In Table IIIb some relevant geometric parameters of the molecule are given with the corresponding standard deviations. In the carbamoyl chloride, the amide bond does not seem to be lengthened (1.325 Å). The nonplanar distortion of the amide group is slightly, but significantly, higher in this molecule than in the cases reported for acetanilide[3] and found for the urethane. This can be explained by the stronger steric interactions between the two substituents of the nitrogen atom on one side and the oxygen and chlorine atoms on the other side. In addition, we must consider the inductive effect of the chlorine atom which we expected to affect the electron density in the amide bond. The fact that the C–N bond length is normal leads us to believe that the withdrawal of electrons by the chlorine is compensated by the donation of electrons to the C–N bond by the nitrogen.

$$CH_3-CH_2$$
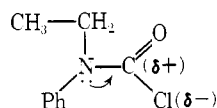
In order to understand this effect it would be useful to compare it with the structure of a molecule, such as N-phenylcarbamoyl chloride.

In the carbamoyl chloride, the benzene ring forms an angle of 70° with the plane C7–N1–C. The nitro group is also out of the benzene plane (11°), as found in other nitrophenyl derivatives.[13] The conformation of the ethyl group is very similar to that found in N,N'-diethyl-N,N'-diphenylurea[2b] and in 4-diethylcarbamoyl-1-cyclohexene-5-carboxylic acid.[2a] All the other conformational parameters are quite normal.

In Figure 2a a projection of the structure on 010 is reported. Inspection of the intermolecular distances below 3.6 Å shows that there are no significant contacts between molecules.

Figure 2b shows the projection of the structure for the urethane on the 100 plane. The molecules form rows through hydrogen bonds between N—H and O=C groups (2.90 Å). The angle N—H···O is about 161°. All the intermolecular contact distances are longer than the sum of the van der Waals radii. Thus, hydrogen-bonding forces are not involved in the distortion from planarity of this amide-like grouping.

Levitt and Lifson[14] have proposed that deviations for peptide bonds in proteins of up to 10° is reasonable. Our results support this view and may indicate that deviations from planarity of peptide bonds in proteins is more general than heretofore recognized.

(13) S. C. Abrahams, *Acta Crystallogr.*, 3, 194 (1950).
(14) M. Levitt and S. Lifson, *J. Mol. Biol.*, 46, 269 (1969).

Reaction of Oxygen Atoms with 1,3-Perfluorobutadiene

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Contribution from the Department of Chemistry and Center for Air Environment Studies, The Pennsylvania State University, University Park, Pennsylvania 16802. Received August 26, 1970

Abstract: The reaction of O(^{3}P), produced from the mercury-photosensitized decomposition of N_2O, with 1,3-C_4F_6 was studied at 32 ± 6° in the absence and presence of O_2. The gaseous products of the reaction are CF_2O, c-C_3F_4, CF_2CFCFO (C_3F_4O), $OCF_2CFCFCF_2$ (C_4F_6O), OCF_2CFCFO ($C_3F_4O_2$), two C_7F_{10} isomers, and C_2F_4. The quantum yields of the first five products are invariant to changes in reactant pressures or absorbed intensities. In the absence of O_2 they are 0.90, 0.68, 0.103, 0.025, and 0.022, respectively. They become 0.96, 0.64, 0.103, 0.20, and 0.21 in the presence of O_2. The quantum yields of the two C_7F_{10} isomers are independent of the absorbed intensity and unaffected by the presence of O_2 but rise slightly with increases in the 1,3-C_4F_6 pressure. A mechanism is presented which explains all but the formation of $C_3F_4O_2$ in the absence of O_2. The initial steps are O(^{3}P) + 1,3-$C_4F_6 \rightarrow CF_2O$ + c-C_3F_4; O(^{3}P) + 1,3-$C_4F_6 \rightarrow C_3F_4O$ + CF_2; O(^{3}P) + 1,3-$C_4F_6 \rightarrow C_4F_6O^*$, where the relative rates of the processes are 0.66, 0.10, and 0.24, respectively. By competitive studies with hydrocarbons, the overall rate constant for the O(^{3}P) + 1,3-C_4F_6 reaction was found to be 2.9 × 10^8 M^{-1} sec^{-1}.

The reaction of ground-state oxygen atoms, O(^{3}P), with C_2F_4 and C_3F_6 has been extensively studied and the mechanism is similar for both molecules.[1] Because of the asymmetry, the mechanism is slightly more complex with C_3F_6, and the first steps are

$$O(^3P) + C_3F_6 \longrightarrow CF_2O + CF_3CF \quad (1)$$

$$\longrightarrow CF_3CFO + CF_2 \quad (2)$$
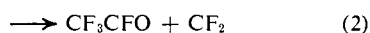
$$\longrightarrow C_3F_6O^* \quad (3)$$

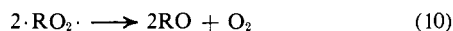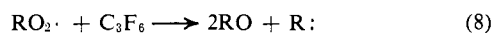Presumably both CF_2 and CF_3CF as well as the excited

molecule $C_3F_6O^*$ are triplets. In the absence of molecular oxygen, C_2F_4 is probably produced (though not detected because of experimental difficulties) from the rearrangement of CF_3CF and dimerization of CF_2. The $C_3F_6O^*$ molecule does not produce propylene oxide but undergoes the reactions

$$C_3F_6O^* + C_3F_6 \longrightarrow C_3F_{10} + CF_2O \quad (4)$$

$$C_3F_6O^* \longrightarrow CF_2O + CF_3CF \quad (5)$$
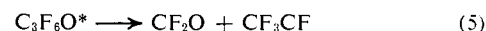
In the presence of molecular oxygen the quantum yields of CF_2O and CF_3CFO are markedly enhanced

(1) J. Heicklen, *Advan. Photochem.*, 7, 57 (1969).

and propylene oxide is produced. The additional reactions that have been shown to occur are

$$C_3F_6O^* + O_2 \longrightarrow RO + \cdot RO_2 \cdot \quad (6)$$

$$R: + O_2 \longrightarrow \cdot RO_2 \cdot \quad (7)$$

$$RO_2 \cdot + C_3F_6 \longrightarrow 2RO + R: \quad (8)$$

$$\longrightarrow RO + C_3F_6O \quad (9)$$

$$2 \cdot RO_2 \cdot \longrightarrow 2RO + O_2 \quad (10)$$
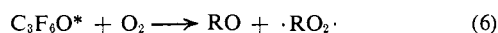
where R: is either CF_2 or CF_3CF.

In this paper we extend the scheme to $1,3\text{-}C_4F_6$, which has two double bonds. A previous study[2] has shown that the major products of the $O(^3P) + 1,3\text{-}C_4F_6$ reaction are CF_2O and $c\text{-}C_3F_4$, both formed with quantum yields of the order of unity. However, no search was made for other products, studies were not done in the presence of O_2, and the mechanism was not elucidated.

Experimental Section

Perfluoroethylene and 1,3-perfluorobutadiene were obtained from Peninsular ChemResearch, Inc. Both compounds were purified by distillation. For C_2F_4 the fraction volatile at $-160°$ but condensable at $-196°$ was used; for $1,3\text{-}C_4F_6$ the fraction used was volatile at $-100°$ but condensable at $-130°$. Gas chromatographic analysis showed no impurities ($<0.01\%$).

CP grade N_2O, C_2H_4, C_3H_8, and $n\text{-}C_4H_{10}$ from the Matheson Co. were used after degassing at $-196°$. No measurable amounts of impurities were found. In particular, the impurity level in the N_2O is $<0.01\%$. Matheson extra dry grade oxygen was used without further purification; the only impurity is N_2 at $\sim0.035\%$.

The technique used was similar to that of Saunders and Heicklen.[3] The oxygen atoms were prepared from the mercury-sensitized photolysis of N_2O. Radiation was from a Hanovia flat-spiral low-pressure mercury resonance arc and passed through a Corning 9-54 filter before entering the stem of a T-shaped Pyrex reaction cell through a quartz window. The top of the T had sodium chloride windows and was situated in the sample beam of a Beckman IR-10 infrared spectrometer for continual analysis of CF_2O. The windows were attached to the cell with Borden's epoxy cement. When reduced intensities were desired, Corning 9-30 filters were inserted between the lamp and reaction vessel. Actinometry was done by the mercury-sensitized photolysis of N_2O in the presence of small amounts of C_2F_4, where $\Phi(CF_2O) = 1.0$.[1]

The reaction cell was connected to a grease-free high-vacuum line containing Teflon stopcocks with Viton "O" rings. After photolysis the reaction mixture was frozen to $-196°$ and the noncondensable gases were removed. The condensables were then warmed slowly and passed through two baths at $-140°$. The N_2O, CF_2O, and C_2F_4 were removed, but the other products were retained in the condensable fraction with the $1,3\text{-}C_4F_6$. In some runs the fraction retained at $-140°$ was separated on a gas chromatographic column 21 ft long $\times$ $^1/_4$-in. outside diameter of copper tubing packed with 30% Kel-F No. 3 oil on chromosorb W(AW). For a helium flow rate of 37 cm³/min with the column at $0°$, the retention times were 15, 24.5, 37, 39.5, and 48 min, respectively for $c\text{-}C_3F_4$, $C_3F_4O_2$, $1,3\text{-}C_4F_6$, C_4F_6O, and C_3F_4O. In other runs the fraction condensable at $-140°$ was passed through a column 12 ft long $\times$ $^1/_8$-in. outside diameter of stainless steel tubing packed with 15% Kel-F No. 3 oil on chromosorb W(HP). For a helium flow rate of 32 cm³/min with the column at $0°$, the retention times were 23 and 33 min for the two C_7F_{10} isomers. The gas chromatograph utilized a Gow Mac power supply, No. 40-012, and thermistor detector No. 9689. Calibrations were performed by collecting the products, measuring their pressures on a dibutyl phthalate manometer, and passing them again through the chromatograph.

To identify the products, infrared and mass spectra were obtained respectively on a Beckman IR-5A infrared spectrometer and an AEI model MS-9 mass spectrometer.

Results

Both in the absence and presence of O_2, the initial gaseous products of the reaction of $O(^3P)$ (produced

(2) W. Stuckey and J. Heicklen, *J. Amer. Chem. Soc.*, **90**, 3952 (1968).
(3) D. Saunders and J. Heicklen, *ibid.*, **87**, 2088 (1965).

Table I. Mass Spectra of C_7F_{10} Isomers on MS-9 at 70 eV

m/e	Rel intensity		Ion
	I	II	
275	1.75	1.93	
274	19.4	25.9	C_7F_{10}
256	0.87	1.34	
255	12.2	17.9	C_7F_9
236	1.4	0.86	C_7F_8
225	0.82	0.85	
224	13.6	13.8	C_6F_8
217	1.4	0.86	C_7F_7
206	7.23	6.55	
205	100	100	C_6F_7
193	1.4	0.86	C_5F_7
187	2.64	2.29	
186	32.2	31.1	C_6F_6
175	1.08	0.88	
174	18.3	15.6	C_5F_6
162	8.3	5.2	C_4F_6
156	3.89	3.76	
155	65.6	65.6	C_5F_5
143	6.9	5.2	C_4F_5
136	2.8	1.7	C_5F_4
132	0.44	0.76	
131	14.5	23.5	C_3F_5
125	1.01	0.73	
124	18.1	14.1	C_4F_4
118	1.10	1.17	
117	20.6	20.7	C_5F_3
113	0.71	1.41	
112	20.8	17.6	C_3F_4
105	5.6	5.2	C_4F_3
98	4.2	3.8	C_5F_2
97	0.46	0.81	
96	6.9	13.6	
94	2.66	1.95	
93	69.4	54.8	C_3F_3
86	2.8	3.5	C_4F_2
82	2.65	4.67	
81	44.7	77.6	C_2F_3
78	0.53	1.24	
77	5.6	15.9	
74	9.2	8.6	C_3F_2
70	0.85	0.81	
69	68.1	62.4	CF_3
64	0.0	4.2	
62	1.5	0.8	C_2F_2
58	0.14	17.2	
57	0.0	3.5	F_3
55	2.8	2.4	C_3F
50	1.4	0.35	CF_2
47	6.38	29.3	CFO
44	45.8	10.0	CO_2
43	0.14	54.8	C_2F
32	4.2	4.8	O_2
31	21.7	19.0	CF
28	17.4	40.2	N_2

from the Hg-sensitized decomposition of N_2O) with $1,3\text{-}C_4F_6$ are CF_2O, $c\text{-}C_3F_4$, C_3F_4O ($CF_2{=}CF{-}CF{=}O$), two isomers of C_7F_{10}, C_4F_6O (1), $C_3F_4O_2$ (2), and C_2F_4.

$$\overline{O{-}CF_2{-}CF}{-}CF{=}CF_2$$
1
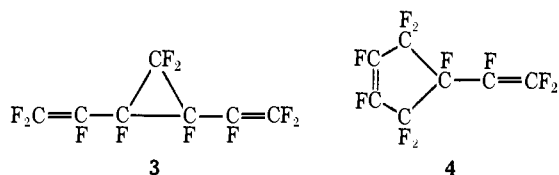
$$\overline{O{-}CF_2{-}CF}{-}CF{=}O$$
2
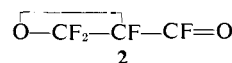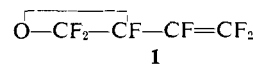
The major products, CF_2O and $c\text{-}C_3F_4$, were previously reported[2] and we have confirmed their presence. Perfluoroacryloyl fluoride (C_3F_4O) and 2,3-epoxyperfluoropropionyl fluoride ($C_3F_4O_2$) were identified from their infrared spectra, which agreed with those previously re-

ported.[4,5] Confirmation of $C_3F_4O_2$ was also obtained from gas chromatographic retention times.[5]

The two isomers of C_7F_{10} and C_4F_6O were unstable and it was difficult to obtain large quantities of them. Therefore, nmr spectra could not be obtained. However, their mass and infrared spectra were measured.

Table I lists the mass spectral peaks for the two C_7F_{10} isomers. The isomer with the shorter chromatographic retention time is labeled I, whereas that with the longer retention time is II. The mass spectra are remarkably similar. The parent peak is at m/e 274 for both isomers, the peak at 275 being due to the ^{13}C isotope. No higher mass spectral peaks were observed (scanned to m/e 400). The infrared spectra of both isomers are shown in Figure 1. Bands occur at 5.60, 6.8, 7.35, 7.52, 7.82, 8.07, 8.43, 8.60, 10.02, 12.2–12.5, 13.05, 13.45, 13.8, and 15.5 μ for isomer I and at 5.61, 6.8, 7.35, 7.55, 7.82, 8.42, 8.69, 10.1, 10.40, 12.40, 13.35, and 15.5 μ for isomer II. Both spectra show one double-bond stretch at 5.61 μ. Presumably this corresponds to an asymmetric double-bond stretch; if no fluorine migration occurs, each isomer contains two double bonds and one ring. Two possible geometric isomers are 3 and 4.

$$F_2C=C\underset{F}{-}\underset{F}{C}\overset{CF_2}{\triangle}\underset{F}{C}\underset{F}{-}C=CF_2$$

3

$$FC\overset{\overset{F_2}{C}}{\underset{FC}{\underset{\|}{C}}}\overset{F}{\underset{C}{\underset{F_2}{C}}}\overset{F}{-}C=CF_2$$

4

The mass spectrum for C_4F_6O is listed in Table II. The parent peak is at m/e 178 and no higher peaks were observed (scanned to m/e 400). The infrared spectrum of the pure compound was difficult to obtain because of partial decomposition of the sample. However, peaks at 5.57 and 6.50 μ were observed in the isolated sample. The former peak corresponds to the C=C stretch, whereas the latter peak is characteristic of the fluorinated epoxides,[6] and was also observed during photolysis. Thus the structure is established as 1. The infrared spectrum of the isolated product also displayed carbonyl bands at 5.29 and 5.38 μ. These bands are oxidation products that are unavoidably produced during isolation and collection. The same difficulty also occurred when attempts were made to isolate 5

$$\overset{\boxed{}}{O-CF_2-CF-CF_3}$$

5
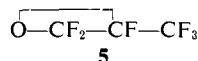
in an earlier study.[6] The spectrum of the isolated sample also contained the band at 5.66 μ due to 1,3-C_4F_6, because of the difficulty in separating small amounts of C_4F_6O from 1,3-C_4F_6.

Quantitative results for C_2F_4 formation could not be obtained because 1,3-C_4F_6 obscured the infrared absorption bands of C_2F_4, and chromatographic analysis could not be effected because of the interference of the large excess of N_2O which has a similar retention time to that of C_2F_4. However, it was established that C_2F_1 was produced by measuring the mass spectrum of the N_2O fraction after the separation of products. The mass spectrum clearly showed the presence of C_2F_4 when O_2 was absent.

(4) P. Tarrant and J. Savory, *J. Org. Chem.*, **28**, 1728 (1963).
(5) W. Stuckey, J. Heicklen, and V. Knight, *Can. J. Chem.*, **47**, 2329 (1969).
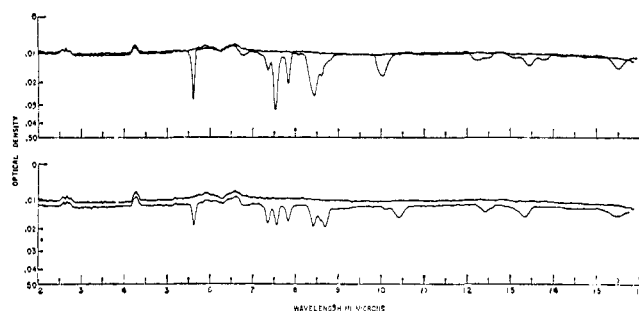(6) J. Heicklen and T. Johnston, *J. Phys. Chem.*, **71**, 1391 (1967).

Figure 1. Infrared spectra of C_7F_{10} isomers. Upper curve is isomer I, lower curve isomer II.

Separate studies indicated that all the products were produced linearly with exposure time, except possibly for C_2F_4 where measurements could not be made. Thus all are primary products and their quantum yields in the reaction of $O(^3P)$ with 1,3-C_4F_6 in the absence of O_2 are listed in Table III. The perfluorobutadiene

Table II. Mass Spectrum of C_4F_6O on MS-9 at 70 eV

m/e	Rel intensity	Ion
178	5.1	C_4F_6O
166	1.11	C_3F_6O
163	2.05	
162	38.9	C_4F_6
159	4.97	C_4F_5O
150	2.54	C_3F_6
143	4.58	C_4F_5
132	0.96	
131	20.7	C_3F_5
128	10.9	C_3F_4O
124	4.03	C_4F_4
113	1.54	
112	29.3	C_3F_4
110	0.82	
109	16.4	C_3F_3O
104	2.05	CF_4O
101	1.01	
100	20.5	C_2F_4
94	3.89	
93	100	C_3F_3
90	2.74	C_3F_2O
86	4.76	C_4F_2
85	77.2	CF_3O
81	14.7	C_2F_3
78	0.74	C_2F_2O
74	10.0	C_3F_2
71	3.69	C_3FO
69	2.87	CF_3
62	11.7	C_2F_2
59	0.86	C_2FO
55	4.22	C_3F
50	6.74	CF_2
47	14.7	CFO
44	9.32	CO_2
43	3.28	C_2F
32	1.94	O_2
31	37.1	CF
28	9.72	N_2

pressure was varied from 1.97 to 106 Torr and the absorbed intensity, I_a, was varied from 9.0 to 698 μ/min. The quantum yields of CF_2O, c-C_3F_4, C_3F_4O, C_4F_6O, and $C_3F_4O_2$ were invariant to changes in these parameters, and their average values and mean deviations were 0.90 ± 0.05, 0.68 ± 0.04, 0.103 ± 0.009, 0.025 ± 0.004, and 0.022 ± 0.004, respectively. The quantum yields of the C_7F_{10} isomers were also invariant to

Table III. Reaction of Oxygen Atoms with 1,3-C_4F_6 at 32 ± 6°

[1,3-C_4F_6], Torr	[N_2O], Torr	I_a, μ/min	Φ(CF_2O)	Φ(c-C_3F_4)	Φ(C_3F_4O)	Φ(C_7F_{10} (I))	Φ(C_7F_{10} (II))	Φ(C_4F_6O)	Φ($C_3F_4O_2$)
1.97	645	278	0.82	0.58				0.030	0.017
2.94	605	604	0.96	0.67					
2.99	637	251				0.157	0.151		
3.05	643	9.0				0.180	0.133		
3.32	610	698	0.83	0.63					
3.7	590	296	0.81	0.73					
6.50	639	279	0.85	0.64					0.024
7.78	599	32.6	0.86	0.62					
7.79	607	32.6	0.86	0.65					
8.34	602	606	0.98	0.75					
8.51	608	673	0.89	0.68					
10.1	630	266	0.84	0.66		0.228	0.198	0.026	0.022
10.1	640	260		0.63	0.102	0.246	0.183		0.019
10.1	630	288		0.66	0.120				0.019
10.2	428	343	0.94						
10.2	691	280	1.00	0.63					0.026
10.2	613	279	0.90	0.67				0.018	0.021
10.2	600	9.0				0.234	0.180		
10.3	648	~11		0.62	0.104	0.242	0.166		0.019
10.6	656	274	0.88	0.66	0.096				
10.7	581	338	0.85						
11.1	438	210	0.93						
27.0	585	631	0.92	0.75					
27.8	593	606	0.95	0.76					
28.0	599	25	0.96	0.77					
28.6	652	301		0.71					
29.8	614	16.8		0.63	0.093				0.020
29.9	600	9.0				0.344			
30.0	640	263	0.85	0.70		0.344	0.246		0.029
30.0	631	9.0				0.343	0.224		
40.2	428	343	0.94						
62	668	297	0.90						
100	579	13.7			0.118				
102	645	270		0.65	0.090				
104	746	270	0.94	0.78					0.047
106	546	20.8	1.02	0.69					
			0.90 ± 0.05	0.68 ± 0.04	0.103 ± 0.009			0.025 ± 0.004	0.022[a] ± 0.004

[a] Neglecting the 0.047 value.

Table IV. Reaction of Oxygen Atoms with 1,3-C_4F_6 in the Presence of O_2 at 32 ± 6°

[1,3-C_4F_6], Torr	[O_2], Torr	[N_2O], Torr	I_a, μ/min	Φ(CF_2O)	Φ(c-C_3F_4)	Φ(C_3F_4O)	Φ(C_7F_{10} (I))	Φ(C_7F_{10} (II))	Φ(C_4F_6O)	Φ($C_3F_4O_2$)
3.5	2.66	646	236		0.62	0.100	0.151	0.131		0.16
9.9	0.47	647	270	1.05	0.71					0.16
9.9	9.5	623	222		0.66	0.097			~0.2	
10.2	9.0	632	222		0.63	0.103				0.20
10.3	8.5	602	11.9		0.51	0.086				0.15
10.5	8.2	655	288		0.66	0.118				0.12
10.6	7.5	618	270		0.55	0.094				
10.7	1.33	703	275	0.97	0.65				0.19	0.19
10.8	8.0	636	263	0.92	0.61		0.240	0.172	0.22	0.25
11.1	3.2	633	222		0.65	0.102				0.18
11.6	3.4	686	338	0.88						
11.8	3.4	706	338	1.05						
16.7	9.9	576	343	1.08						
26.2	18.5	661	338	1.02						
27.7	17.5	749	355	0.86						
27.8	16.9	~630	280	0.86	0.72					
28	25.2	705	251				0.360	0.255		
29.8	4.4	672	280	1.01	0.62					
29.9	3.8	657	301	0.88						
30.2	19.8	612	270		0.62	0.115				0.22
30.2	10.0	670	9.0				0.345	0.202		
31.4	2.9	613	251				0.352	0.248		
32	26.4	670	13.7		0.64	0.111				0.32
32.2	8.4	567	13.7		0.71	0.107				0.26
32.3	8.8	655	251				0.379	0.266		
35	25.0	728	251				0.317	0.209		
				0.96 ± 0.08	0.64 ± 0.04	0.103 ± 0.006			0.20	0.21 ± 0.05

Table V. Reaction of Oxygen Atoms with Mixtures of $1,3-C_4F_6$ and a Hydrocarbon at $32 \pm 6°$

$[1,3-C_4F_6]$, Torr	$[X]$, Torr	$[N_2O]$, Torr	I_a, μ/min	$\Phi(CF_2O)^a$
		$X = C_3H_8$		
5.91	243	532	198	0.34
10.5	160	591	194	0.57
10.7	110	612	204	0.63
10.9	335	546	192	0.40
		$X = n-C_4H_{10}$		
10.2	45	520	173	0.65
10.3	142	594	167	0.38
10.4	452	379	170	0.135
10.5	141	603	174	0.41
		$X = C_2H_4$		
10.1	13.2	558	262	0.264
10.2	12.3	576	262	0.251
10.3	73.2	607	8.2	0.035
10.4	51.8	654	253	0.080
10.4	147	607	202	0.048
10.9	44.6	674	253	0.085
20.0	71	644	8.7	0.118
20.0	107	611	312	0.069
20.1	45.9	536	319	0.177
20.2	199	551	312	0.031
24.3	20.0	690	8.2	0.34
28.9	15.4	456	389	0.40
29.1	15.3	653	326	0.48
29.3	15.1	587	346	0.51
96.5	110	455	210	0.274
98.8	108	550	202	0.31

[a] All values of $\Phi(CF_2O)$ were corrected for quenching of Hg* by hydrocarbon and $1,3-C_4F_6$.

changes in I_a, but they did increase by about a factor of 2 as the $1,3-C_4F_6$ pressure was raised from 3.0 to 30 Torr.

The results with O_2 added are given in Table IV. The perfluorobutadiene pressure was varied from 3.48 to 35 Torr, the O_2 pressure from 0.47 to 26.4 Torr, and I_a from 9.0 to 355 μ/min. The quantum yields of the C_7F_{10} isomers were the same as in the absence of O_2 for any $1,3-C_4F_6$ pressure. The other product yields were invariant to changes in the parameters, but not necessarily the same as in the absence of O_2. The average value of $\Phi(CF_2O)$ increased slightly from 0.90 to 0.96, whereas $\Phi(c-C_3F_4)$ fell slightly from 0.68 to 0.64. In both cases these changes are within the experimental uncertainties. $\Phi(C_4F_4O)$ remained unchanged at 0.103 when O_2 was added, but both $\Phi(C_4F_6O)$ and $\Phi(C_3F_4O_2)$ increased noticeably from about 0.02 to about 0.21.
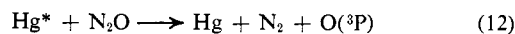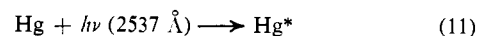
In order to measure the rate constant for the reaction of $O(^3P)$ with $1,3-C_4F_6$, experiments were done with mixtures of $1,3-C_4F_6$ and C_3H_8, $n-C_4H_{10}$, or C_2H_4. In these experiments, listed in Table V, only $\Phi(CF_2O)$ was measured, and it dropped as the hydrocarbon-to-$1,3-C_4F_6$ pressure ratio was augmented. In computing $\Phi(CF_2O)$, corrections were made for any quenching of the excited mercury atom by either the hydrocarbon or $1,3-C_4F_6$, since quenching was significant in some instances. The quenching constants relative to N_2O which were used were 0.095, 0.285, 1.75, and 1.38 respectively for C_3H_8,[7] $n-C_4H_{10}$,[7] C_2H_4,[7] and $1,3-C_4F_6$.[8]
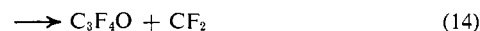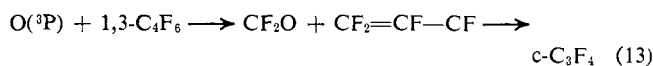
Discussion

The primary photolytic act is the formation of $O(^3P)$ from the mercury-sensitized decomposition of N_2O[9]

(7) R. J. Cvetanović, *Progr. React. Kinet.*, **2**, 39 (1964).
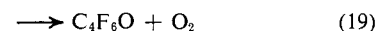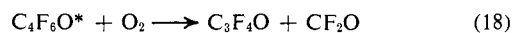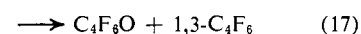(8) W. Stuckey and J. Heicklen, *Can. J. Chem.*, **46**, 1361 (1968).

$$Hg + h\nu \ (2537 \ Å) \longrightarrow Hg^* \quad (11)$$

$$Hg^* + N_2O \longrightarrow Hg + N_2 + O(^3P) \quad (12)$$

where Hg* is the $6(^3P_1)$ state of Hg. The oxygen atoms then react with $1,3-C_4F_6$ in steps analogous to those for C_2F_4 and C_3F_6

$$O(^3P) + 1,3-C_4F_6 \longrightarrow CF_2O + CF_2=CF—CF \longrightarrow$$

$$c-C_3F_4 \quad (13)$$

$$\longrightarrow C_3F_4O + CF_2 \quad (14)$$

$$\longrightarrow C_4F_6O^* \quad (15)$$

where presumably both CF_2 and C_4F_6O are in triplet states by spin conservation. The reaction sequence is apparently the same in the presence and absence of O_2. $\Phi(c-C_3F_4)$ and $\Phi(C_3F_4O)$ give the relative importance of reactions 13 and 14 respectively to be 0.66 (0.68 in the absence of O_2 and 0.64 in the presence of O_2) and 0.103. By difference, the relative importance of reaction 15 is 0.24.

In the absence of O_2 the CF_2 radicals would either combine to form C_2F_4, which was found, or add to $1,3-C_4F_6$ to produce a C_5F_8 compound. A search was made for C_5 fluorocarbons with no success. However, it would be a minor product difficult to separate from $1,3-C_4F_6$. Consequently, the presence or absence of C_5 compounds is difficult to establish.

The $C_4F_6O^*$ behaves differently from the excited epoxides produced in the C_2F_4 or C_3F_6 reactions. In the first place C_4F_6O is found as a minor product in the absence of O_2, contrary to the fact that epoxides are not found under similar conditions with the lighter perfluoroolefins. Apparently about 10% of the $C_4F_6O^*$ can somehow lose its excitation energy and be stabilized. Second, the lighter excited epoxides either react with the perfluoroolefin to produce CF_2O and cyclic perfluorocarbons (reaction 4), decompose to produce CF_2O and a diradical (reaction 5), or react with O_2 to produce acyl fluorides and oxygenated diradicals. The $C_4F_6O^*$ molecule does yield CF_2O, and C_7F_{10} compounds are produced. Thus reactions analogous to those in C_3F_6 are suggested. However, there are two important differences: (1) the sum of the quantum yields for the C_7F_{10} compounds can exceed the yield of $C_4F_6O^*$ production, and (2) the C_7F_{10} yields are not reduced in the presence of O_2. As a result the mechanism of C_7F_{10} formation probably does not involve $C_4F_6O^*$ as a precursor. To account for the other facts we introduce the reactions

$$C_4F_6O^* + 1,3-C_4F_6 \longrightarrow CF_2O + polymer \quad (16)$$

$$\longrightarrow C_4F_6O + 1,3-C_4F_6 \quad (17)$$

$$C_4F_6O^* + O_2 \longrightarrow C_3F_4O + CF_2O \quad (18)$$

$$\longrightarrow C_4F_6O + O_2 \quad (19)$$

If the above mechanism is valid, the ratio k_{16}/k_{17} can be found from the expression

$$k_{17}/(k_{16} + k_{17}) =$$

$$\Phi(C_4F_6O)/[1 - \Phi(c-C_3F_4) - \Phi(C_3F_4O)] \quad (I)$$

which applies in the absence of O_2. The ratio k_{16}/k_{17} is about 9.

To complete the mechanism in the presence of O_2 we

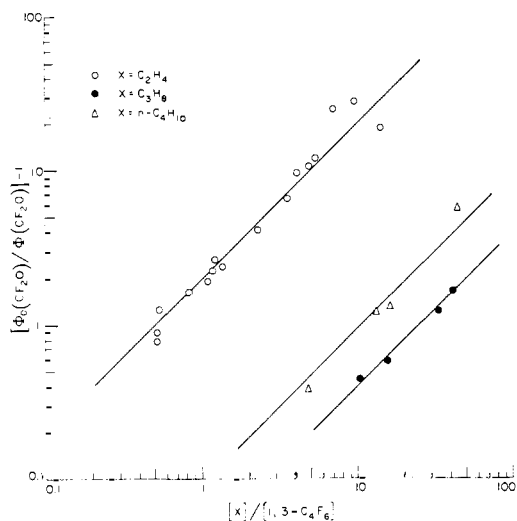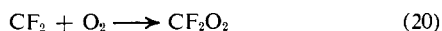(9) R. J. Cvetanović, *Advan. Photochem.*, **1**, 115 (1963).

Figure 2. Log–log plot of $[\Phi_0(CF_2O)/\Phi(CF_2O)] - 1$ vs. the ratio of hydrocarbon and $1,3\text{-}C_4F_6$ pressures in the mercury-photosensitized decomposition of N_2O in the presence of hydrocarbons and $1,3\text{-}C_4F_6$ at $32 \pm 6°$.

add the expected steps

$$CF_2 + O_2 \longrightarrow CF_2O_2 \qquad (20)$$
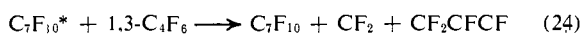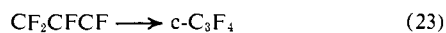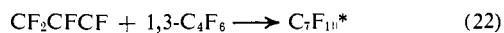
$$CF_2O_2 + 1,3\text{-}C_4F_6 \longrightarrow CF_2O + C_4F_6O \qquad (21)$$

The formation of $C_3F_4O_2$ as a primary product in the absence of O_2 is difficult to understand, since two oxygen atoms must be incorporated into the same molecule. We carefully checked to be sure that molecular O_2 was absent, but were never able to eliminate $C_3F_4O_2$ production. However, $\Phi(C_3F_4O_2)$ is small in the absence of O_2 and does not seriously affect our findings. The increase with O_2 added is easily attributed to reaction 18, and k_{18}/k_{19} can be found from the expression

$$k_{18}/(k_{18} + k_{19}) =$$
$$\Phi(C_3F_4O_2)/[1 - \Phi(c\text{-}C_3F_4) - \Phi(C_3F_4O)] \qquad (II)$$

which applies in the presence of O_2. The ratio k_{18}/k_{19} is ~ 6.

It is interesting to speculate on the mechanism of formation of the C_7F_{10} compounds. Their large quantum yields suggest that they come from the major process, reaction 13. Since the quantum yields of $c\text{-}C_3F_4$ and the C_7F_{10} compounds are not affected by the presence of O_2, the CF_2CFCF diradical produced in that reaction apparently does not react with O_2. The following processes can be envisioned for the fate of the diradical produced in reaction 13.

$$CF_2CFCF + 1,3\text{-}C_4F_6 \longrightarrow C_7F_{11}* \qquad (22)$$

$$CF_2CFCF \longrightarrow c\text{-}C_3F_4 \qquad (23)$$

$$C_7F_{10}* + 1,3\text{-}C_4F_6 \longrightarrow C_7F_{10} + CF_2 + CF_2CFCF \qquad (24)$$

The CF_2CFCF diradical produced in reaction 24 presumably has less energy than that produced in reaction 13 and always closes to $c\text{-}C_3F_4$. The CF_2 produced in reaction 24 must be a singlet, which does not react with O_2, to be in accord with the fact that $\Phi(CF_2O)$ does not exceed unity in the presence of O_2. Production of C_7F_{10} and $c\text{-}C_3F_4$ in reaction 24 or some variation of it is

required by the fact that the combined quantum yields of these products exceed unity.

The value for $\Phi(C_4F_6O)$ when O_2 is added should be given by the expression

$$\Phi(C_4F_6O) = 1 - \Phi(c\text{-}C_3F_4) - \Phi(C_3F_4O_2) \qquad (III)$$

The value computed from eq III for $\Phi(C_4F_6O)$ in the presence of O_2 is 0.15, in acceptable agreement with the value of 0.20 found experimentally.

Finally, the mechanism predicts that $\Phi(CF_2O)$ should increase from 0.90 in the absence of O_2 to 1.00 in the presence of O_2. The observed increase is to 0.96 ± 0.08. In addition, the mechanism predicts that C_2F_4 should disappear in the presence of O_2, but it was too difficult to verify this prediction experimentally.

The relative rate constant for the reaction of oxygen atoms with $1,3\text{-}C_4F_6$ and a hydrocarbon can be found from studies of mixtures of the two gases. The general reaction of oxygen atoms with the hydrocarbon X can be written

$$O + X \longrightarrow \text{not } CF_2O \qquad (25)$$
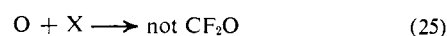
The competition leads to the prediction

$$[\Phi_0(CF_2O)/\Phi(CF_2O)] - 1 =$$
$$k_{25}[X]/(k_{13} + k_{14} + k_{15})[1,3\text{-}C_4F_6] \qquad (IV)$$

where $\Phi_0(CF_2O)$ is $\Phi(CF_2O)$ in the absence of the hydrocarbon. Plots based on eq IV are shown in Figure 2 for the three hydrocarbons. The log–log plots are well fitted with straight lines of slope 1.00. The values of $k_{25}/(k_{13} + k_{14} + k_{15})$ obtained from the plots are 2.0, 0.093, and 0.039 respectively for C_2H_4, $n\text{-}C_4H_{10}$, and C_3H_8. These yield rate constants, relative to C_2H_4, for the reaction of oxygen atoms with $n\text{-}C_4H_{10}$ and C_3H_8 of 0.0465 and 0.0195, respectively, in excellent agreement with the reported values of 0.045^9 and $0.016,^{10}$ respectively. From the absolute value of $5.7 \times 10^8\ M^{-1}\ \sec^{-1}$ for the room-temperature rate constant for $O(^3P)$ with $C_2H_4,^9$ $k_{13} + k_{14} + k_{15}$ becomes $2.9 \times 10^8\ M^{-1}\ \sec^{-1}$. The rate constant data obtained in this study are summarized in Table VI.

Table VI. Summary of Rate Constant Data

Ratio	Value	Units	Source
$k_{13}/(k_{13} + k_{14} + k_{15})$	0.66	None	$\Phi(c\text{-}C_3F_4)$
$k_{14}/(k_{13} + k_{14} + k_{15})$	0.103	None	$\Phi(C_3F_4O)$
$k_{15}/(k_{13} + k_{14} + k_{15})$	0.24	None	$1 - \Phi(c\text{-}C_3F_4) - \Phi(C_3F_4O)$
k_{16}/k_{17}	~ 9	None	Eq 1
k_{18}/k_{19}	~ 6	None	Eq II
$k_{13} + k_{14} + k_{15}$	2.9×10^8	M^{-1} $\sec^{-1}$	Eq IV Figure 2

(10) D. Saunders and J. Heicklen, *J. Phys. Chem.*, **70**, 1950 (1966).