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It can be verified directly for the examples given in Table I that the mth-order approximation correctly gives the first m coefficients of the expansions of γ and $\varphi=\theta/(1-\theta)$ as functions of α. That this must be the case is easily seen from the definition of $z=\gamma-1$ [Eq. (2.4) of I] and the fact that the first m z_j's are exact in the mth approximation.

V. DISCUSSION

The limiting form of Δ^* given by Eq. (4.8) is essentially the one-dimensional analog of the suggestion advanced in Ref. 10, except that the argument of the singular function is $\rho=N_{11}/N$ rather than $\theta=N/L$. The difference is not too serious since as θ approaches one, ρ must also. In fact, a random-mixing argument quickly leads to the prediction $\rho_{\text{Av}}=\theta$ for the linear lattice. There is a difference, however; in terms of ρ, Δ^* discourages configuration with many molecules in a few clusters. There are "some" such configurations with θ not near one, and these "should" be discouraged.

The results presented in the previous section warn against attempting to discard high-order correlations. In two- or three-dimensional problems it will be necessary to include estimates of Δ^* or some analogous many-body interaction if thermodynamic properties are to be predicted faithfully over the entire density range.

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Mercury-Photosensitized Oxidation of Tetrafluoroethylene*

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The mercury-photosensitized reactions of C_2F_4 were studied in the absence and the presence of oxygen at room temperature. In the absence of oxygen, the only product was cyclo-C_3F_6, whereas CF_2O and another unidentified product were also formed in the presence of oxygen. The cyclo-C_3F_6 formation rate was unaffected by oxygen or nitrogen and was proportional to the C_2F_4 pressure and the square root of the incident intensity. The results are explained. The oxidation apparently does not involve the CF_2 radical. Two processes are introduced to explain the oxygenated products. One of these is attack of C_2F_4 by oxygen atoms produced from the mercury-photosensitized decomposition of oxygen. The other involves the reaction of molecular oxygen with an electronically excited C_2F_4 molecule. The first oxidation process can be suppressed by the addition of nitrogen, whereas the second cannot. The oxidation mechanism presented is not complete but does explain the major trends.

INTRODUCTION

THE mercury-photosensitized decomposition of tetrafluoroethylene has been studied by Atkinson.[1] His excellent paper demonstrates in a convincing fashion that CF_2 radicals are produced. For low conversions the only product is perfluorocyclopropane, and its yield increases with the C_2F_4 pressure. It is unlikely that this product could be formed if CF_2 radicals were absent. He also found that at 50 mm pressure the cyclo-C_3F_6 yield is nearly independent of intensity but that it drops with increasing intensity at higher pressures.

The results above 50 mm pressure can be explained by the mechanism

$$Hg+h\nu\rightarrow Hg^*, \tag{a}$$

$$Hg^*+C_2F_4\rightarrow Hg+C_2F_4^*, \tag{b}$$

$$C_2F_4^*\rightarrow 2CF_2, \tag{c}$$

$$2CF_2\rightarrow C_2F_4, \tag{d}$$

$$CF_2+C_2F_4\rightarrow c\text{-}C_3F_6, \tag{e}$$

where the asterisk denotes an excited electronic state. Actually, the intermediate state $C_2F_4^*$ is not needed to explain Atkinson's data, but it has been included in anticipation of the results of the present work. We have reexamined this problem, especially at lower pressures (0.6 to 60 mm), to extend and clarify some of the prior experiments done at pressures ranging from 10 to 350 mm. In most of our work, the system has been studied in the presence of oxygen, and, in some cases, nitrogen also was added.

EXPERIMENTAL

Tetrafluoroethylene was prepared by decomposing Teflon under vacuum at 450° to 480°C. The effluent gas contained over 90% monomer, about 5% perfluoropropylene, and a few percent carbon dioxide. This gas was passed over solid potassium hydroxide to remove the carbon dioxide and then fractionated on a Beckman GC-2A preparative gas–liquid chromatograph with a 16-ft silica gel column. The resulting tetrafluoroethylene contained less than 0.01% of any impurity. Matheson research-grade oxygen and nitrogen were used.

Appropriate mixtures of the three gases were prepared in either a 10-cm-long Pyrex cell with sodium

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[1] B. Atkinson, J. Chem. Soc. **1952**, 2684.

chloride windows or a 5-cm-long quartz cell. Each cell was 5.0 cm in diameter. Irradiation was from Hanovia Type-SH, medium-pressure, U-shaped mercury arcs at both ends of the cell. The light was collimated by quartz lenses and passed through Corning 9–54 glass before entering the cell. This removed unwanted radiation below 2200 Å. Where reduced intensities were desired, screens with 20% or 45% transmission were used.

When the Pyrex cell with sodium chloride windows was used, the run was interrupted periodically and infrared spectra were taken on a Perkin–Elmer Model 21 spectrometer. At the conclusion of the run, the gases were collected and passed through the Beckman GC–2A programmed dual-column chromatograph. When the quartz cell was used, only chromatographic analysis was done.

The products found by chromatographic analysis—CO_2 and perfluorocyclopropane—were calibrated so that chromatographic areas could be converted to pressures. Corrections were also made for the very small amounts of atmospheric CO_2 that was introduced during transfer of the gas sample tube from the vacuum line to the chromatograph. This correction was less than 10% in most cases, and never larger than 30%.

Identification of the perfluorocyclopropane was made by chromatographic and infrared analysis. The product of the photolysis of pure tetrafluoroethylene had a chromatographic retention time on the 16-ft silica gel column which could only correspond to a C_3 fluorocarbon that was neither C_3F_8 nor C_3F_6.[2] This product was then isolated and the infrared spectrum obtained. Very few bands appeared, indicating a high degree of symmetry. Satisfactory assignments could be made for the perfluorocyclopropane molecule.[3]

RESULTS

A mixture of 20 mm of C_2F_4 and 30 mm of oxygen was photolyzed, and the infrared spectrum was measured periodically throughout the run. Initially, bands appeared at 5.16, 7.96, 8.05, 10.27, 10.50, 12.65, and 12.92 μ, all of which can be attributed to CF_2O.[4,5] However, this product did not accumulate linearly with exposure, and was found to decay even in the dark. Other initial product bands appeared at 6.20, 7.82, 8.85, and 11.65 μ. All of these bands intensified continuously with exposure and were stable in the dark. The 7.82 and 11.65 bands belong to perfluorocyclopropane.[3] The bands at 6.20 and 8.85 μ could not be associated with any known carbon–fluorine–oxygen compound.

With continued irradiation, secondary products were produced. The CO_2 bands at 4.33 and 15.00 μ and the SiF_4 bands at 5.41, 5.50, and 9.70 μ were easily recognized. Two other bands also appeared: a weak one at 9.25 μ and a strong one at 13.95 μ. All of these products were stable. The unimportant band at 9.25 μ was never identified, but the 13.95 μ band almost surely belongs to sodium fluoride. Because SiF_4 was produced, the presence of fluorine atoms is indicated. These atoms, besides attacking the Pyrex to produce SiF_4, would surely react with the sodium chloride windows to yield sodium fluoride. Furthermore, when the reaction cell was evacuated and the gases collected for chromatographic analysis, an infrared spectrum of the evacuated cell still showed the band at 13.95, indicating a solid deposit.

Chromatographic analysis of the reaction mixture gave roughly 39% C_2F_4, 39% CO_2, 4% perfluorocyclopropane, 5% of something heavier than perfluorocyclopropane, and 3% of assorted other products.

The run described above was repeated under slightly different conditions. The incident intensity was somewhat lower, and since the same cell was used, the windows were now coated with sodium fluoride. The infrared results were essentially identical, but the chromatographic analysis did not show any of the heavy product. Some lighter product, probably C_2F_2, was found in about the same amount as the perfluorocyclopropane.

A run with 2 mm of C_2F_4 and 300 mm of oxygen showed only CF_2O as a product on infrared analysis. Undoubtedly the other products were too small to be detected.

All other runs were done in the quartz cell, and only chromatographic analyses were performed. The results are shown in Tables I through III and Figs. 1 through 5. The exposure times were kept small to avoid the complications of secondary reactions. The only products were perfluorocyclopropane and carbon dioxide. In the absence of oxygen, no carbon dioxide was produced. Interspersed among the tables are runs in which only the exposure time was altered. In the absence of oxygen, the rate of perfluorocyclopropane formation

TABLE I. Photolysis in the absence of oxygen ($T=23°C$, 2537 Å, quartz cell).

(C_2F_4) (mm)	Exposure time (h)	$R(c\text{-}C_3F_6)$ (mm/h)
1.9	3.00	0.0016
7.0	3.00	0.0086
18.0	1.00	0.017
19.5	1.00	0.028
19.5	3.00	0.022
20.5	13.50	0.021
60.5	1.033	0.062

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[2] S. A. Greene and F. M. Wachi, Anal. Chem. **35**, 928 (1963).

[3] J. Heicklen, F. M. Wachi, and V. Knight, "The Infrared Spectra of Perfluorocyclopropane and *Cis*- and *Trans*-Perfluorobutene-2," J. Phys. Chem. (to be published).

[4] P. J. H. Woltz and E. A. Jones, J. Chem. Phys. **17**, 502 (1949).

[5] A. H. Neilsen, T. G. Burke, P. J. H. Woltz, and E. A. Jones, J. Chem. Phys. **20**, 596 (1952).

Table II. Photolysis of C_2F_4–O_2 mixtures ($T=23°C$, 2537 Å, quartz cell).

(C_2F_4) (mm)	(O_2) (mm)	(N_2) (mm)	Exposure time (h)	$R(c\text{-}C_3F_6)$ (mm/h)	$R(CO_2)$ (mm/h)
(C_2F_4)∼0.60 mm					
0.63	0.99	824	1.25	···	0.078
0.63	1.1	0.0	1.25	···	0.070
0.60	2.8	0.0	0.75	···	0.074
0.61	11.4	0.0	0.75	···	0.108
0.55	11.5	0.0	0.75	···	0.086
0.62	37	0.0	0.25	···	0.190
0.52	34	0.0	0.75	···	0.069
0.60	32	788	0.833	···	0.062
0.60	28	712	1.00	···	0.062
0.59	128	0.0	0.25	···	0.325
0.67	112	0.0	0.50	···	0.123
0.65	101	715	0.75	···	0.093
0.63	297	0.0	0.25	···	0.49
0.65	297	0.0	0.25	···	0.124
0.65	299	0.0	0.50	···	0.123
0.61	705	0.0	0.167	···	1.38
0.61	851	0.0	0.75	···	0.16
0.61	839	0.0	0.75	···	0.15
0.65	810	0.0	1.00	···	0.32
0.60	>1000	0.0	0.25	···	1.69
(C_2F_4)∼2.0 mm					
2.0	0.87	0.0	0.784	···	0.20
2.3	14.7	0.0	1.50	0.0018	0.19
2.1	31	0.0	0.50	···	0.176
1.9	31	0.0	1.00	0.0028	0.145
2.1	29	767	1.083	0.0021	0.115
2.1	32	0.0	2.00	0.0021	0.41
2.2	31	0.0	3.00	0.0029	0.35
2.2	101	0.0	3.00	0.0025	0.24
2.0	301	0.0	0.50	0.0021	0.41
2.2	288	0.0	1.00	0.0025	0.33
2.1	298	0.0	2.083	0.0022	0.29
1.9	310	0.0	3.00	0.0019	0.35
2.2	828	0.0	0.333	···	0.60
2.3	800	0.0	0.50	···	0.38
1.7	778	0.0	0.50	···	0.31
2.2	>1000	0.0	1.00	···	1.05
(C_2F_4)∼6.0 mm					
6.6	29	0.0	1.00	0.0076	0.36
6.0	29	773	1.00	0.0108	0.23
6.0	103	0.0	1.00	0.0069	0.35
6.5	296	0.0	1.00	0.0069	0.52
7.0	773	0.0	0.50	···	0.37
7.0	800	0.0	0.50	···	0.53
6.5	806	0.0	0.50	···	0.56
6.0	>1000	0.0	0.50	···	1.18
(C_2F_4)∼20 mm					
21.5	0.335	0.0	0.083	0.033	0.70
21.0	1.00	0.0	0.167	0.029	1.39
19.9	1.09	0.0	0.50	···	1.39
21	1.15	0.0	0.50	0.031	1.65

TABLE II (*Continued*)

(C_2F_4) (mm)	(O_2) (mm)	(N_2) (mm)	Exposure time (h)	R(c-C_3F_6) (mm/h)	R(CO_2) (mm/h)
		(C_2F_4)$\sim$20 mm (*Continued*)			
21.5	3.0	0.0	0.167	0.025	0.62
21.0	27	789	1.00	0.024	0.48
20.5	29	0.0	1.00	0.025	0.62
21.0	105	0.0	1.51	0.023	0.45
22.0	261	0.0	0.25	0.029	$\sim$0.55
21.0	274	0.0	0.25	0.024	···
18.5	273	0.0	0.50	0.024	···
18.5	274	0.0	0.50	0.021	$\sim$0.46
21.0	306	0.0	1.00	0.021	0.50
22.0	286	0.0	2.00	···	0.54
21	779	0.0	0.55	0.026	1.05
19.5	>1000	0.0	1.00	0.022	1.00
		(C_2F_4)$\sim$60 mm			
60.5	29	0.0	0.667	0.084	$\lesssim$1.0
59	29	0.0	1.067	0.092	···
58.5	33	0.0	3.167	0.091	0.73
57	785	0.0	3.00	0.103	0.71

is independent of exposure time even for 13.5-h exposure. In the presence of oxygen, the rates of product formation are independent of length of irradiation for at least 1 h and are not much affected even for exposures up to 3 h. All runs listed in Table II are for times of this duration or less. Table III gives results at reduced intensities. The exposure times are longer to compensate for the reduction, but the percent conversion is still sufficiently small that secondary reactions are unimportant.

Figures 1 and 2 are log–log plots of the rate of perfluorocyclopropane formation, R(c-C_3F_6), versus the C_2F_4 pressure at various intensities. The plots are linear over a 30-fold variation in pressure with unit slope indicating that R(c-C_3F_6) varies as the first power of the C_2F_4 pressure. The presence of even 1 atm of oxygen or nitrogen does not affect the results.

Figure 3 shows the variation of R(c-C_3F_6)/(C_2F_4) with the intensity. The log–log plot is linear with a slope of 0.5 indicating a dependence proportional to the square root of the intensity.

Figure 4 is a log–log plot of the rate of CO_2 formation, R(CO_2), versus the oxygen pressure at five different C_2F_4 pressures ranging from 0.6 to 60 mm. The oxygen pressure was varied from 0.3 mm to over 1000 mm. With 0.6 mm C_2F_4, the rate of CO_2 production rises steadily with the oxygen pressure from about 0.07 mm/h to at least twice that value at oxygen pressures exceeding 1 atm. The data are badly scattered at the high oxygen pressures, and the CO_2 rate may be as high as 1.6 mm/h at 1000 mm of oxygen. With 2.0 mm C_2F_4, the CO_2 rate is about 0.2 mm/h at low oxygen pressures and is not much affected until the oxygen pressure exceeds 100 mm. Then it begins

TABLE III. Photolysis of C_2F_4–O_2 mixtures at reduced intensities (T=23°C, 2537 Å, quartz cell).

(C_2F_4) (mm)	(O_2) (mm)	% transmission	Exposure time (h)	R(c-C_3F_6) (mm/h)	R(CO_2) (mm/h)
2.15	0.0	45	6.00	0.00172	···
2.16	285	20	5.00	···	0.049
2.16	0.0	20	16.00	0.00110	···
2.15	0.0	20	21.0	0.00116	···
6.0	111	45	3.00	0.0044	···
6.5	97.5	45	4.00	0.0062	0.142
6.5	0.0	20	6.25	0.0031	···
21.0	0.0	45	2.00	0.013	···
21.0	267	45	2.167	0.021	<0.39
21.0	257	20	5.00	0.0118	0.120
21.0	9.8	20	5.083	0.0110	0.091

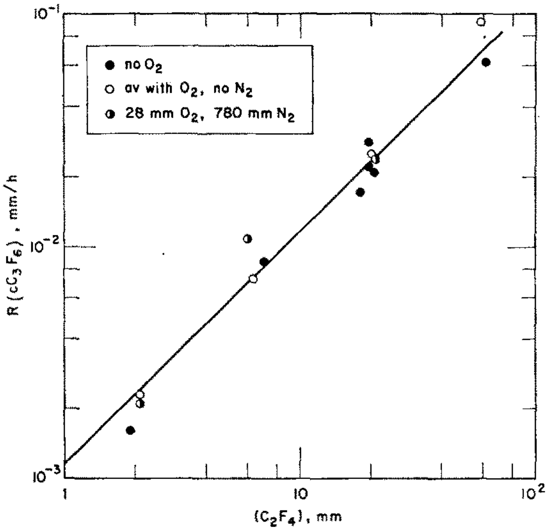

FIG. 1. Plot of $R(c\text{-}C_3F_6)$ versus (C_2F_4) at full intensity.

to climb toward a rate of about 1.0 mm/h at 1000 mm of oxygen. With 6 mm of C_2F_4, it is not convenient to prepare mixtures of low oxygen pressure. However, at the higher pressures, the CO_2 rate is fairly constant at about 0.5 mm/h, at least up to 1 atm of oxygen. With 20 mm of C_2F_4 the results are more complex. One point with 0.3 mm of oxygen gives $R(CO_2)$ as 0.7 mm/h. This value rises to 1.5 mm/h at 1 mm of oxygen and then drops with further increases of oxygen to 0.5 mm/h at 100 mm of oxygen. Above this pressure, $R(CO_2)$ again rises reaching 1.0 mm/h for oxygen pressures greater than 1 atm. Two points at 60 mm of C_2F_4 give $R(CO_2)$ as 0.7 mm/h. The results at 0.6 mm C_2F_4 are uncertain because of the scatter, but at least for the other four series, and probably for all

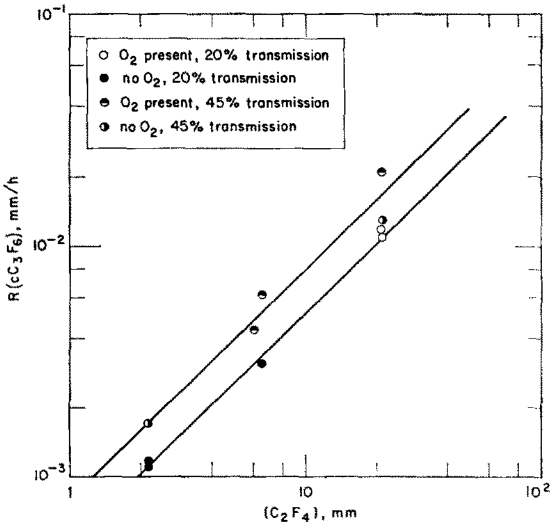

FIG. 2. Plot of $R(c\text{-}C_3F_6)$ versus (C_2F_4) at reduced intensities.

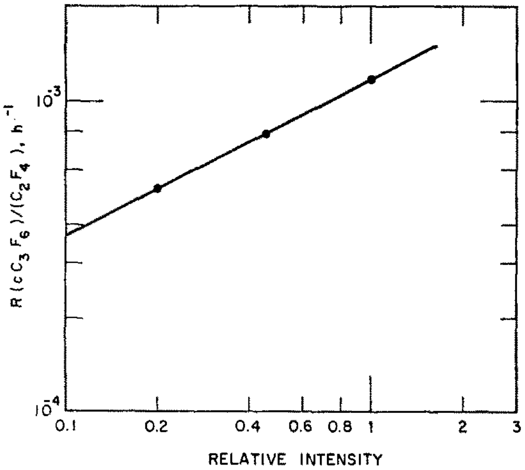

FIG. 3. Plot of $R(c\text{-}C_3F_4)/(C_2F_4)$ versus relative intensity.

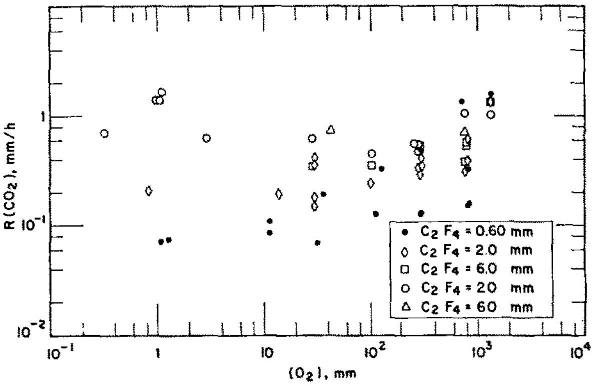

FIG. 4. Plot of $R(CO_2)$ versus (O_2) for C_2F_4 pressures of 0.60, 2.0, 6.0, 20, and 60 mm.

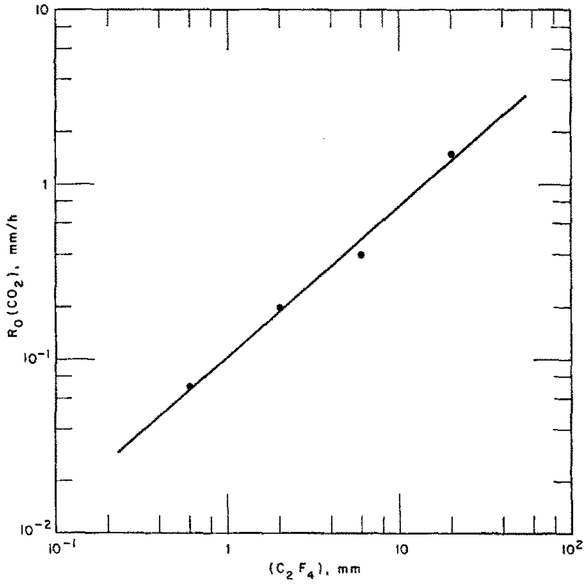

FIG. 5. Plot of $R_0(CO_2)$ versus (C_2F_4).

five, $R(CO_2)$ is in the neighborhood of 1.0 mm/h (to a factor of 2) at the highest oxygen pressures. The limiting low values of the CO_2 rate of formation $R_0(CO_2)$ are plotted versus the C_2F_4 pressure in Fig. 4. For the series with 20 mm of C_2F_4, the value used is that for 1.0 mm of oxygen. The log–log plot is linear with slope of 0.87. Thus, $R_0(CO_2)$ rises with C_2F_4; the variation is almost, but slightly less than, linear.

In Table II are a number of runs with over 1 atm of nitrogen present. The nitrogen reduces the CO_2 rate to the minimum value in the absence of N_2 for that C_2F_4 pressure. In no case does the nitrogen prevent CO_2 formation. In fact, for the run with 0.63 mm C_2F_4 and 1.0 mm of O_2, the addition of 824 mm of nitrogen had no effect.

$R(CO_2)$ is proportionately smaller at the reduced intensities in contrast to $R(c\text{-}C_3F_6)$.

DISCUSSION

The infrared analysis clearly establishes the primary products of photolysis as CF_2O, cyclo-C_3F_6, and an unidentified product with infrared bands at 6.20 and 8.85 μ. Fluorocarbons are sufficiently stable to pass through the chromatograph, whereas carbon–fluorine–oxygen compounds will be converted to CO_2 and HF on the column or by contact with the stopcock grease present in our system. The HF does not pass through the column, but the CO_2 does. Repeated attempts to put CF_2O through our column have resulted in the appearance of CO_2 only. Apparently the conversion is quantitative. The failure to obtain any products other than cyclo-C_3F_6 and CO_2 by chromatographic analysis in the short-term runs strongly indicates that the unidentified product is a carbon–fluorine–oxygen compound.

For the runs carried to extended conversions, NaF, SiF_4, and CO_2, as well as an unidentified band at 9.25 μ, were found. The CO_2 results from reactions of the oxygenated products. The NaF and SiF_4 indicate the presence of fluorine atoms that are probably generated from the reaction

$$CF_2O+h\nu\rightarrow FCO+F \text{ (or } CO+2F).$$

The NaF is solid and remains in the reaction cell. The SiF_4 reacts rapidly with water on the column to give SiO_2 and HF, neither of which yields a chromatographic peak. Several attempts to pass SiF_4 through the column yielded nothing. Carbon monoxide would not be detected either by infrared analysis (because its band is too weak) or by chromatographic analysis (because it cannot be collected at −196°C).

Thus, the cyclo-C_3F_6 can be measured directly, whereas we believe the CO_2 yield to be a quantitative measure of oxygenated products. In the subsequent discussion, it is understood that CO_2 yield is equated with the yield of oxygenated fluorocarbons.

In the absence of oxygen, the sole product is perfluorocyclopropane in agreement with the findings of Atkinson.[1] The rate of its formation is proportional to the C_2F_4 pressure and the square root of the light intensity. Thus, our results confirm Atkinson's at high pressure and extend them to much lower pressures. Reactions (a) through (e) yield the expression

$$R(c\text{-}C_3F_6)=k_e(C_2F_4)\left[\frac{2I_a}{2k_d+k_e(C_2F_4)/(CF_2)}\right]^{\frac{1}{2}}, \qquad (1)$$

where I_a is the absorbed intensity. If $k_e(C_2F_4)/(CF_2)\ll 2k_d$, then Eq. (1) reduces to

$$R(cC_3F_6)=(k_e/k_d^{\frac{1}{2}})(C_2F_4)I_a^{\frac{1}{2}}, \qquad (2)$$

and the observed results are explained. However, Eq. (2) presupposes that all the Hg* is removed by collisional quenching and none by radiation. The value of the radiation rate constant is generally accepted to be 9.1×10^6 sec^{-1}.[6] Because of resonance entrapment the effective value will be much reduced, perhaps by a factor of 10 to 100 in our system. At 2 mm of pressure, the collision frequency with C_2F_4 is about 1×10^7 sec^{-1}. Consequently, our results require Reaction (a) to be extremely efficient, occurring on almost every collision. This requirement is at variance with the findings of Atkinson who reported that the mercury fluorescence was not completely quenched even in the presence of 25 mm of C_2F_4 in a reaction vessel of comparable dimensions to ours. Nevertheless, we are unable to explain our results in any other reasonable manner.

In the presence of oxygen, the results are more difficult to explain. However, it is indicated that CF_2 radicals do not react with oxygen. If they did, either the cyclo-C_3F_6 would have decreased with the addition of oxygen, or, if a chain that regenerated CF_2 were involved, the CO_2 would have increased rapidly with the oxygen pressure. The results clearly establish that oxygen has no influence on the cyclo-C_3F_6 yield. With high C_2F_4 pressures, there is no marked increase of CO_2 production with increases in oxygen. Even at the lower C_2F_4 pressures, there is a region where alteration of the oxygen pressure has little effect. Consequently, other mechanisms must be sought to account for the oxidation products.

The mercury-photosensitized decomposition of oxygen is well known. The mechanism is almost surely[7]

$$Hg^*+O_2\rightarrow Hg+O_2^*, \qquad (f)$$

$$O_2^*+O_2\rightarrow O+O_3, \qquad (g)$$

$$O_2^*+N_2\rightarrow O_2+N_2, \qquad (h)$$

where O_2^* is probably an electronically excited oxygen molecule, although a vibrationally excited molecule has not been ruled out. The oxygen atoms and possibly the

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[6] P. H. Garrett, Phys. Rev. **40**, 779 (1932); also see A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, New York, 1934), p. 147.

[7] For a review, see D. H. Volman, Advan. Photochem. **1**, 43 (1963).

ozone, could then react with C_2F_4:

$$O+C_2F_4 \rightarrow \text{products (not } CF_2).$$

This reaction scheme is consistent with the cyclo-C_3F_6 results if additional CF_2 is not produced by the reaction and if the removal of Hg* by O_2 and N_2 is always small compared to Reaction (b). D. Saunders of this laboratory has reacted O atoms with C_2F_4, and has found the sole oxidation product to be CF_2O. A full report will be published in the near future. Consequently, the reaction is most likely

$$O+C_2F_4 \rightarrow C_2F_4O \xrightarrow{O_2} 2CF_2O+O. \quad \text{(i)}$$

A chain reaction is involved which can account for large amounts of products even if Reaction (i) is small. The chain length should be very sensitive to conditions. The lack of reproducibility of the CO_2 yield at high oxygen pressures reflects this sensitivity.

Volman[8] has shown that the ozone yield in the absence of C_2F_4 is only 0.03 with 1 atm of oxygen. The deactivation of Hg* by collision with N_2 is 67 times slower than with O_2.[9] Thus, even under the most unfavorable conditions, Reaction (b) is the most important step for removal of Hg*. However, Reaction (h) is significant, and the oxidation due to the above mechanism should be suppressed by the addition of nitrogen.[9] At oxygen pressures of 30 and 100 mm, the addition of N_2 gives a moderate reduction in CO_2 yield. With 1 mm of oxygen and 0.63 mm of C_2F_4, where the inhibiting effect of N_2 should be more pronounced, no reduction in oxidation occurs with the addition of 824 mm of N_2. Clearly another mechanism must be introduced to explain the results.

A method to explain the oxidation is through an electronically excited C_2F_4 molecule that reacts with oxygen. We introduce the reactions

$$C_2F_4^{*}+C_2F_4 \rightarrow C_2F_4^{**}+C_2F_4, \quad \text{(j)}$$

$$C_2F_4^{**}+O_2 \rightarrow 2CF_2O, \quad \text{(l)}$$

where $C_2F_4^{**}$ is the new electronic state. To retain consistency with all the results, it is necessary that Reaction (j) be slower than (c) for all C_2F_4 pressures employed, and that $C_2F_4^{*}$ not be converted to $C_2F_4^{**}$ by collision with O_2 or N_2. Even though the oxidation products exceed the c-C_3F_6 formed, Reaction (c) can be much more important than (j) as almost all the CF_2 radicals recombine to form C_2F_4. The restrictions that O_2 or N_2 do not collisionally convert $C_2F_4^{*}$ to $C_2F_4^{**}$ seems rather artificial, and it is not intended that the details of this mechanism be considered as absolutely correct. In all likelihood, the oxidation process is more complicated. However, an excited molecule is apparently needed to account for the oxidation. This excited state must be metastable (presumably a triplet) as even 0.3 mm of oxygen gives significant amounts of oxidation products. This scheme is reminiscent of that in the simple ketones.[10–15] Above a certain low oxygen pressure, $C_2F_4^{**}$ is quenched by oxygen and no further increase in oxidation occurs by Reactions (j) and (l) as the oxygen pressure is raised. The increase observed can be attributed to the excited oxygen mechanism. Recent experiments have been performed in our laboratory in which the Hg-photosensitized reaction of C_3F_6 has been studied. In the absence of oxygen, no products are formed. However, with oxygen present, CF_2O and CF_3CFO are produced in equal amounts, thus confirming the excited molecule mechanism. These experiments will be published in the near future.

At low oxygen pressures or high nitrogen or C_2F_4 pressures, the mechanism predicts that

$$R_0(CO_2)=(2kj/kc)(C_2F_4)I_a. \quad (3)$$

$R_0(CO_2)$ should be linear with I_a in conformance with our observations. Figure 5 is a log–log plot of $R_0(CO_2)$ versus the C_2F_4 pressure. The plot is linear and has a slope of 0.87 in reasonable agreement with expectation. That the slope is less than unity indicates that the mechanism is more complex than developed here. The mechanism fails to explain the detailed dependence of $R(CO_2)$ on oxygen pressure with 20 mm C_2F_4. Accounting for the minimum, if it is real, requires additional steps.

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