superfluous. The results of cell misalignment can be calculated in the normal, elementary way because of the relatively small magnitude of the aberrations established in this work.

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The Production of Perfluorocyclopropane in the Reaction of Oxygen Atoms with Tetrafluoroethylene

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The reaction of $O(^3P)$ with C_2F_4 proceeds by the reaction scheme

$$O + C_2F_4 \xrightarrow{k_{11}} CF_2O + CF_2$$

$$O + C_2F_4 \xrightarrow{k_5} C_2F_4O^*$$

$$2CF_2 \xrightarrow{k_2} C_2F_4$$

$$CF_2 + C_2F_4 \xrightarrow{k_3} \text{cyclo-}C_3F_6$$

$$C_2F_4O^* + C_2F_4 \xrightarrow{k_6} CF_2O + \text{cyclo-}C_3F_6$$

$$C_2F_4O^* \xrightarrow{k_7} CF_2O + CF_2$$

where $C_2F_4O^*$ is an excited intermediate. The ratio $k_5/(k_{11} + k_5)$ is 0.15 at 22° and drops slightly as the temperature is raised. The CF_2 radicals produced give the same values for $k_3/k_2^{1/2}$ as do singlet CF_2 radicals produced in another system.

Introduction

In recent reports from this laboratory,[1,2] it has been shown that the reaction of triplet oxygen atoms with C_2F_4 yields CF_2O as the sole oxygen-containing product independent of conditions for temperatures from 23 to 125°. However, at room temperature the cyclo-C_3F_6 formed was about 0.15 that of the CF_2O for C_2F_4 pressures up to 30 mm. This invariance with pressure is contrary to that expected from the sequence of reactions

$$O + C_2F_4 \longrightarrow CF_2O + CF_2 \text{ (singlet)} \qquad (1)$$

$$2CF_2 \longrightarrow C_2F_4 \qquad (2)$$

$$CF_2 + C_2F_4 \longrightarrow \text{cyclo-}C_3F_6 \qquad (3)$$

Therefore, two possible alternatives were suggested[1,3]

$$O + C_2F_4 \longrightarrow CF_2O + CF_2 \text{ (triplet)} \qquad (4)$$

$$O + C_2F_4 \longrightarrow C_2F_4O^* \qquad (5)$$

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(1) D. Saunders and J. Heicklen, *J. Am. Chem. Soc.*, **87**, 2088 (1965).

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

(3) J. Heicklen, N. Cohen, and D. Saunders, *ibid.*, **69**, 1774 (1965).

where the triplet CF_2 from reaction 4 would disappear by (2) or (3) but with different rate constants from the singlet reactions. The product of reaction 5 is an excited C_2F_4O molecule which never becomes stabilized (neither tetrafluoroethylene oxide nor CF_3CFO is a product of the reaction) but may react *via*

$$C_2F_4O^* + C_2F_4 \longrightarrow CF_2O + \text{cyclo-}C_3F_6 \qquad (6)$$

$$C_2F_4O^* \longrightarrow CF_2O + CF_2 \qquad (7)$$

The results[1] in the presence of molecular oxygen favored reaction 4, but reaction 5 could not be eliminated as a possibility. Therefore, we studied the cyclo-C_3F_6 yield over a wide range of conditions to see if we could decide among the possibilities. The results of that study are reported here.

Experimental Section

The experimental procedure was identical with that of an earlier study,[4] except that an excess of N_2O (Matheson, degassed), usually 500 mm, was present in all runs, and the C_2F_4 was prepared by reacting Zn with 1,2-$C_2F_4Br_2$.[2] The amount of nitrogen produced was computed from the residual pressure of the gas noncondensable at −196°.

Results

The quantum yield of cyclo-C_3F_6 formation from mercury-sensitized photolyses of mixtures of 500 mm N_2O with smaller amounts of C_2F_4 is shown in Tables I–III and Figures 1–3. The quantum yields Φ(cyclo-C_3F_6) are computed as the amount of cyclo-C_3F_6 produced divided by the N_2 produced.

At 22°, Φ(cyclo-C_3F_6) rises proportionately (slope = 1.0 on log–log plot of Figure 1) with C_2F_4 pressure for C_2F_4 pressures up to 0.6 mm. For C_2F_4 pressures between 0.6 and 30 mm, Φ(cyclo-C_3F_6) is constant at about 0.15, but at higher pressures Φ(cyclo-C_3F_6) rises. The data for ref 1 are included in Figure 1; they lie on the same curve as the data from this study. A variation of the absorbed intensity by a factor of 50 had no effect for C_2F_4 pressures below 30 mm. Possible trends at higher pressures are obscured by the scatter in the data, but the low-intensity points lie above those at the higher intensities.

At 95° and C_2F_4 pressures between 1 and 4 mm, Φ(cyclo-C_3F_6) is about 0.11 irrespective of intensity, as shown in Figure 2. At higher C_2F_4 pressures, Φ(cyclo-C_3F_6) rises toward unity with increasing pressure; the steeper the rise, the lower the intensity.

At 150°, there is no intensity-independent, pressure-independent region. Φ(cyclo-C_3F_6) is increased by raising the C_2F_4 pressure or lowering the intensity. The limiting high-pressure, low-intensity limit for

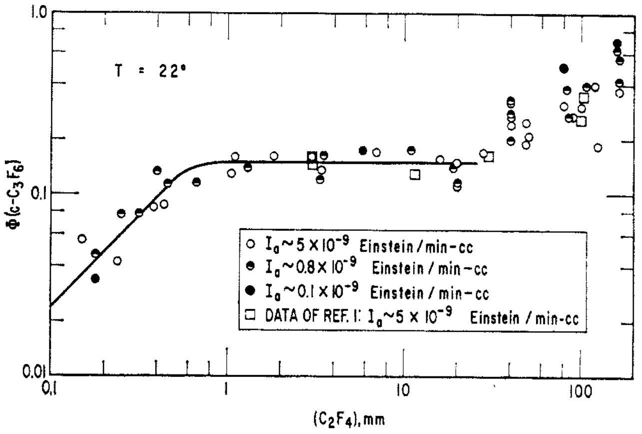

Figure 1. Plot of Φ(cyclo-C_3F_6) *vs.* (C_2F_4) at 22°.

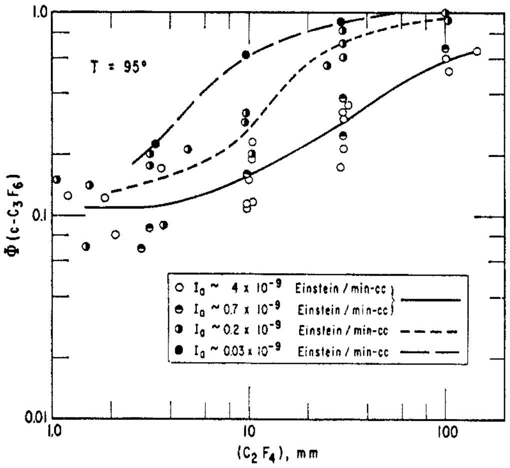

Figure 2. Plot of Φ(cyclo-C_3F_6) *vs.* (C_2F_4) at 95°.

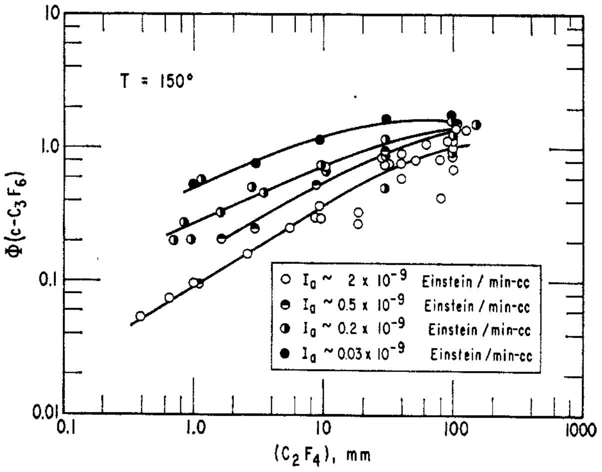

Figure 3. Plot of Φ(cyclo-C_3F_6) *vs.* (C_2F_4) at 150°.

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[4] N. Cohen and J. Heicklen, *J. Chem. Phys.*, **43**, 871 (1965).

Table I: Mercury-Sensitized Photolysis of N_2O–C_2F_4 Mixtures at 22°; $N_2O \sim 500$ mm

(C_2F_4), mm	$R(N_2) \times 10^9$, moles/min cc	Φ(cyclo-C_3F_6)
	$I_a \sim 5 \times 10^{-9}$ einstein/min cc	
0.15	4.3	0.056
0.24	4.9	0.042
0.38	5.7	0.085
0.44	6.0	0.088
1.05	6.6	0.13
1.1	3.7	0.16
1.83	6.6	0.16
3.0	6.0	0.16
3.4	6.6	0.13
6.9	7.4	0.17
16	4.8	0.15
20	2.7	0.11
20	2.6	0.15
28	...	0.17
40	3.0	0.24
40	2.5	0.27
49	3.1	0.25
49	5.9	0.19
51	3.4	0.21
80	2.8	0.31
90	5.7	0.27
100	2.7	0.31
120	2.2	0.40
122	5.4	0.185
165	2.5	0.37
	$I_a \sim 0.8 \times 10^{-9}$ einstein/min cc	
0.18	0.78	0.046
0.25	0.70	0.078
0.32	0.88	0.078
0.40	1.05	0.144
0.46	0.65	0.115
0.67	1.22	0.116
1.3	0.98	0.14
3.35	1.23	0.12
3.5	0.85	0.162
10.1	1.15	0.176
19	...	0.14
20	1.44	0.113
40	0.56	0.20
40	0.34	0.27
40	0.61	0.33
83	0.39	0.38
85	0.53	0.27
108	0.42	0.40
160	0.27	0.63
163	0.34	0.56
165	0.52	0.42
	$I_a \sim 0.1 \times 10^{-9}$ einstein/min cc	
0.18	...	0.034
5.8	0.21	0.174
40	0.090	0.33
80	0.090	0.50
160	0.107	0.70

Table II: Mercury-Sensitized Photolysis of N_2O–C_2F_4 Mixtures at 95°; $N_2O \sim 500$ mm

(C_2F_4), mm	$R(N_2) \times 10^9$, moles/min cc	Φ(cyclo-C_3F_6)
	$I_a \sim 4 \times 10^{-9}$ einstein/min cc	
1.2	3.8	0.125
1.85	4.4	0.12
2.1	...	0.08
3.6	...	0.17
9.8	3.9	0.11
9.8	...	0.113
10.0	4.7	0.15
10.2	4.6	0.19
10.3	3.7	0.23
10.4	3.5	0.118
29.5	3.4	0.175
30	3.1	0.32
31	3.5	0.22
31	3.5	0.30
32	4.6	0.35
100	4.2	0.60
106	2.7	0.52
147	4.2	0.65
	$I_a \sim 0.7 \times 10^{-9}$ einstein/min cc	
2.85	0.66	0.069
3.15	0.72	0.087
9.8	0.72	0.16
30	0.78	0.25
30	0.62	0.38
100	0.70	0.67
	I_a 0.2×10^{-9} einstein/min cc	
1.05	0.20	0.15
1.50	0.18	0.07
1.56	0.23	0.14
3.1	0.22	0.175
3.15	0.126	0.2
3.7	0.18	0.09
4.95	0.20	0.21
9.6	0.163	0.29
9.8	0.157	0.32
10.2	0.169	0.2
25	0.20	0.55
30	0.17	0.70
30	0.149	0.82
30	0.18	0.60
100	0.080	1.0
102	0.177	0.92
	I_a 0.03×10^{-9} einstein/min cc	
3.35	0.032	0.22
9.8	0.032	0.62
29	0.033	0.90

Φ(cyclo-C_3F_6) is about 1.5. At all intensities the slopes of the log–log plots on Figure 3 of Φ(cyclo-C_3F_6) *vs.* (C_2F_4) are less than unity, indicating that the dependence of Φ(cyclo-C_3F_6) on (C_2F_4) is less than linear.

Table III: Mercury-Sensitized Photolysis of N_2O–C_2F_4 Mixtures at 150°; $N_2O \sim 500$ mm

(C_2F_4), mm	$R(N_2) \times 10^9$, moles/min cc	Φ(cyclo-C_3F_6)
$I_a \sim 2 \times 10^{-9}$ einstein/min cc		
0.39	1.44	0.053
0.66	1.6	0.073
1.0	2.6	0.095
2.53	1.73	0.16
5.5	1.92	0.25
8.7	1.7	0.30
9.2	1.92	0.37
9.5	1.76	0.29
10.5	5.8	0.72
18.5	1.8	0.27
18.5	2.1	0.33
28	1.12	0.85
30	2.9	0.77
33	2.4	0.87
40	4.2	0.59
40	3.8	0.77
40	...	0.93
52	1.12	0.81
61	1.0	1.08
80	3.2	0.82
80	3.2	0.42
90	1.2	1.15
100	4.0	0.87
100	4.8	0.69
100	2.3	1.15
100	3.2	1.0
104	1.68	1.4
125	1.87	1.35
$I_a \sim 0.5 \times 10^{-9}$ einstein/min cc		
1.1	0.65	0.093
1.65	0.38	0.21
2.9	0.80	0.25
8.6	0.73	0.53
31	0.75	0.94
101	0.68	1.5
$I_a \sim 0.2 \times 10^{-9}$ einstein/min cc		
0.71	0.21	0.20
0.84	0.139	0.27
0.95	0.21	0.20
1.18	0.175	0.58
1.6	0.22	0.34
2.85	0.160	0.50
3.5	0.23	0.46
9.8	0.147	0.75
10.3	0.25	0.67
30	0.28	1.18
30	0.172	0.50
31	0.150	0.88
98	0.21	1.6
100	0.174	1.27
100	0.096	1.15
100	0.067	0.96
150	0.22	1.5
$I_a \sim 0.03 \times 10^{-9}$ einstein/min cc		
1.0	0.027	0.53
3.0	0.037	0.77
9.35	0.036	1.15
31	0.033	1.66
99	0.035	1.8

Discussion

In this system, the initial photolytic act is excitation of the mercury vapor

$$Hg + h\nu \longrightarrow Hg^* \qquad (8)$$

The excited mercury atom might react with either N_2O or C_2F_4

$$Hg^* + N_2O \longrightarrow Hg + N_2 + O(^3P) \qquad (9)$$

$$Hg^* + C_2F_4 \longrightarrow Hg + 2CF_2 \text{ (singlet)} \qquad (10)$$

Reaction 9 is a well-known method for producing oxygen atoms and is the only reaction by which N_2O quenches Hg^*.[5] Reaction 10 is almost the only result of quenching Hg^* by C_2F_4.[6,7] A small fraction of the quenching leads to excited C_2F_4 molecules which can deactivate. However, in this work this process is negligible under all conditions and can be ignored. The relative rate constants k_9/k_{10} have been measured to be about 3.0 at room temperature.[1,8] We measured this ratio at elevated temperatures and found it to be insensitive to temperature.[9] In the experiments reported in this paper, the ratio $(N_2O)/(C_2F_4)$ was always greater than 3.0. Thus at least 90% of the quenching of the mercury was by reaction 9.

The oxygen atom produced then reacts exclusively with C_2F_4 to yield ultimately one molecule of CF_2O for every oxygen atom consumed. The possible reactions are (1), (4), and (5). At present we are unable to distinguish between (1) and (4), so we combine them into a composite reaction (11).

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

(6) B. Atkinson, *J. Chem. Soc.*, 2684 (1952).

(7) J. Heicklen, V. Knight, and S. A. Greene, *J. Chem. Phys.*, **42**, 221 (1965).

(8) A. J. Yarwood, O. P. Strausz, and H. E. Gunning, *ibid.*, **41**, 1705 (1964).

(9) Unpublished work of this laboratory.

$$O + C_2F_4 \longrightarrow CF_2O + CF_2 \qquad (11)$$

where the multiplicity of the CF_2 is unspecified.

If CF_2 radicals were the only precursors to cyclo-C_3F_6 formation (*i.e.*, reaction 5 is unimportant) and the only reactions of CF_2 are (2) and (3), then application of a stationary-state treatment to O atoms and to CF_2 radicals as determined by reactions 9, 2, 3, and 11 gives two limiting expressions for Φ(cyclo-C_3F_6), depending on the relative rates of reactions 2 and 3

$$\Phi(\text{cyclo-}C_3F_6) = 1 \qquad (R_2 < R_3) \qquad (12)$$

$$\Phi(\text{cyclo-}C_3F_6) = k_3\left(\frac{I_a}{2k_2}\right)^{1/2}(C_2F_4) \qquad (R_3 < R_2) \qquad (13)$$

Thus, Φ(cyclo-C_3F_6) would depend on the intensity and the C_2F_4 pressure ($R_2 > R_3$) or it would be independent of both variables ($R_3 > R_2$); it could not depend on one variable and be independent of the other. The data at 22° and C_2F_4 pressures less than 0.6 mm show that Φ(cyclo-C_3F_6) increases with C_2F_4 pressure but is unaffected by variations in the intensity. Thus another reaction must be playing a role; we presume it is reaction 5. Conversely, if reaction 5 were the only result of oxygen atom–C_2F_4 encounters, then

$$\Phi(\text{cyclo-}C_3F_6) = 1 \qquad (R_2 < R_3) \qquad (14)$$

$$\Phi(\text{cyclo-}C_3F_6) = k_3(C_2F_4)\left\{\frac{k_7}{2I_ak_2[k_6(C_2F_4) + k_7]}\right\}^{1/2} + \frac{k_6(C_2F_4)}{k_6(C_2F_4) + k_7} \qquad (R_3 < R_2) \qquad (15)$$

but at all pressures of C_2F_4 greater than 1 mm, $k_6(C_2F_4) > k_7$ as will be shown. Therefore, the last equation reduces to

$$\Phi(\text{cyclo-}C_3F_6) \cong 1 \qquad (16)$$

That is, Φ(cyclo-C_3F_6) would be unity under all conditions except at the very lowest C_2F_4 pressures. The results indicate that this is not the case. Thus, reaction 11 must participate. Henceforth, discussion is based on the mechanism consisting of reactions 2, 3, 5–9, and 11.

If we apply the steady-state approximation to (CF_2), (O), and ($C_2F_4O^*$), recognizing that reaction 7 is an unimportant source of CF_2 radicals, we obtain

$$\Phi(\text{cyclo-}C_3F_6) = 1.0 \qquad (R_2 < R_3) \qquad (17)$$

$$\Phi(\text{cyclo-}C_3F_6) = \frac{k_3(C_2F_4)}{I_a^{1/2}}\left[\frac{k_{11}}{2k_2(k_{11} + k_5)}\right]^{1/2} + \frac{k_5k_6(C_2F_4)}{(k_{11} + k_5)[k_6(C_2F_4) + k_7]} \qquad (R_3 < R_2) \qquad (18)$$

An important prediction of the mechanism is that in the high C_2F_4 pressure, low-intensity limit, Φ(cyclo-C_3F_6) = 1.0 as long as reaction 10 is negligible. Since we have defined Φ(cyclo-C_3F_6) as (cyclo-C_3F_6)/(N_2), then the actual limit for Φ(cyclo-C_3F_6) called Φ_∞(cyclo-C_3F_6), is

$$\Phi_\infty(\text{cyclo-}C_3F_6) = 1.0 + 2\frac{k_{10}}{k_9}\frac{(C_2F_4)}{(N_2O)} \qquad (19)$$

Under our experimental conditions, the last term on the right side of (19) can approach 0.20. At 22 and 95°, Φ_∞(cyclo-C_3F_6) is about unity, whereas at 150° it is about 1.5 compared to the theoretical limit of 1.2. Presumably this discrepancy reflects errors in our analytical procedure.

Equation 18 will hold reasonably well for Φ(cyclo-C_3F_6) $\leq$ 0.5 and will become more and more exact as Φ(cyclo-C_3F_6) decreases.

Let us first examine the results at 22°. For C_2F_4 pressures less than 30 mm, Φ(cyclo-C_3F_6) is independent of intensity. Consequently, the first term on the right side of (18) must be unimportant. At very low pressures, $k_7 \gg k_6(C_2F_4)$ and (18) reduces to

$$\Phi(\text{cyclo-}C_3F_6) \approx \frac{k_5k_6(C_2F_4)}{k_7(k_{11} + k_5)} \qquad (20)$$

In accordance with (20), Figure 1 shows that Φ(cyclo-C_3F_6) is proportional to (C_2F_4) at low C_2F_4 pressures and is independent of I_a. From the intercept of the log–log plot, $k_5k_6/k_7(k_{11} + k_5)$ is estimated to be 0.24 mm^{-1}. As the C_2F_4 pressure is raised, $k_6(C_2F_4) \gg k_7$, and (18) becomes

$$\Phi(\text{cyclo-}C_3F_6) \approx \frac{k_5}{k_{11} + k_5} \qquad (21)$$

Again, Figure 1 shows a large region where Φ(cyclo-C_3F_6) is independent of (C_2F_4) and I_a. The ratio $k_5/(k_{11} + k_5)$ is 0.15. Finally, at higher pressures eq 18 can be rearranged to yield

$$I_a^{1/2}\left[\Phi(\text{cyclo-}C_3F_6) - \frac{k_5}{k_{11} + k_5}\right] = k_3(C_2F_4)\left[\frac{k_{11}}{2k_2(k_{11} + k_5)}\right]^{1/2} \qquad (22)$$

Using the value of 0.15 for $k_5/(k_{11} + k_5)$, we can compute the left side of (22) [$I_a = R(N_2)$], and in Figure 4 it is plotted *vs.* (C_2F_4). The data are limited (only values for Φ(cyclo-C_3F_6) between 0.2 and 0.5 are used) and are scattered. Nevertheless, we force the best straight line of slope unity through the points and from the intercept estimate $k_3/k_2^{1/2}$ to be 1.0 × 10^{-2} (l./mole

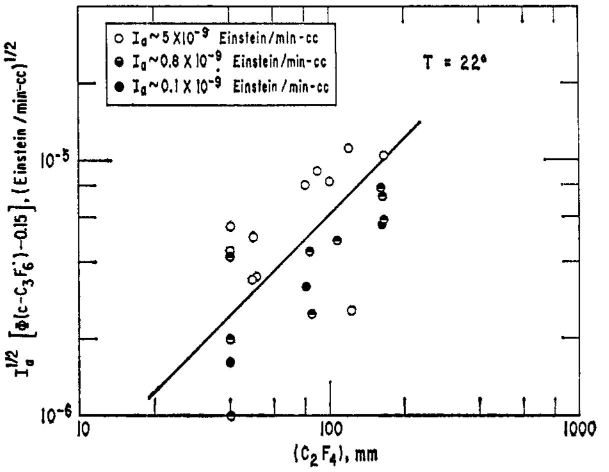

Figure 4. Plot of $I_a^{1/2}[\Phi(\text{cyclo-}C_3F_6) - 0.15]$ *vs.* (C_2F_4) at 22° for values of $\Phi(\text{cyclo-}C_3F_6) < 0.5$.

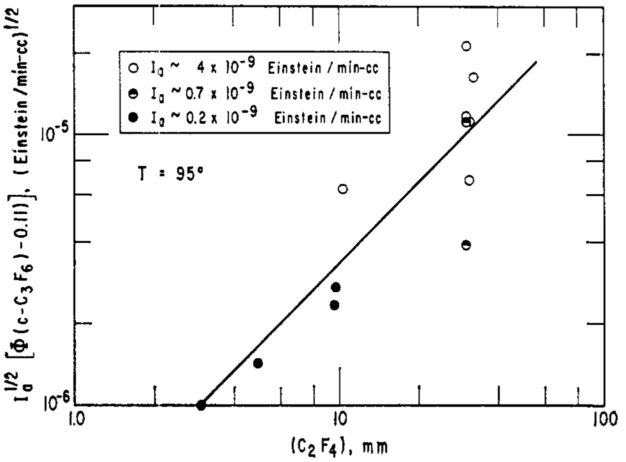

Figure 5. Plot of $I_a^{1/2}[\Phi(\text{cyclo-}C_3F_6) - 0.11]$ *vs.* (C_2F_4) at 95° for values of $\Phi(\text{cyclo-}C_3F_6) < 0.5$.

sec)$^{1/2}$. This estimate is probably good to about a factor of 2.

At 95° the same analysis can be made as at 22°. The very low-pressure region was not reached, and $k_5k_6/k_7(k_{11} + k_5)$ cannot be estimated. The flat region in Figure 2 is below 4 mm and yields a value of about 0.11 for $k_5/(k_{11} + k_5)$. The left side of (22) is plotted *vs.* (C_2F_4) in Figure 5, and again the best straight line of unit slope if forced through the badly scattered data. The estimate of $k_3/k_2^{1/2}$ at 95° is 3.1 × 10^{-2} (l./mole sec)$^{1/2}$.

At 150°, Figure 3 shows that there is no intensity-independent region. Consequently, the first term on the right side of (18) must always be important. However, there is no region where $\Phi(\text{cyclo-}C_3F_6)$ is proportional to (C_2F_4), so the second term on the right side of (18) must also play a role. In fact, $k_5/(k_{11} + k_5)$ must be about 0.10. If it were much smaller, then there would be a linear region for $\Phi(\text{cyclo-}C_3F_6) \sim 0.3$; but if it were much larger, then there would be a linear region for $\Phi(\text{cyclo-}C_3F_6) < 0.10$. If we use a value of about 0.10 for $k_5/(k_{11} + k_5)$, then $k_5k_6/k_7(k_{11} + k_5)$ must be similar to that at room temperature and $k_3/k_2^{1/2}$ can be estimated from the appropriate plot, Figure 6, based on eq 22. The estimate is 0.13 (l./mole sec)$^{1/2}$.

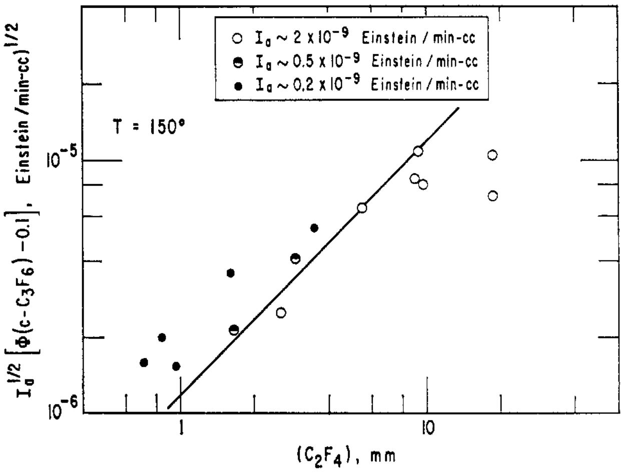

Figure 6. Plot of $I_a^{1/2}[\Phi(\text{cyclo-}C_3F_6) - 0.10]$ *vs.* (C_2F_4) at 150° for values of $\Phi(\text{cyclo-}C_3F_6) < 0.5$.

Table IV summarizes the rate constant data. Reactions 5 and 11 are the competing reactions for the highly exothermic O + C_2F_4 reaction. The chemical energy greatly exceeds any thermal energy, and the activation energy is only about 0.6 kcal/mole;[2] thus temperature variations should have little effect on the rates. However, if there is any effect it should be such that reaction 11 is favored with increasing temperature, as the $C_2F_4O^*$ would be more unstable. Our results agree with expectation. Reactions 6 and 7 are highly exothermic, and no temperature effect would be expected for them. Again our crude results agree with this hypothesis. The ratio k_6/k_7 is about 2.0 mm^{-1}, so reaction 7 is unimportant for C_2F_4 pressures in excess of 1 mm. Reaction 3 might well have an activation energy, and thus $k_3/k_2^{1/2}$ could be markedly enhanced at elevated temperatures. In fact, this occurs, and Table IV shows a comparison of the ratio obtained with that obtained in another study for singlet CF_2 radicals. Within experimental error, the results are identical.

We may now address ourselves to the question of what is the nature of the excited species designated $C_2F_4O^*$. Thermochemical considerations indicate that $C_2F_4O^*$ has at least 70 kcal/mole excess energy over the ground state. If all this energy appeared as vi-

Table IV: Rate Constant Data

Temp, °C	$k_5/(k_{11} + k_5)$	$k_6k_5/[k_7(k_{11} + k_5)]$, mm^{-1}	$10^3 \times k_3/k_2^{1/2}$ (l./mole sec)$^{1/2}$ This work	$10^3 \times k_3/k_2^{1/2}$ (l./mole sec)$^{1/2}$ Ref 4
22	0.15	0.24	10.0	4.3
95	~0.11	...	31	40
150	~0.10	[a]	130	130

[a] Similar to value at 22°.

brational energy, $C_2F_4O^*$ would never be stabilized under our conditions and would always dissociate. Consequently, $C_2F_4O^*$ must be an excited electronic level, presumably a triplet in accordance with the spin conservation rules.

Finally we return to the problem of the multiplicity of the CF_2 radicals formed in reaction 11. Originally, the suggestion that the CF_2 radicals in this system were triplets was based on their excessive reactivity with C_2F_4 and O_2. However, the results of this study have shown that their reactivity toward C_2F_4 is identical with that for singlet CF_2 radicals. Thus if they are triplets, the evidence must rest on the reactivity with O_2. The appropriate experiments are being conducted in the Aerospace Laboratories, and will be the subject of a future report.

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Photolysis of Methyl Iodide in the Presence of Nitric Oxide

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Methyl iodide was photolyzed in the presence of NO at room temperature. Iodine is both a primary and secondary product. Nitrosomethane is a primary product, while $(CH_3NO)_2$, NO_2, CH_3ONO, N_2, and N_2O are secondary products, and CH_3ONO_2, CH_2O, and HNO_2 are tertiary products. The complete reaction sequence is given. Methyl iodide enters the chain step to give CH_3O radicals. The important steps in removing CH_3NO are $2CH_3NO \rightarrow (CH_3NO)_2$ and $CH_3NO + NO \rightarrow CH_3O + N_2O$. The rate constants for both reactions were obtained and are tabulated with several other rate constants. Where comparisons could be made with existing results, agreement was good.

I. Introduction

The methyl radical addition to nitric oxide has been studied extensively, and the rate constant is reasonably well known.[1-6] The adduct has been observed by the use of infrared analysis[7] as well as mass spectral analysis.[8]

Nitrosomethane can be removed in a number of reactions. If the NO pressure is sufficiently low that all methyl radicals are not scavenged by NO, then two methyl radicals can react with CH_3NO. Such a reaction was proposed by Hoare[6] to account for the fact

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(1) R. W. Durham and E. W. R. Steacie, *J. Chem. Phys.*, **20**, 582 (1952).

(2) F. P. Lossing, K. V. Ingold, and A. W. Tickner, *Discussions Faraday Soc.*, **14**, 34 (1953).

(3) W. A. Bryce and K. V. Ingold, *J. Chem. Phys.*, **23**, 1968 (1955).

(4) M. I. Christie, *Proc. Roy. Soc.* (London), **A249**, 248 (1958).

(5) W. C. Sleppy and J. G. Calvert, *J. Am. Chem. Soc.*, **81**, 769 (1959).