

THE PYROLYSIS OF TETRAFLUOROETHYLENE

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### ABSTRACT

The pyrolysis of tetrafluoroethylene was studied in the temperature and pressure range 300 to 455°C and 25 to 760 torr. The rate of reaction was determined to be second order with respect to the tetrafluoroethylene, and three independent numerical values of the second order rate constant were determined by simultaneously measuring the tetrafluoroethylene concentration, the octafluorocyclobutane concentration and the total pressure as a function of reaction time. The temperature dependence of the reaction rate constants are given by

$$K_2 = 10^{11.05 \pm 0.07} \exp \left( \frac{-25,555 \pm 200}{RT} \right) \quad \text{cc/mole-sec}^{-1}$$

$$K_2^I = 10^{10.81 \pm 0.14} \exp \left( \frac{-25,136 \pm 420}{RT} \right) \quad \text{cc/mole-sec}^{-1}$$

$$K_2^{II} = 10^{11.33 \pm 0.20} \exp \left( \frac{-26,407 \pm 590}{RT} \right) \quad \text{cc/mole-sec}^{-1}$$



## 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<sup>(1)</sup>. 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  $16.5 \times 10^{10}$  cc/mole-sec<sup>-1</sup>. Atkinson and co-workers<sup>(2,3)</sup> 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 ranges 300-550°C and 200 to 550 torr 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  $10.3 \times 10^{10}$  cc/mole-sec<sup>-1</sup>.

Butler<sup>(4)</sup> studied the first order thermal decomposition of  $c\text{-C}_4\text{F}_8$  to  $\text{C}_2\text{F}_4$  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  $c\text{-C}_4\text{F}_8$ , Butler calculated that the second order rate constant ( $k_2$ ) for the rate of decrease of  $\text{C}_2\text{F}_4$  had an activation energy of 24.0 kcal/mole and a frequency factor of  $20 \times 10^{10.4}$  cc/mole-sec<sup>-1</sup>. Butler also found that during the course of  $c\text{-C}_4\text{F}_8$  decomposition that a slow parallel decomposition forming perfluoropropene ( $\text{C}_3\text{F}_6$ ) occurred with a first order rate constant ( $k_3$ ). The Arrhenius parameters for  $k_3$  were determined to be  $10^{17.2}$  sec<sup>-1</sup> and 87.2 kcal/mole. Atkinson and Atkinson<sup>(3)</sup> also showed that the formation of  $\text{C}_3\text{F}_6$  from  $c\text{-C}_4\text{F}_8$  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  $3.9 \times 10^{16}$  sec<sup>-1</sup>.

In order to evaluate the second order rate constant ( $k_2$ ) for the dimerization of  $\text{C}_2\text{F}_4$  based on the experimental determination of total pressure as a function of reaction time, the previous investigators<sup>(1,2)</sup> 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  $c-C_4F_8$  concentration, and the total pressure as a function of reaction time. The concentrations of  $C_2F_4$  and  $c-C_4F_8$  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 References (1) and (2), 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.

#### EXPERIMENTAL

Apparatus. 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-H<sub>2</sub>O 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 6mm Vycor tubing. Both the sampling and pump tubes were terminated outside of the furnace by 2 mm greaseless vacuum stopcocks.

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  $300-4000\text{ cm}^{-1}$  was used as a back up instrument for the identification of any species which escaped detection by the gas chromatograph. A 4 foot column of 50/80 mesh Poropak (Waters Associate, Inc.) Type N maintained at  $100^{\circ}\text{C}$  was used to separate the  $\text{C}_2\text{F}_4$  pyrolysis products. The column was packed in 1/4 inch 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  $200^{\circ}\text{C}$  while purging with helium (75 ml/min) for two hours. 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  $20^\circ C$ . 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  $c-C_4F_8$  and that traces of  $CO_2$ ,  $CF_4$  and  $C_2F_6$  were also present. The mole fraction of the  $c-C_4F_8$  impurity was determined to be approximately  $9 \times 10^{-3}$ . 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 pyrolyzed. 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  $-126^\circ C$  and condensable at  $-196^\circ C$ . Heicklen and Knight<sup>(5)</sup> 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  $c-C_4F_8$  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.

Procedure. 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.

The actual experimental data have been obtained by applying standard experimental techniques. 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 sample from the reactor at various reaction times and analyzing the sample with the aid of the gas chromatograph and the IR spectrophotometer. These data which were obtained with temperature, initial pressure and reactant composition as independent variables were used for the evaluation of the necessary rate equations and the appropriate Arrhenius parameters.

## RESULTS

Data Analysis. 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

$$\frac{d [C_2F_4]}{dt} = -k_2 [C_2F_4]^2 + k_1 [c-C_4F_8] \quad (1)$$

Butler<sup>(4)</sup> has shown that if the temperature is less than 500°C the second term on the right hand side of Eq. (1) 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

$$\frac{d [C_2F_4]}{dt} = -k_2 [C_2F_4]^2 \quad (2)$$

The integrated form of Eq. (2) yields the rate constant ( $k_2$ ) as a function of parameters which were experimentally determined

$$k_2 = \frac{1}{t} \left[ \frac{1}{[C_2F_4]_t} - \frac{1}{[C_2F_4]_0} \right] \text{ cc/mole-sec}^{-1} \quad (3)$$

where  $t$  is the reaction time in seconds and  $[C_2F_4]_t$  and  $[C_2F_4]_0$  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  $c-C_4F_8$ , Eq. (1) can be rewritten in terms of the  $c-C_4F_8$  concentration.

$$\frac{d [c-C_4F_8]}{dt} = \frac{k_2}{2} \left( ([C_2F_4]_0 - 2 [c-C_4F_8]_0) - 2 [c-C_4F_8]_t \right) \text{cc/mole-sec}^{-1} \quad (4)$$

The numerical value of the second order rate constant for  $C_2F_4$  pyrolysis ( $k_2'$ ) can be determined by integrating Equation (4).

$$k_2' = \frac{1}{t} \left( \frac{2([c-C_4F_8]_t - [c-C_4F_8]_0)}{[C_2F_4]_0 ([C_2F_4]_0 - 2([c-C_4F_8]_t - [c-C_4F_8]_0))} \right) \text{cc/mole-sec}^{-1} \quad (5)$$

The numerical value of  $k_2'$  as calculated from Eq. (5) should be equal to the value of  $k_2$  calculated from Eq. (3). 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  $k_2''$

$$k_2'' = \frac{RT}{t} \left[ \frac{1}{(2P_t) - (P_{C_2F_4})_0} - \frac{1}{(P_{C_2F_4})_0} \right] \text{cc/mole-sec}^{-1} \quad (6)$$

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.

C<sub>2</sub>F<sub>4</sub> Pyrolysis. The order of the C<sub>2</sub>F<sub>4</sub> pyrolysis reaction was determined at 365°C by applying the half-life method. During the course of these experiments, the initial C<sub>2</sub>F<sub>4</sub> pressure was varied from 740 to 175 torr, and the C<sub>2</sub>F<sub>4</sub> half-life was approximately  $2 \times 10^3$  sec when the initial C<sub>2</sub>F<sub>4</sub> 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<sub>2</sub>F<sub>4</sub> is given by Eq. (2).

Once the reaction was established to be second order, the pyrolysis of C<sub>2</sub>F<sub>4</sub> was studied over the temperature and initial pressure ranges 300 to 450°C and 50 to 200 torr. The three independent rate constants given by Eqs. (3), (5) and (6) were calculated from the experimentally determined time dependence of the C<sub>2</sub>F<sub>4</sub> concentration, c-C<sub>4</sub>F<sub>8</sub> concentration and total pressure. The numerical values of these rate constants based on a series of experiments with a reaction temperature and initial C<sub>2</sub>F<sub>4</sub> pressure of 452°C and 50.8 torr are listed in Table 1. The average values of the three rate constants as a function of temperature are given in Table 2. The numerical value of each of the rate constants listed in Table 2 are based on 5 to 10 data points.

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

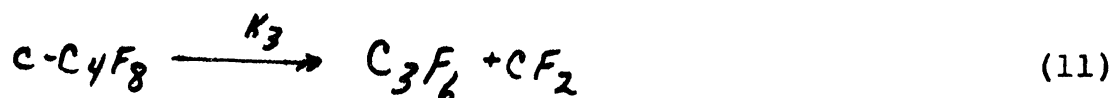
$$k_2 = 10^{11.05 \pm .07} \exp\left(\frac{-25,555 \pm 200}{RT}\right) \text{ cc/mole-sec}^{-1} \quad (7)$$

$$K_2' = 10^{10.81 \pm .14} \exp\left(\frac{-25,136 \pm 420}{RT}\right) \quad \text{cc/mole-sec}^{-1} \quad (8)$$

$$K_2'' = 10^{11.33 \pm .20} \exp\left(\frac{-26,407 \pm 590}{RT}\right) \quad \text{cc/mole-sec}^{-1} \quad (9)$$

c-C<sub>4</sub>F<sub>8</sub> Pyrolysis. The thermal decomposition of c-C<sub>4</sub>F<sub>8</sub> 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-C<sub>4</sub>F<sub>8</sub> from C<sub>2</sub>F<sub>4</sub> and the first order decomposition of c-C<sub>4</sub>F<sub>8</sub>. The results of these experiments confirmed the validity of the assumption that the term representing the first order back reaction in Eq. (1) is insignificant with respect to the contribution of the second order term for temperatures less than 460°C.

It has been previously shown<sup>(3,4)</sup> that both C<sub>2</sub>F<sub>4</sub> and C<sub>3</sub>F<sub>6</sub> are formed by parallel, unimolecular reactions during the course of c-C<sub>4</sub>F<sub>8</sub> pyrolysis. These unimolecular reactions are given by



Butler<sup>(4)</sup> has shown that both  $k_1$  and  $k_3$  can be determined if  $k_2$  is known and the concentrations of  $c\text{-C}_4\text{F}_8$ ,  $\text{C}_2\text{F}_4$  and  $\text{C}_3\text{F}_6$  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<sup>(4)</sup>.

#### DISCUSSION

The pyrolysis of  $\text{C}_2\text{F}_4$  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  $\text{C}_2\text{F}_4$  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  $\text{C}_2\text{F}_4$  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<sup>(1,2)</sup>. In the temperature range of interest, the values of  $k_2''$  reported in References (1) and (2) 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. The experimental determination of the second order rate constants  $k_2$ ,  $k_2'$  and  $k_2''$  were based on two assumptions: (1)  $\text{C}_2\text{F}_4$  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  $452^\circ\text{C}$ . 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  $452^\circ\text{C}$ . The possible effects of any heterogeneous effects were also considered. The previous studies<sup>(1,2)</sup> 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.

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Table 1 SECOND ORDER RATE CONSTANT FOR  
TETRAFLUOROETHYLENE PYROLYSIS AT 725°K.

t	$k_2$	$k_2'$	$k_2''$
(seconds)	(cc/mole-sec <sup>-1</sup> )		
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

Table 2 TEMPERATURE DEPENDENCE OF SECOND ORDER  
RATE CONSTANT FOR TETRAFLUOROETHYLENE PYROLYSIS

T	$k_2$	$k_2'$	$k_2''$
$^{\circ}\text{K}$	(cc/mole-sec <sup>-1</sup> )		
588	36.0	30.5	34.2
638	194	156	183
663	411	328	361
688	828	620	937
725	2305	1877	2420

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13. ABSTRACT

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$$K_2^I = 10^{10.81 \pm .14} \exp\left(\frac{-25,136 \pm 420}{RT}\right) \text{ cc/mole} \cdot \text{sec}^{-1}$$

$$K_2^{II} = 10^{11.33 \pm .20} \exp\left(\frac{-26,407 \pm 590}{RT}\right) \text{ cc/mole} \cdot \text{sec}^{-1}$$

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WT

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**Pyrolysis**

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**Octafluorocyclobutane**

**Thermal Decomposition of Fluoro-  
carbons**

**Chemical Kinetics**

**Rate Expressions**

**Rate Constants**