# Rate Parameters for Reaction of Oxygen Atoms with $C_2F_4$ , $CF_2CFCl$ and $CF_2CCl_2$

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Ground-state  $CF_2$  was monitored by kinetic spectroscopy after long wavelength flash photolysis of  $C_2F_4+NO_2+N_2$  mixtures and was ascribed as a product of the overall reaction

 $O(2^{3}P)+C_{2}F_{4}\rightarrow CF_{2}O+CF_{2}.$ 

(1)

From the decrease in the CF<sub>2</sub> yield in competitive systems, rate constants relative to  $k_1$  were determined for CF<sub>2</sub>CFCl and CF<sub>2</sub>CCl<sub>2</sub>. The reactivities of the chlorofluoroethylenes show a similar trend with ionization potential to that established for hydrocarbon olefins. From preliminary measurements of the overall decomposition of C<sub>2</sub>F<sub>4</sub> flashed in O<sub>2</sub> at 25°C, it is proposed that singlet CF<sub>2</sub> reacts with O<sub>2</sub> about 0.2 times as rapidly as with C<sub>2</sub>F<sub>4</sub>. Although there was no direct evidence for triplet CF<sub>2</sub> molecules formed in (1), the results are consistent with an earlier analysis of continuous photolysis experiments, if CF<sup>\*</sup><sub>2</sub> is rapidly relaxed in collisions with NO<sub>2</sub> or NO.

Reactions of ground-state oxygen atoms with tetrafluoroethylene and perfluoropropene have been studied by Heicklen and collaborators <sup>1,2</sup> and those with some partially fluorinated olefins by Moss and Jennings.<sup>3, 4</sup> The reactivities of fluoroolefins compared to the corresponding hydride at first decrease with substitution of F atoms adjacent to the double bond, but further substitution apparently reverses this trend so that  $C_2F_4$  and  $C_2H_4$  are about equally reactive at room temperature. Saunders and Heicklen <sup>1</sup> studied the Hg-sensitized decomposition of N<sub>2</sub>O in the presence of  $C_2F_4$  and found that, in the absence of O<sub>2</sub>, the yields of CF<sub>2</sub>O and N<sub>2</sub> were equal. With small partial pressures of O<sub>2</sub> present, tetrafluoroethylene epoxide could also be isolated, and the yield of CF<sub>2</sub>O was tripled. It was proposed that the reaction O+C<sub>2</sub>F<sub>4</sub> forms *triplet* CF<sub>2</sub> (85 %) and an excited C<sub>2</sub>F<sub>4</sub>O (15 % at 23°C)<sup>2</sup> and that both species react with O<sub>2</sub>.

Long-wavelength flash-photolysis of NO<sub>2</sub> is a convenient <sup>6, 7</sup> source of O(2<sup>3</sup>P). Preliminary experiments with  $C_2F_4 + NO_2 + N_2$  mixtures <sup>8</sup> showed that ground state CF<sub>2</sub> molecules were present immediately after the photoflash and that CF<sub>2</sub> was not formed from CF<sub>2</sub>CFCl or CF<sub>2</sub>CCl<sub>2</sub>. These reactions have been studied further, to establish whether or not triplet carbenes are formed, and because photometry of the CF<sub>2</sub> bands provides a simple method of measuring relative rate constants in competitive systems.

#### EXPERIMENTAL

The flash-photolysis apparatus was of conventional design, with a quartz photolysis flashlamp mounted parallel to a reaction cell 80 cm in length. A Pyrex cell was used in all experiments where it was necessary to restrict photolytic light to  $\lambda > 300$  nm, to prevent direct photolysis of the olefins and to avoid formation of excited O atoms by photolysis of NO<sub>2</sub>. Photolytic flash energies were 1065-1650 J, and the energy of the spectroscopic flash was 100 J. The intensities of the flashes decayed to half their maximum values in 40 and 10 µsec after initiation, respectively. The complete cell, photolamp and reflector assembly

was surrounded by a furnace which could be heated electrically to  $\sim 150^{\circ}$ C and the temperature at various points along the cell could be measured by a thermocouple. Spectra were photographed in a Hilger Quartz Littrow spectrograph on Ilford HP3 plates, which were developed in Ilford Contrast FF developer (diluted 1+4) for 3 min. Plates were photometered with a Joyce-Loebl double-beam recording microdensitometer (model E12 mk III).

Preliminary experiments with a calibrated step-wedge established that the plate density varied linearly with logarithmic exposure in the density range obtained. Four bands of CF<sub>2</sub> were measured, all arising from molecules with no quanta of vibrational energy <sup>9</sup> and with  $v'_2 = 7$  (246 nm), 6 (249 nm), 4 (255 nm) and 3 (258 nm). The shorter wavelength bands are more intense, but could not be measured on all plates because of inadequate background intensity, particularly in the experiments with CF<sub>2</sub>CCl<sub>2</sub>. Fig. 1 compares the CF<sub>2</sub> peak heights in experiments when C<sub>2</sub>F<sub>4</sub>+NO<sub>2</sub>+N<sub>2</sub> mixtures were flashed in the whole cell and with half the cell blanked off. When an absorber is so dilute that pressure broadening is determined only by diluent molecules, the exponents of *l* and *c* in the Beer-Lambert relationship must be equal; fig 1 shows that, within experimental error, these exponents are unity for all the bands measured here. A similar conclusion was reached by Dalby,<sup>10</sup> who monitored CF<sub>2</sub> absorption at 248.8 nm photoelectrically.



Peak height (mm) with 40 cm pathlength

FIG. 1.—Comparison of CF<sub>2</sub> peak heights for pathlengths of 80 and 40 cm.  $\lambda$ (nm)  $\bigcirc$ , 255;  $\triangle$ , 258;  $\Box$ , 246; and  $\blacksquare$ , 249.

Even at room temperature and a few torr total pressure, the colour of  $NO_2$ +fluoroethylene mixtures bleached in 4-5 h. (Haszeldine <sup>11</sup> has described addition reactions of  $NO_2$  to fluorinated ethylenes at 50-65°C and higher total pressures.) Gas mixtures were therefore prepared immediately before photolysis in a glass vessel fitted with an electrically driven stirrer, pressures being measured by means of a glass spiral gauge of sensitivity 1·4 : 1. The preparation of the four-component gas mixtures probably introduces the major experimental uncertainties here. In the high temperature studies, there was no difference in CF<sub>2</sub> yield from mixtures which had been allowed to stand at 146°C for various periods up to 5 min, and therefore reaction of  $NO_2$  with the olefins is unimportant under these conditions. In all experiments in which relative rate parameters were measured, the



FIG. 2.—Variation with time of CF<sub>2</sub> bands after flash photolysis of mixtures containing 0.09 torr NO<sub>2</sub>, 2.0 torr C<sub>2</sub>F<sub>4</sub> and (a) 48 torr N<sub>2</sub> (b) 25 torr O<sub>2</sub> and 23 torr N<sub>2</sub>. Flash energy 1350 J, Pyrex cell.

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partial pressure of NO<sub>2</sub> was 0.09 torr and the total pressure was made up to 50 torr by addition of N<sub>2</sub>, in order to minimize flash heating of the reaction mixtures.

Continuous photolysis was carried out in 1 l. Pyrex bulbs placed a few inches from a 60 W electric lamp, and products were sought by infra-red analysis with a Perkin-Elmer 257 spectrophotometer. Although the colour of NO<sub>2</sub> vanished rapidly on irradiation of mixtures with each of the fluoroethylenes, the only product identified was CF<sub>2</sub>O, from C<sub>2</sub>F<sub>4</sub>. CF<sub>2</sub>O, CFClO and CCl<sub>2</sub>O were not detected in photolyzed CF<sub>2</sub>CFCl or CF<sub>2</sub>CCl<sub>2</sub>+NO<sub>2</sub> mixtures.

#### MATERIALS

Tetrafluoroethylene was obtained by destructive distillation of degassed polymer; the products were first distilled from 196°K and then from 147°K. The final fraction contained about 1 % of perfluoropropylene, which is relatively inert to attack by  $O(2^{3}P)^{2}$ .

Nitrogen dioxide and CF<sub>2</sub>CFCl (Matheson) and CF<sub>2</sub>CCl<sub>2</sub> (Phase Separations Ltd.) were degassed and distilled on the vacuum line. No impurities were detected by infra-red analysis of these reagents. Nitrous oxide, ethylene (B.O.C. grade X) and SF<sub>6</sub> (I.C.I.) were degassed and used without further purification. N<sub>2</sub> (B.O.C., O<sub>2</sub> free) and O<sub>2</sub> (B.O.C.) were dried before use by slow passage through a packed trap at 77°K.

#### RESULTS

#### FORMATION OF GROUND STATE $CF_2$

Fig. 2 shows kinetic absorption spectra of the CF<sub>2</sub> bands after flashing  $C_2F_4$ + NO<sub>2</sub>+N<sub>2</sub> or  $C_2F_4$ +NO<sub>2</sub>+O<sub>2</sub> mixtures. The rate of appearance of CF<sub>2</sub> and the final intensity were not affected by addition of up to 200 torr O<sub>2</sub>, 40 torr SF<sub>6</sub> or 100 torr N<sub>2</sub>O. With 37.5 torr  $C_2F_4$ , 0.04 torr NO<sub>2</sub> and 700 torr O<sub>2</sub>, the CF<sub>2</sub> intensity was decreased by 25 %, relative to a mixture with 700 torr N<sub>2</sub> in place of the O<sub>2</sub>. Under these conditions, the reaction O+O<sub>2</sub>+O<sub>2</sub>→O<sub>2</sub>+O<sub>3</sub> is expected to be ~0.4 times as fast as O+C<sub>2</sub>F<sub>4</sub>, in agreement with the observed decrease in CF<sub>2</sub> yield. The constancy of the peak heights with various diluents also shows that the pressure broadening of the CF<sub>2</sub> bands varies little for the gases and pressures employed.

It was assumed that the  $CF_2$  formed by the pseudo-first order decay of O atoms or an excited species and  $\ln [(CF_2)_{t'} - (CF_2)_t]$  was plotted against t (where t' is a delay time ~200  $\mu$ sec.) The  $CF_2$  intensity did not decrease appreciably from its maximum value in 1 msec after the flash. Despite the large scatter, satisfactory straight lines were obtained (fig. 3) and fig. 4 illustrates the variation of the measured gradients with  $C_2F_4$  concentration. The data of fig. 4 are consistent with the scheme:

$$O(2^{3}P) + C_{2}F_{4} \rightarrow CF_{2}O + CF_{2}$$

$$\tag{1}$$

$$O(2^{3}P) + NO_{2} \rightarrow NO + O_{2}$$
<sup>(2)</sup>

and agree well with the published values of  $k_1^{1}$  and  $k_2^{6}$ , at low partial pressures of  $C_2F_4$ , assuming 30 % decomposition of the NO<sub>2</sub> during the flash. At higher  $C_2F_4$  concentrations,  $CF_2$  appearance follows the "tail" of the photoflash, corresponding to  $k_{\text{effective}} = 5 \times 10^4 \text{ sec}^{-1}$ . Singlet  $CF_2$  must therefore form either directly or by rapid deactivation of an excited species.

The absolute  $CF_2$  yield was measured approximately by comparing the  $CF_2$ intensities with those from  $CF_2CFCl$  or  $CF_2CCl_2$  (when these olefins were flashed in a quartz cell). The extents of decomposition were taken to be the ratios of  $CF_2$ intensities in repeatedly flashed single mixtures. In one flash, 30 % of a mixture containing 0.09 torr NO<sub>2</sub>, 37.5 torr  $C_2F_4$  and 12.4 torr N<sub>2</sub> was decomposed, and the  $CF_2$  peak heights (at 199  $\mu$ sec delay) were 0.6 those from 2.0 torr  $CF_2CFCl$  (in 48 torr N<sub>2</sub>) and 1.0 times those from 1.0 torr  $CF_2CCl_2$  (in 49 torr N<sub>2</sub>). The extents of decomposition of the olefins were estimated to be respectively 3 and 6 %, leading to values of 0.036 and 0.06 torr for the partial pressure of  $CF_2$  in the  $C_2F_4$ +NO<sub>2</sub>

mixture. These estimates are probably high because CFClCFCl and  $C_2Cl_4$  are ultimate products of the photolyses <sup>12, 13</sup> as well as polymers, which lead to overestimation of the extent of decomposition. Furthermore, the absorption spectrum



FIG. 3.—Variation with time of CF<sub>2</sub> concentration. Partial pressures (torr): 0.045 NO<sub>2</sub> and 0.5, •; or  $\Box$ ,  $\blacksquare$ , 1.1 C<sub>2</sub>F<sub>4</sub>. 0.09 NO<sub>2</sub> and  $\triangle$ ,  $\blacktriangle$  2.0,; or  $\bigcirc$ ,  $\bigcirc$ , 4.5 C<sub>2</sub>F<sub>4</sub>.



FIG. 4.—Dependence of rate of  $CF_2$  formation on concentration of  $C_2F_4$ . 0.09 torr  $NO_2$ , total pressure 50 torr  $\bigcirc$  (N<sub>2</sub>) or  $\bigcirc$  (SF<sub>6</sub>); 0.045 torr  $NO_2$ , total pressure 25 torr  $N_2$ ,  $\triangle$ .

of CCl can be observed strongly after flashing  $CF_2CCl_2$ ,<sup>12</sup> and so the quantum yield of  $CF_2$  is possibly less than unity. The overestimation of  $CF_2$  yields will be partly compensated if  $CF_2$  reacts rapidly with CFCl or  $CCl_2$ . The analysis of the continuous photolysis experiments <sup>1</sup> suggest that there is an 85% yield of  $CF_2^*$  from reaction (1) at 23°C, in good general agreement with the approximate measurement made here.

#### RELATIVE RATE CONSTANTS FOR REACTIONS OF O ATOMS

Relative rate parameters were determined by measuring the  $CF_2$  yield when  $C_2H_4$ ,  $CF_2CFCl$  or  $CF_2CCl_2$  were present to compete with  $C_2F_4$  for O atoms. The chlorinated olefins absorb only weakly in the region of the  $CF_2$  bands, and do not form  $CF_2$  on flashing with NO<sub>2</sub> either at 296 or 419°K. If all the O atoms are removed by reactions (1), (2) and (3):

$$O + olefin \rightarrow products$$
(3)  
$$[CF_2]^{-1} = [CF_2]_0^{-1} (1 + \{k_2[NO_2] + k_3[R]\}/k_1[C_2F_4]),$$
(A)

where [R] is the concentration of competing olefin and  $[CF_2]_0$  is a constant, proportional to the number of O atoms produced in the cell. If  $k_3[R]/k_2$  is sufficiently large, only small errors arise from the change in  $[NO_2]$  due to photolysis and to consumption in (2). Although all the O atoms apparently release a  $CF_2$  molecule, the analysis will still be valid if only a fraction release  $CF_2$ , so long as this fraction remains constant within any experiment. There was no evidence for reaction of the initial adduct with  $C_2F_4$  or the other olefins at room temperature.

Results were derived in two ways: by plotting reciprocals of CF<sub>2</sub> peak heights either against [R], keeping  $[C_2F_4]$  fixed, or against  $1/[C_2F_4]$  with [R] constant within an experiment. The second method was necessary for the experiments with chlorinated olefins because they absorb light weakly in the region of the  $CF_2$  bands. With ethylene, experiments of each type were possible. In essence, the analysis of measurements consists of extrapolation to the intercept where  $[CF_2]^{-1} = 0$ . This intercept is the (negative) value of  $[C_2F_4]^{-1}$  or  $[C_2H_4]$  required to make the right-hand side of eqn. (A) equal to zero. Fig. 5-7 are typical plots, and fig. 8 and 9 show reciprocal intercepts plotted against [R], in experiments at 296  $(\pm 1)^\circ$  and 419  $(\pm 2)^\circ$ K. Because of the long extrapolations in some experiments, the values of the intercepts are accurate only to  $\pm 10$  %. At room temperature, the results for ethylene either at constant  $[C_2F_4]$  or constant  $[C_2H_4]$  agree well, confirming that the CF<sub>2</sub> has no precursor which can be scavenged by the olefin. The agreement of  $k_1 = (1.05 \pm 0.05)k_{C_2H_4}$  with the previous ratio  $(1\cdot 1\pm 0\cdot 1)^{1}$  at 296°K is good evidence that the CF<sub>2</sub> and CF<sub>2</sub>O monitored in the two sets of experiments are produced in the same process, which is presumably reaction (1). Experiments were also carried out with mixtures containing fixed amounts of  $C_2F_4$  and varying the  $C_2H_4$  at 419°K. The resulting graphs were adequately linear, but corresponding to  $k_1 = (0.3 \pm 0.1)k_{C_{2H_4}}$  which is much less than the value from measurement of CF<sub>2</sub>O,  $k_1 = 0.66k_{C_{2H_4}}$  at 398°K, indicating that CF<sub>2</sub> may react with  $C_2H_4$  or a product at this temperature. Since Saunders and Heicklen were able to measure the more stable product, their value for the relative rate constant at high temperatures is adopted, and provides absolute rate constants for the other olefins (table 1). Relative activation energies were calculated from the equation

$$E_{\rm rel} = R \left[ \frac{\ln k_{\rm rel_T} - \ln k_{\rm rel_{T'}}}{1/T' - 1/T} \right],$$

and the error limits quoted are derived from the standard deviations of the  $k_{rel}$  measurements shown on fig. 8 and 9.



FIG. 5.—Reciprocal relative yield of CF<sub>2</sub> against C<sub>2</sub>H<sub>4</sub> partial pressure (with C<sub>2</sub>F<sub>4</sub> constant) at 296°K.  $\bigcirc$ ,  $\bigcirc$ , 12.5; and  $\square$ ,  $\blacksquare$ , 6.25 torr C<sub>2</sub>F<sub>4</sub>;  $\bigcirc$ ,  $\blacksquare$ , from band at  $\lambda$  249 nm; and  $\bigcirc$ ,  $\square$ , from band at 246 nm.



FIG. 6.—Reciprocal relative yield of CF<sub>2</sub> against  $[C_2F_4]^{-1}$ , at 296°K. CF<sub>2</sub>CCl<sub>2</sub>;  $\bullet$ , 12.5; and  $\bigcirc$ , 18.8 torr; CF<sub>2</sub>CFCl:  $\triangle$ , 9.4 torr;  $\blacktriangle$ , no other olefin.

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# FLASH PHOTOLYSIS OF $C_2F_4+O_2$ mixtures

If they are formed at all, triplet  $CF_2$  molecules must be relaxed rapidly. If they are never formed, the discrepancies between these results and the analysis of the continuous photolysis experiments indicate that  $O_2$  reacts either with excited  $C_2F_4$ 



FIG. 7.—Reciprocal relative yield of CF<sub>2</sub> against  $[C_2F_4]^{-1}$ , at 419°K. CF<sub>2</sub>CCl<sub>2</sub>: •, 12.5; and  $\bigcirc$ , 6.25 torr; CF<sub>2</sub>CFCl,  $\triangle$  12.5 torr;  $\blacktriangle$ , no other olefin.



FIG. 8.—Variation of reciprocal intercepts with olefin partial pressure, 296°K.  $\bigcirc$ , CF<sub>2</sub>CCl<sub>2</sub>;  $\bigcirc$ , CF<sub>2</sub>CFCl;  $\square$ , C<sub>2</sub>H<sub>4</sub>

molecules (possibly formed by recombination of  $CF_2$ ) or with singlet  $CF_2$ . This reaction could be more important than was realized,<sup>10</sup> if the spin-allowed and exothermic process

$$CF_2 + O_2 \rightarrow CF_2 O + O(2^3 P) \tag{4}$$

were followed rapidly by (1), regenerating  $CF_2$ . Reaction (4) is relatively slow, for  $CF_2$  decay is not appreciably affected by  $O_2$  in flashed  $CF_2CCl_2$  or  $CF_2CFCl^{13}$ 



olefin pressure (torr)

FIG. 9.—Variation of reciprocal intercepts with olefin partial pressure,  $419^{\circ}$ K.  $\bigcirc$ , CF<sub>2</sub>CCl<sub>2</sub>;  $\bigcirc$ , CF<sub>2</sub>CFCl.

TABLE 1.	-RATE	PARAMETERS	FOR	REACTIONS	OF	$O(2^{3}P)$	)
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olefin	k <sub>rel</sub> (296°K) ª	k <sub>rel</sub> (419°K) <sup>a</sup>	E <sub>rel</sub> (eV) <sup>a</sup>	A <sub>rel</sub> <sup>a</sup>	10 <sup>11</sup> A(cm <sup>3</sup> mol <sup>-1</sup> sec <sup>-1</sup> )	E(eV)	IP(eV)
C <sub>2</sub> F <sub>4</sub>	1	1	0	1	0.26	0.026	9.3 c
CF <sub>2</sub> CFCl	$0.51 \pm 0.04$	$1.36 \pm 0.10$	$0.087 \pm 0.015$	$15\pm9$	3.9	0.113	10·4 c
CF <sub>2</sub> CCl <sub>2</sub>	$0.67 \pm 0.06$	$0.95 \pm 0.10$	$0.030 \pm 0.015$	$2 \cdot 3 \pm 1 \cdot 5$	0.22	0.026	10·0 ¢
CF <sub>2</sub> CFCF <sub>3</sub>			0.069	0.2	0.13	0·095 b	
$C_2 H_4$	$0.95\pm0.05$		0.039	4.4	1.15	0·065 <sup>b</sup>	10.6

(a),  $k_{rel} = k_{olefin}/k_{C_2F_4}$ ;  $E_{rel} = E_{olefin} - E_{C_2F_4}$ ;  $A_{rel} = A_{olefin}/A_{C_2F_4}$ ; (b), data of ref. (1); (c), data of ref. (23).

which do not reform  $CF_2$  in analogues of reaction (1). This scheme was discounted by Heicklen, Knight and Greene <sup>14</sup> who studied the Hg-sensitized oxidation of  $C_2F_4$ and found that at high pressures of  $C_2F_4$ , the yield of oxidation products did not increase markedly with  $O_2$  pressure. Nevertheless, it was decided to seek for this reaction by comparing  $CF_2$  intensities in repeatedly flashed single samples of  $C_2F_4$ 

diluted in  $O_2$ ,  $N_2$  or  $O_2 + N_2$  mixtures (fig. 10). If  $CF_2$  is removed only by reactions (5) and (6):

$$CF_2 + CF_2 \rightarrow C_2F_4 \tag{5}$$

$$CF_2 + C_2F_4 \rightarrow cyclo - C_3F_6 \tag{6}$$

all of which are slow compared to the lifetime of the photoflash, the ratio of the overall extent of decomposition of  $C_2F_4$  with and without added  $O_2$  equals  $1+2k_4[O_2]/3k_6[C_2F_4]$ .

Decomposition of mixtures with  $O_2$  was increased relative to those with  $N_2$ , and continuous absorption built up below 270 nm in the repeatedly flashed samples. At the same time, emission lines from the photolamp were *enhanced*, showing that the continuum is due to scattering of light, presumably by a solid product. Solid



number of previous flashes

FIG. 10.—[CF<sub>2</sub>] yield in repeatedly flashed  $C_2F_4$  mixtures with  $N_2$  and  $O_2$ . 1 %  $C_2F_4$  with  $\bigoplus$ , 99;  $\bigoplus$ , 25; or  $\blacktriangle$ , 0 torr  $O_2$ , total pressure 100 torr; 1 %  $C_2F_4$  with  $\bigoplus$ , 24.8;  $\bigcirc$ , 6.3; or  $\triangle$ , 0 torr  $O_2$ , total pressure 25 torr.

polymers were formed also in Hg-sensitized  $C_2F_4+O_2$  systems.<sup>15</sup> The continuum was much reduced in intensity by decreasing the  $C_2F_4$  and  $O_2$  partial pressures, and data from several experiments at 25°C suggest  $k_4 \sim 0.2 k_6$ , assuming that no product absorbs significantly in the region of the  $C_2F_4$  spectrum (i.e., ~200 nm).

Repeatedly flashed samples were passed slowly through packed traps at 77°K, in order to condense products and unchanged  $C_2F_4$ , and the trapped residues were then distilled into infra-red cells. In one experiment, 3·4 µmoles of CF<sub>2</sub>O were retained from a mixture containing originally 0·5 torr  $C_2F_4$  and 25 torr each of  $N_2$ and  $O_2$  and flashed 7 times (total energy 6000 J); (the extinction coefficient of CF<sub>2</sub>O at 5·12 µ was taken to be 205 M<sup>-1</sup> cm<sup>-1</sup>, from ref. (1)). About 12 % of the original  $C_2F_4$  was converted to CF<sub>2</sub>O. The yield of CF<sub>2</sub>O was the same for a similar mixture with the total pressure increased to 780 torr by addition of N<sub>2</sub>, showing that the CF<sub>2</sub>O does not form from vibrationally-excited  $C_2F_4$  or CF<sub>2</sub>. Although perfluorocyclopropane is a stronger absorber in the infra-red than CF<sub>2</sub>O,<sup>1</sup> it was not detected in

the experiments either with or without  $O_2$  present; this is consistent with the slow rate of reaction (6) compared to (5), with small partial pressures of  $C_2F_4$ .

Values for  $k_6/(k_5)^{\frac{1}{2}}$  have been derived by Cohen and Heicklen <sup>16</sup> from Hgsensitized decomposition of  $C_2F_4$ , and by Atkinson and McKeagan <sup>15</sup> from thermal decomposition of perfluorocyclopropane. With the absolute value of  $k_5$  reported by Dalby,<sup>10</sup> the respective values of  $k_6$  at 25°C become 40 and 95 M<sup>-1</sup> sec<sup>-1</sup> and therefore  $k_4 \sim 13$  M<sup>-1</sup> sec<sup>-1</sup>.

#### DISCUSSION

# photolysis of $NO_2$ in presence of $C_2F_4$

Smith <sup>6, 7</sup> has discussed the flash photolysis of NO<sub>2</sub> as a source of  $O(2^{3}P)$  and measured the relative importance of the reactions

$$O + NO_2 \rightarrow NO + O_2$$

$$O + CS_2 \rightarrow CS + SO$$

in mixtures containing  $CS_2$ , by photometering the absorption bands of CS.  $CS_2$  proved an excellent monitor for O atom reactions because of the high absorption intensity and low reactivity of CS. One difficulty was that the CS was initially vibrationally excited and relaxed relatively slowly; this problem does not arise for  $CF_2$ , which partly compensates for the weaker bands that it is necessary to measure. A further advantage in working with  $C_2F_4$  is that, unlike  $CS_2$ , there is no long wavelength absorption system which could lead directly to photolysis or, as with  $CS_2$ , to production of reactive excited molecules..

Besides photolysis, long wavelength irradiation of NO<sub>2</sub> produces long-lived metastable molecules with a radiative lifetime of 44  $\mu$ sec at 4348 Å.<sup>17, 18</sup> Complex molecules are efficient deactivators, and possibly most of the NO<sub>2</sub><sup>\*</sup> is deactivated by C<sub>2</sub>F<sub>4</sub> at a rate limited by the collision frequency. Experiments with added N<sub>2</sub>O or SF<sub>6</sub>, which are also rapid deactivators <sup>17</sup> show that there is no significant yield of CF<sub>2</sub> due to such reactions, however. Furthermore, the measurement of the absolute yield of CF<sub>2</sub>, though approximate, and the rate constant determined relative to C<sub>2</sub>H<sub>4</sub> show that CF<sub>2</sub> forms from O-atom reactions; thus NO<sub>2</sub> decomposition is by photolysis and not by reaction with C<sub>2</sub>F<sub>4</sub>.

Cvetanović<sup>5</sup> noted that NO<sub>2</sub> reacts rapidly with isobutene epoxide, and it also might react with the chlorofluoroethylene epoxides. The initial adduct of  $O + C_2F_4$  is apparently too short lived to react significantly with NO<sub>2</sub>. In any case the kinetic analysis will hold, so long as a fixed fraction of  $C_2F_4O^*$  yields  $CF_2$  in each set of experiments.

# MECHANISM OF REACTION OF $O(2^{3}P)$ with $C_{2}F_{4}$

Using the Hg-sensitized decomposition of  $N_2O$  as source of atomic oxygen, Heicklen and collaborators have studied the reaction of  $O+C_2F_4$ . In the absence of  $O_2$  the quantum yield of  $CF_2O$  is unity, and by monitoring the  $CF_2O$  in competitive systems, rate parameters were derived for reactions of O atoms with hydrocarbon olefins <sup>1</sup> which agree excellently with previously published data.<sup>5</sup> The relative rate constant  $k_1/k_{C_2H_4}$  measured here is in close agreement with the results of Saunders and Heicklen,<sup>1</sup> confirming that the overall reaction (1) accounts for most of the O atoms. In a mechanism which fitted most features of the continuous photolysis

experiments,<sup>14, 16, 19, 20</sup> both with and without added  $O_2$ , two primary steps were proposed :

$$O + C_2 F_4 \rightarrow CF_2 O + CF_2^* \tag{1a}$$

$$\mathbf{O} + \mathbf{C}_2 \mathbf{F}_4 \to \mathbf{C}_2 \mathbf{F}_4 \mathbf{O}^{**}. \tag{1b}$$

At 23°C, (1*a*) accounts for 85 % of the O atoms, and the remainder form an excited epoxide, which reacts readily with  $C_2F_4$  or  $O_2$ . No direct evidence was found here for the presence or absence of long-lived  $C_2F_4O^{**}$  molecules; they are presumably scavenged by  $C_2F_4$  or  $O_2$  and never release  $CF_2$ .

The formation of *triplet*  $CF_2$  molecules was postulated partly to conform with spin conservation in (1*a*), and also to explain the increase in  $CF_2O$  yield with added  $O_2$ ; singlet  $CF_2$  was thought completely inert towards reaction with  $O_2$ . Relative rate constants for recombination and reaction with  $C_2F_4$  of the  $CF_2$  were equal to the value for singlet  $CF_2$ ,<sup>20</sup> showing that the triplet  $CF_2$  is rapidly relaxed. The reactivity towards  $O_2$  was considered to show that the  $CF_2$  was initially formed in an excited state. In the flash photolysis experiments the singlet  $CF_2$  appears more rapidly than triplet-triplet annihilation:

$$CF_2^* + CF_2^* \rightarrow CF_2 + CF_2 \tag{1c}$$

which could occur at a maximum rate corresponding to 2/9 the collision frequency.  $NO_2$  and NO are inevitably present in the flash-photolyzed mixtures and the rapid formation of singlet  $CF_2$  could be explained if  $CF_2^*$  is relaxed by NO<sub>2</sub> and NO at a rate greater than  $2 \times 10^{10}$  M<sup>-1</sup> sec<sup>-1</sup> (which is equivalent to one tenth of the collision rate). It was not possible to check if formation of singlet CF<sub>2</sub> was delayed with decreased partial pressures of  $NO_2$  since the  $CF_2$  bands were then too weak to be measured accurately. The experiments with 700 torr added  $O_2$  give an upper limit for the reaction rate of  $CF_2^*$  with  $O_2$  of  $6 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ , if less than 5 % of the CF<sub>2</sub><sup>\*</sup> was scavenged in processes not returning CF<sub>2</sub> to the system. Johnston and Heicklen <sup>20</sup> deduced an upper limit of  $6 \times 10^6$  M<sup>-1</sup> sec<sup>-1</sup> for this rate constant at  $23^{\circ}$ C, on the assumption that reaction (1c) occurs at every collision, and the true rate constant may be much smaller. If the rate constant for reaction (4) of singlet  $CF_2$ with  $O_2$  is 13 M<sup>-1</sup> sec<sup>-1</sup> it could not account for more than a few percent of the  $CF_2O$  yield under the conditions of the continuous photolysis studies, although it might be responsible for some of the scatter in the measured quantum yields. Vibrationally excited  $CF_2$  was not observed here or in flash-photolyzed  $C_2F_4$ , although in each case  $CF_2$  must originally bear large amounts of excess energy (~1.5 eV per  $CF_2$  group from  $C_2F_4$  photolyzed at 200 nm). This may indicate that  $CF_2$  itself, or  $C_2F_4$ , is an efficient deactivator of the "hot"  $CF_2$ .

# **REACTION OF O(2<sup>3</sup>P)** WITH CHLOROFLUOROETHYLENES

Absolute rate constants were derived from the relative rate constants for  $C_2H_4$  reported by Saunders and Heicklen<sup>1</sup> and

$$k_{C_{2H_4}} = (1.15)10^{-11} \exp(-0.065/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

(with the activation energy in eV) which was based on the results of Elias and Schiff<sup>21</sup> and Cvetanović.<sup>5</sup> The value of 0.065 eV for the activation energy has been confirmed by Smith,<sup>22</sup> but the value of the pre-exponential factor may be in error by  $\pm 50$  %. Table 1 shows that the chlorofluoroethylenes exhibit a similar trend in reactivity to that of the hydrocarbon olefins which was recognized by Cvetanović,<sup>5</sup> i.e., the activation energies correlate with the ionization potentials of the olefins. The recorded pre-exponential factors vary more than those of the hydrocarbons, and both Arrhenius

parameters for  $CF_2CFCl$  are abnormally high, which may indicate that secondary reactions remove  $CF_2$  in the high-temperature experiments. Reaction of  $CF_2^*$  with  $C_2H_4$  may also be significant at 146°C and contribute to the discrepancy between these results and those from the continuous photolysis studies.

Neither  $CF_2CFCI$  nor  $CF_2CCl_2$  release  $CF_2$  which is consistent with the observation of Haszeldine and Steele <sup>24</sup> that atom or free radical attack on  $CF_2CFCI$  occurs exclusively at the  $CF_2$  group. The absence of  $CF_2O$  as a product suggests that the epoxides are stabilized, in contrast to  $C_2F_4O^*$ , but subsequently react with NO<sub>2</sub>. There was no new infra-red absorption in the carbonyl or epoxide regions; although a number of weak bands were observed, their carriers were not identified.

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