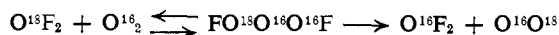


Because of the restricting nature of the matrix, this intermediate could rearrange in only two ways giving either O_2F_2 or $OF_2 + O$.

In the latter system the steady production of $O^{16}F_2$ during the photolysis of $O^{18}F_2$ in O^{16}_2 suggests an exchange mechanism involving O_3F_2 .



Although this may be an oversimplification of the actual mechanism, the end result would be the loss of O^{18} to molecular oxygen where its presence would go undetected.

Acknowledgments. The author wishes to thank Dr. Stanley A. Francis for many helpful discussions throughout the course of this work. The development of a computer program by Mrs. Barbara Victor and Mr. John Berry is also gratefully acknowledged.

The Reaction of Oxygen Atoms with Perfluoropropene

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Contribution from the Aerospace Corporation, El Segundo, California.
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Oxygen atoms, $O(^3P)$, were generated by the mercury-sensitized decomposition of N_2O at 24° . In the presence of C_3F_6 , the products are N_2 , CF_2O , CF_3CFO , and a C_3F_{10} compound. C_2F_4 also may be formed, but our analytical scheme was incapable of measuring its presence. The sum of CF_2O and CF_3CFO was approximately equal to the N_2 formed, but CF_2O accounts for about 85% of the sum. In the presence of molecular oxygen, $\Phi(CF_2O)$ is equal to $\Phi(CF_3CFO)$ and varies from 0 to 20 depending on the conditions. The mechanism of the oxidation is outlined in both the presence and the absence of molecular oxygen. Several rate constant ratios are established and tabulated. The C_3F_6 is 0.27 times as efficient as N_2O in quenching the excited mercury atoms. The absolute rate of the reaction of atomic oxygen with C_3F_6 was measured by competition with C_2H_4 . The rate constant for C_3F_6 is 2.1×10^7 l./mole sec.

I. Introduction

As a continuation of our studies on the vapor phase oxidation of perfluorocarbons, we have studied the reactions of oxygen atoms with perfluoropropene. The oxygen atoms were generated from the mercury-sensitized decomposition of nitrous oxide. This method of generating oxygen atoms has been studied extensively by Cvetanović¹⁻⁶ and recently applied by us to the study of oxygen atom reactions with C_2F_4 .⁷ The method was recently reviewed by Cvetanović.⁸ The advantages of the method are that the only oxygen species produced is $O(^3P)$ and that N_2O is nonreactive with this species and most radicals. In his initial work,² Cvetanović believed the quantum yield of oxygen atom production to be 0.78, but more recent studies have shown that the quantum yield is unity.^{9,10}

- (1) R. J. Cvetanović, *J. Chem. Phys.*, **23**, 1203 (1955).
- (2) R. J. Cvetanović, *ibid.*, **23**, 1208 (1955).
- (3) R. J. Cvetanović, *ibid.*, **23**, 1375 (1955).
- (4) R. J. Cvetanović, *ibid.*, **25**, 376 (1956).
- (5) R. J. Cvetanović, *Can. J. Chem.*, **36**, 623 (1958).
- (6) R. J. Cvetanović and L. C. Doyle, *ibid.*, **38**, 2187 (1960).
- (7) D. Saunders and J. Heicklen, Aerospace Corp. Report TDR-469 (5250-40)-2, Feb. 15, 1965; *J. Am. Chem. Soc.*, **87**, 2088 (1965).
- (8) R. J. Cvetanović, *Advan. Photochem.*, **1**, 115 (1963).
- (9) R. J. Cvetanović, W. E. Falconer, and K. R. Jennings, *J. Chem. Phys.*, **35**, 1225 (1961).
- (10) M. G. Bellas, Y. Rousseau, O. P. Strausz, and H. E. Gunning, *ibid.*, **41**, 768 (1964).

II. Experimental

Matheson Company research grade nitrous oxide and ethylene and Peninsular Chemical Research Company hexafluoropropene were used after degassing by pumping through a spiral trap at -196° . Gas chromatograms of these compounds showed no extraneous peaks. Matheson extra-dry grade oxygen (99.6%) was used without further purification.

The vacuum system, optical system, analytical system, and procedures have been described previously.⁷ During photolysis, infrared absorption peaks at 5.12 and 5.30 μ were monitored intermittently. The final full scan was made 3 to 5 min. after irradiation was discontinued.

Calibrations for cyclo- C_3F_6 and CF_2O have been described previously.⁷ CF_3CFO was calibrated from the mercury-sensitized photolysis of mixtures of C_3F_6 and O_2 . Because equal quantities of CF_2O and CF_3CFO should be produced by this method, the latter product was calibrated *via* the former by taking the ratio of absorbances. The absorption coefficient of CF_3CFO at 5.30 μ (to base 10) is 0.056 mm.⁻¹/cm. of path length. It must be cautioned that this value may be somewhat different in another instrument. As a check that indeed equal amounts of CF_2O and CF_3CFO were produced in the mercury-sensitized oxidation of C_3F_6 , the reacted mixture was fractionated at -160° and the two fractions were passed through a gas chromatograph. Approximately equal amounts of CO_2 were found in each fraction (the fluorocarbonyl compounds quantitatively convert to CO_2 in our system), and the total amount of CO_2 was twice that expected from the CF_2O alone.

Attempts to calibrate the cell pressure of the C_5F_{10} compound from its chromatographic peak area failed due to an apparent decomposition of the compound. The previously obtained calibration factor for cyclo- C_3F_6 in our system was 5 in.² of area per millimeter of pressure. Considering the trend of higher molecular weight compounds to have larger calibration factors, we assumed the reasonable value of 8 in.²/mm.

III. Results

Initially, a mixture of 5 mm. of C_3F_6 and 6 mm. of N_2O was photolyzed for 30 min. The final infrared

Table I. Mercury-Sensitized Photolysis of C₃F₆-N₂O Mixtures at 24°

C ₃ F ₆ , mm.	N ₂ O, mm.	Exposure time, min.	Φ(N ₂)	Φ(CF ₂ O)	Φ(CF ₃ CFO)	~Φ(C ₅ F ₁₀)	[Φ(CF ₂ O) + Φ(CF ₃ CFO)]/ Φ(N ₂)
$I_a = 5.8 \times 10^{18}$ quanta/cc. sec.							
4.90	4.6	4.50	0.67	0.53	0.078	0.127	0.91
5.28	17.0	4.00	0.85	0.63	0.105	0.142	0.86
5.03 ^a	51.0	2.50	0.98	0.74	0.117	0.193	0.87
5.48 ^a	148.5	3.50	0.97	0.63	0.093	0.160	0.73
5.65 ^a	507.8	4.08	1.02	0.72	0.126	0.161	0.83
16.0	5.60	3.00	0.53	~0.047	0.044	...	~0.17
14.0	5.12	6.00	0.53	0.39	0.070	...	0.86
15.5	16.5	6.00	0.74	0.63	0.093	...	0.98
15.5	52.0	9.00	0.92	0.68	0.113	...	0.85
16.0 ^a	149.0	8.00	1.02	0.83	0.083	...	0.90
15.5 ^a	499.0	10.00	0.98	0.72	0.128	0.28	0.86
49.0	5.03	12.00	0.26	0.22
49.8	16.0	16.00	0.49	0.41	0.060	...	0.96
51.0	57.5	27.00	0.76	0.64	0.096	...	0.96
50.2	147.0	24.00	0.96	0.79	0.108	...	0.94
49.5 ^a	505.5	26.00	1.02	0.78	0.128	0.41	0.89
146.7	5.27	20.08	0.099	0.117	~0.013	...	~1.36
153.0	15.0	34.00	0.22	0.20	0.027	...	1.04
151.5	50.5	35.00	0.53	0.45	0.096	...	1.03
149.0	148.0	25.08	0.82	0.74	0.129	...	1.06
151.5	503.5	35.00	0.94	0.70	0.112	0.45	0.86
516.3	5.20	31.00	0.036	0.019	~0.006	0.003	0.72
503.0	16.0	60.00	0.087	0.085	~0.028	0.053	1.29
506.5	51.5	60.00	0.24	0.119	~0.024	0.147	0.61
505.0	150.0	50.00	0.49	0.33	~0.056	0.30	0.80
$I_a = 1.02 \times 10^{18}$ quanta/cc. sec.							
4.90	7.1	14.00	0.97	0.72	0.13	...	0.87
4.70	15.8	14.00	1.01	0.84	0.14	...	0.97
4.48	50.5	10.00	1.24	0.98	0.15	...	0.91
4.50	153.5	12.00	1.38	1.01	0.20	...	0.88
4.98	501.0	14.00	1.26	1.06	0.14	...	0.96
15.5	502.0	30.00	1.37	1.08	0.19	...	0.93
49.3	505.7	70.00	1.27	1.02	0.13	...	0.91
151.5	506.0	30.00	1.11	0.96	0.13	...	0.98

^a Used in calculation of I_a .

spectrum revealed new peaks at 5.12, 5.20, 5.30, 6.88, and 8.00 μ and a broad peak at 9.05 to 9.20 μ . The bands at 5.12, 5.20, and 8.00 μ can be attributed to CF₂O; those at 5.30 and 9.05-9.20 μ , to CF₃CFO. The other bands of these products were obscured by those of the reactant or the sodium fluoride windows and consequently were not observed. The peak at 6.88 μ could not, to our knowledge, be associated with any known carbon-fluorine or carbon-fluorine-oxygen compound.

Subsequent runs were for short conversions (usually less than 10%). Plots of the absorbed intensity at 5.12 and 5.30 μ vs. time showed that the products were not being consumed during exposure. All mixtures containing 5 mm. or 500 mm. of C₃F₆ or 500 mm. of N₂O were chromatographed. Other than excess reactants and CO₂ (formed from the CF₂O and CF₃CFO), the only products were very small amounts of C₄F₈ compounds and larger amounts of a compound having a retention time in the C₄-C₅ region. C₂F₄ might also have been formed in small amounts, but its presence would have been obscured by the large amounts of N₂O, which has a similar retention time on our chromatograph column.

Two runs containing mixtures of 130 mm. of C₃F₆ and 475 mm. of N₂O were photolyzed for 2 hr. each. The mixtures were chromatographed and the C₅F₁₀ was collected from the effluent gas. The combined product was purified by alternately freezing the gas into one of two traps located on either side of a third trap

containing dry KOH. The infrared spectrum of about 13 mm. of the purified gas is shown in Figure 1. Major peaks are at 7.57, 7.87, and 8.19 μ , and smaller peaks at 6.84, 9.23, and 9.53 μ were observed. To our knowl-

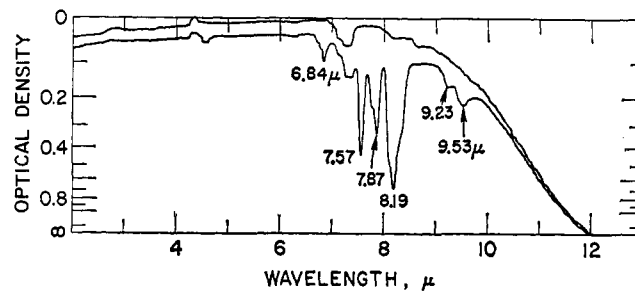


Figure 1. Infrared spectrum of C₅F₁₀ compound.

edge, the spectra correspond to no known carbon-fluorine or carbon-fluorine-oxygen compound. The identification of the compound can be considerably narrowed from the following considerations: (1) chromatographic retention times show that the compound is most likely a C₅ fluorocarbon; (2) to within experimental error, all of the oxygen can be accounted for in the CF₂O and CF₃CFO; (3) carbon-fluorine mass balance considerations require that the C-to-F ratio be 0.50; (4) any C₅ monoolefin cannot have a center of symmetry; thus, a double bond stretch should appear in the infrared spectrum. The absence of such a band eliminates the possibility that the molecule is an olefin. The remaining possibilities are

Table II. Mercury-Sensitized Photolysis of $C_3F_6-N_2O$ Mixtures in the Presence of Oxygen^a

O ₂ , mm.	C ₃ F ₆ , mm.	N ₂ O, mm.	Exposure time, min.	Φ(CF ₂ O)	Φ(CF ₃ CFO)	Φ(c-C ₃ F ₆)	~Φ(C ₅ F ₁₀)
4.8	5.13	499.2	3.50	0.41	0.38	0.000	0.000
5.00	18.0	498.5	4.00	0.94	0.92	0.000	Trace
4.74	50.3	492.0	7.00	1.74	1.64	0.023	0.005
5.47	154.0	485.5	6.00	4.18	4.43	0.100	0.013
12.7	5.23	498.5	4.00	0.21	0.21
13.5	16.5	495.0	4.00	0.81	0.78
14.8	51.2	491.0	8.00	1.49	1.39	0.059	Trace
17.0	154.0	505.0	4.00	4.03	3.44	0.190	0.014
52.1	4.40	501.0	47.00	0.029	0.011
48.0	16.0	512.5	35.00	0.079	0.036
52.0	52.0	557.0	7.00	1.35	0.68
50.0	177.5	505.0	5.00	2.92	2.48	0.086	Trace
150.0	4.92	500.5	20.00	0.000	0.0000
154.5	15.5	491.0	35.00	0.017	0.0095
158.0	50.0	521.0	35.00	0.047	0.0200

^a At 24°; $I_a = 5.8 \times 10^{13}$ quanta/cc. sec.

Table III. Mercury-Sensitized Photolysis of $C_3F_6-N_2O$ Mixtures in the Presence of Oxygen for Various Intensities at 24°

C ₃ F ₆ , mm.	O ₂ , mm.	N ₂ O, mm.	$I_a \times 10^{-13}$, quanta/cc. sec.	Exposure time, min.	Φ(CF ₂ O)	Φ(CF ₃ CFO)
18.0	5.00	498.5	5.8	4.00	0.94	0.92
13.8	5.70	499.0	1.02	10.00	1.69	1.46
14.7	5.31	498.2	0.179	30.00	3.60	2.73
15.8	4.21	494.0	0.031	30.00	9.10	7.73
50.3	4.74	492.0	5.8	7.00	1.74	1.64
49.0	5.56	508.0	1.02	10.00	2.50	2.17
50.2	4.83	498.0	0.179	20.00	6.52	6.44
48.0	5.08	507.0	0.031	25.00	13.12	13.90
154.0	5.47	485.5	5.8	6.00	4.18	4.43
154.2	5.32	500.5	1.02	10.00	3.88	3.28
155.0	4.93	490.0	1.02	4.00	5.92	5.01
154.9	5.62	496.1	0.179	40.00	8.16	6.56
155.0	5.00	521.0	0.179	12.00	8.34	7.69
150.1	5.38	510.0	0.031	40.00	21.8	18.3

that the product is perfluorocyclopentane, perfluoromethylcyclobutane, perfluoro-1,1-dimethylcyclopropane, or perfluoro-1,2-dimethylcyclopropane. From the mechanistic considerations, the last-named compound would be expected as a product; furthermore, it is difficult to see how any of the other products could be formed. Thus, our tentative conclusion is that the C₅ product is perfluoro-1,2-dimethylcyclopropane.

The results of the low-conversion runs are listed in Table I. Runs were performed at two intensities. For the high intensity runs, I_a was computed by setting the average value of $\Phi(N_2) = 1.00$ for the runs with $(C_3F_6)/(N_2O) \leq 0.1$. The lower intensities were taken as 0.176 of the higher intensity in conformance with the absorption coefficient for two Corning 9-30 filters at 2537 Å. as determined by measurement in our laboratory. The results of Table I are essentially independent of intensity and show that $\Phi(N_2) = \Phi(CF_2O) + \Phi(CF_3CFO)$, in conformance with mass-balance requirements. Furthermore, $\Phi(N_2)$ increases as $(C_3F_6)/(N_2O)$ diminishes and $\Phi(CF_2O)$ is about 6.5 times greater than $\Phi(CF_3CFO)$ under all conditions. At total pressures greater than 250 mm., the previously described⁷ diffusion effect was observed. After photolysis, sufficient time was allowed for homogeneity to be reached before the final infrared analysis was made.

A series of experiments was run with 500 mm. of

Table IV. Mercury-Sensitized Photolysis of $C_3F_6-N_2O$ Mixtures in the Presence of C₂H₄^a

C ₂ H ₄ , mm.	C ₃ F ₆ , mm.	N ₂ O, mm.	Exposure time, min.	Φ(N ₂)	Φ(CF ₂ O)	Φ(CF ₃ CFO)
5.48	20.0	531.5	5.00	1.04	0.100	0.012
5.41 ^b	56.6	509.0	6.00	1.00	0.23	0.052
5.60	157.9	474.5	6.00	0.84	0.40	0.061
17.0	47.0	490.0	15.00	1.12	0.071	0.014
16.0	150.0	497.5	20.00	0.90	0.184	0.033
50.0	152.0	488.0	60.00	0.94	0.065	0.010

^a At 24°; $I_a = 7.4 \times 10^{13}$ quanta/cc. sec. ^b Used for calculation of I_a .

N₂O and various mixtures of O₂ and C₃F₆ at full intensity. The intensity was assumed to be the same as for runs in the absence of O₂. The results are listed in Table II. Subsequently, a second series was run with 500 mm. of N₂O, 5 mm. of O₂, and 15, 50, and 500 mm. of C₃F₆ for various reduced intensities. The results of these experiments are listed in Table III. The results of Tables II and III can be summarized as follows. (1) The C₅F₁₀ compound was not found except in very reduced amounts at the highest C₃F₆ pressures. (2) An additional product with a retention time equivalent to cyclo-C₃F₆ was found in small amounts and increased with the C₃F₆ pressure. This compound was never positively identified, and, rather than cyclo-C₃F₆, it might be the product of the mercury-sensitized oxidation of C₃F₆.¹¹ In any event, it is not an important product and need not be considered further. (3) The $\Phi(CF_2O)$ and $\Phi(CF_3CFO)$ are approximately equal. (4) The quantum yields of the carbonyl products range from 0 to 20; they increase with the C₃F₆ pressure, but fall with enhancement of both the O₂ pressure and the absorbed intensity.

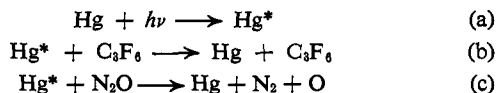
Finally, a series of 500 mm. of N₂O and various mixtures of C₃F₆ and C₂H₄ was run so that their competition for the oxygen atoms could be measured. Table IV lists the results, which show that $\Phi(CF_2O)$ and $\Phi(CF_3CFO)$ diminish as $(C_2H_4)/(C_3F_6)$ is enlarged.

IV. Discussion

No products are formed from the mercury-sensitized photolysis of C₃F₆ at room temperature.¹¹ Thus, the

(11) J. Hecklen and V. Knight, Aerospace Corp. Report TDR-469(5250-40)-5, Feb. 15, 1965; *J. Phys. Chem.*, in press.

mechanism for $C_3F_6-N_2O$ mixtures can be written as

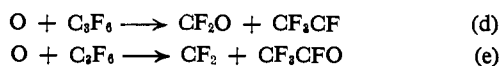


where Hg^* refers to an excited mercury atom. Actually, reaction b goes *via* an excited C_3F_6 molecule,¹¹ but since this molecule only deactivates, there is no need to consider it. The simple three-step mechanism predicts that

$$\frac{1}{\Phi(N_2)} = 1 + \frac{k_b(C_3F_6)}{k_c(N_2O)} \quad (1)$$

Figures 2 and 3 are plots of $1/\Phi(N_2)$ vs. $(C_3F_6)/(N_2O)$. Although there is some scatter at ratios less than unity, a well-defined slope of 0.27 corresponding to k_b/k_c is found for $(C_3F_6)/(N_2O)$ ratios up to 100. The reciprocals of the sum of the quantum yields of the oxygenated products were not plotted in Figures 2 and 3 because the nature of their analysis is less reliable.

C_3F_6 quantitatively scavenges the oxygen atoms to form products

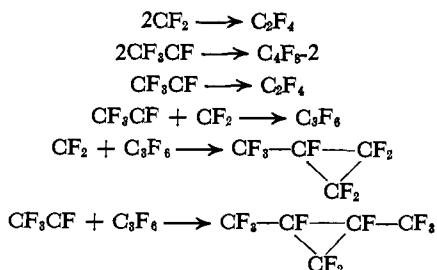


where reactions d and e might proceed *via* an unstable C_3F_6O intermediate molecule. However, no such intermediate was observed; if it exists it must be short-lived. If the spin conservation rules are obeyed, then the radical products of (d) and (e) should be triplets, which we believe to be the case.¹² The ratio of rate constants k_d/k_e can be obtained from the expression

$$\frac{k_d}{k_e} = \frac{\Phi(CF_2O)}{\Phi(CF_3CFO)} \quad (2)$$

The ratio is found to be 6.5.

The radical fragments can disappear by any of the following processes.



The more important radical is CF_2CF and apparently it adds to C_3F_6 much more readily than it recombines as $\Phi(C_5F_{10}) > \Phi(C_4F_8)$. In all likelihood, all the radical-radical reactions are small and the C_4F_8 compound we observed is the perfluorinated methylcyclopropane. An alternative explanation is that radicals are never formed and that the C_3F_6O intermediate reacts directly with C_3F_6 to give the oxygenated products and the cyclopropanes. A powerful argument in favor of this alternative is the very low quantum yield of C_4F_8 compounds. On the other hand, this alternative mechanism requires that $\Phi(CF_2O) = \Phi(C_5F_{10})$ and $\Phi(CF_3CFO) = \Phi(C_4F_8)$. The data in Table I clearly indicate that this is not the case. Thus, this alternative mechanism, although it cannot be ruled out entirely, cannot be the exclusive mechanism.

(12) J. Heicklen, N. Cohen, and D. Saunders, Aerospace Corp. Report TDR-469(5250-40)-4, Dec. 30 1964; *J. Phys. Chem.*, **69**, 1774 1965.

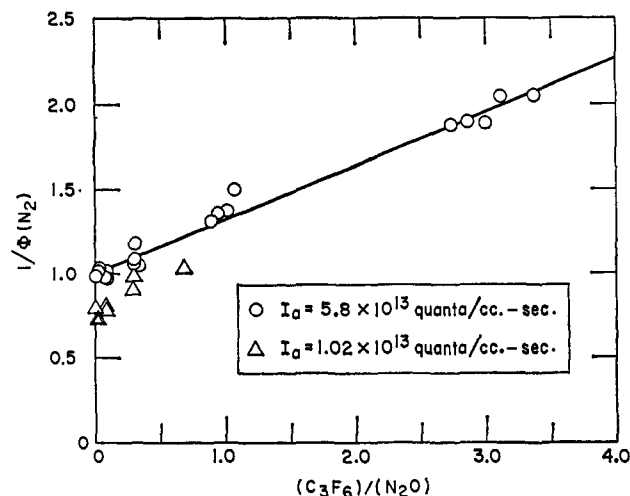


Figure 2. Plot of $1/\Phi(N_2)$ vs. $(C_3F_6)/(N_2O)$ for small ratios.

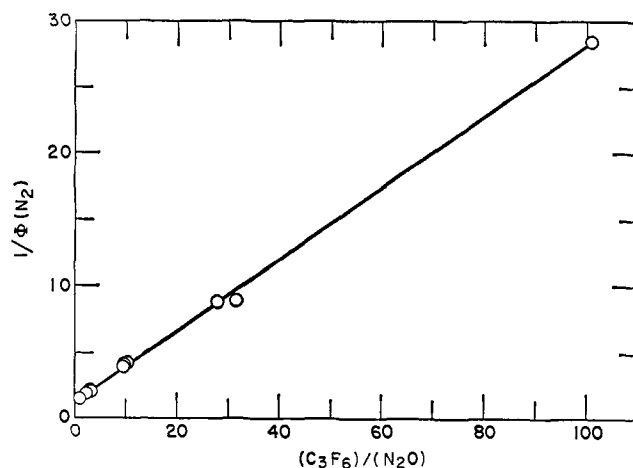
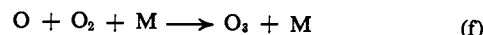


Figure 3. Plot of $1/\Phi(N_2)$ vs. $(C_3F_6)/(N_2O)$ for large ratios.

For simplicity, we will ignore it in the ensuing discussion.

Figure 4 is a plot of $\Phi(C_5F_{10})$ vs. N_2O for C_3F_6 pressures of 5 and 500 mm. At the lower C_3F_6 pressure, $\Phi(C_5F_{10})$ quickly rises with N_2O to an upper limit of about 0.16. For the larger C_3F_6 pressure, it requires more N_2O to initiate C_5F_{10} formation because of the competition of N_2O and C_3F_6 for the Hg^* atom. Ultimately, however, $\Phi(C_5F_{10})$ reaches a larger value with 500 mm. than with 5 mm. of C_3F_6 . These results clearly show that the C_5F_{10} production is associated with oxygen atom formation. Furthermore, $\Phi(C_5F_{10})$ rises with C_3F_6 , as would be expected if the CF_2CF radical were also being removed by rearrangement to C_2F_4 as well as by addition to C_3F_6 .

In the presence of molecular oxygen, $\Phi(CF_2O)$ is equal to $\Phi(CF_3CFO)$ within experimental error. At the highest intensities, $\Phi(CF_2O)$ and $\Phi(CF_3CFO)$ first remain constant and then fall as the oxygen pressure is raised, as shown in Figure 5. The fall-off starts sooner, the lower the C_3F_6 pressure. For sufficiently high $(O_2)/(C_3F_6)$, the oxidation products can be completely suppressed. Clearly, the molecular oxygen must be competing with the C_3F_6 for the oxygen atom. The indicated reaction is



Under some conditions (high C_3F_6 , low I_a), $\Phi(CF_2O)$ and $\Phi(CF_3CFO)$ rise way beyond unity. (Under our

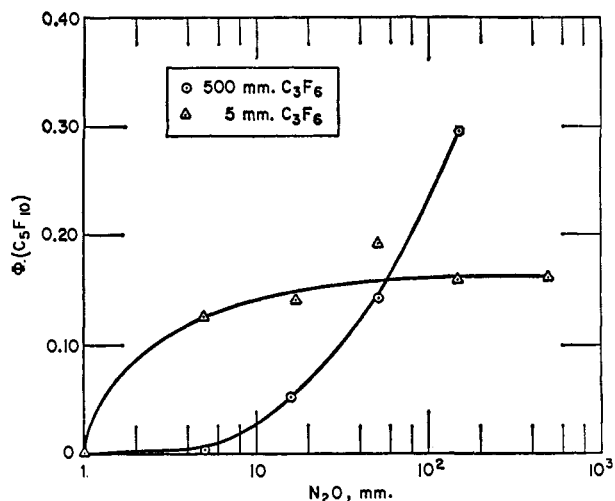


Figure 4. Plot of $\Phi(C_3F_{10})$ vs. N_2O pressure.

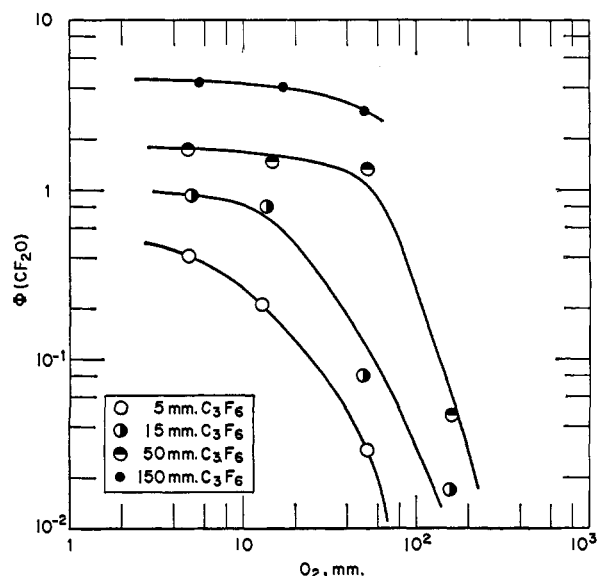
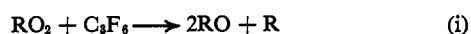
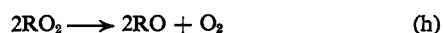


Figure 5. Plot of $\Phi(CF_2O)$ vs. (O_2) for $I_a = 5.8 \times 10^{13}$ quanta/cc. sec. with 500 mm. of N_2O present.

experimental conditions they have reached 20.) Thus a chain mechanism must be introduced. The chain-terminating step cannot involve reactions of R radicals with themselves or C_3F_6 for the data in Table II clearly indicate that oxygen suppresses the products of those reactions. Reaction f cannot be a terminating step for then $\Phi(CF_2O)$ and $\Phi(CF_3CFO)$ would be independent of intensity and dependent on oxygen pressure over the whole range of variables contrary to our findings. Thus we introduce the radicals RO_2 , and the simplest scheme is



where R is either CF_2 or CF_3CF . Steps g and h are analogous to those involved in the oxidation of alkyl radicals.¹³ (If the intermediate C_3F_6O is formed, then perhaps it too could be scavenged by oxygen and produced by RO_2 attack on C_3F_6 .)

(13) For example, see P. A. Leighton, "Photochemistry of Air Pollution," Academic Press Inc., New York, N. Y., 1961.

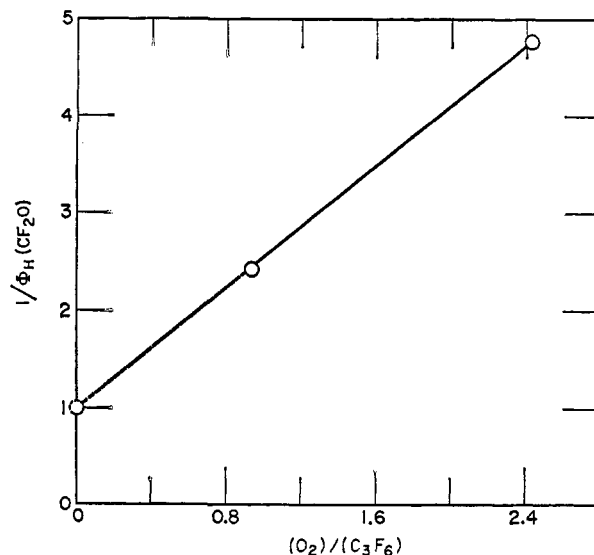


Figure 6. Plot of $1/\Phi_H(CF_2O)$ vs. $(O_2)/(C_3F_6)$ for $I_a = 5.8 \times 10^{13}$ quanta/cc. sec. and $C_3F_6 = 5$ mm. with 500 mm. of N_2O present.

This oxidation mechanism predicts that

$$\Phi(CF_2O) =$$

$$\Phi(CF_3CFO) = \frac{(k_d + k_e)(C_3F_6)}{(k_d + k_e)(C_3F_6) + k_f(M)(O_2)} + \frac{k_f(C_3F_6)}{(2k_h I_a)^{1/2}} \left[\frac{(k_d + k_e)(C_3F_6)}{(k_d + k_e)(C_3F_6) + k_f(M)(O_2)} \right]^{1/2} \quad (3)$$

For small values of C_3F_6 and large values of I_a , the second term on the right-hand side of eq. 3 becomes negligible, and the reduced expression can be rearranged to

$$\frac{1}{\Phi_H(CF_2O)} = 1 + \frac{k_f(M)(O_2)}{(k_d + k_e)(C_3F_6)} \quad (4)$$

where $\Phi_H(CF_2O)$ is $\Phi(CF_2O)$ for high I_a (5.8×10^{13} quanta/cc. sec.) and 5 mm. of C_3F_6 . Figure 6 is a plot of $1/\Phi_H(CF_2O)$ vs. $(O_2)/(C_3F_6)$ for 500 mm. of N_2O and 5 mm. of C_3F_6 . The plot is linear and the slope yields a value of about 54 l./mole for $k_f/(k_d + k_e)$. The dashed portion shows that the intercept is unity as would be expected from eq. 4.

Since $\Phi_H(CF_2O)$ can be estimated from Figure 6, eq. 3 can be rewritten

$$\frac{\Phi(CF_2O) - \Phi_H(CF_2O)}{\Phi_H(CF_2O)^{1/2}} = \frac{k_f(C_3F_6)}{(2k_h I_a)^{1/2}} \quad (5)$$

Figure 7 is a log-log plot of the left-hand side of (5) vs. I_a . The data points are fitted with the best straight line of slope -0.5 for each pressure. While there is some deviation at the highest intensities [the plots are the least reliable here because $\Phi(CF_2O)$ and $\Phi_H(CF_2O)$ are becoming more similar], the data points confirm the prediction. We had thought that at sufficiently low I_a , the termination step might become



However, were this so, then at low I_a the plots would level off. There is no indication that this occurs.

Further rearrangement of eq. 3 leads to

$$\frac{[\Phi(CF_2O) - \Phi_H(CF_2O)]I_a^{1/2}}{[\Phi_H(CF_2O)]^{1/2}} = \frac{k_f(C_3F_6)}{(2k_h)^{1/2}} \quad (6)$$

The values for the left-hand side of eq. 6 were obtained, for each of the three C_3F_6 pressures, from the plots in

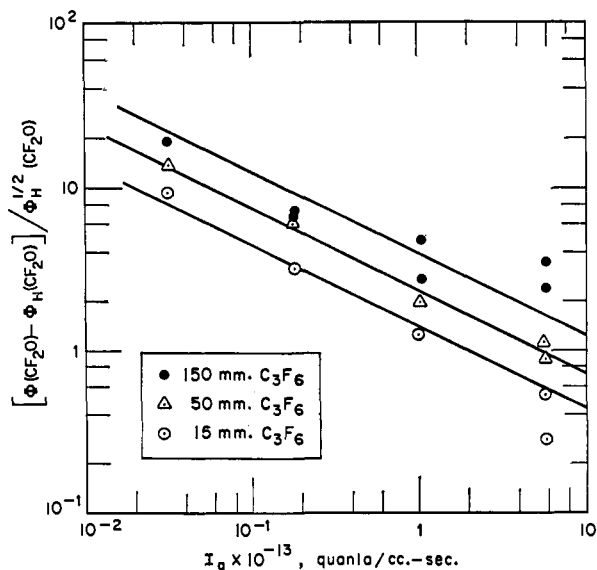


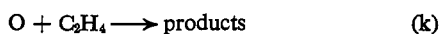
Figure 7. Plot of $[\Phi(\text{CF}_2\text{O}) - \Phi_{\text{H}}(\text{CF}_2\text{O})]/[\Phi_{\text{H}}(\text{CF}_2\text{O})]^{1/2}$ vs. I_a with 500 mm. of N_2O present.

Figure 7. These values are plotted vs. the C_3F_6 pressure in Figure 8. Although the plot is linear, it does not pass through the origin as predicted by eq. 6. If indeed the intercept is truly nonzero, then an additional chain-propagating step is required that does not depend on the C_3F_6 pressure. Such a step is



However, if reaction j does occur, it must be less important than reaction h to conform with our analysis of the data. From the slope of Figure 8, k_1^2/k_h is estimated to be about 0.0044 l./mole sec. This rate constant ratio is a lower limit, for it assumes that a uniform distribution of radicals exists throughout the cell. In mercury-sensitized reactions, this is often not the case, and thus k_1^2/k_h may be larger than calculated.

The absolute rate of reactions d + e was measured from the competition of oxygen atoms with C_3F_6 and C_2H_4 . In the presence of C_2H_4 , the additional reaction



must be considered. Introducing this reaction leads to the expression

$$\frac{\Phi(\text{N}_2) - \Phi(\text{RO})}{\Phi(\text{RO})} = \frac{k_k}{(k_d + k_e)} \frac{(\text{C}_2\text{H}_4)}{(\text{C}_3\text{F}_6)} \quad (7)$$

where $\Phi(\text{RO}) = \Phi(\text{CF}_2\text{O}) + \Phi(\text{CF}_3\text{CFO})$. The log of the left-hand side of eq. 7 is plotted vs. the log of $(\text{C}_2\text{H}_4)/(\text{C}_3\text{F}_6)$ in Figure 9. The graph is fitted with the best straight line of slope unity. The intercept yields a value of 29 for $k_k/(k_d + k_e)$. The absolute value for k_k is about 0.60×10^9 l./mole sec.^{8,14} This gives a value for $k_d + k_e$ of 2.1×10^7 l./mole sec. From this latter value and the value of $k_f/(k_d + k_e)$ of 54 l./mole, k_f is estimated to be 1.1×10^9 l.²/mole² sec. The constant k_f has been investigated by many workers¹⁵⁻²⁰

(14) L. Elias and H. I. Schiff, *Can. J. Chem.*, **38**, 1657 (1960).

(15) S. W. Benson and A. E. Axworthy, Jr., *J. Chem. Phys.*, **26**, 1718 (1957).

(16) F. Kaufman, *Proc. Roy. Soc. (London)*, **A247**, 123 (1958).

(17) F. Kaufman, *J. Chem. Phys.*, **28**, 352 (1958).

(18) L. Elias, E. A. Ogryzlo, and H. I. Schiff, *Can. J. Chem.*, **37**, 1680 (1959).

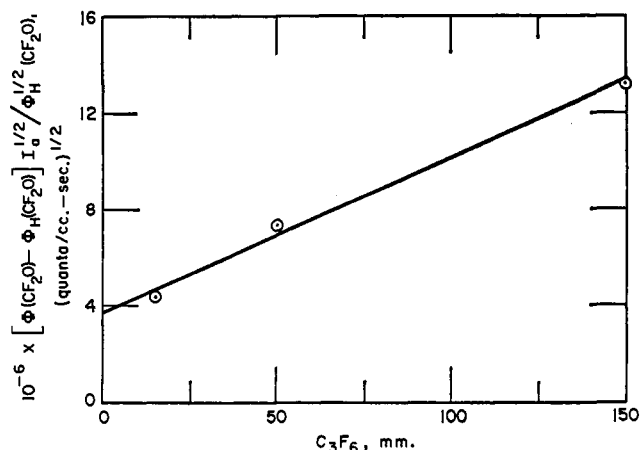


Figure 8. Plot of $[\Phi(\text{CF}_2\text{O}) - \Phi_{\text{H}}(\text{CF}_2\text{O})]I_a^{1/2}/[\Phi_{\text{H}}(\text{CF}_2\text{O})]^{1/2}$ vs. C_3F_6 pressure.

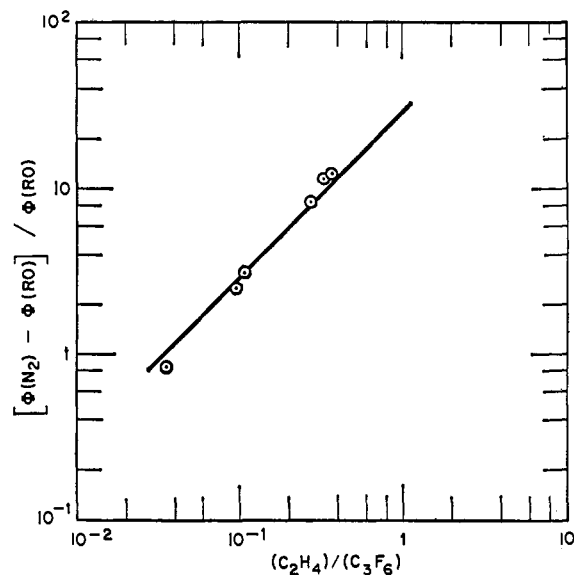


Figure 9. Plot of $[\Phi(\text{N}_2) - \Phi(\text{RO})]/\Phi(\text{RO})$ vs. $(\text{C}_2\text{H}_4)/(\text{C}_3\text{F}_6)$ with 500 mm. of N_2O present.

and the results were critically analyzed by Leighton¹⁸ and by Kaufman.²¹ The generally accepted rate constant is about 1×10^8 l.²/mole² sec. to within a factor of two with O_2 as the third body. Kaufman and Kelso²² have recently found k_f to be 5.5×10^8 l./mole sec. with N_2O as a third body, which is a factor of two lower than our value.

The discrepancy may be due to an inaccuracy in the reported rate constant for reaction k, or more likely to inaccuracies in our data and the resulting analysis.

One puzzling feature is our finding that O_3 production diminishes RO formation. Recent work in our laboratory has shown that O_3 reacts rapidly with perfluoroolefins to produce RO. There seem to be two possible explanations. One is that the mercury catalytically converts O_3 to O_2 , so that O_3 never becomes important. A second possibility is that the O_3 absorbs the radiation to yield O_2 plus $\text{O}(^1\text{D})$ atoms which are then preferentially removed by the N_2O to yield

(19) J. A. Zaslowsky, H. B. Urback, F. Leighton, R. J. Wnuk, and J. A. Wojtowicz, *J. Am. Chem. Soc.*, **82**, 2682 (1960).

(20) P. G. Dickens, R. D. Gould, J. W. Linnett, and A. Richmond, *Nature*, **187**, 686 (1960).

(21) F. Kaufman, *Progr. Reaction Kinetics*, **1**, 115 (1961).

(22) F. Kaufman, private communication, 1965.

products which we would not detect (*i.e.*, N₂, O₂, or NO). The absorption of O₃ of 2537-Å. radiation is intense; the absorption coefficient (to base 10) is 0.176 mm.⁻¹ cm.⁻¹. Thus only microns of O₃ could remove significant portions of the radiation, and the O₃ pressure would be kept small. An attractive feature of this possibility is that for every O(³P) atom removed by reaction f, another is prevented from forming because of the O₃ absorption at 2537 Å. Thus our reported rate constant for reaction f would be reduced by a factor of two to give excellent agreement with that of Kaufman and Kelso.

Table V is a compilation of the rate constant ratios determined in this study.

Table V. Rate Constant Ratios

Ratio	Value	Source
k_b/k_c	0.27	Eq. 1, Figure 3
k_d/k_e	6.5	Eq. 2
$k_f/(k_d + k_e)$	54 l./mole	Eq. 4, Figure 6
k_i^2/k_h	≥ 0.0044 l./mole sec.	Eq. 6, Figure 8
$k_k/(k_d + k_e)$	29	Eq. 7, Figure 9

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Oxygen Exchange between Periodate and Water Studied by ¹⁷O Nuclear Magnetic Resonance

I. Pecht and Z. Luz

Contribution from the Isotope Department, Weizmann Institute of Science, Rehovoth, Israel. Received April 17, 1965

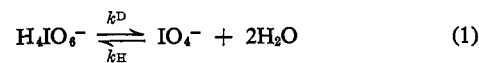
Oxygen exchange between periodate and water was studied by ¹⁷O nuclear magnetic resonance (n.m.r.). In aqueous solutions of periodate, the water ¹⁷O n.m.r. line is broadened and no signal due to the ¹⁷O of periodate is observed. This is due to fast oxygen exchange between water and periodate. From the concentration and temperature dependence of the water ¹⁷O line width, the kinetic parameters for the exchange reactions were determined. The pseudo-first-order rate constant of the exchange reaction, H₅IO₆ + H₂O* ⇌ H₅IO₆O* + H₂O, is 4.5 × 10³ sec.⁻¹ at 25° and its activation energy is 13.5 kcal. mole⁻¹. The reaction is not catalyzed by hydrogen or chloride ions. For the oxygen-exchange rate of water with IO₄⁻, an upper limit of 1.2 × 10³ sec.⁻¹ at 25° is found. The exchange with I₂O₈⁴⁻ ions is faster than 2.8 × 10⁴ sec.⁻¹ at the same temperature. The results are discussed in terms of hydration-hydrolysis equilibria and are compared with previous investigations of similar systems.

Introduction

The study of the oxygen exchange between solvent water and oxy compounds is important for the understanding of their structure and kinetic behavior.¹ The rates of these reactions span a wide range; some are immeasurably slow, and others are too fast to be measured by conventional tracer techniques. Oxygen exchange of telluric, periodic, and xenic acids is extremely fast in comparison with other oxy compounds. Reuben, Samuel, Selig, and Shamir² showed that oxygen exchange between water and xenic acid [Xe(OH)₆] is complete within 3 min.; when a concentrated aqueous solution of Xe(OH)₆ was mixed with water highly enriched with ¹⁷O, the n.m.r. signal of ¹⁷O

due to xenic acid was completely developed within the time necessary to make the first observation. By a similar procedure we were able to follow the increase in the intensity of the ¹⁷O signal of telluric acid [Te(OH)₆] dissolved in ¹⁷O-enriched water. From this experiment, the half-life of the oxygen-exchange reaction was found to be ~10 min. at 25°.³

Anbar and Guttmann⁴ have shown that the half-life of the oxygen exchange between periodate and water at pH 4 and 7 is less than 5 sec. and hence cannot be followed by the conventional tracer technique. More recently Kustin and Lieberman⁵ using the temperature jump method studied the dehydration-hydration reactions



a process through which oxygen exchange between periodate and water takes place. The rate constants determined, $k_D = 5.6 \times 10^3$ and $k_H = 1.9 \times 10^2$ sec.⁻¹ in the pH range 3.4 to 5.0 at 20°, are consistent with the lower limit for the exchange rate given by Anbar and Guttmann.⁴ Using the nuclear magnetic resonance (n.m.r.) line-broadening technique we have extended the study of oxygen exchange between periodate species and water.

It is well known that the n.m.r. line shape is sensitive to chemical exchange processes in which the resonating nuclei exchange their magnetic environment.⁶ If the exchange rate is slow, the n.m.r. spectrum will appear as a superposition of the spectra due to the various species. At fast rates of exchange the spectrum will exhibit the time average of the discrete spectra. If the exchange rate is of the order of the width of the spectrum, measured in cycles per second, the n.m.r. line

(3) I. Pecht and Z. Luz, unpublished.

(4) M. Anbar and S. Guttmann, *J. Am. Chem. Soc.*, **83**, 781 (1961).

(5) K. Kustin and E. C. Lieberman, *J. Phys. Chem.*, **68**, 3869 (1964).

(6) For a recent review, see A. Loewenstein and T. M. Connor, *Ber. Bunsenges. Physik. Chem.*, **67**, 280 (1963).

(1) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, Chapter 8.

(2) J. Reuben, D. Samuel, H. Selig, and J. Shamir, *Proc. Chem. Soc.*, 270 (1963).