a.	n.a.	n.a.	n.a.
CF ₃ -C=CF ₂	n.a.	n.a.	n.a.	n.a.
CF ₃				

(a) t_m = retention time in minutes to peak.

(b) RRV = relative retention volume with respect to perfluoroethane.

Helium Carrier gas flow rate: 60 ml/min

Column Material: 50/80 mesh

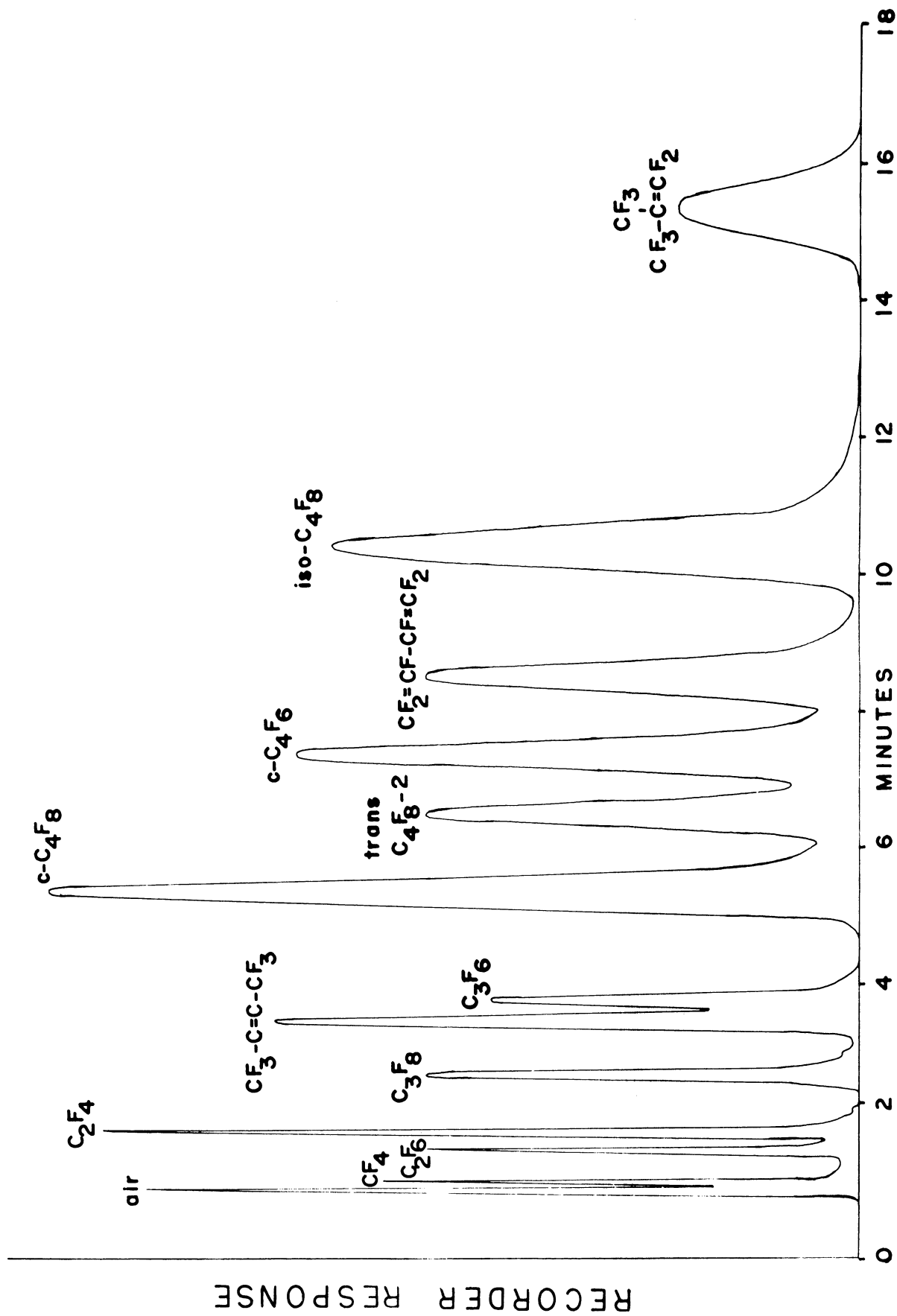


Fig. 1. Gas-solid chromatogram of fluorocarbons.

III. PYROLYSIS OF C_2F_4 AND C_3F_6

A. C_2F_4 PYROLYSIS

1. Introduction

The vapor phase dimerization of tetrafluoroethylene (C_2F_4) in the temperature and pressure ranges 290-470°C and 100 to 700 torr have been studied by Lacher, Tompkin, and Park.⁷ Their experiments were conducted in a one-liter Pyrex vessel, and the kinetic results were based on total pressure measurements as a function of reaction time. The rate of consumption of C_2F_4 was found to be second order with respect to C_2F_4 and the second order Arrhenius rate constant (k_2) was reported to have an activation energy of 26.299 kcal/mole and a frequency factor of 16.5×10^{10} cc/mole-sec⁻¹. Atkinson and co-workers^{8,9} studied the decomposition of C_2F_4 at temperatures from 300 to 800°C. At temperatures below 600°C, they reported that the second order dimerization of C_2F_4 to octafluorocyclobutane (c- C_4F_8) and the first order back reaction were much faster than any of the other reactions which were taking place. In the temperature range 600 to 800°C hexafluoroethane (C_2F_6) and octafluorobutenes were also formed, and at temperatures above 800°C C_2F_6 and tars were the primary products. The dimerization of C_2F_4 in the temperature and pressure range 300-550°C and 200 to 550 torr respectively was studied in a static Pyrex reactor. The kinetic data were based on the measurement of total pressure as a function of reaction time, and the second order Arrhenius rate constant (k_2) for the dimerization of C_2F_4 in this temperature range was reported to have an activation energy of 25.4 kcal/mole and a frequency factor of 10.3×10^{10} cc/mole-sec⁻¹.

Butler¹⁰ studied the first order thermal decomposition of c- C_4F_8 to C_2F_4 in the temperature range 360 to 560°C. These experiments were conducted in a one-liter Pyrex flask, and initial reactant pressures between 0.003 and 600 torr were considered. Based on the measured equilibrium composition in this system and the numerical value of the first order rate constant for the decomposition of c- C_4F_8 , Butler calculated that the second order rate constant (k_2) for the rate of decrease of C_2F_4 and an activation energy of 24.0 kcal/mole and a frequency factor of $10^{10.4}$ cc/mole-sec⁻¹. Butler also found that during the course of c- C_4F_8 decomposition that a slow parallel decomposition forming perfluoropropene (C_3F_6) occurred with a first order rate constant (k_3). The Arrhenius parameters for k_3 were determined to be $10^{17.2}$ sec⁻¹ and 87.2 kcal/mole. Atkinson and Atkinson⁹ also showed that the formation of C_3F_6 from c- C_4F_8 is a first order reaction. Their experiments were conducted in a nickel pyrolysis tube and covered the temperature range 550 to 650°C. Based on these experiments, the first order rate constant (k_3) was reported to have an activation energy of 79.0 kcal/mole and a frequency factor of 3.9×10^{16} sec⁻¹.

Lifshitz et al.,¹¹ have studied the thermal decomposition of $c\text{-C}_4\text{F}_8$ behind reflected shock waves in a single-pulse shock tube over the temperature range 770 to 930°C. During the course of these experiments, shock waves were driven into highly diluted $c\text{-C}_4\text{F}_8$ argon mixtures and the initial partial pressures of $c\text{-C}_4\text{F}_8$ behind the reflected shock waves were approximately 7 mm. The rate of decomposition of $c\text{-C}_4\text{F}_8$ was found to be first order with respect to $c\text{-C}_4\text{F}_8$, and the first order Arrhenius rate constant (k_1) was reported to have an activation energy of 74.300 kcal/mole and a frequency factor of $2.1 \times 10^{16} \text{ sec}^{-1}$. These results can be used in conjunction with the known temperature dependence equilibrium constant for the $c\text{-C}_4\text{F}_8 \rightleftharpoons 2 \text{C}_2\text{F}_4$ equilibrium system (i.e., see Ref. 10) to estimate k_2 .

In order to evaluate the second order rate constant (k_2) for the dimerization of C_2F_4 based on the experimental determination of total pressure as a function of reaction time, the previous investigators^{7,8} were forced to make certain assumptions. The present investigation was undertaken in order to determine three independent numerical values of the rate constant (k_2). The three independent values of k_2 were determined by simultaneously measuring the C_2F_4 concentration, the $c\text{-C}_4\text{F}_8$ concentration, and the total pressure as a function of reaction time. The concentrations of C_2F_4 and $c\text{-C}_4\text{F}_8$ were determined with the aid of GSC chromatography. The numerical values of k_2 based on total pressure are compared directly to the values reported in Refs. 7 and 8, and the values of k_2 based on the concentration measurements were used to check the assumptions which were made in order to determine k_2 from the total pressure measurements. The present series of experiments were conducted in the temperature and pressure ranges 300-455°C and 25-760 torr.

2. EXPERIMENTAL

The experiments were conducted in a cylindrical, Vycor reactor which was enclosed in a horizontal wire-wound furnace. The vessel was approximately 250 mm long and had a volume of 455 ml. Prior to instillation in the furnace the reactor was cleaned with a 5% HF-H₂O solution. Power was supplied to the furnace from a commercially available temperature controller which was capable of controlling the temperature 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 installed 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 6 mm Vycor tubing. Both the sampling and pump tubes were terminated outside of the furnace by 2 mm greaseless vacuum stopcocks. The dead volume between the furnace and the stopcocks was approximately 0.6 ml. Since large gas samples were extracted from the reactor, this small dead volume did not have a significant effect on the results. The experimental facilities utilized for these experiments are described in detail in a previous publication.⁶

An Aerograph model 202-B dual column, hot wire, thermal conductivity gas chromatograph was used to identify and quantitatively determine the gaseous products as a function of reaction time. A Beckman IR-10 infrared spectrophotometer with a spectral range 300-4000 cm^{-1} was used as a back up instrument for the identification of any species which escaped detection by the gas chromatograph. A 4 ft column of 50/80 mesh Poropak (Waters Associate, Inc.) Type N maintained at 100°C was used to separate the C_2F_4 pyrolysis products. The column was packed in 1/4 in. O.D. type 316 stainless steel tubing, and the helium carrier gas flow rate was maintained at 75 ml/min. Prior to final installation in the chromatograph, the column was activated by heating it to 200°C while purging with helium (75 ml/min) for 2 hr. 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 C_2F_4 used in this study was purchased from Columbia Organic Chemicals, Inc., Columbia, South Carolina, and it was stored in a steel cylinder as a liquified gas under its own vapor pressure of approximately 20 atm. at 20°C. The manufacturer stabilized the liquid phase, by adding 1% by weight of alpha-pinene to the liquid. The supplier specified that the minimum purity of the gas phase was 99%. Subsequent gas chromatographic analysis of the C_2F_4 indicated that the major gas phase impurity was $\text{c-C}_4\text{F}_8$ and that traces of CO_2 , CF_4 , and C_2F_6 were also present. The mole fraction of the $\text{c-C}_4\text{F}_8$ impurity was determined to be approximately 9×10^{-3} . In order to determine if the rate of C_2F_4 pyrolysis was effected by residual inhibitor which may have been present in the gaseous C_2F_4 supplied from the cylinder, a number of preliminary experiments were conducted in which both purified C_2F_4 and C_2F_4 taken directly from the cylinder were pyrolysed. Purified C_2F_4 was obtained by withdrawing a sample of C_2F_4 from the cylinder and collecting that fraction of the sample which was volatile at -126°C and condensible at -196°C. Heicklen and Knight¹² report that this purification technique yields C_2F_4 with less than 0.1% of any impurity. In all cases the experimental results were identical for both purified and cylinder C_2F_4 . Therefore in all experiments the C_2F_4 was taken directly from the cylinder and used without further purification. The $\text{c-C}_4\text{F}_8$ and C_3F_6 used in these experiments were purchased from the Matheson Company, East Rutherford, New Jersey and Air Products and Chemicals, Inc., Allentown, Pennsylvania, respectively. Both of the gases had impurities of less than 1% and were used directly without further purification.

Reactants and calibration mixtures were introduced into the reactor and gas chromatograph through a glass manifold equipped with greaseless vacuum stopcocks. A 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 Tiernan 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.

During any series of experiments, the reactants were introduced into the reactor, which was maintained at a controlled temperature, and the time dependence of the total pressure, and the concentration of both reactants and products was determined by withdrawing a large sample from the reactor at various reaction times and analyzing the sample with the aid of the gas chromatograph and the IR spectrophotometer. The experimental data at the lowest temperature were determined for reactions in which the extent of reaction, with respect to $c\text{-C}_4\text{F}_8$, ranged from approximately 10 to 35%. At the highest temperature the extent of reaction varied from approximately 20 to 75%. 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.

3. RESULTS

The results of previous investigators have indicated that the rate of C_2F_4 pyrolysis, in the temperature range 300-550°C, can be represented by

$$\frac{d[\text{C}_2\text{F}_4]}{dt} = -k_2[\text{C}_2\text{F}_4]^2 + k_1[c\text{-C}_4\text{F}_8] \quad (3)$$

Butler¹⁰ has shown that if the temperature is less than 500°C the second term on the right-hand side of Eq. (3) is insignificant with respect to the first term. Therefore the rate expression for the pyrolysis of C_2F_4 at temperatures below 500°C can be represented by the equation

$$\frac{d[\text{C}_2\text{F}_4]}{dt} = -k_2[\text{C}_2\text{F}_4]^2 \quad (4)$$

The integrated form of Eq. (4) yields the rate constant (k_2) as a function of parameters which were experimentally determined

$$k_2 = \frac{1}{t} \left[\frac{1}{[\text{C}_2\text{F}_4]_t} - \frac{1}{[\text{C}_2\text{F}_4]_0} \right] \text{ cc/mole-sec}^{-1} \quad (5)$$

where t is the reaction time in seconds and $[\text{C}_2\text{F}_4]_t$ and $[\text{C}_2\text{F}_4]_0$ are the measured concentrations of C_2F_4 (moles/cc) at time t and $t = 0$ respectively. Assuming that the back reaction is insignificant and that the only important products are C_2F_4 and $c\text{-C}_4\text{F}_8$, Eq. (3) can be rewritten in terms of the $c\text{-C}_4\text{F}_8$ concentration.

$$\frac{d[c\text{-C}_4\text{F}_8]}{dt} = \frac{k_2}{2} \left(([\text{C}_2\text{F}_4]_0 - 2[c\text{-C}_4\text{F}_8]_0) - 2[c\text{-C}_4\text{F}_8]_t \right) \text{ cc/mole-sec}^{-1} \quad (6)$$

The numerical value of the second order rate constant for C_2F_4 pyrolysis (k_2') can be determined by integrating Eq. (6).

$$k_2' = \frac{1}{t} \left(\frac{2[c-C_4F_8]_t - [c-C_4F_8]_0}{[C_2F_4]_0([C_2F_4]_0 - 2([c-C_4F_8]_t - [c-C_4F_8]_0))} \right) \text{ cc/mole-sec}^{-1} \quad (7)$$

The numerical value of k_2' as calculated from Eq. (7) should be equal to the value of k_2 calculated from Eq. (5). However, since the two k_2 's are based on independent experimental measurements, the "prime" nomenclature is used to differentiate between the two experimental values of the rate constant k_2 .

Since the stoichiometry of the reaction has been assumed and the only products are C_2F_4 and $c-C_4F_8$, the numerical value of k_2 can also be determined by measuring the total pressure of the products as a function of time. The numerical value of k_2 based on total pressure measurements is given the symbol k_2''

$$k_2'' = \frac{RT}{t} \left[\frac{1}{(2P_t) - (P_{C_2F_4})_0} - \frac{1}{(P_{C_2F_4})_0} \right] \text{ cc/mole-sec}^{-1} \quad (8)$$

where R is the universal gas constant, T is the reaction temperature, P_t is the total system pressure at time t and P_0 is the initial pressure.

The order of the C_2F_4 pyrolysis reaction was determined at 365°C by applying the half-life method. During the course of these experiments, the initial C_2F_4 pressure was varied from 740 to 175 torr, and the C_2F_4 half-life was approximately 2×10^3 sec when the initial C_2F_4 pressure was 175 torr. A least mean square fit to the data indicated that the order of reaction was 1.98, and hence for all practical purposes the rate equation for the pyrolysis of C_2F_4 is given by Eq. (4).

Once the reaction was established to be second order, the pyrolysis of C_2F_4 was studied over the temperature and initial pressure ranges 300 to 450°C and 50 to 200 torr, respectively. The three independent rate constants given by Eqs. (5), (7), and (8) were calculated from the experimentally determined time dependence of the C_2F_4 concentration, $c-C_4F_8$ concentration and total pressure. The numerical values of these rate constants based on a series of experiments with a reaction temperature and initial C_2F_4 pressure of 452°C and 50.8 torr are listed in Table 5. Arrhenius plots of the three second order rate constants k_2 , k_2' , and k_2'' are given in Figs. 2-4. Each of these curves is based on 31 data points. The Arrhenius curves for k_2'' as calculated from the results given in Refs. 7 and 8 are also given in Fig. 4.

TABLE 5

SECOND ORDER RATE CONSTANT FOR TETRAFLUOROETHYLENE PYROLYSIS AT 725°K

t (sec)	k_2	k_2'	k_2''
	(cc/mole-sec ⁻¹)		
300	2240	1947	2520
300	2278	1904	2520
600	2379	1791	2380
600	2355	1865	2380
900	2295	1871	2250
900	2260	1886	2250
1200	2250		2502
1800	2381		2561
Average	2305	1877	2420

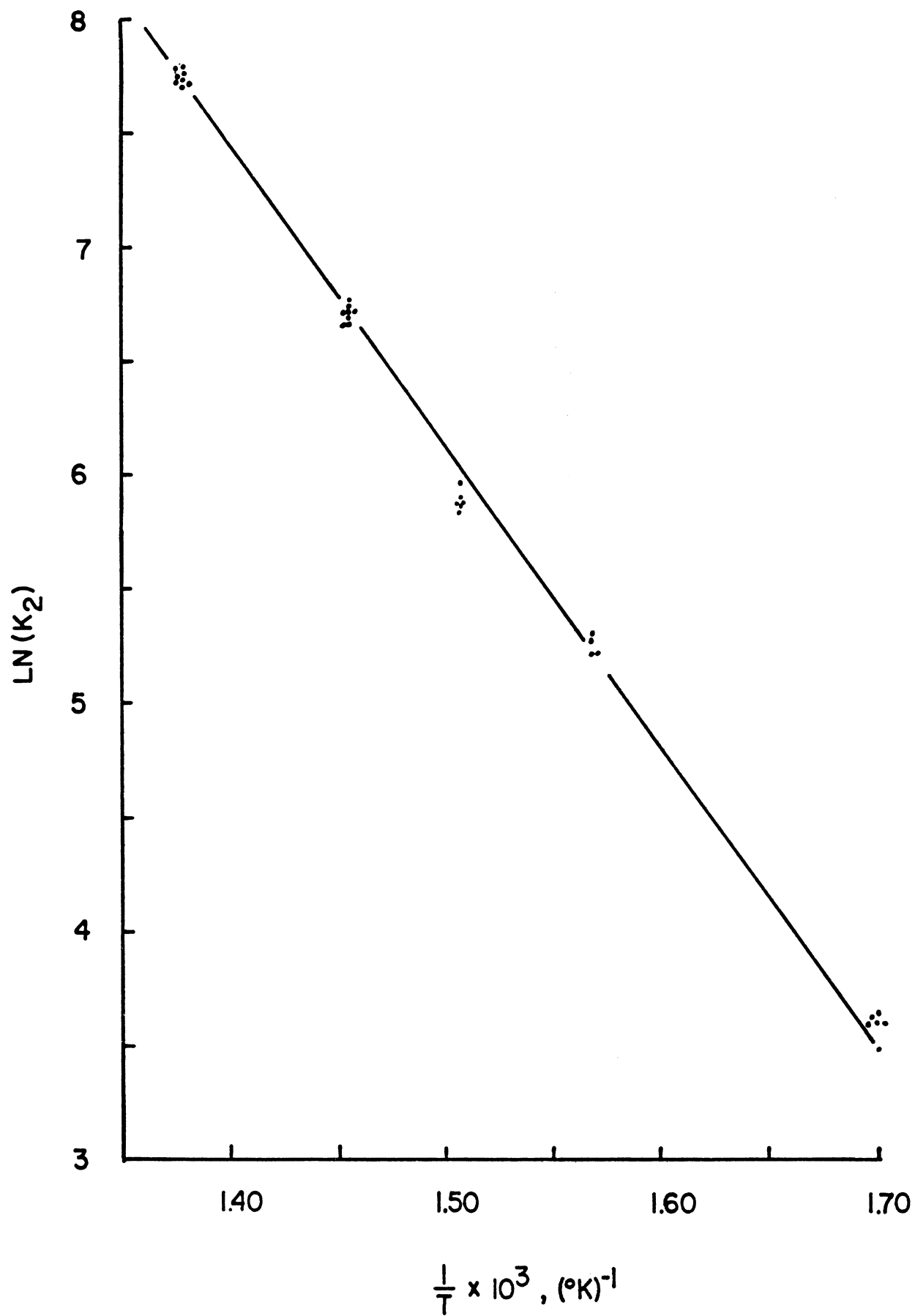


Fig. 2. Arrhenius temperature dependence of k_2 .

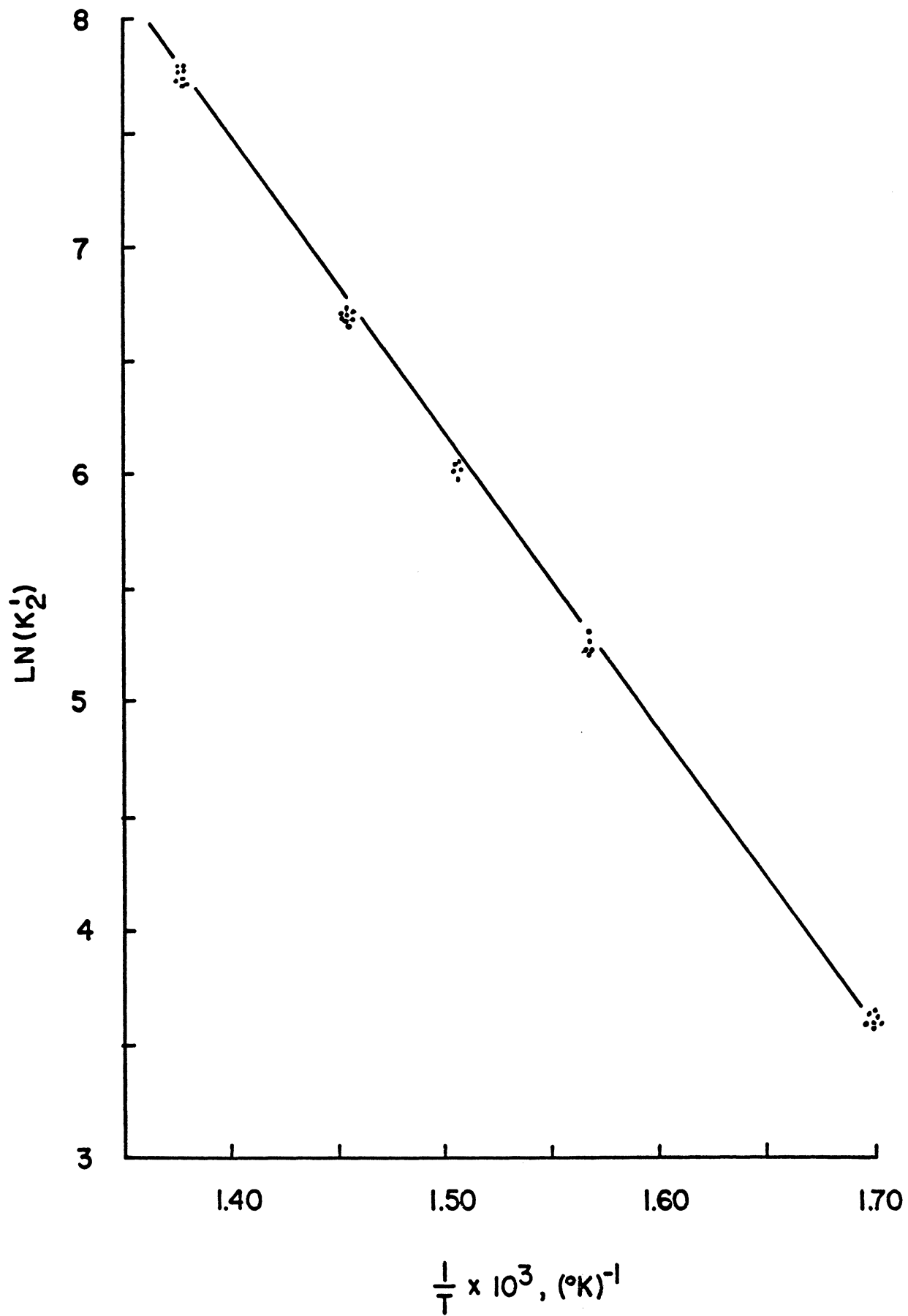


Fig. 3. Arrhenius temperature dependence of k_2' .

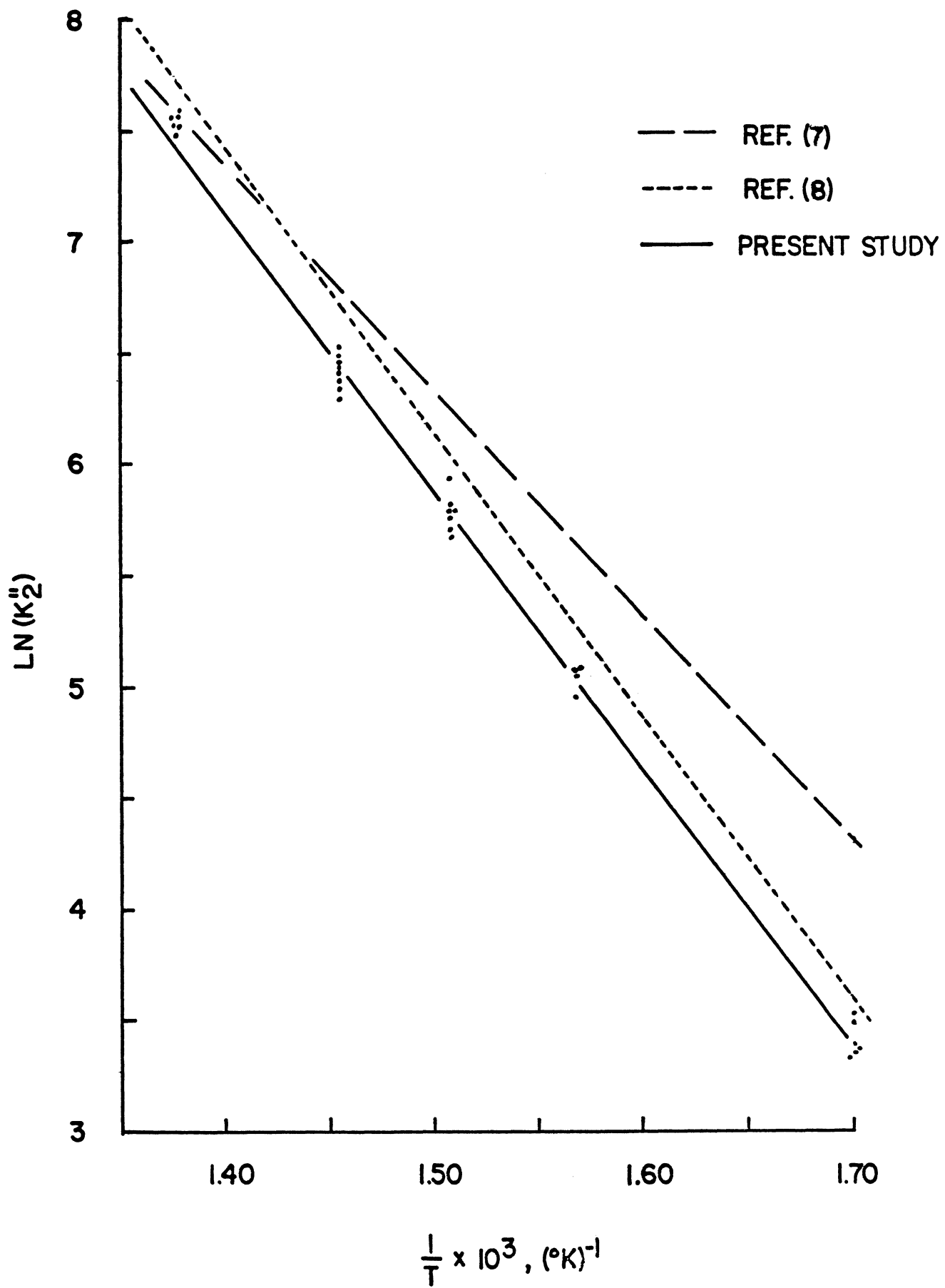


Fig. 4. Arrhenius temperature dependence of k_2'' .

The Arrhenius expressions for the temperature dependence of the three rate constants obtained by a least-mean-squares fit of the experimental data are given by

$$k_2 = 10^{11.07 \pm .03} \exp\left(\frac{-25,635 \pm 90}{RT}\right) \text{ cc/mole-sec}^{-1} \quad (9)$$

$$k_2' = 10^{10.81 \pm .07} \exp\left(\frac{-25,140 \pm 200}{RT}\right) \text{ cc/mole-sec}^{-1} \quad (10)$$

$$k_2'' = 10^{11.36 \pm .07} \exp\left(\frac{-26,500 \pm 200}{RT}\right) \text{ cc/mole-sec}^{-1} . \quad (11)$$

The thermal decomposition of $c\text{-C}_4\text{F}_8$ was studied in the temperature and pressure ranges 452 to 552°C and 100 to 200 torr. These experiments were conducted in order to confirm the results of previous investigators concerning the relative rates of the second order production of $c\text{-C}_4\text{F}_8$ from C_2F_4 and the first order decomposition of $c\text{-C}_4\text{F}_8$. The results of these experiments confirmed the validity of the assumption that the term representing the first order back reaction in Eq. (3) is insignificant with respect to the contribution of the second order term for temperatures less than 460°C.

It has been previously shown^{9,10} that both C_2F_4 and C_3F_6 are formed by parallel, unimolecular reactions during the course of $c\text{-C}_4\text{F}_8$ pyrolysis. These unimolecular reactions are given by



Butler¹⁰ has shown that both k_1 and k_3 can be determined if k_2 is known and the concentrations of $c\text{-C}_4\text{F}_8$, C_2F_4 , and C_3F_6 are measured during the course of $c\text{-C}_4\text{F}_8$ pyrolysis. The numerical values of k_1 and k_3 based on our limited $c\text{-C}_4\text{F}_8$ pyrolysis data at both 452 and 552°C are in reasonable agreement with the results given by Butler.¹⁰

4. DISCUSSION

The pyrolysis of C_2F_4 has been studied in the temperature and pressure ranges 290 to 470°C and 100 to 700 torr. This reaction was shown to be second order with respect to the concentration of C_2F_4 and the numerical value of the second order rate constant based on three independent experimental measurements has been determined. These results were obtained by simultaneously measuring the C_2F_4 concentration, the $c\text{-C}_4\text{F}_8$ concentration and the total pressure as a function of reaction time.

The temperature dependence of the second order rate constant (k_2'') based solely on total pressure measurements, has been previously reported in the literature.^{7,8} In the temperature range of interest, the values of k_2'' reported in Refs. 7 and 8 vary by approximately 26%. The numerical values of k_2 and k_2'' evaluated in the present study are within approximately 5 to 12% of each other and they generally fall between the results of the previous investigators. However, the second order rate constant (k_2') based on the measured $c\text{-C}_4\text{F}_8$ concentration, is approximately 20% lower than k_2 .

A number of possible reasons for the variance between k_2 and k_2' and k_2'' were considered. An error analysis was made in order to determine if the variance in the rate constants was due to experimental errors. This analysis revealed that the expected deviation in the rate constants based on the estimated experimental errors were not large enough to account for the measured deviations. To experimental determination of the second order rate constants k_2 , k_2' , and k_2'' were based on two assumptions: (1) C_2F_4 and $c\text{-C}_4\text{F}_8$ were the only important products; (2) the first order rate of decomposition of $c\text{-C}_4\text{F}_8$ was negligible with respect to the second order rate of formation of $c\text{-C}_4\text{F}_8$. Careful gas chromatographic analysis of the reaction products indicated that no significant side reactions were occurring when the reaction temperature was less than or equal to 452°C . As discussed earlier, the validity of the second assumption was confirmed by studying the thermal decomposition of $c\text{-C}_4\text{F}_8$ at 452°C . The possible effects of any heterogeneous effects were also considered. The previous studies^{7,8} were conducted in Pyrex reactor vessels in which the surface to volume ratios were varied by a factor of 100 with no significant effect on the rate of reaction. The present investigation was conducted in a Vycor reactor with yet another surface to volume ratio. Since heterogeneous reactions are strongly influenced by both the reactor material and surface to volume ratio it was concluded that the consistency of the results obtained by similar methods over a broad range of experimental conditions preclude any significant surface effects.

The frequency factor associated with the second order rate constant k_2 can be estimated from either simple kinetic theory considerations or the theory of absolute reaction rates. The molecular diameter of C_2F_4 , which is required for the kinetic theory calculations, is assumed to be 5.12\AA .¹³ The molecular diameter reported in Ref. 13 was determined by correlating viscosity measurements with the aid of the Lennard-Jones (6-12) intermolecular potential energy function. The calculated frequency factor, based on kinetic theory, at 455°C is 1.35×10^{14} cc/mole-sec⁻¹. This result is approximately one thousand times the experimentally determined frequency factor, and hence the steric factor for this reaction is approximately 10^{-3} . Since C_2F_4 has a number of internal degrees of freedom, a steric factor of 10^{-3} is reasonable.

The theory of absolute reaction rates can be employed to estimate the theoretical bimolecular rate constant¹⁴

$$k_{th} = \frac{kT}{h} \frac{Q^\ddagger}{Q^2 C_{2F_4}} e^{-E_0/RT} \quad (14)$$

where k is Boltzmann's constant, h is Planck's constant, E_0 is the activation energy at absolute zero and Q^\ddagger and $Q_{C_2F_4}$ are the partition functions of the activated complex and C_2F_4 respectively.⁴ The relationship between the experimental activation energy, E_a , and E_0 is determined by equating the logarithmic differential of Eq. (14) to E_a/RT^2 .

$$\frac{d(\ln k)}{dT} = E_a/RT^2 = \frac{d(\ln k_{th})}{dT} \quad (15)$$

Combining Eqs. (14) and (15) with the temperature dependence of the reactant and activated complex partition function yields

$$E_0 = E_a - RT \left[\sum_i \frac{x_i^\ddagger}{e^{x_i^\ddagger} - 1} - 2 \sum_j \frac{x_j}{e^{x_j} - 1} - 1 \right] \quad (16)$$

$$x \equiv \frac{hc\omega}{kT} \quad (17)$$

where ω is the molecular vibration wave number and x_i^\ddagger and x_0 are calculated from the known vibrational wave numbers of the activated complex and C_2F_4 respectively. The experimental frequency factor can be estimated by combining the results of Eqs. (14) and (16).

$$A = \frac{kT}{h} \frac{Q^\ddagger}{Q^2 C_{2F_4}} \exp \left[\sum_i \frac{x_i^\ddagger}{e^{x_i^\ddagger} - 1} - 2 \sum_j \frac{x_j}{e^{x_j} - 1} - 1 \right] \quad (18)$$

The partition function for C_2F_4 is readily calculated with the aid of the molecular parameters listed in the JANAF Tables.¹⁵ The partition function of the activated complex is calculated based on the assumption that it has the same geometrical arrangement as $c-C_4F_8$. The 23 fundamental vibrational frequencies of $c-C_4F_8$ are available in the literature.¹⁶ However, the numerical value of a number of these frequencies are not known accurately. Electron diffraction studies¹⁷ have been used to evaluate the spatial configuration of $c-C_4F_8$, and these results have indicated that $c-C_4F_8$ is nonplanar. Therefore the symmetry number of this molecule is two. The frequency factor, as calculated from Eq. (18) at 455°C, is approximately 1.5×10^7 cc/mole-sec⁻¹. This result is approximately 10^4 lower than the experimentally observed frequency factor. The statistical evaluation of the equilibrium constant for the reaction $c-C_4F_8 \rightleftharpoons 2 C_2F_4$ requires that the partition functions of both C_2F_4 and $c-C_4F_8$ be known. Since the partition functions of both C_2F_4 and $c-C_4F_8$ had been evaluated at 455°C, the equilibrium constant of the reaction mentioned above is

readily evaluated at 455°C. The calculated equilibrium constant is in excellent agreement with the experimental value,¹⁰ and hence the discrepancy between the measured and calculated frequency factors can not be attributed to numerical details. Since the partition function of C₂F₄ is accurately known, the theoretical frequency factor can only approach the measured value if the partition function of the activated complex is increased by approximately 10⁴. The rotational and translational contributions to Q_{c-C₄F₈} are relatively well known, and hence any increase in the total partition function would most probably have to come from vibrational contributions. The discrepancy between the experimental and calculated frequency factors could be reduced significantly if the actual activated complex is geometrically similar to c-C₄F₈ and is loosely bound. The loosely bound complex could have a number of low vibrational frequencies which would increase Q[‡] significantly.

The hydrocarbon system analogous to the fluorocarbon system of interest has also been studied.



The heat of reaction at 427°C and the equilibrium constant at 455°C for the dissociation of cyclobutane, see Eq. (19), are 18.92 Kcal/mole and 7.43 x 10⁻² moles/cc respectively.¹⁸ The corresponding heats of reaction and equilibrium constant for the dissociation of c-C₄F₈, see Eq. (12), are 49.92 Kcal/mole and 4.12 x 10⁻¹¹ moles/cc respectively.¹⁸ These thermochemical data indicate that the c-C₄F₈ is considerably more stable than c-C₄H₈.

The pyrolysis of C₂H₄ has been studied by a number of investigators¹⁹⁻²² Since the pyrolysis of C₂H₄ is considerably more complex than the analogous fluorocarbon reaction, a direct comparison between the present results and the C₂H₄ system can not be made. The thermal decomposition of c-C₄H₈ has been investigated by Walters and co-workers²³⁻²⁵ and Pritchard and co-workers.²⁶ The first order Arrhenius rate constant, k₀, for the decomposition of c-C₄F₈ is reported to have a frequency factor of 10^{15.71} sec⁻¹ and an activation energy of 62.8 Kcal/mole.¹⁴ Butler¹⁰ has reported that the frequency factor and activation energy of the unimolecular rate constant for the decomposition of c-C₄F₈ are 10^{16.0} sec⁻¹ and 74.3 Kcal/mole respectively. The two unimolecular frequency factors are in good agreement. However, the activation energy for the perfluoro compound is 11.5 Kcal/mole higher than the analogous hydrocarbon. Since the c-C₄F₈ is more stable than c-C₄H₈ this result is reasonable.

B. C₃F₆ PYROLYSIS

1. Introduction

Atkinson and Atkinson⁹ have studied the pyrolysis of perfluoropropene and perfluoroisobutene in the temperature ranges 600 to 675 and 700 to 750°C respectively. They reported that their data could be represented by a reaction of order 1.5. The Arrhenius rate constant for this reaction was reported to have an activation energy of 53.5 Kcal/mole and a frequency factor of $7.2 \times 10^{10} \text{ l}^{1/2}\text{-mole}^{1/2}\text{-sec}^{-1}$. The purpose of the present investigation was to study the thermal decomposition of perfluoropropene in the temperature and pressure ranges 550-675°C and 50-410 torr respectively.

2. Experimental

The experiments were conducted in a cylindrical Vycor reactor vessel (250 mm long by 60 mm I.D.) which was maintained at a constant temperature by an electrically heated furnace. The reactor temperature, which was measured with the aid of four chromel-alumel thermocouples, was controlled to within $\pm 1/2^\circ\text{C}$ over a period of several hours. An Aerograph model 202-B dual column, hot wire, thermal conductivity gas chromatography and a Beckman IR-10 infrared spectrophotometer with a spectral range $300\text{-}4000 \text{ cm}^{-1}$ were used to identify and quantitatively determine the gaseous products as a function of reaction time. A five foot column of 50/80 mesh Poropak Type N maintained at 135°C was used in conjunction with the gas chromatograph. The perfluoropropene used in these experiments was purchased from Air Products and Chemicals, Inc. Gas chromatographic analysis of the C₃F₆ indicated that it had a minimum purity of 99.8%.

3. Results And Discussion

The pyrolysis of perfluoropropene (C₃F₆) was studied over the temperature and initial pressure ranges 552-676°C and 50-410 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 the rate equation for the pyrolysis of perfluoropropene can be represented by the first order expression

$$\frac{d[\text{C}_3\text{F}_6]}{dt} = -k_4[\text{C}_3\text{F}_6] \quad (20)$$

The average values of the rate constant (k_4) calculated from the integrated form of Eq. (20) as a function of initial pressure and temperature are given in Table 6. An Arrhenius plot of the first order rate constant (k_4) as determined from the data is given in Fig. 5. A least mean squares fit to the experimental data yields

$$k_4 = 10^{8.08 \pm 0.26} \exp\left(\frac{-47,200 \pm 1,000}{RT}\right) \text{ sec}^{-1} \quad (21)$$

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 microns.⁹ 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 Fig. 6. In all cases the rate of perfluorobutene-2 production increased, and the order of the rate of production of perfluorobutene-2 with respect to the perfluoropropene concentration 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 Fig. 7. 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 thermal conductivity detector had the same sensitivity to perfluoroisobutene as the average of the perfluorobutene-2 and octafluorocyclobutane sensitivities. The rate of production of perfluoroisobutene with respect to perfluoropropene also had 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. Butler¹⁰ 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% occurred. This mass loss was attributed to the small flakes of white dust that condensed in the cooler parts of the system.

The present experimental results indicate that the pyrolysis of perfluoropropene, in the temperature and initial pressure ranges 550-675°C and 50-410 torr, can be represented by a first order reaction. When the pyrolysis of perfluoropropene was carried out in a nickel vessel in the same temperature

TABLE 6

AVERAGE VALUES OF THE FIRST-ORDER RATE CONSTANT, k_4

T (°C)	Initial Pressure (torr)	Number of Data Points	$k_4 \times 10^5$ (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

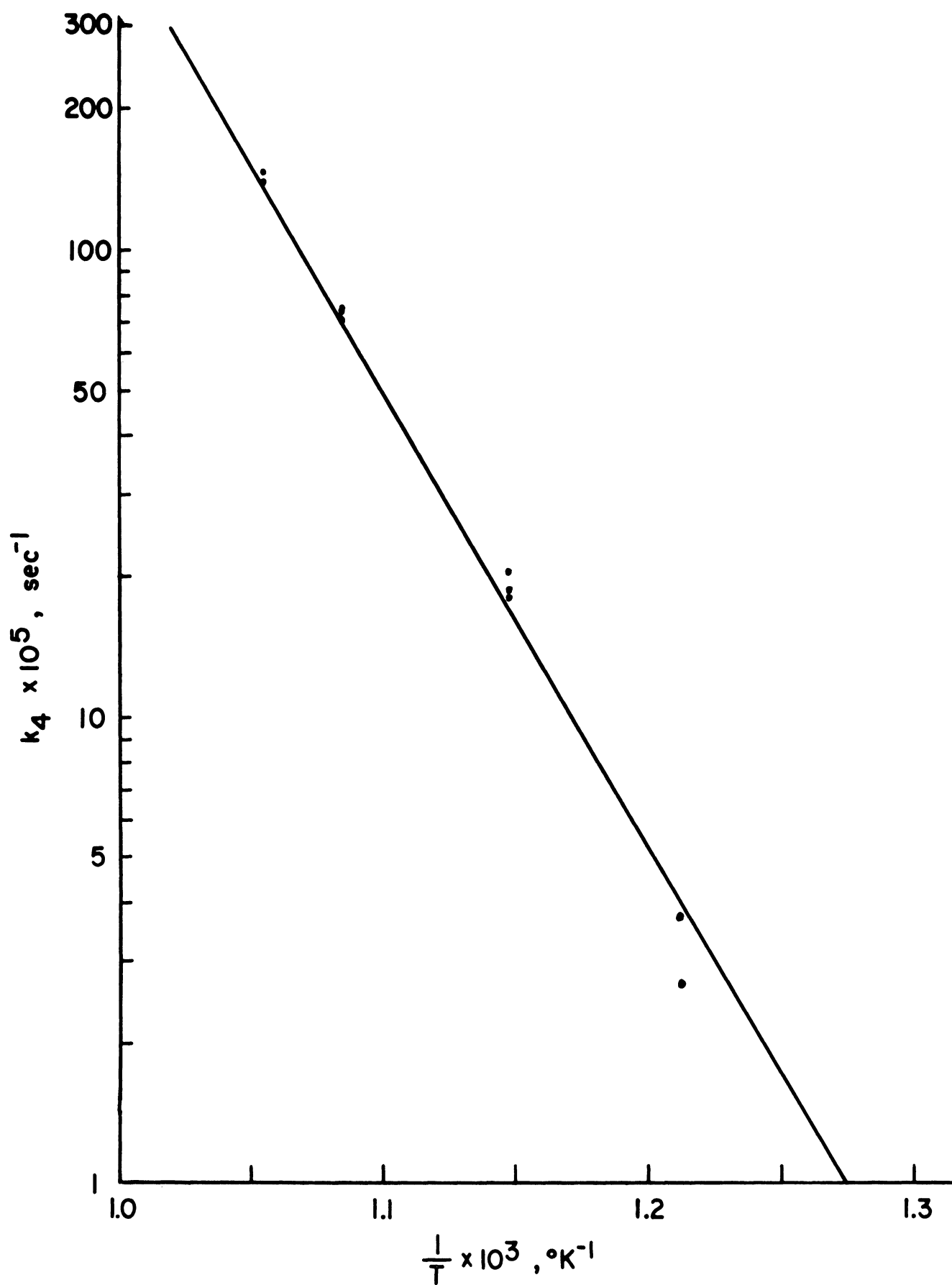


Fig. 5. Arrhenius plot of k_4 vs. $1/T$.

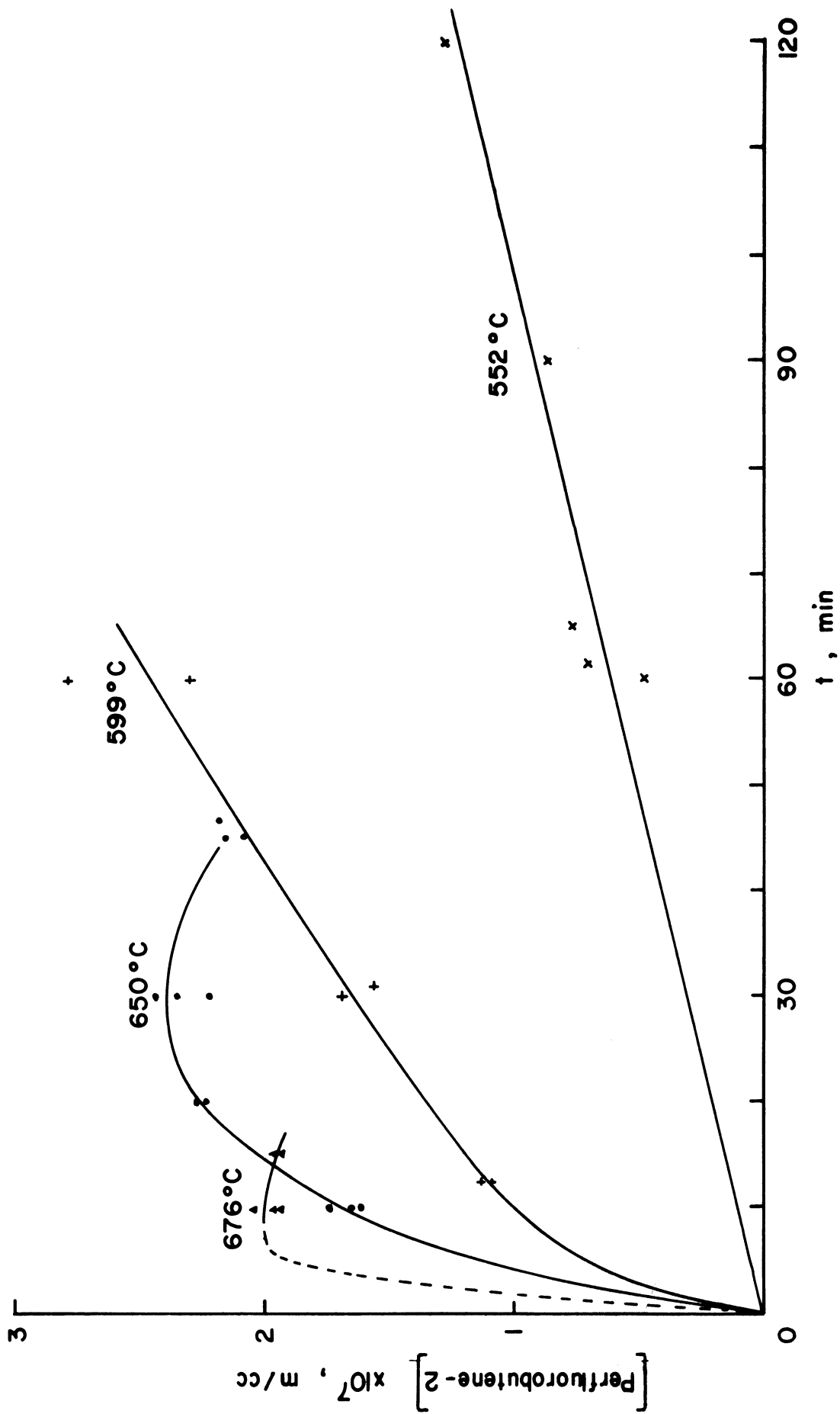


Fig. 6. Perfluorobutene-2 production in perfluoropropene pyrolysis.

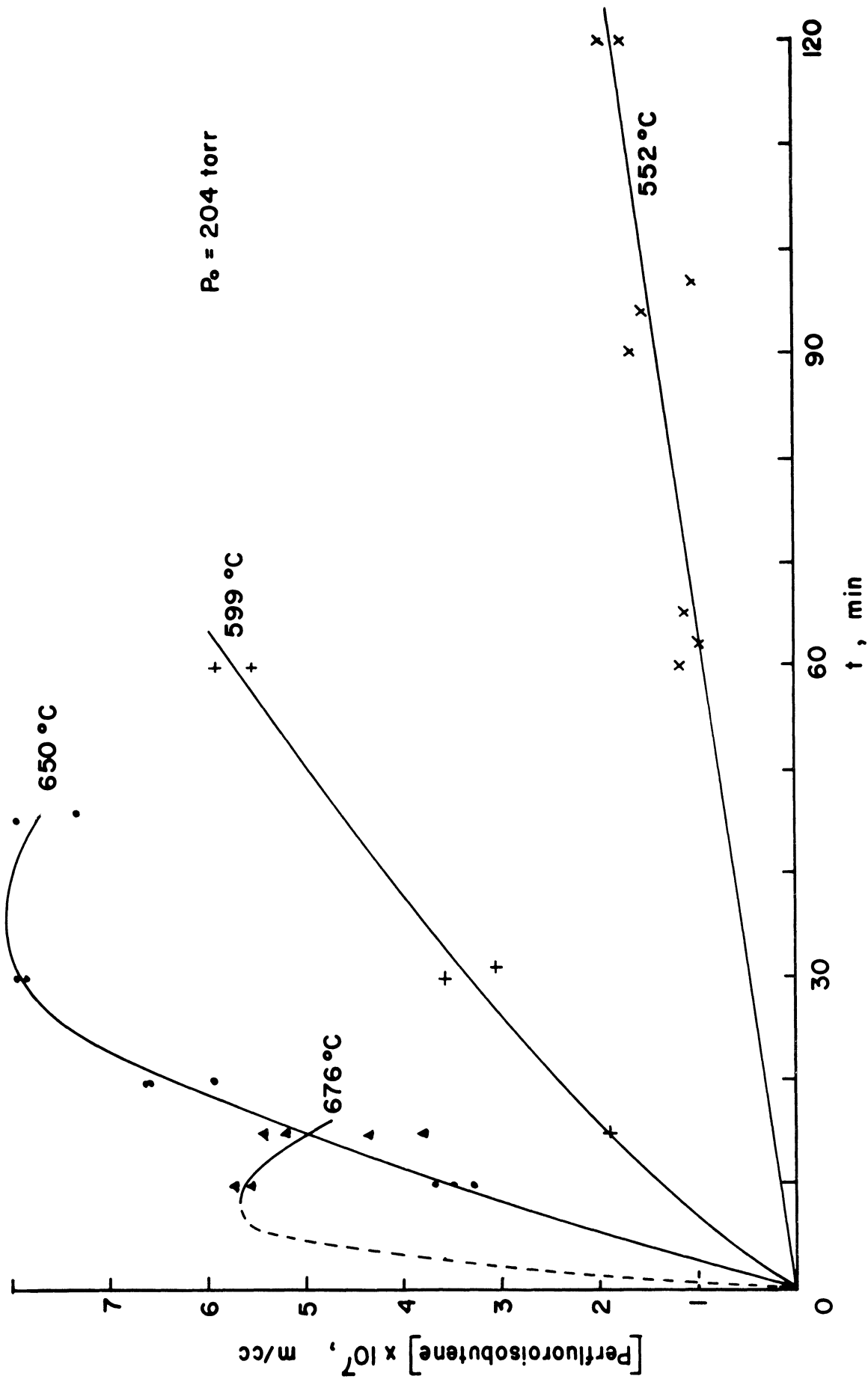


Fig. 7. Perfluoroisobutene production in perfluoropropene pyrolysis.

range, Atkinson and Atkinson⁹ reported that their data could be represented by a reaction of order 1.5. In their paper Atkinson and Atkinson⁹ do not specify the range of initial C_3F_6 concentrations which were considered. However, these authors reported that the perfluoropropene half-life was approximately 60 min when the reaction temperature and initial C_3F_6 pressure were approximately 600°C and 400 torr respectively.

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. 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 Atkinson⁹ is approximately the same as determined in this investigation it is reasonable to suggest that the pyrolysis of perfluoropropene is a first order reaction.

IV. PYROLYSIS OF CF₂O

A. INTRODUCTION

Both the thermodynamic and kinetic properties of carbonyl fluoride, CF₂O, have been studied by several investigators. The heat of formation has been evaluated based on both experimental results²⁷⁻²⁹ and theoretical bond energy considerations.³⁰ The equilibrium constant for the reaction $2 \text{CF}_2\text{O} \rightleftharpoons \text{CF}_4 + \text{CO}_2$ has been experimentally determined over the temperature range 300 to 1100°C.^{29,31} Modica and La Graff³² have investigated the pyrolysis of CF₂O in excess Ar behind reflected shock waves. Mixtures containing 5% CF₂O and 95 percent Ar were shock heated to temperatures between 2430 and 3330°C at total pressures near 0.8 atm. Assuming that the rate law was given by

$$\frac{-d[\text{CF}_2\text{O}]}{dt} = k_{\text{Ar}} [\text{Ar}][\text{CF}_2\text{O}] \quad (22)$$

the second order rate constant k_{Ar} was found to be

$$k_{\text{Ar}} = 4.29 \times 10^{11} \text{ T}^{1/2} \exp(-55,575/\text{RT}) \text{ cc/mole-sec}^{-1} \quad (23)$$

The purpose of the present investigation was to study the thermal decomposition of CF₂O in the temperature and pressure ranges 330-480°C and 25-600 torr respectively.

B. EXPERIMENTAL

The experiments were conducted in a cylindrical fused quartz reactor vessel (170 mm long by 60 mm I.D.) with a surface-to-volume ratio of approximately 0.76 cm⁻¹. The reaction temperature, maintained by an electrically heated furnace, was measured with the aid of four chromel-alumel thermocouples. The temperature was controlled to within ±1/2°C. over a period of several hours. An Aerograph model 202-B dual column thermal conductivity gas chromatograph and a Beckman IR-10 infrared spectrophotometer were used to identify and quantitatively determine the gaseous products as a function of reaction time. A six foot composite column, consisting of two feet of 50/80 mesh Poropak Type T followed by four feet of 50/80 mesh Poropak Type N was used in conjunction with the gas chromatograph.⁵ The CF₂O used in this investigation was purchased from the Matheson Company, Inc. The manufacturer indicated that the minimum purity of the CF₂O was 98 percent. However, subsequent analysis in our laboratory, using both gas chromatographic and infrared spectroscopic techniques,

showed that the CF_2O had only trace CO and CF_4 impurities, but the gas also had a CO_2 impurity of approximately 10%. This CF_2O was used without further purification, and in all cases the initial CO_2 impurity was taken into account. All of the experimental data were obtained with CO_2 production less than 50 percent of its equilibrium value.

C. RESULTS AND DISCUSSION

The pyrolysis of CF_2O was studied in a fused quartz reactor vessel in the initial pressure temperature and pressure ranges 330-480°C and 25-600 torr respectively. The reaction was found to be heterogeneous and the major gas phase products were CF_2O , CO_2 and SiF_4 . The order of reaction was determined by using both the differential method and the method of integration.³³ Both the rate of production of CO_2 and the rate of consumption of CF_2O were found to be half-order with respect to the CF_2O concentration. Thus the heterogeneous rate equation for the pyrolysis of carbonyl fluoride can be represented by the half-order expression

$$\frac{-d[\text{CF}_2\text{O}]}{dt} = k_5[\text{CF}_2\text{O}]^{1/2} \quad (24)$$

and similarly for the production of carbon dioxide

$$\frac{d[\text{CO}_2]}{dt} = k_6[\text{CF}_2\text{O}]^{1/2} \quad (25)$$

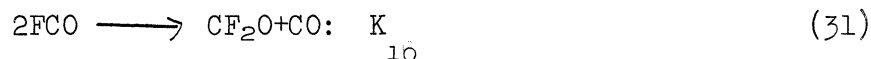
Arrhenius plots of the half-order rate constants k_5 and k_6 are given in Figs. 8 and 9. A least mean square fit to the experimental data yielded

$$k_5 = (10^{-2.21 \pm 0.23}) \exp[-14,360 \pm 140 \text{ IRT}] \left(\frac{\text{mole}}{\text{cc}}\right)^{1/2} \cdot \text{sec}^{-1} \quad (26)$$

$$k_6 = (10^{-1.41 \pm 0.22}) \exp[-16,6 \pm 680 \text{ IRT}] \left(\frac{\text{mole}(1/2)}{\text{cc}}\right)^{\text{sec}^{-1}} \quad (27)$$

Since silicon tetrafluoride (SiF_4) was consistently detected as a reaction product, it is suggested that the pyrolysis of CF_2O in a fused quartz reactor vessel is heterogeneous in nature.

A possible reaction scheme, which accounts for the experimentally observed kinetics, is



where R is an intermediate radical.

When a steady-state analysis is performed on the R and FCO radicals, the pyrolysis of carbonyl fluoride and the production of carbon dioxide are given by

$$\frac{d[\text{CF}_2\text{O}]}{dt} = -k_9 \left(\frac{2k_7}{k_{10}} \right)^{1/2} [\text{CF}_2\text{O}]^{1/2} \quad (32)$$

$$\frac{d[\text{CO}_2]}{dt} = +k_9 \left(\frac{2k_7}{k_{10}} \right)^{1/2} [\text{CF}_2\text{O}]^{1/2} \quad (33)$$

Inspection of the two rate Eqs. (32) and (33), which were derived based on the assumed mechanism, indicates that the two experimentally determined overall rate constants should be equal. The least mean square results given in Eqs. (26) and (27) are in reasonable agreement, but the Arrhenius curve for k_5 lies below the corresponding curve for k_6 . The numerical values of k_5 and k_6 are equal within the experimental errors at 367 and 413°C, and k_5 tends to fall slightly below k_6 at 425 and 462°C. However, even at the higher temperatures the average values of the two experimentally determined overall rate constants vary by only approximately thirty percent. The proposed reaction mechanism is consistent with the experimentally determined reaction orders within the experimental error, the theoretical and experimental rate constants are also in agreement.

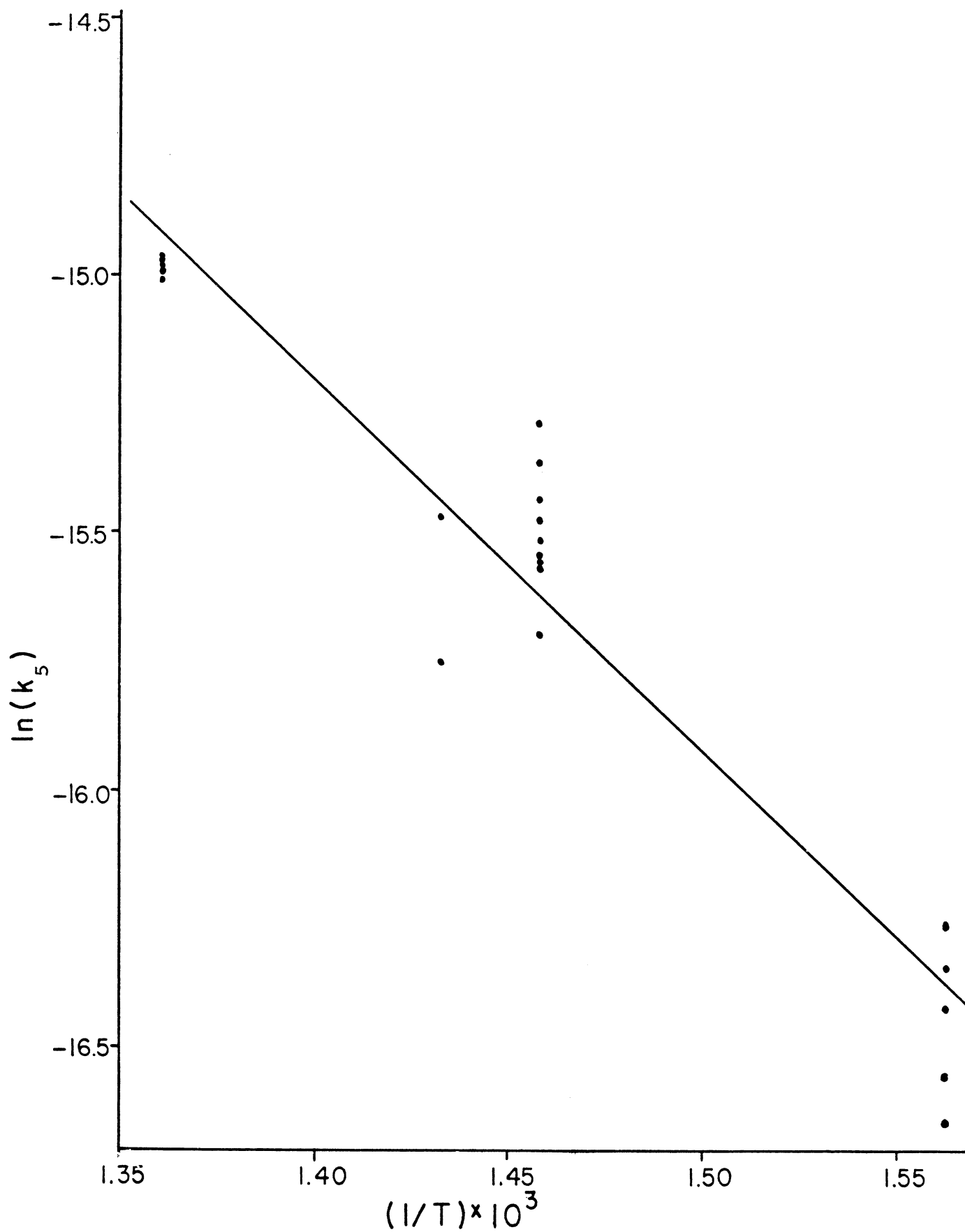


Fig. 8. Arrhenius plot for k_{CF_2O} .

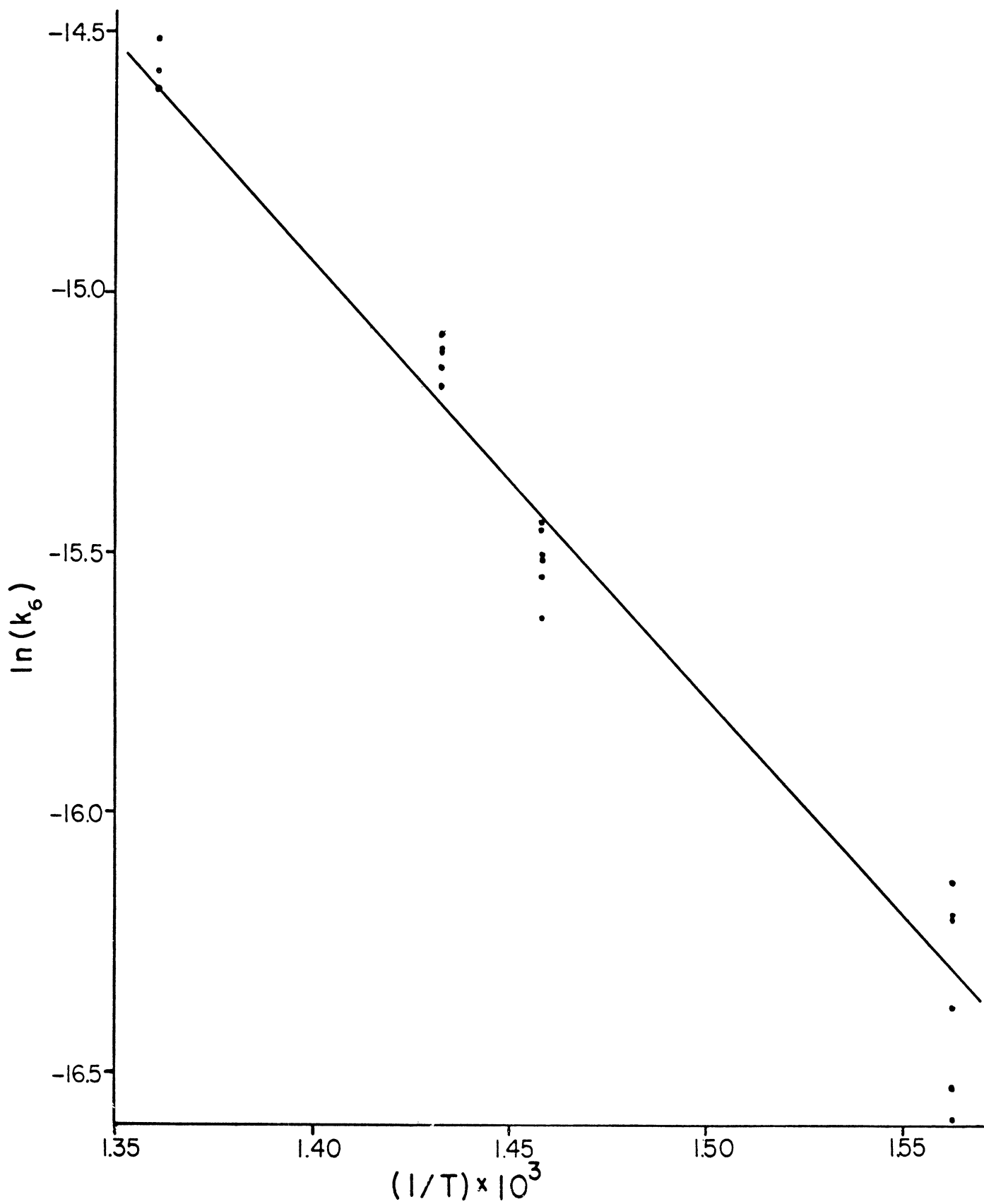


Fig. 9. Arrhenius plot for k_{CO_2} .

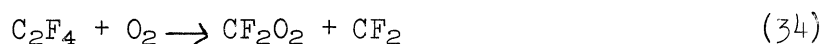
V. PRELIMINARY C₂F₄ OXIDATION RESULTS

A. INTRODUCTION

A number of authors have considered reaction systems involving both C₂F₄ and O₂. Caglioti et al.,³⁴ have studied the radiation induced oxidation of C₂F₄ at room temperature. Their experiments were carried out with 1/1 mixtures of C₂F₄/O₂ initially, at a total pressure of one atmosphere. The primary reaction products were shown to be: CF₂O, (CF₂)₂O and a liquid polyperoxide. The authors did not attempt to explain the experimental data. Heicklen, et al.,³⁵ have studied the mercury-photosensitized oxidation of C₂F₄ at room temperature. Their results led them to conclude that CF₂ radicals did not react to any significant extent with O₂ molecules. They also concluded that the primary source of CF₂O was a reaction between O₂ and an electronically excited C₂F₄ molecule.

Modica and LaGraff³⁶ have studied the high temperature oxidation of C₂F₄-O₂-Ar mixtures. These experiments were conducted in the temperature range 1225 to 2125°C, and the time dependence of the various product concentrations were determined with the aid of both TOF mass spectrometric and UV spectroscopic techniques. Their experimental results led them to suggest that the oxidation reaction was taking place between CF₂ radicals and O₂ molecules rather than as a direct molecular reaction between C₂F₄ and O₂. In this temperature range the oxidation products included CO and CF₄, and the mass spectrometric data indicated that CF₂O was not a reaction product. Bauer, Ho and Resler³⁷ have studied the thermal oxidation of C₂F₄ in a single-pulse shock tube. Mixtures of C₂F₄ and O₂, highly diluted in argon, were shock heated for periods of about 1.3 milliseconds to temperatures in the range 900-1725°C. Based on mass spectrometric analysis of the shocked mixtures, the major reaction products were found to include CF₂O, CO, CF₄ and C₃F₆, and small amounts of CO₂ and C₃F₈ were also produced. A plausible mechanism for the oxidation reaction has also been suggested.

The thermal explosion limits of C₂F₄/O₂ mixtures at both high and moderate pressures have been studied.³⁸⁻³⁹ Heicklen and Knight⁴⁰ have considered the thermal oxidation of perfluoroolefins. Mixtures of O₂ and C₂F₄ were heated in a flow system at temperatures from 225-725°C. In the C₂F₄-O₂ system, the major product was CF₂O and smaller amounts of c-C₃F₆, C₃F₆ and c-C₄F₈ were also formed. The analytical measurements were made with the aid of an infrared spectrophotometer. Their results were not conclusive, but they have made a number of suggestions. They presume that the initiating step is



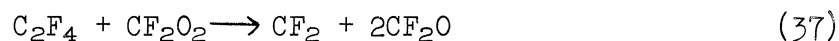
where reaction (34) may occur on the wall. It is further suggested that the major product, CF_2O , is probably produced by a chain.



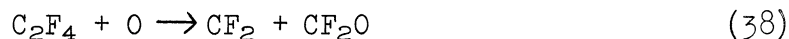
or



and



or



Even though the extent of reaction was kept low the rate constants varied with contact time, and therefore no rate equations or Arrhenius rate constants were suggested by the authors.

The thermal oxidation of C_2F_4 in the temperature range 150 to 300°C is presently under investigation. Preliminary experimental results are reported in the subsequent paragraphs.

B. EXPERIMENTAL

The C_2F_4 oxidation studies were conducted in the same basic facility that was employed for the pyrolysis of C_2F_4 . Preliminary data have been obtained in the temperature and total pressure ranges 150-300°C and 25-250 torr respectively, and a number of $\text{C}_2\text{F}_4/\text{O}_2$ mixtures with C_2F_4 mole fractions from 0.1 to 0.9 have been studied. The gas phase reaction products have been analyzed with the aid of GSC chromatographic techniques, and the various reaction products were separated with the aid of the columns described in Reference 6.

C. RESULTS AND DISCUSSION

In all cases, the major reaction product was found to be CF_2O . During a number of the experiments, small amounts of CO_2 and $\text{c-C}_3\text{F}_6$ were also

detected. A typical curve representing the concentration of the reactants and CF_2O as a function of reaction time is shown in Fig. 10. These data correspond to an equimolar mixture of C_2F_4 and O_2 reacting at a temperature and initial reactant pressure of 175°C and 100 mm of Hg. respectively. The shape of the CF_2O curve indicates that there is an initial induction period during which the rate of production of CF_2O is relatively low followed by a relatively linear region. Finally the rate of production of CF_2O decreases as the C_2F_4 and O_2 are consumed. Since the rate of consumption of C_2F_4 is higher than the rate of consumption of O_2 , the simple stoichiometric reaction



is not obeyed. In order to estimate the relative composition of any unknown products, atomic carbon, atomic fluorine and atomic oxygen mass balances were evaluated. When the mass balances were evaluated for the data shown in Fig. 10, all of the oxygen was accounted for and deficiencies in both carbon and fluorine were found in the gaseous products. Assuming that all of the carbon and fluorine were combined in a single molecule the molecule must have the chemical formula $(\text{CF})_n$. The carbon and fluorine deficiencies were approximately 4.7 and 10.5% at reaction times of 60 and 180 min respectively. The trace amounts of $\text{c-C}_3\text{F}_8$ in the reaction products were not included in the mass balances, but these contributions were not significant in any of the experiments.

An attempt was made to correlate the kinetic data with the aid of the following overall rate expressions

$$\frac{d[\text{CF}_2\text{O}]}{dt} = k_{11}[\text{C}_2\text{F}_4]^u [\text{O}_2]^v \quad (40)$$

$$\frac{d[\text{C}_2\text{F}_4]}{dt} = -k_{12}[\text{C}_2\text{F}_4]^w [\text{O}_2]^x \quad (41)$$

$$\frac{d[\text{O}_2]}{dt} = -k_{13}[\text{C}_2\text{F}_4]^y [\text{O}_2]^z \quad (42)$$

The kinetic data were not amenable to consistent analysis with the aid of Eqs. (34)-(36). The same general problem was encountered by Heicklen and Knight.⁴⁰ At the present time, supplementary experiments are in progress, and additional data analysis techniques are under consideration. It is anticipated that more light will be shed on this reaction system in the future.

0.5 C₂F₄ + 0.5 O₂

T = 175 °C

P₀ = 100mm Hg

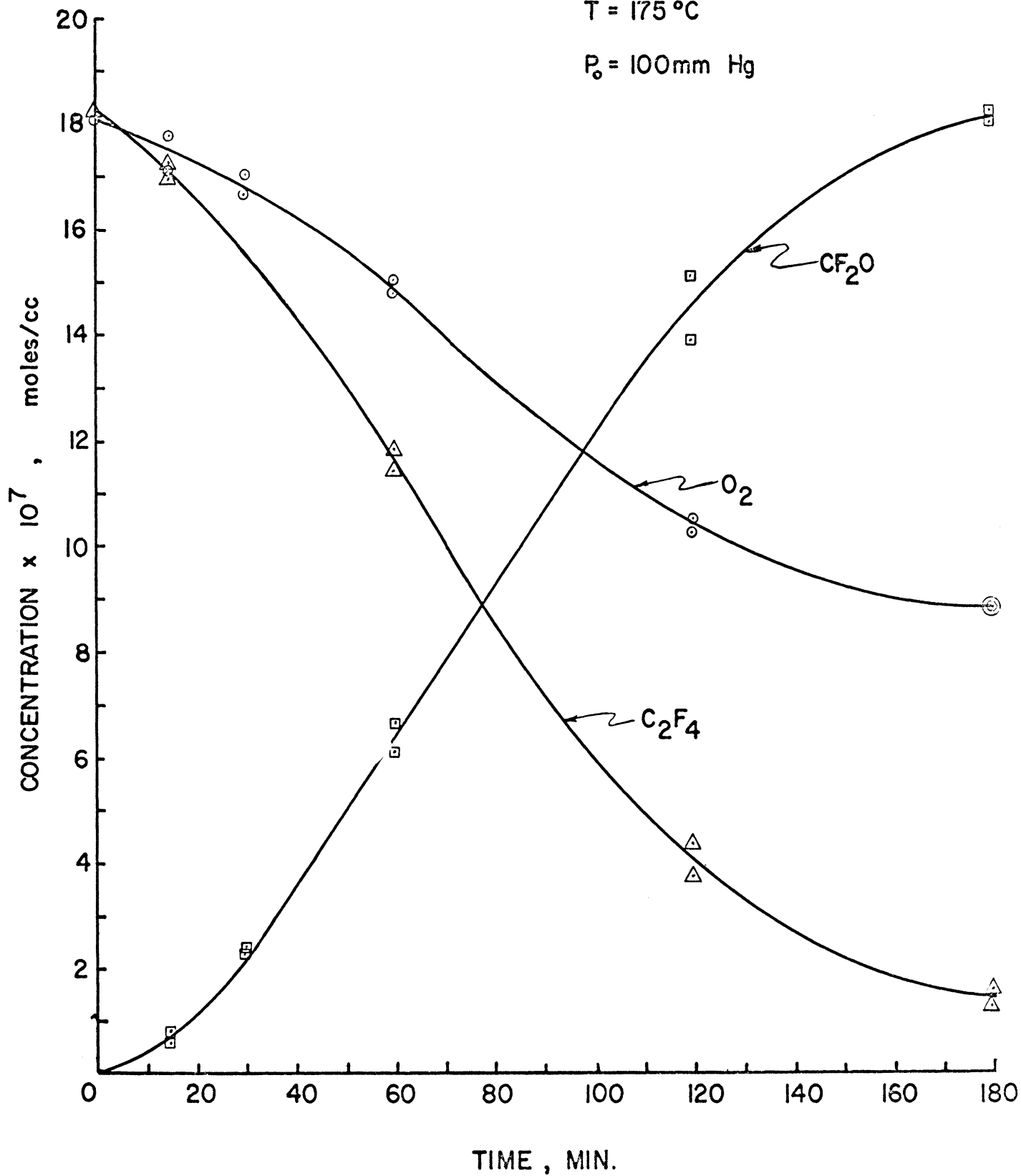


Fig. 10. Oxidation of C₂F₄.

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13. ABSTRACT The pyrolysis of C ₂ F ₄ , C ₃ F ₆ , and CF ₂ O have been studied in the temperature and pressure ranges 300-455°C, 25-760 torr; 550-675°C, 50-410 torr; and 330-480°C, 25-600 torr, respectively. The rate equations and appropriate Arrhenius rate constants for these three reactions are reported. The oxidation kinetics of C ₂ F ₄ are also being investigated and preliminary results in the temperature and pressure ranges 175-300°C and 25-200 torr are discussed. Finally the application of gas-solid chromatography techniques to the separation of low molecular weight fluorocarbons and the analysis of the C ₂ F ₄ oxidation products are discussed.			

14. KEY WORDS	LINK A		LINK B		LINK C	
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Oxygen						
Perfluoropropene						
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