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Mercury-Sensitized Photolysis of $C_2F_4^{\dagger}$

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Tetrafluoroethylene was decomposed by mercury photosensitization at temperatures from 21° to 224°C. At pressures below 60 mm, the only product was $c-C_8F_6$ and its production was linear with the C_2F_4 pressure and enhanced by raising the temperature. The CF2 radicals produced during photolysis can either recombine or add to the substrate:

 $2CF_2 \rightarrow C_2F_4$

k7 $CF_2+C_2F_4\rightarrow c-C_3F_6.$

The rate constant ratio $k_7/k_6^{\frac{1}{2}}$ was found to be 395 exp(-6700/RT) (liter/mole·sec)^{$\frac{1}{2}$}.

I. INTRODUCTION

THE room-temperature mercury-sensitized photoly- \mathbf{I} sis of C₂F₄ yields perfluorocyclopropane (cyclo- C_3F_6) as a product, and the yield of this product increases linearly with the C₂F₄ pressure.¹⁻³ It was proposed that the $c-C_3F_6$ results from the addition of singlet CF₂ radicals⁴ to C₂F₄. Recently Cordischi, Lenzi, and Mele⁵ have subjected C₂F₄-O₂ mixtures to x and γ radiation and found c-C₃F₆ as one of the products. Its yield was linear with the C₂F₄ pressure, and it was produced with an activation energy of 6.7 kcal/mole over the temperature range -20° to $+25^{\circ}$ C. Presumably, the $c-C_3F_6$ was formed by the same mechanism as in the photolysis. We have re-examined the photolysis in detail from room temperature to 224°C to determine the Arrhenius parameters of the reaction-rate constant.

II. EXPERIMENTAL

Tetrafluoroethylene was prepared and purified as discussed elsewhere.² The Hg-sensitized photolysis was carried out in a 5-cm-long quartz cell of 5.0-cm diam. The cell was in a 10-cm-long, asbestos-wrapped aluminum oven. A quartz window at the open end of the oven prevented cooling by convection. Irradiation was from a Hanovia low-medium pressure spiral-shaped mercury-resonance arc at one end of the cell. A Corning 9-54 glass filter removed unwanted radiation below 2200 A. In all cases, the lamp was allowed to warm up for at least 15 min before photolysis was begun.

At the conclusion of each run, the contents of the cell were collected and passed through a Beckman

GC-2A gas chromatograph, utilizing a 16-ft silica gel column. Identification of products was made by previously determined retention times for various fluorocarbons, and the principal product c-C₃F₆, was calibrated so that peak areas could be converted to concentration units.

The lamp intensity was determined by irradiation of mixtures of N_2O (Matheson, degassed) and C_2F_4 in approximate ratios of 40:1. The N₂O is sensitized by $Hg(6^{3}P_{1})$ to give N₂+O with a quantum yield of unity,^{6,7} and the trace amounts of C_2F_4 consume the O atoms formed.⁸ From the N₂ yield, the 2537-Å radiation entering the cell was thus determined to be 5.6×10^{15} quantum/sec.

Experiments were performed at several temperatures from 21° to 224°C. At higher temperatures, the c-C₃F₆ was found to decompose. Typical C₂F₄ pressures ranged from about 1 to 30 mm. At 175°C, C₂F₄ pressures up to 320 mm were investigated. In several instances, the duration of photolysis was varied to ensure that c-C₃F₆ yields were linear with time.

The temperature variation from run to run at a given nominal temperature was $\pm 2^{\circ}$ C as measured by a thermocouple.

The C₂F₄ pressures of less than 10 mm were measured with a McLeod gauge; higher pressures were measured with a manometer.

III. RESULTS

In all runs at temperatures of 224°C or lower and at C₂F₄ pressures of 60 mm or less, the only product formed was $c-C_3F_6$. Furthermore, the $c-C_3F_6$ yield was found to be linear with C_2F_4 pressure and with duration of photolysis, within experimental error. At temperatures of 287° and 337°C, the c-C₃F₆ yield was considerably less than expected on the basis of lower-

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¹B. Atkinson, J. Chem. Soc. **1952**, 2684. ²J. Heicklen, V. Knight, and S. A. Greene, J. Chem. Phys. **42**, 221 (1965).

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TABLE I. Photolysis of C₂F₄.

(C ₂ F ₄) (mm)	$(C_2F_4) \times 10^4$ (mole/liter)	Exposure time (min)	$\Phi(c-C_8F_6)$		
<i>T</i> =21°C					
2.3 4.25 7.9 8.4 13.5 19.5 24.5 26.5	1.25 2.3 4.3 4.6 7.4 10.6 13.3 14.4	70.0 32.0 30.0 30.0 30.0 32.0 30.0 26.0	0.0024 0.0038 0.0061 0.0085 0.010 0.0052 0.015 0.016		
	1 = 30°C 0 47 65 0 0 00006				
0.9 3.0 8.85 19.5 30.5 30.5	0.47 1.5 4.6 10.1 15.8 15.8	65.0 30.0 30.0 30.0 30.0 45.0	0.00096 0.0029 0.0094 0.027 0.013 0.029		
<i>T</i> =122°C					
1.0 3.75 8.4 20.5 21	$0.41 \\ 1.53 \\ 3.4 \\ 8.3 \\ 8.6$	15.0 30.0 30.0 15.5 7.5	0.012 0.042 0.096 0.23 0.25		
	T =	175°C			
0.865 2.0 5.05 9.25 9.35 9.6 18 19 32 39 63 65 99 153 187 200 227 265 319	$\begin{array}{c} 0.31 \\ 0.72 \\ 1.8 \\ 3.3 \\ 3.35 \\ 3.4 \\ 6.45 \\ 6.8 \\ 11.5 \\ 14 \\ 22.5 \\ 23.5 \\ 35.5 \\ 54.5 \\ 67 \\ 72 \\ 81.5 \\ 95 \\ 114 \end{array}$	20.5 16.0 15.0 9.16 3.5 14.5 15.5 3.0 30.0 6.25 3.0 2.0 2.0 1.0 4.25 2.1 1.0 1.0 224°C	0.021 0.067 0.15 0.22 0.23 0.13 0.26 0.53 0.84 1.04 1.05 0.55 0.48 0.79 1.23 0.83 1.1 2.06		
1.2	0.39	15.0	0.054		
2.5 8.3 22	0.81 2.7 7.1	30.0 10.4	0.11 0.39 0.83		

temperature runs because of thermal decomposition. At 175°C and pressures of 100 mm or higher, a secondary product was formed in trace amounts that was tentatively identified as n-C₃F₆. The data are tabulated in Table I. It can be seen that the reproducibility is not very good, particularly at the greater pressures. In most cases the errors were such as to cause $\Phi(c-C_3F_6)$ (c-C₃F₆ yield, molecule per quantum) to appear too small, probably due to thermal decomposition of c-C₃F₆. Log-log plots (Fig. 1) of $\Phi(c-C_3F_6)$ as a function of initial C₂F₄ concentration for C₂F₄ concentrations less than about 10⁻⁸ mole/liter at five different temperatures are all linear with slope unity, indicating that the

production of $c-C_8F_6$ is first order in C_2F_4 , as was determined previously.¹⁻³

IV. DISCUSSION

The results are consistent with the previously given mechanism²

$$Hg+h\nu \rightarrow Hg^*, \qquad (1)$$

$$Hg^* + C_2 F_4 \rightarrow Hg + C_2 F_4^*, \qquad (2)$$

$$C_2F_4^* + C_2F_4 \rightarrow C_2F_4^{**} + C_2F_4,$$
 (3)

$$C_2F_4 \stackrel{\kappa_4}{\longrightarrow} C_2F_4, \tag{4}$$

$$C_2F_4^* \rightarrow 2CF_2,$$
 (5)

$$2CF_2 \xrightarrow{\kappa_4} C_2F_4, \qquad (6)$$

$$CF_2 + C_2F_4 \rightarrow c - C_3F_6. \tag{7}$$

The sequence of Reactions (3) and (4), although kinetically indistinguishable in this work from a onestep deactivation, has been included to conform with previous results.² Reaction (2) is the only possible fate of the Hg* atoms, so that the rate of formation of upper vibrational levels of electronically excited C_2F_4 (designated $C_2F_4^*$) is controlled by I_a only, which is presumed to be constant throughout all the experi-



FIG. 1. $\Phi(c-C_3F_6)$ vs (C₂F₄).

ments. The $C_2F_4^*$ molecule can either fission to form two CF₂ radicals, presumably in the singlet electronic state [Reaction (5)], or be collisionally deactivated into lower vibrational levels with insufficient energy to decompose [Reaction (3)]. These states are designated $C_2F_4^{**}$ and presumably belong to the same electronic state as $C_2F_4^{**}$. The only possible fate of $C_2F_4^{**}$ is deexcitation to ground-state C_2F_4 [Reaction (4)].

From this mechanism, two limiting cases can be distinguished for the quantum yield of $c-C_3F_6$ formation, $\Phi(c-C_3F_6)$:

$$\Phi(c-C_3F_6) = [k_7/(I_ak_6)^{\frac{1}{2}}](C_2F_4) \qquad (R_6 \gg R_7), \quad (8)$$

$$\Phi(c-C_3F_6) = 2\{k_5/[k_5+k_3(C_2F_4)]\} \qquad (R_7 \gg R_6), \quad (9)$$

where R_6 and R_7 stand for the rates of Reactions (6) and (7), respectively. If $\Phi(c-C_3F_6)$ be plotted vs C_2F_4 concentration, the limiting low-pressure value for the slope will be $k_7/(k_6I_a)^{\frac{1}{2}}$. The intercepts of the plots of $\log\Phi(c-C_3F_6)$ vs $\log(C_2F_4)$ give $k_7/k_6^{\frac{1}{2}}I_a^{\frac{1}{2}}$ from which $k_7/k_6^{\frac{1}{2}}$ can be calculated, since I_a is known. These values are tabulated in Table II. An Arrhenius plot of $k_7/k_6^{\frac{1}{2}}$ vs T^{-1} is shown in Fig. 2. The points up to 224°C are seen to be on a straight line, the slope of which gives a value of 6.7 ± 0.2 kcal/mole for $E_7-(\frac{1}{2})E_6$. The preexponential factor is 395 (liter/mole · sec)^{\frac{1}{2}}.

Recently, Dalby⁹ has obtained from the flash photolysis of C₂F₄ a value of $k_6=1.3\times10^8(T/300)^{\frac{3}{2}}\times$ $\exp(-1200/RT)$ liter/mole·sec. This expression becomes $k_6=2.6\times10^8 \exp(-1600/RT)$ liter/mole·sec when put in the ordinary Arrhenius form. Using

TABLE II. $k_7/k_6^{\frac{1}{2}}$ at various temperatures.

 T (°C)	$k_7/k_6^{\frac{1}{2}} \times 10^3$ (liter/mole·sec) ^{\frac{1}{2}}	
 21 36 122 175 224	4.3 6.2 89 216 430	

⁹ F. W. Dalby, J. Chem. Phys. 41, 2297 (1964).



FIG. 2. $k_6/k_7^{\frac{1}{2}}$ vs T^{-1} .

this expression gives $k_7 = 6.4 \times 10^6 \exp(-7500/RT)$ liter/mole·sec.

In order that the value of k_5/k_8 could be determined, experiments at 175°C were carried to C₂F₄ pressures high enough to obtain the falloff in the slope of $\Phi(c-C_8F_8)$ vs (C₂F₄). Although a definite falloff is observed, the scatter in the data is so large that k_5/k_8 can only be estimated roughly; the best estimate is 10^{-2} mole/liter.

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