

Final Technical Report

COMBUSTION KINETICS OF TETRAFLUOROETHYLENE

Richard A. Matula  
Department of Mechanical Engineering  
The University of Michigan

Supported by:

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH  
GRANT NO. AF-AFOSR-1144-66

September 1967



## TABLE OF CONTENTS

	Page
LIST OF ILLUSTRATIONS	iv
ABSTRACT	v
I. INTRODUCTION	1
II. EXPERIMENTAL FACILITIES AND TECHNIQUES	2
A. Facilities	2
B. Experimental Techniques and Procedures	2
III. ANALYTICAL DEVELOPMENTS	7
A. Infrared Analysis	7
B. Gas Chromatographic Analysis	7
IV. EXPERIMENTAL RESULTS	11
A. Preliminary $\text{CF}_2\text{O}$ Pyrolysis Results	11
B. Preliminary $\text{C}_2\text{F}_4$ Reaction Rate Studies	15
1. $\text{C}_2\text{F}_4$ Pyrolysis	15
2. $\text{C}_2\text{F}_4$ Oxidation Experiments	18
REFERENCES	19

## LIST OF ILLUSTRATIONS

Table	Page
1. Column Materials Studied for General C/F/O Compound Separations	8
2. CO <sub>2</sub> Rate Constant in CF <sub>2</sub> O Pyrolysis	14
3. CF <sub>2</sub> O Rate Constant in CF <sub>2</sub> O Pyrolysis	14
4. Temperature Dependence of k <sub>1</sub> (T) and k <sub>2</sub> (T)	15
5. Rate Constants for the Pyrolysis of C <sub>2</sub> F <sub>4</sub>	18

Figure	Page
1. Static facility system schematic.	3
2. The furnace.	4
3. Static reactor vessel.	5
4. Typical chromatogram of CO <sub>2</sub> - CF <sub>2</sub> O mixture.	9
5. Typical chromatogram of C <sub>2</sub> F <sub>4</sub> oxidation products.	10
6. Rate of production of CO <sub>2</sub> as a function of initial CF <sub>2</sub> O concentration.	12
7. Rate of consumption of CF <sub>2</sub> O as a function of initial CF <sub>2</sub> O concentration.	13
8. C <sub>2</sub> F <sub>4</sub> half-life as a function of initial C <sub>2</sub> F <sub>4</sub> concentration.	16

## ABSTRACT

The oxidation kinetics of tetrafluoroethylene and the pyrolysis of carbonyl fluoride are being experimentally studied in the temperature range 500-750°K. Both infrared spectroscopic and gas chromatographic techniques have been developed for the quantitative analysis of all important reaction products.

The pyrolysis of  $\text{CF}_2\text{O}$  has been studied in the temperature range 500-750°K. When the studies are conducted in a quartz reactor vessel, the only significant gaseous products are  $\text{CF}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{SiF}_4$ . Preliminary analysis of the kinetic data indicate that both the heterogeneous rate of production of  $\text{CO}_2$  and rate of consumption of  $\text{CF}_2\text{O}$  are half order with respect to  $\text{CF}_2\text{O}$ .

Prior to the initiation of the  $\text{C}_2\text{F}_4$  oxidation experiments, the pyrolysis of  $\text{C}_2\text{F}_4$  was studied at 636°K. The only important product was *c*- $\text{C}_4\text{F}_8$ , and the rate was shown to be second order with respect to  $\text{C}_2\text{F}_4$ . The second order rate constants as evaluated from both the experimentally determined rate of production of *c*- $\text{C}_4\text{F}_8$  and the rate of decrease of  $\text{C}_2\text{F}_4$  are reported. Preliminary oxidation experiments employing an equimolar mixture of  $\text{O}_2$  and  $\text{C}_2\text{F}_4$  at 636°K and an initial pressure of 50 mm of Hg indicate that the oxidation reaction is fast and that the only significant reaction products are  $\text{CF}_4$ ,  $\text{CO}_2$ , and  $\text{CF}_2\text{O}$ . Additional work with these systems is being continued under the sponsorship of the Air Force Office of Scientific Research Grant No. AF-AFOSR-1144-66.

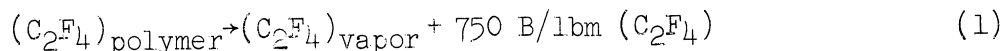


## I. INTRODUCTION

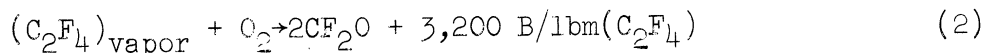
In many practical applications the detailed flow fields about reentry vehicles can only be calculated if the kinetics of the flow field are known. The flow field chemistry may be particularly important when combustion reactions are possible. Frequently, the ablation products of reentry vehicles may, 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.<sup>1-4</sup> 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 the present research project is to study the oxidation kinetics of tetrafluoroethylene and the thermal stability of one of the important oxidation products,  $CF_2O$ , in the temperature range 500-1000°K. Preliminary experimental results are included in this report. Additional work with these systems is being continued under the sponsorship of the Air Force Office of Scientific Research Grant No. AF-AFOSR-1144-66.

## II. EXPERIMENTAL FACILITIES AND TECHNIQUES

### A. FACILITIES

A schematic diagram of the static reaction system is shown in Fig. 1. The vacuum system has been constructed from special greaseless vacuum stopcocks and glass to metal seals which are rated at  $10^{-8}$  torr. The two furnaces are designed for a maximum operating temperature of  $1500^{\circ}\text{K}$ . Temperature control to within  $\pm 2^{\circ}\text{K}$  is obtained by automatically regulating the power input to the heaters. In order to insure that the longitudinal temperature gradients in the furnace cavity are negligible, guard heaters have been installed at each end of the furnaces. A sketch of a typical furnace is shown in Fig. 2. The present design can be readily adapted for flow system operation in the event that this becomes necessary. A schematic diagram of a typical quartz reactor is shown in Fig. 3.

Excellent analytical facilities are available for the analysis of C/F/O compounds. A Beckmann IR-10 spectrophotometer with a spectral range from  $300\text{-}4000\text{ cm}^{-1}$  is available, and gas analysis cells with path lengths up to one meter can be employed for the required infrared analyses. A library consisting of the spectra of many of the important C/F/O compounds has been developed in the past year. Gas chromatography instrumentation including both thermal conductivity and ionization detectors are also available for product analysis. Methods have been obtained for the gas chromatographic determination of all important compounds. In particular a column has been developed which will allow the simultaneous determination of  $\text{CO}_2$  and  $\text{CF}_2\text{O}$  (see Section III).

### B. EXPERIMENTAL TECHNIQUES AND PROCEDURES

The gases utilized in this research program were purchased from commercial sources. Ultra high purity oxygen (minimum purity = 99.95%), and  $\text{CF}_2\text{O}$  with a suggested minimum purity of 97% were purchased from the Matheson Company. Gas chromatographic analysis of the  $\text{CF}_2\text{O}$  indicated that the only significant impurity was  $\text{CO}_2$ . However, it was determined that the  $\text{CO}_2$  impurity in the  $\text{CF}_2\text{O}$  had a mole fraction of approximately 0.08. The tetrafluoroethylene used in the present experiments was purchased from the Columbia Organic Chemicals Company. The manufacturer specified that the minimum purity of the  $\text{C}_2\text{F}_4$  was 99%. Gas chromatographic analysis of the  $\text{C}_2\text{F}_4$  indicated that the majority impurity was  $\text{c-C}_4\text{F}_8$  which had a mole fraction of approximately 0.6%.

The actual experimental data has been obtained by applying the standard experimental procedures that have been developed in our laboratory. The re-



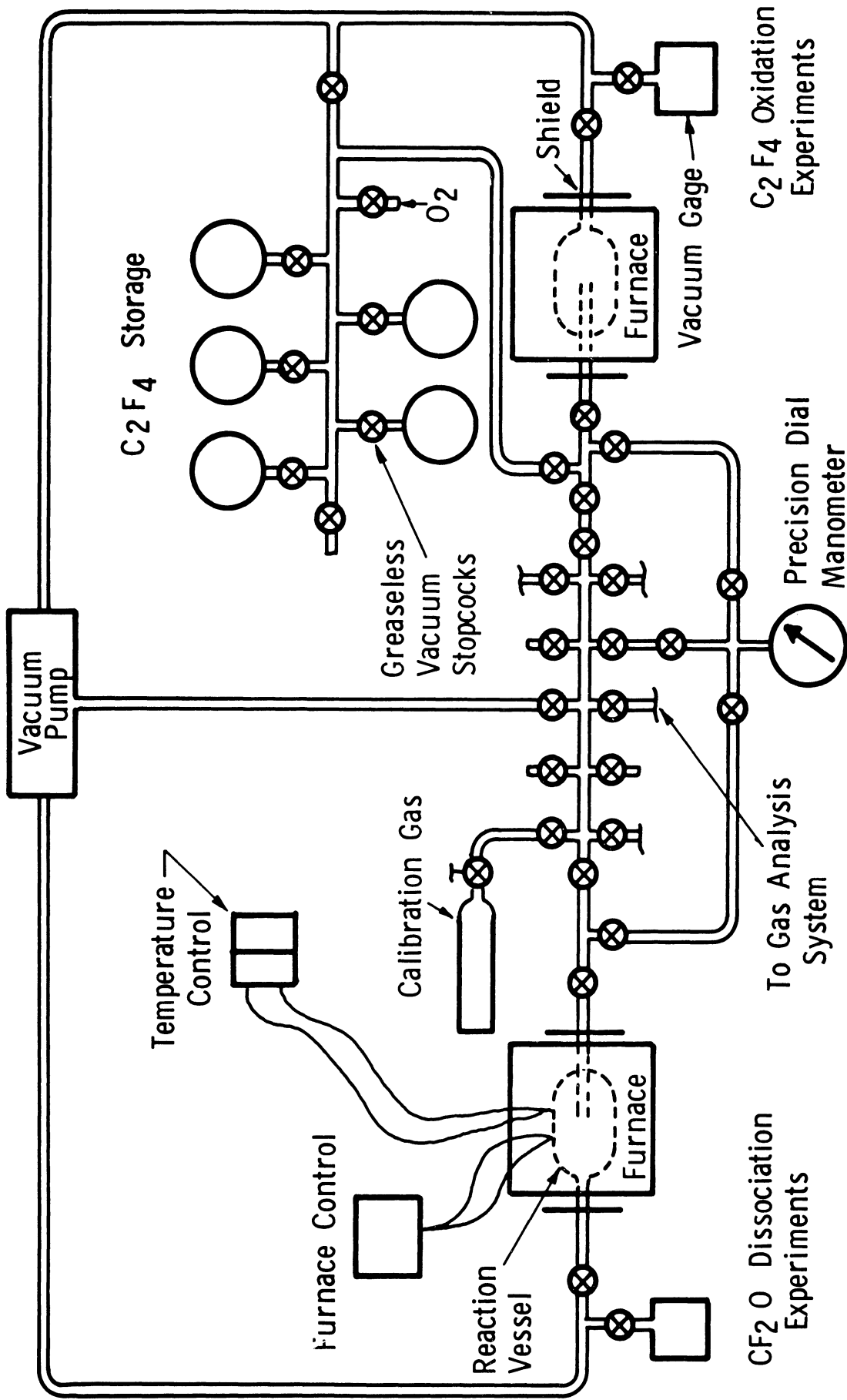


Fig. 1. Static facility system schematic.

Furnace Cavity is 5" O. D.  
and  $9\frac{1}{2}$ " Long

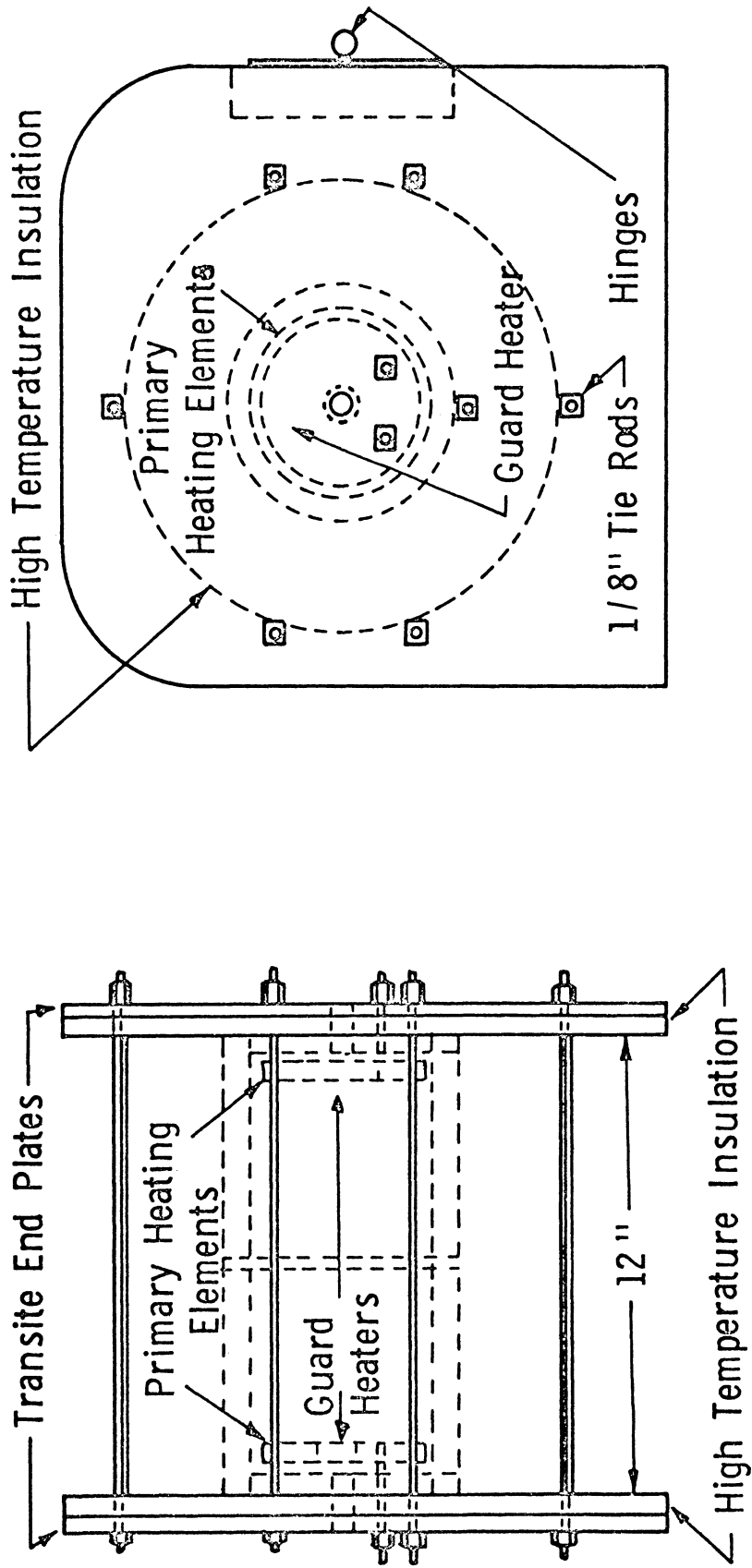


Fig. 2. The furnace.

actants are introduced into the reactor, which is maintained at a controlled temperature, and the time dependence of the concentration of both the reactants and products are determined by withdrawing samples from the reactor at variable time intervals and analyzing the sample with the aid of both the gas chromatographic and infrared analysis equipment. These data which are obtained at variable temperature, initial pressure and reactant composition are used for the evaluation of the necessary rate equations and the appropriate Arrhenius parameters.

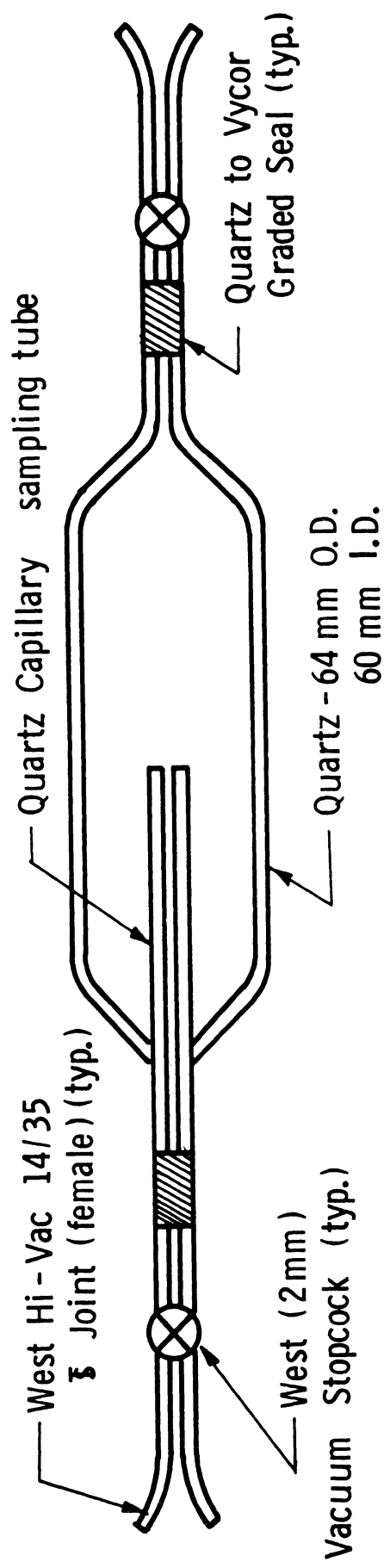


Fig. 3. Static reactor vessel.

### III. ANALYTICAL DEVELOPMENTS

#### A. INFRARED ANALYSIS

Considerable effort has been expended in the past year to develop the techniques necessary for both the qualitative and quantitative analysis of compounds that are important in the C/F/O system. A Beckmann IR-10 infrared spectrophotometer with a spectral range 300-4000  $\text{cm}^{-1}$  was received during the year. This instrument has been put into operation and a library of pure component spectra of the various fluorocarbons has been established. The spectra of  $\text{CF}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{CO}$ , all of which are important compounds in the C/F/O reaction system, are also included in the library. Gas absorption cells with path lengths from 5 to 100 cm are available for the required analysis. This flexibility allows a wide range of concentrations of a given molecule to be measured. In order to decrease the reaction of  $\text{CF}_2\text{O}$  and other reactive fluorocarbon compounds with the gas cell windows special window materials including AgBr and AgCl must be used. The IR facilities have also been used for the quantitative evaluation of  $\text{CO}_2$  and  $\text{CF}_2\text{O}$  in gas mixtures. The data obtained in these experiments are in substantial agreement with the data from gas chromatography analysis of the same mixture.

#### B. GAS CHROMATOGRAPHIC ANALYSIS

The most important factor in the effectiveness of a gas chromatograph to quantitatively analyze gas mixtures is the selection of a column which will adequately separate all of the components in the mixture. For our purposes columns had to be developed which could separate two classes of mixtures: (1)  $\text{C}_2\text{F}_4$  - c- $\text{C}_4\text{F}_8$  mixtures and (2)  $\text{O}_2$  -  $\text{C}_2\text{F}_4$  -  $\text{CF}_4$  -  $\text{CO}_2$  -  $\text{CF}_2\text{O}$  mixtures.

The separation of  $\text{C}_2\text{F}_4$  - c- $\text{C}_4\text{F}_8$  mixtures was readily obtained by employing a 6-ft column of 3% squalane on silica gel maintained at 25°C. The  $\text{C}_2\text{F}_4$  - c- $\text{C}_4\text{F}_8$  separation was also obtained by utilizing a 4-ft column of 50/80 mesh type N Poropak maintained at 100°C. Both of the above analyses were performed with a He carrier gas flow rate of 60 ml/min.

A literature search indicated that the simultaneous gas chromatographic quantitative analysis of  $\text{CO}_2$  -  $\text{CF}_2\text{O}$  mixtures has not been reported. In order to obtain the required separation of  $\text{CO}_2$  and  $\text{CF}_2\text{O}$  a systematic column evaluation program was undertaken. The various columns tested are listed in Table 1. It was found that excellent separation of  $\text{CO}_2$  -  $\text{CF}_2\text{O}$  mixtures could be obtained by using a 6-ft composite column consisting of 2 ft of 50/80 mesh Poropak (Waters Associate, Inc.) Type I followed by 4 ft of 50/80 mesh Poropak Type N. The column was packed in 1/4 in. O.D. type 315 stainless steel tubing. Before final installation in the chromatograph the column was heated

to 180°C and purged with helium (60 ml/min for two hours). Prior to each series of runs the column was conditioned by passing three 250 mm of Hg samples through it.

TABLE 1  
 COLUMN MATERIALS STUDIED  
 FOR GENERAL C/F/O COMPOUND SEPARATIONS

<u>Solid Support</u>	<u>Stationary Phase</u>
Activated Alumina	
Activated Silica-Gel	
Activated Alumina with 10% NaCl	
Activated Charcoal	
Activated Molecular Sieve, 5A	
Activated Molecular Sieve, 13x	
Poropak Type N	
Poropak Type Q	
Poropak Type R	
Poropak Type S	
Poropak Type T	
Tee Six (Teflon)	10% Carbowax 300
Tee Six	5% Kel F Oil No. 10
Kel F 300 LD	5% Kel F Oil No. 10
Tee Six	5% Fluorolube
Chromosorb W	5% SE-30
Chromosorb T	5% DC-702
Chromosorb P	20% Silicone Oil DCFS 1265
Chromosorb P	20% Silicone Oil DC 710
Chromosorb P	20% QF-1 Fluoro-Silicone Oil
Chromosorb P	20% Versilube F-20
Chromosorb P	20% SE-S2
Chromosorb W	20% Kel F Oil No. 10

A typical chromatogram indicating the separation of CF<sub>2</sub>O and CO<sub>2</sub> as obtained with the column described above is shown in Fig. 4. The operating conditions corresponding to the results given in Fig. 4 are: column temperature 23°C; carrier gas (helium) flow rate 60 ml/min. The detector response was determined to be linear when the CF<sub>2</sub>O concentration was varied by a factor of approximately eleven and the curve of detector response vs. concentration of CF<sub>2</sub>O extrapolated to the origin. This indicates that, once the column is conditioned, CF<sub>2</sub>O absorption on the column is essentially nonexistent. A typical chromatogram showing the separation of O<sub>2</sub>, CF<sub>4</sub>, CO<sub>2</sub>, CF<sub>2</sub>O, and C<sub>2</sub>F<sub>4</sub> on the column described above is given in Fig. 5.

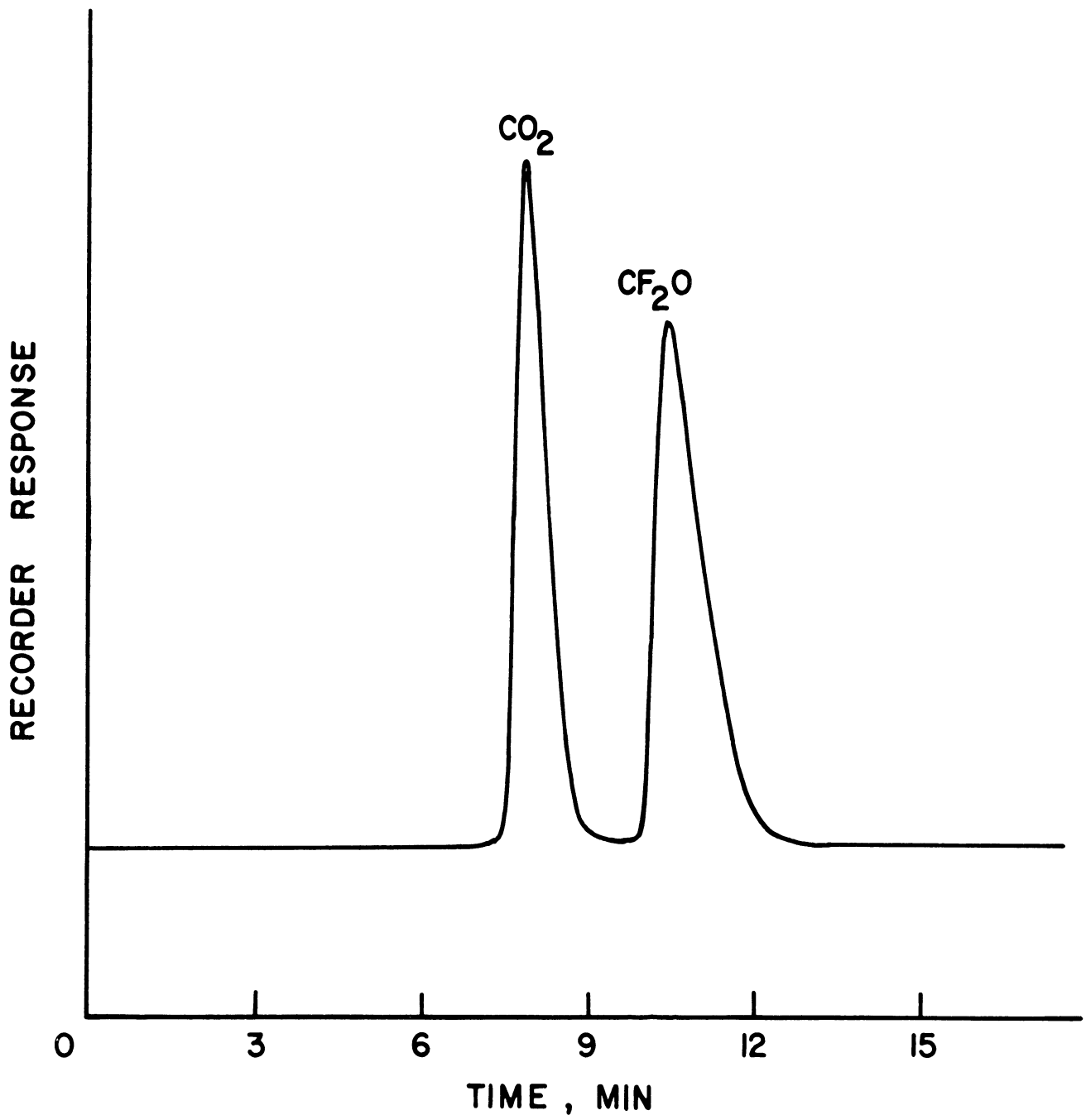


Fig. 4. Typical chromatogram of CO<sub>2</sub> - CF<sub>2</sub>O mixture.

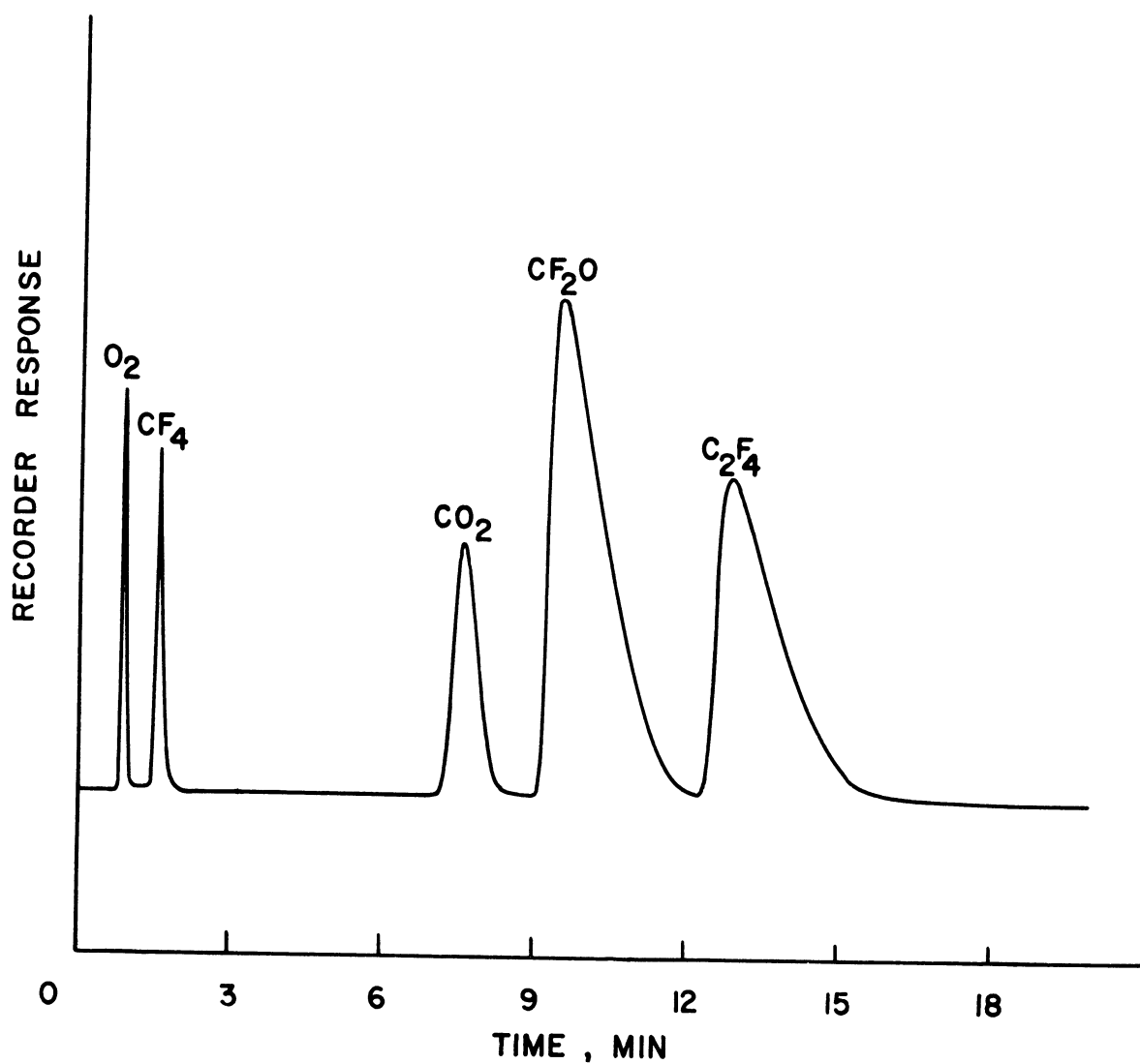


Fig. 5. Typical chromatogram of  $C_2F_4$  oxidation products.



#### IV. EXPERIMENTAL RESULTS

##### A. PRELIMINARY CF<sub>2</sub>O PYROLYSIS RESULTS

The pyrolysis of CF<sub>2</sub>O with initial CF<sub>2</sub>O pressures ranging from 25 to 600 mm of Hg has been studied in the temperature range 500-750°K. When the studies were conducted in a quartz reactor vessel, gas chromatographic and infrared analysis of the gaseous reaction products indicated that the only important products were CF<sub>2</sub>O, CO<sub>2</sub>, and SiF<sub>4</sub>. Preliminary experiments have been undertaken in order to determine the form of the rate equation for this heterogeneous reaction. The following rate laws were assumed

$$R_{\text{CO}_2} = \frac{d[\text{CO}_2]}{dt} = k_1(T) [\text{CF}_2\text{O}]^\alpha \quad (3)$$

$$R_{\text{CF}_2\text{O}} = -\frac{d[\text{CF}_2\text{O}]}{dt} = k_2(T) [\text{CF}_2\text{O}]^\beta \quad (4)$$

The numerical values of  $\alpha$  and  $\beta$  in Eqs. (3) and (4) were determined by measuring the initial rate of formation and decay of CO<sub>2</sub> and CF<sub>2</sub>O, respectively, as a function of initial CF<sub>2</sub>O concentration. The initial rates were evaluated by employing the following equations:

$$R_{\text{CO}_2} = \frac{[\text{CO}_2]_t - [\text{CO}_2]_0}{\Delta t} \quad (5)$$

$$R_{\text{CF}_2\text{O}} = \frac{[\text{CF}_2\text{O}]_0 - [\text{CF}_2\text{O}]_t}{\Delta t} \quad (6)$$

As indicated in Section II the concentrations of CO<sub>2</sub> and CF<sub>2</sub>O as a function of time were determined by gas chromatographic techniques. The reaction time ( $\Delta t$ ) used in Eqs. (5) and (6) was held constant for any series of runs at a given temperature. In order to insure that the finite difference approximation of the actual slopes of the CO<sub>2</sub> and CF<sub>2</sub>O vs. time curves were a reasonable approximation, the reaction times were varied from 30 min at the low temperature to 5 min at the highest temperature. This technique insured that the change in CF<sub>2</sub>O concentration for an experiment was relatively small (5-10%). Typical curves for the rate of production of CO<sub>2</sub> and the rate of decrease of CF<sub>2</sub>O concentration are given in Figs. 6 and 7, respectively. It is apparent from these results that both  $\alpha$  and  $\beta$  are approximately one half and that the preliminary data can be conveniently represented by the following rate expressions:

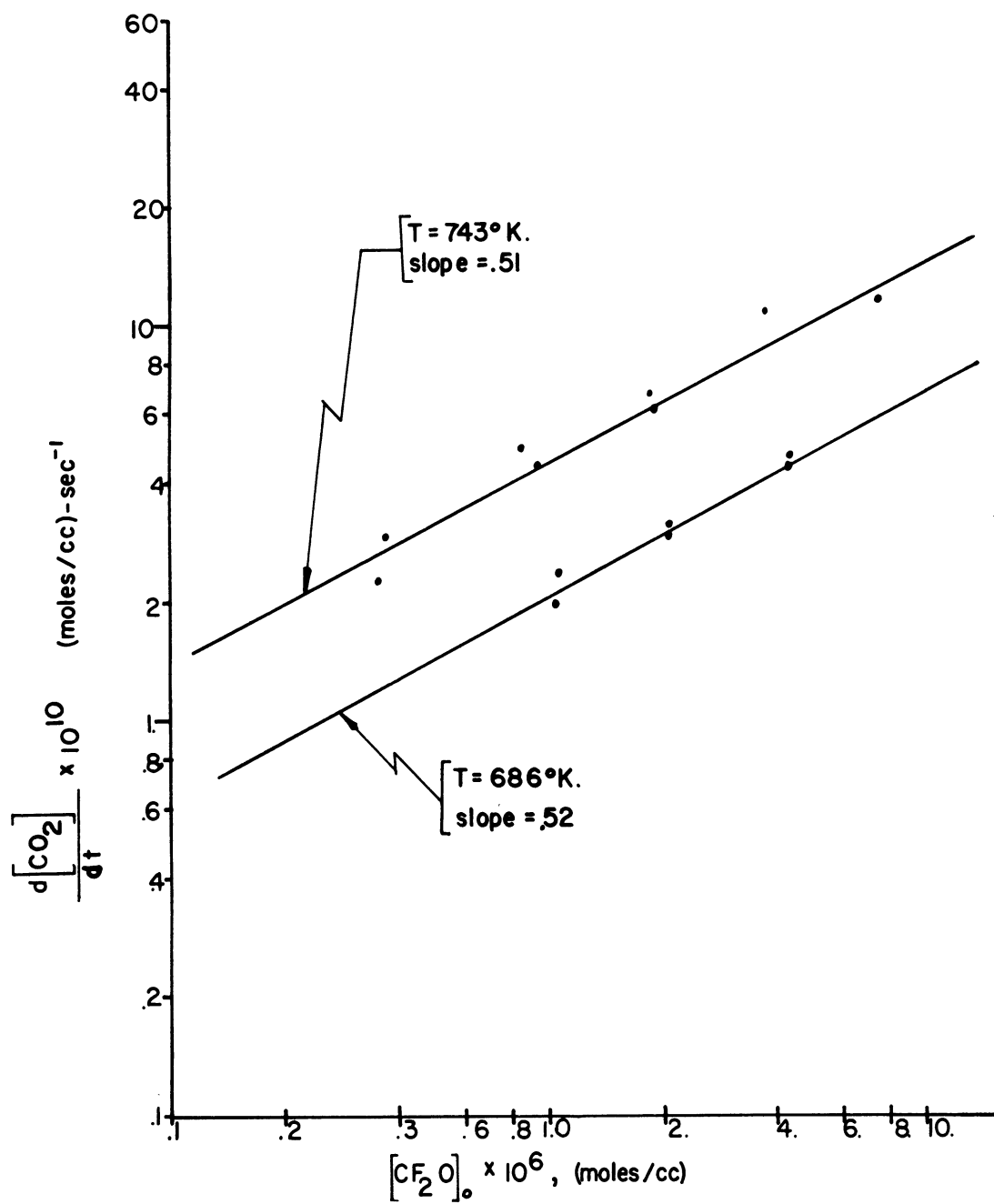


Fig. 6. Rate of production of  $CO_2$  as a function of initial  $CF_2O$  concentration.

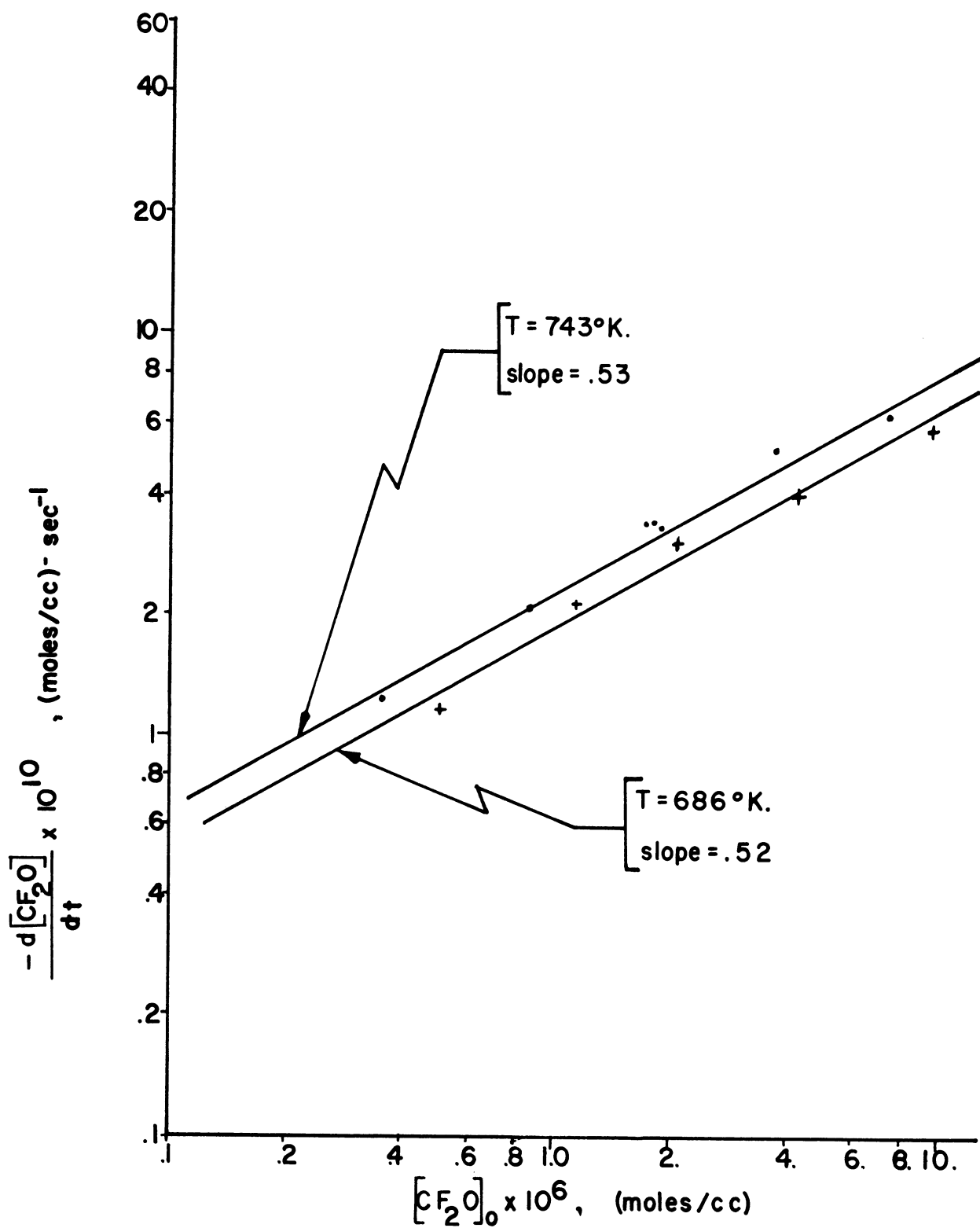


Fig. 7. Rate of consumption of CF<sub>2</sub>O as a function of initial CF<sub>2</sub>O concentration.

$$R_{\text{CO}_2} = k_1(T) [\text{CF}_2\text{O}]^{1/2} \quad (7)$$

$$R_{\text{CF}_2\text{O}} = k_2(T) [\text{CF}_2\text{O}]^{1/2} \quad (8)$$

Numerical values of  $k_1$  and  $k_2$  based on Eqs. (7) and (8) and the experimental data are given in Tables 2 and 3, respectively. It should be noted that the rate constants as determined from the experimental data are relatively insensitive to the initial concentration of  $\text{CF}_2\text{O}$  and hence the data are adequately represented by the rate expressions given in Eqs. (7) and (8). The average values of  $k_1$  and  $k_2$  as a function of temperature are listed in Table 4. An Arrhenius plot of these data indicate that  $k_1$  and  $k_2$  have activation energies of approximately 17 kcal/mole and 15 kcal/mole, respectively.

TABLE 2

$\text{CO}_2$  RATE CONSTANT IN  $\text{CF}_2\text{O}$  PYROLYSIS

$$R_{\text{CO}_2} = \frac{d[\text{CO}_2]}{dt} = k_1[\text{CF}_2\text{O}]^{1/2}$$

T - 735°K		T - 698°K		T - 686°K		T - 640°K	
$[\text{CF}_2\text{O}]_0 \times 10^6$	$k \times 10^7$	$[\text{CF}_2\text{O}]_0 \times 10^6$	$k \times 10^7$	$[\text{CF}_2\text{O}]_0 \times 10^6$	$k \times 10^7$	$[\text{CF}_2\text{O}]_0 \times 10^6$	$k \times 10^7$
moles/cc	(moles/cc) <sup>1/2</sup> sec <sup>-1</sup>	moles/cc	(moles/cc) <sup>1/2</sup> sec <sup>-1</sup>	moles/cc	(moles/cc) <sup>1/2</sup> sec <sup>-1</sup>	moles/cc	(moles/cc) <sup>1/2</sup> sec <sup>-1</sup>
0.956	4.660	1.03	2.82	1.05	1.632	9.490	0.660
1.987	4.522	2.07	2.72	4.33	1.835	4.679	1.272
1.014	4.975	4.19	2.64	2.14	1.845	2.302	0.987
		12.87	2.55	4.36	1.941	0.563	0.795
				2.14	1.827	1.089	0.622
				1.06	1.972	2.313	0.917
				2.15	1.765	4.680	0.920

TABLE 3

$\text{CF}_2\text{O}$  RATE CONSTANT IN  $\text{CF}_2\text{O}$  PYROLYSIS

$$R_{\text{CF}_2\text{O}} = -\frac{d[\text{CF}_2\text{O}]}{dt} = k[\text{CF}_2\text{O}]^{1/2}$$

T - 735°K		T - 698°K		T - 686°K		T - 640°K	
$[\text{CF}_2\text{O}]_0 \times 10^6$	$k \times 10^7$	$[\text{CF}_2\text{O}]_0 \times 10^6$	$k \times 10^7$	$[\text{CF}_2\text{O}]_0 \times 10^6$	$k \times 10^7$	$[\text{CF}_2\text{O}]_0 \times 10^6$	$k \times 10^7$
moles/cc	(moles/cc) <sup>1/2</sup> sec <sup>-1</sup>	moles/cc	(moles/cc) <sup>1/2</sup> sec <sup>-1</sup>	moles/cc	(moles/cc) <sup>1/2</sup> sec <sup>-1</sup>	moles/cc	(moles/cc) <sup>1/2</sup> sec <sup>-1</sup>
8.120	3.015	1.03	1.437	8.70	1.713	4.679	0.838
0.956	2.353	2.07	1.873	4.36	1.688	2.302	0.710
0.442	2.983	4.19	1.154	2.14	1.802	1.163	0.478
8.264	3.022			1.06	1.970	2.313	0.625
1.987	3.047			2.19	1.845	4.680	0.593
1.014	2.028			0.498	1.808		
				0.506	1.655		

TABLE 4

TEMPERATURE DEPENDENCE OF  $k_1(T)$  AND  $k_2(T)$ 

T, °K	$\bar{k}_1(T) \times 10^7,$ (moles/cc) <sup>1/2</sup> sec <sup>-1</sup>	$\bar{k}_2(T) \times 10^7,$ (moles/cc) <sup>1/2</sup> sec <sup>-1</sup>
735	4.72	2.91
698	2.68	1.68
686	1.84	1.18
640	0.882	0.648

B. PRELIMINARY  $C_2F_4$  REACTION RATE STUDIES1.  $C_2F_4$  Pyrolysis

Prior to initiation of the  $C_2F_4$  oxidation studies, the pyrolysis of  $C_2F_4$  was considered. These experiments served a dual purpose: (1) check out and shake down of the experimental apparatus, and (2) results of these experiments could be checked against data previously reported in the literature.<sup>5-7</sup>

When the pyrolysis of  $C_2F_4$  was carried out at 636°K, the only important reaction products were found to be  $C_2F_4$  and *c*- $C_4F_8$ . It was assumed that the equation for the rate of loss of  $C_2F_4$  was given by

$$R_{C_2F_4} = - \frac{d[C_2F_4]}{dt} = k_3(T) [C_2F_4]^n \quad (9)$$

The numerical value of  $n$  was evaluated by the half-life method. It is readily shown<sup>8</sup> that the measured half life ( $t_{1/2}$ ) of a reaction can be utilized to evaluate  $n$ .

$$\ln(t_{1/2}) = \ln(f(n,k)) - (n-1) \ln([C_2F_4]_0) \quad (10)$$

A plot of the experimentally measured half life of  $C_2F_4$  at a reaction temperature of 636°K is shown in Fig. 8. The slope of the curve is -0.98 and hence

$$-(n-1) = -0.98 \quad (11)$$

Therefore the numerical value of  $n$  in Eq. (9) is 1.98 and for all practical purposes the rate equation for  $C_2F_4$  is taken to be

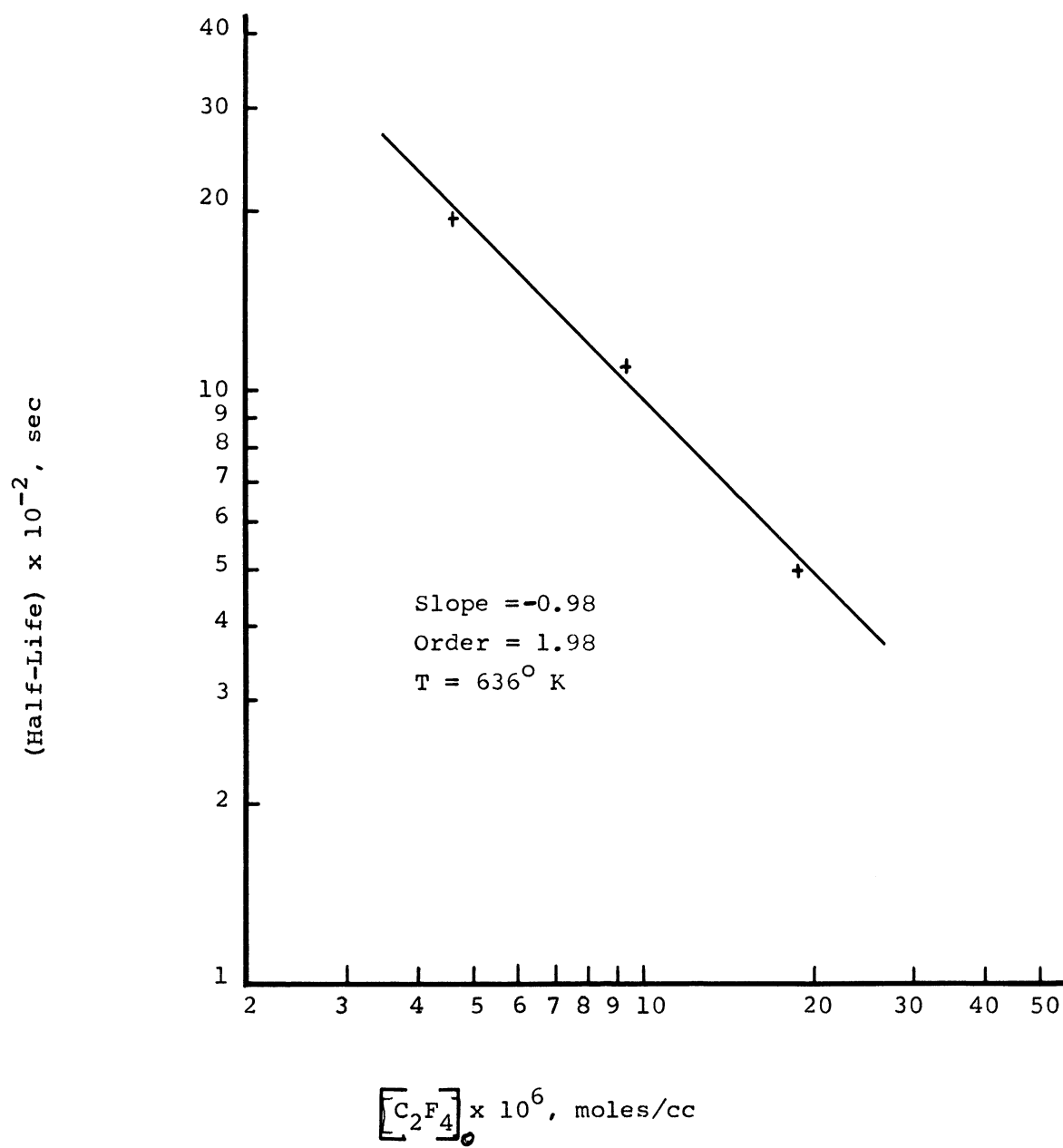


Fig. 8.  $C_2F_4$  half-life as a function of initial  $C_2F_4$  concentration.

$$R_{C_2F_4} = k_3(T) [C_2F_4]^2 \quad (12)$$

The results as given in Eq. (12) are consistent with data previously reported in the literature.<sup>5-7</sup>

In order to evaluate the numerical value of  $k_3$  at 636°K the concentrations of both *c*-C<sub>4</sub>F<sub>8</sub> and C<sub>2</sub>F<sub>4</sub> were measured as a function of reaction time. These experiments were conducted with initial C<sub>2</sub>F<sub>4</sub> pressures of approximately 50 and 100 of Hg. Since the only products are *c*-C<sub>4</sub>F<sub>8</sub> and C<sub>2</sub>F<sub>4</sub> and we have shown that the rate of decrease of C<sub>2</sub>F<sub>4</sub> is second order, the value of  $k_3$  can be determined from both the measured time dependence of the concentrations of C<sub>2</sub>F<sub>4</sub> and *c*-C<sub>4</sub>F<sub>8</sub>.

The value of  $k_3$  can be evaluated from the integrated form of Eq. (12)

$$k_3(T) = \frac{1}{t} \left( \frac{1}{[C_2F_4]_t} - \frac{1}{[C_2F_4]_0} \right) \quad (13)$$

The rate constant can also be evaluated in terms of the *c*-C<sub>4</sub>F<sub>8</sub> measurements. The following stoichiometric reaction is valid for the pyrolysis experiments



It can be shown that the rate constant  $k_3$  can also be evaluated in terms of the initial C<sub>2</sub>F<sub>4</sub> concentration and the concentration of *c*-C<sub>4</sub>F<sub>8</sub> at time *t*

$$k_3 = \frac{1}{t} \frac{2[c-C_4F_8]}{[C_2F_4]_0 ([C_2F_4]_0 - 2[c-C_4F_8])} \quad (15)$$

The numerical value of  $k_3$  at 636°K, for two initial C<sub>2</sub>F<sub>4</sub> pressures, as calculated from both Eqs. (13) and (15) are listed in Table 5. The average value of  $k_3$  at 636°K based on the C<sub>2</sub>F<sub>4</sub> and *c*-C<sub>4</sub>F<sub>8</sub> data are 199 (cc/gm-mole) sec<sup>-1</sup> and 180 (cc/gm-mole) sec<sup>-1</sup>, respectively. These two independent numerical values are in good agreement with each other. The numerical values of  $k_3$  reported in References 6 and 7 are 192 and 153 (cc/mole) sec<sup>-1</sup>, respectively. The excellent agreement between the present data and the data presented in References 6 and 7 indicates that our experimental facilities and techniques are adequate.

TABLE 5

RATE CONSTANTS FOR THE PYROLYSIS OF  $C_2F_4$ 

$$R_{C_2F_4} = - \frac{d[C_2F_4]}{dt} = k_3 [C_2F_4]^2$$

$t_R$ (min)	$k_{C_2F_4}$ (cc/gm-mole-sec)	$k_{C-C_4F_8}$ (cc/gm-mole-sec)
$P_0 = 101.6 \text{ mm Hg}; T = 636^\circ K$		
15	206.2	176.5
30	185.2	155.8
30	185.2	173.7
60	199.3	175.0
	$(k_{C_2F_4})_{avg} 193.9$	$(k_{C-C_4F_8})_{avg} 175.1$
$P_0 = 50.8 \text{ mm Hg}; T_R = 636^\circ K$		
15	218.7	186.1
15	193.2	196.0
30	197.7	187.4
30	189.4	175.2
60	222.8	174.2
	$(k_{C_2F_4})_{avg} 204.4$	$(k_{C-C_4F_8})_{avg} 183.8$

## 2. $C_2F_4$ Oxidation Experiments

Preliminary oxidation experiments employing an equimolar mixture of  $O_2$  and  $C_2F_4$  at  $636^\circ K$  and an initial pressure of 50 mm of Hg indicate that the reaction is fast at these conditions and that the only significant reaction products are  $CF_4$ ,  $CO_2$ , and  $CF_2O$ . Additional work with these systems is being continued under the sponsorship of the Air Force Office of Scientific Research Grant No. AF-AFOSR-1144-66.



## REFERENCES

1. Economos, C., "Ablation Tests on Plastic Models in a Hypersonic Wind Tunnel," ARS J., 1074-1081 (July 1962).
2. Steg, L., and Lew, H., "Hypersonic Ablation," AGARD Hypersonic Conference TCEA, Rhode-St. Genese, Belgium (April 3-6, 1962).
3. Steg, L., "Materials for Reentry Heat Protection of Satellites," ARS J., 815-822 (September 1960).
4. Adams, M., "Recent Advances in Ablation," ARS J., 625-632 (September 1959).
5. Atkinson, B., and Atkinson, V. A., "The Thermal Decomposition of Tetrafluoroethylene," J. Chem. Soc. (London), 2086 (April-June 1957).
6. Atkinson, B., and Trendwith, A. B., "The Thermal Decomposition of Tetrafluoroethylene," J. Chem. Soc. (London), 2082 (April-July 1953).
7. Lacher, J., Tompkin, G., and Park, J., "The Kinetics of the Vapor Phase Dimensions of Tetrafluoroethylene," J. Am. Chem. Soc., 74, 1963 (1952).
8. Frost, R. G., and Pearson, A. A., Kinetics and Mechanism, 2nd Edition, John Wiley and Sons, Inc., p. 42 (1965).



Security Classification

**DOCUMENT CONTROL DATA - R&D**

*(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)*

<b>1. ORIGINATING ACTIVITY (Corporate author)</b> The University of Michigan Department of Mechanical Engineering Ann Arbor, Michigan		<b>2a. REPORT SECURITY CLASSIFICATION</b> Unclassified	
		<b>2b. GROUP</b>	
<b>3. REPORT TITLE</b> COMBUSTION KINETICS OF TETRAFLUOROETHYLENE			
<b>4. DESCRIPTIVE NOTES (Type of report and inclusive dates)</b> Final Technical Report			
<b>5. AUTHOR(S) (Last name, first name, initial)</b> Matula, Richard A.			
<b>6. REPORT DATE</b> September 1967		<b>7a. TOTAL NO. OF PAGES</b> 23	<b>7b. NO. OF REFS</b> 8
<b>8a. CONTRACT OR GRANT NO.</b> AF-AFOSR-1144-66		<b>9a. ORIGINATOR'S REPORT NUMBER(S)</b>	
<b>b. PROJECT NO.</b> c. d.		<b>9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)</b>	
<b>10. AVAILABILITY/LIMITATION NOTICES</b> Copies are available from the originator.			
<b>11. SUPPLEMENTARY NOTES</b>		<b>12. SPONSORING MILITARY ACTIVITY</b> Air Force Office of Scientific Research	
<b>13. ABSTRACT</b> The oxidation kinetics of tetrafluoroethylene and the pyrolysis of carbonyl fluoride are being experimentally studied in the temperature range 500-750°K. Both infrared spectroscopic and gas chromatographic techniques have been developed for the quantitative analysis of all important reaction products. The pyrolysis of CF <sub>2</sub> O has been studied in the temperature range 500-750°K. When the studies are conducted in a quartz reactor vessel, the only significant gaseous products are CF <sub>2</sub> O, CO <sub>2</sub> , and SiF <sub>4</sub> . Preliminary analysis of the kinetic data indicate that both the heterogeneous rate of production of CO <sub>2</sub> and rate of consumption of CF <sub>2</sub> O are half order with respect to CF <sub>2</sub> O. Prior to the initiation of the C <sub>2</sub> F <sub>4</sub> oxidation experiments, the pyrolysis of C <sub>2</sub> F <sub>4</sub> was studied at 636°K. The only important product was c-C <sub>4</sub> F <sub>8</sub> , and the rate was shown to be second order with respect to C <sub>2</sub> F <sub>4</sub> . The second order rate constants as evaluated from both the experimentally determined rate of production of c-C <sub>4</sub> F <sub>8</sub> and the rate of decrease of C <sub>2</sub> F <sub>4</sub> are reported. Preliminary oxidation experiments employing an equimolar mixture of O <sub>2</sub> and C <sub>2</sub> F <sub>4</sub> at 636°K and an initial pressure of 50 mm of Hg indicate that the oxidation reaction is fast and that only the significant reaction products are CF <sub>4</sub> , CO <sub>2</sub> , and CF <sub>2</sub> O. Additional work with these systems is being continued under the sponsorship of the Air Force Office of Scientific Research Grant No. AF-AFOSR-1144-66.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Tetrafluoroethylene Oxygen Carbonyl Fluorine Reaction rates Gas phase reactions Reaction kinetics Combustion kinetics Gas chromatography						

**INSTRUCTIONS**

**1. ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

**2a. REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

**2b. GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

**3. REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

**4. DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

**5. AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

**6. REPORT DATE:** Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

**7a. TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

**7b. NUMBER OF REFERENCES:** Enter the total number of references cited in the report.

**8a. CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.

**8b, 8c, & 8d. PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

**9a. ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

**9b. OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

**10. AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through \_\_\_\_\_."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through \_\_\_\_\_."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through \_\_\_\_\_."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

**11. SUPPLEMENTARY NOTES:** Use for additional explanatory notes.

**12. SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

**13. ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

**14. KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.



