PHOTO-OXIDATION OF CF$_2$ClBr AND COMPETITIVE REACTIONS OF CF$_2$Cl RADICALS WITH O$_2$, Br$_2$, Cl$_2$ AND HBr
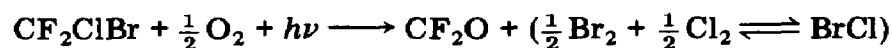
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Summary

The photo-oxidation of CF$_2$ClBr vapour was studied at 20 °C using light of wavelength 248 nm. The overall reaction is

$$CF_2ClBr + \tfrac{1}{2}O_2 + h\nu \longrightarrow CF_2O + (\tfrac{1}{2}Br_2 + \tfrac{1}{2}Cl_2 \rightleftharpoons BrCl)$$

The quantum yield of CF$_2$O is unity over a wide range of pressures of CF$_2$ClBr and O$_2$. The results are interpreted in terms of a mechanism involving the initiation steps

$$CF_2ClBr + h\nu \longrightarrow CF_2Cl + Br$$

$$CF_2Cl + O_2 + M \longrightarrow CF_2ClOO + M \tag{5}$$
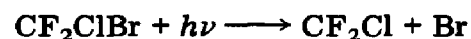
CF$_2$ClBr was also photolyzed with O$_2$ plus Br$_2$ or Cl$_2$ or HBr. Reaction (5) competed with each of the reactions

$$CF_2Cl + Br_2 \longrightarrow CF_2ClBr + Br \tag{10}$$

$$CF_2Cl + Cl_2 \longrightarrow CF_2Cl_2 + Cl \tag{11}$$

$$CF_2Cl + HBr \longrightarrow CF_2ClH + Br \tag{12}$$

The following were obtained at 20 °C: $k_5/k_{10} = 1.4 \pm 0.1$; $k_5/k_{11} = 39 \pm 3$; $k_5/k_{12} = 147 \pm 20$. From this data we estimate that $k_5 = 8.7 \times 10^{11}$ cm^3 mol^{-1} s^{-1}. There was no indication of a pressure dependence for reaction (5) at pressures above 23 Torr.

1. Introduction

The compound bromochlorodifluoromethane (CF$_2$ClBr) is sold commercially, mainly under the name BCF. Its major use is in fire extinguishers and hence it is eventually released into the atmosphere. BCF could thus contribute to stratospheric ozone depletion so its photochemistry and photo-oxidation are of particular interest. We have previously described an investigation of the photochemistry of BCF vapour at room temperature [1]

but no quantitative or mechanistic studies of the photo-oxidation of BCF have been reported. Francis and Haszeldine [2] showed that irradiation of BCF plus O_2 with light of wavelength greater than 220 nm gave the products CF_2O, CO_2, SiF_4 and Br_2. Kagiya et al. noted that the rate of photo-decomposition of ozone is increased if BCF is present [3].

We now report the results of a study of the photo-oxidation of BCF. Results on the competitive reactions of CF_2Cl radicals with O_2, Cl_2, Br_2 and HBr are also presented.

2. Experimental details

2.1. Materials

O_2 was dried by passage through $CaCl_2$ and P_2O_5. BCF, Cl_2, Br_2 and HBr were as in ref. 1. CF_2Cl_2 and CF_2ClH were from ICI Mond Division. No impurities were detected using gas–liquid chromatography (GLC) or IR spectroscopy.

CF_2O was made from CCl_2O by the method of Fawcett et al. [4], in which phosgene is bubbled through a stirred slurry of NaF in acetonitrile at 35 °C. All the reagents and apparatus were thoroughly dried before use. The acetonitrile was fractionally distilled under nitrogen. The products were passed through two traps at −80 °C to remove HF and CCl_2O and the CF_2O was collected at −196 °C. Traces of CCl_2O and CFClO were removed by distillation from −130 to −196 °C. The only detectable impurity in the distillate using GLC or IR spectroscopy was CO_2 which could not be removed from the CF_2O. The CF_2O content of the mixture was determined by measuring the fluorine content using a modification of the method of Strouts et al. [5]. A known amount of the CF_2O–CO_2 mixture was dissolved in 1 M NaOH under vacuum to produce Na_2CO_3 plus NaF. The fluoride ion was determined by titration of the solution (buffered at pH 3.0) against 0.004 M thorium nitrate which was standardized with sodium fluoride solution. The CF_2O–CO_2 sample was found to contain 78.2 mol.% CF_2O. It was stored at −196 °C.

2.2. Apparatus

The apparatus used was mainly as in ref. 1. Photolyses were performed at 20 ± 2 °C in one of two reaction vessels. Vessel A was a cylinder made of silica with Suprasil windows, of length 97 mm, internal diameter 48 mm and volume 187.2 cm^3. Reaction vessel B was in the form of a cross with two opposite NaCl windows and two opposite silica windows, all attached with Apiezon wax. The path length was 65 mm between the NaCl windows and 67 mm between the silica windows. The volume was 124.8 cm^3. A parallel beam of light from an A.E.G. Wotan 200 W HBO W/2 high pressure mercury lamp was used for the photolyses. The beam passed through two filters. The first consisted of a silica cell containing a drop of mercury plus 300 Torr cis-but-2-ene vapour to remove any unreversed emission from the lamp at

253.7 nm. The second filter was aqueous cyanine perchlorate. The light then traversed the reaction vessel after which it passed through a $NiSO_4$–$CoSO_4$ solution and a Chance–Pilkington OX7 filter. The intensity of the emergent monochromatic radiation at 248 nm was monitored. Further information on the filters and monitoring are given in ref. 1. The transmittance of the first two filters together with the absorption spectrum of BCF ensured that 248 nm radiation alone caused photolysis.

3. Results of preliminary photolyses

Initial photolyses of mixtures of BCF and O_2 were carried out in vessel B so that IR spectra could be recorded at intervals during the photolysis of a given mixture. During a 2 h photolysis of 25 Torr BCF plus 25 Torr O_2, the distinctive IR absorptions of CF_2O appeared. There were no other new peaks. Unlike Francis and Haszeldine [2], we found no CO_2 or SiF_4. Next, 10 Torr BCF plus 10 Torr O_2 were photolyzed for 10 h, with the UV–visible spectra recorded at intervals using a Cary 17 spectrophotometer. An absorption developed with λ_{max} = 380 nm. After photolysis, residual O_2 was pumped away from the products at −196 °C and the residues were analysed using GLC. A single peak with the same appearance time as CO_2 was obtained. This would be expected if the product of photolysis were CF_2O, since this is converted quantitatively to CO_2 on the column.

To measure the yields of CF_2O, an IR Beer's law plot was constructed using the synthetic CF_2O–CO_2 mixture (see Section 2.1). Absorptions were measured at the maximum of the P branch at 1930 cm^{-1}. A good straight line through the origin was obtained. However, if a pressure of BCF equivalent to that used in the photolyses was added to the samples of CF_2O, the absorption by CF_2O at 1930 cm^{-1} increased by about 20% even though BCF is transparent in this region. A new calibration curve for CF_2O was therefore prepared with 25 Torr BCF added to each sample. Pressures of BCF above 25 Torr had no effect on this curve. A further Beer's law plot for BCF itself was constructed using the absorption at 1152 cm^{-1}. This was used to determine the pressure of BCF consumed during the photolysis.

If CF_2O is the only carbon-containing species produced on photolysis of BCF–O_2 mixtures, the overall reaction should be

$$CF_2ClBr + \tfrac{1}{2}O_2 + h\nu \longrightarrow CF_2O + \tfrac{1}{2}Br_2 + \tfrac{1}{2}Cl_2 \tag{1}$$
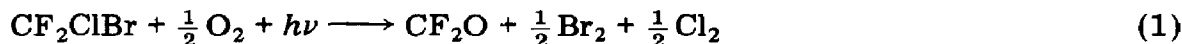
Cl_2 and Br_2 would then rapidly equilibrate to give BrCl. To measure the halogen yield, a UV Beer's law plot for Br_2–Cl_2 mixtures was prepared. Various mixtures of equal pressures of Br_2 and Cl_2 were irradiated for 30 min in vessel B with visible light from the mercury lamp. The resulting mixtures had λ_{max} = 380 nm, as was observed in the BCF–O_2 photolyses.

A mixture of 8.8 Torr BCF plus 9.6 Torr O_2 was irradiated for 14 h with the IR and UV absorption spectra recorded at intervals. The growth of products and removal of BCF are shown in Fig. 1. The estimated errors in
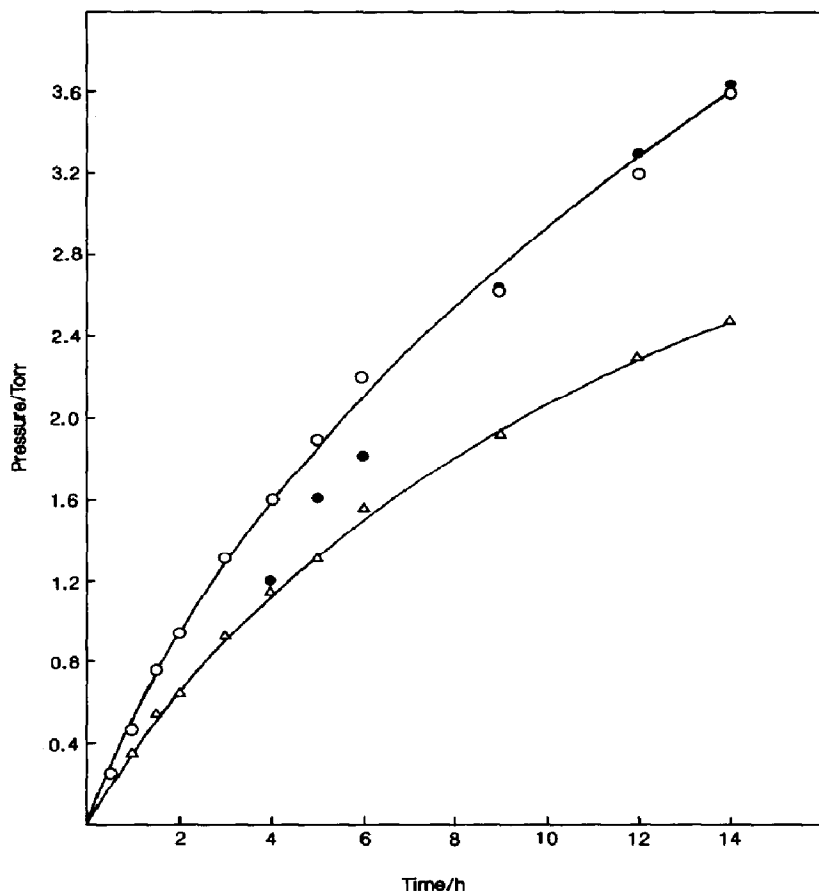
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Fig. 1. Photolysis of 8.8 Torr BCF plus 9.6 Torr O_2 for different times: ●, pressure of BCF lost; ○, pressure of CF_2O formed; △, pressure of ($\frac{1}{2}Br_2$ + $\frac{1}{2}Cl_2$ + BrCl) formed.

the quantities plotted are: CF_2O formed, ±5%; BCF lost, ±10%; ($\frac{1}{2}Br_2$ + $\frac{1}{2}Cl_2$ + BrCl) formed, ±5%. If reaction (1) is appropriate, the pressure of CF_2O formed should equal the pressure of BCF removed. Within experimental error, this is true. (Measurements of BCF loss at short photolysis times are inaccurate so values for photolyses less than 4 h are not given in Fig. 1.) The value $[\frac{1}{2}Cl_2 + \frac{1}{2}Br_2 + BrCl]/[CF_2O]$ should equal unity but it was found to be 0.71 ± 0.02 for all samples for photolyses from 1 to 14 h. This agrees with the results of Jayanty et al. [6] on the photo-oxidation of CF_2Cl_2 and $CFCl_3$. The yield of halogen was less than expected and this could be explained by the reaction of Cl_2 and Br_2 with the Apiezon wax used to fix the windows on to the cross-shaped cell B. This was confirmed by photolyzing a Br_2–Cl_2 mixture in the cross-shaped cell. The absorbance at 380 nm decreased steadily during a 2 h photolysis. Next, three runs were performed in which BCF plus O_2 was photolyzed in vessel A (see Section 2.2) which was free of Apiezon. The magnitude of $[\frac{1}{2}Cl_2 + \frac{1}{2}Br_2 + BrCl]$ was determined spectroscopically when the products were still in vessel A. The products were then quantitatively transferred to vessel B and the values of

CF$_2$O formed and BCF lost were measured using IR spectroscopy as described above. The value $[\frac{1}{2}Cl_2 + \frac{1}{2}Br_2 + BrCl]/[CF_2O]$ was then close to unity for all photolysis times.

4. Determination of quantum yields of products

The above discussion shows that eqn. (1) quantitatively describes the photo-oxidation of BCF. To determine the quantum yield of CF$_2$O, various pressures of BCF in the range 5 - 100 Torr plus 1 - 25 Torr O$_2$ were irradiated at room temperature in vessel A. Quantum yields were measured as in ref. 1 with HBr as an actinometer. After photolysis, the products were condensed at -196 °C and residual O$_2$ was pumped away. The residue was transferred to vessel B and the IR spectrum was recorded to obtain the yield of CF$_2$O. The results are given in Table 1. In a further four photolyses, the CF$_2$O yield was measured by GLC analysis of the products with the column calibrated for CF$_2$O using CO$_2$ since CF$_2$O is quantitatively converted to CO$_2$ on the column. This technique is much more sensitive than the IR analysis, so much shorter photolysis times can be used. The results are included in Table 1.

TABLE 1

Quantum yield of CF$_2$O from the photolysis of CF$_2$ClBr vapour in the presence of O$_2$ at 20 °C

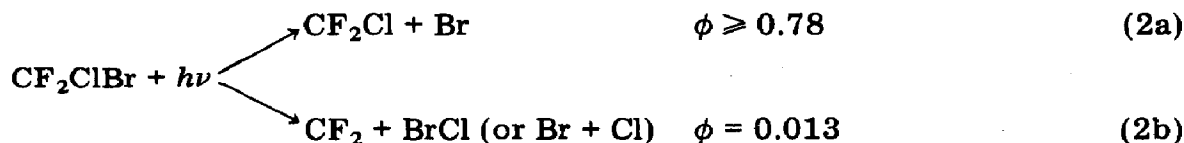| Pressure (Torr)		Photolysis time (min)	$\phi(CF_2O)$
CF$_2$ClBr	O$_2$		
20.3	1.0	30	0.95
20.4	2.0	60	1.00
20.3	4.0	60	1.02
20.0	8.0	60	1.02
20.4	15.9	60	1.09
20.1	10.4	60	1.08
40.7	9.4	60	0.98
101.5	10.0	60	0.99
69.8	5.3	60	1.01
6.2	6.2	120	1.18
25.9	25.6	120	0.81
27.3	26.9	60	0.91
20.4	2.0	2	1.14[a]
20.2	2.0	2	0.98[a]
20.4	2.0	3	1.04[a]
20.4	1.9	3	0.98[a]

[a]Products analysed using GLC.

5. Discussion of the mechanism of the photo-oxidation of CF$_2$ClBr

The results in Sections 3 and 4 show that eqn. (1) describes the overall photo-oxidation of BCF and that the quantum yield of CF$_2$O is unity

(within experimental error) over a wide range of pressures of BCF and O_2. It is also independent of photolysis time.
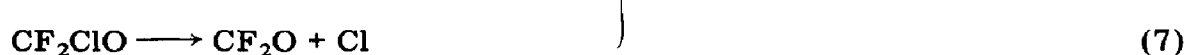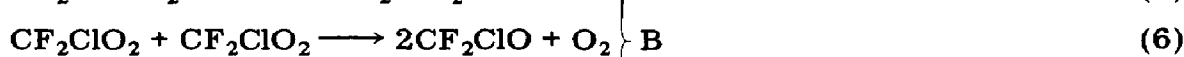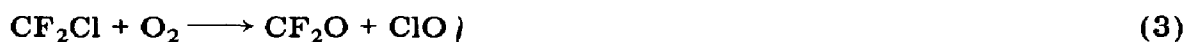
We have shown previously [1] that the photolysis of BCF involves two competing primary processes

$$CF_2ClBr + h\nu \begin{cases} \nearrow CF_2Cl + Br & \phi \geqslant 0.78 \quad (2a) \\ \\ \searrow CF_2 + BrCl \text{ (or Br + Cl)} & \phi = 0.013 \quad (2b) \end{cases}$$

For most of the present discussion, we shall neglect the minor channel (reaction (2b)).

The quantum yield for process (2a) was found [1] to be no less than 0.78 using radical scavengers, with extrapolation to zero photolysis time to allow for the observed quantum yields being less than the primary quantum yields owing to the occurrence of back reactions. The uncertainties in this extrapolation led us to suggest that the true quantum yield for the primary decomposition of BCF could well be unity, i.e. ϕ(2a) + ϕ(2b) = 1. Our new observation that $\phi(CF_2O)$ is unity when BCF is photolyzed with O_2 present fully supports this proposal (see the discussion of the mechanism below).

The photo-oxidation of BCF can be considered in terms of the following mechanisms.

$$CF_2ClBr + h\nu \longrightarrow CF_2Cl + Br \tag{2a}$$

$$CF_2Cl + O_2 \longrightarrow CF_2O + ClO \left.\begin{matrix} \\ \end{matrix}\right\} A \tag{3}$$

$$ClO + ClO \longrightarrow Cl_2 + O_2 \tag{4}$$

$$CF_2Cl + O_2 + M \longrightarrow CF_2ClO_2 + M \left.\begin{matrix} \\ \\ \end{matrix}\right\} B \tag{5}$$

$$CF_2ClO_2 + CF_2ClO_2 \longrightarrow 2CF_2ClO + O_2 \tag{6}$$

$$CF_2ClO \longrightarrow CF_2O + Cl \tag{7}$$

$$Cl + Cl + M \longrightarrow Cl_2 + M \tag{8}$$

$$Br + Br + M \longrightarrow Br_2 + M \tag{9}$$

Br and Cl will ultimately form an equilibrium mixture of Br_2 plus Cl_2 plus 2BrCl. In the above scheme, there are two possible routes to CF_2O. Mechanism A involves reactions (3) and (4) while mechanism B involves reactions (5) - (7). These alternatives have been considered by several authors. Heicklen and coworkers originally favoured a type A mechanism for formation of CF_2O in the photo-oxidation of CF_3I [7] and CFClO in the photo-oxidation of $CFCl_3$ [8]. However, they later favoured mechanism B for the photo-oxidations of $CFCl_3$ and CF_2Cl_2 [9] and for the production of CCl_2O from the reaction between CCl_3 and O_2 [9]. Recent work by Ryan and Plumb [10] strongly suggests that the reactions of CF_3 and CCl_3 radicals with O_2 involve the analogues of reaction (5) rather than reaction (3). Hackett et al.

[11] studied the multiphoton dissociation of CF_2Cl_2 in the presence of O_2. They assumed that CF_2O is formed via mechanism A but did not consider mechanism B.

The most recent work on the reaction of CF_2Cl radicals with O_2 at room temperature is that of Suong and Carr [12] who photolyzed $CF_2ClCOCF_2Cl$ in the presence of O_2. They found CF_2O to be the only organic product, with a quantum yield of 2 at O_2 pressures of 3 Torr or above. They discussed the formation of CF_2O in terms of reactions (3) - (7) above and comprehensively surveyed the evidence concerning mechanisms A and B. They strongly favour mechanism B and we fully accept their arguments. Our own work does not permit a clear distinction between the two mechanisms. We find that $\phi(CF_2O)$ is unaffected by varying the pressures of BCF and O_2 over a wide range, with a total pressure of 12 - 112 Torr (see Table 1). At first sight, this seems to favour mechanism A since reaction (5) (mechanism B) could well be in the region of pressure dependence (but see discussion in Section 6.4). However, in mechanism B, all the CF_2ClO_2 formed by reaction (5) is ultimately converted to CF_2O and hence the possible pressure dependence of reaction (5) does not affect $\phi(CF_2O)$. The possibility of reaction (5) being pressure dependent under our conditions is discussed in more detail in Section 6.

Our result $\phi(CF_2O) = 1$ in the photo-oxidation of BCF is in accord with previous work on the photo-oxidation of CF_2Cl_2 and related compounds. Thus Milstein and Rowland [13] photolyzed CF_2Cl_2 plus O_2 at 185 nm and obtained $\phi(CF_2O) = \phi(-CF_2Cl_2) = 1$. Also, the photo-oxidations of CF_2Cl_2 and $CFCl_3$ [6] give CF_2O and $CFClO$ respectively with close to unit quantum efficiency.

The results in Table 1 show that, in our present work, $\phi(CF_2O) = 1$ irrespective of photolysis time. This indicates that the primary quantum yield of decomposition of BCF by reaction (2a) is 1 (or more precisely 0.99 if we allow for the occurrence of channel (2b) — see discussion below). Yet when BCF is photolyzed in the presence of radical scavengers such as Cl_2 or HBr, the quantum yield for loss of BCF falls rapidly as the photolysis time increases [1]. Thus, when 25 Torr BCF was photolyzed with 2 Torr Cl_2, we obtained $\phi(CF_2Cl_2) = \phi(-BCF) = 0.78$ on extrapolation to zero photolysis time; however, after photolysis for 5 min, $\phi(CF_2Cl_2)$ was only 0.46. This is because of the occurrence of the efficient back reaction

$$CF_2Cl + Br_2 \longrightarrow CF_2ClBr + Br \tag{10}$$

with the Br_2 formed via reactions (2a) and (9). The fact that in the BCF–O_2 system $\phi(CF_2O)$ is *not* dependent on photolysis time shows that scavenging of CF_2Cl radicals by O_2 (reaction (5)) is substantially faster than the back reaction (10). This is discussed further in Section 6.

We noted above that the photolysis of BCF involves only 1.3% decomposition by channel (2b). In the presence of O_2 the fate of the resulting CF_2 radical depends on the spin state of the CF_2. Following the work of Simons and Yarwood [14] on the flash photolysis of CF_2Br_2, we expect singlet CF_2

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to be formed. This and other work [15 - 17] suggests that the reaction between $^1CF_2$ and O_2 is very slow. It is therefore likely that $^1CF_2$ would react with Br_2 to give CF_2Br_2 or with Cl_2 to give CF_2Cl_2. However, by analogy with the reaction of ^3CFCl with O_2 [17], $^3CF_2$ should react with O_2 as follows:

$$^3CF_2 + O_2 \longrightarrow F + CO + FO$$
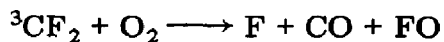
Thus channel (2b) does not contribute to the yield of CF_2O whatever the spin state of CF_2. This channel is so unimportant that products from it other than CF_2O would probably not be detected.

6. Competitive reactions of CF_2Cl radicals with O_2, Cl_2, HBr and Br_2

Three series of runs were performed. Each involved the photolysis of BCF with O_2 plus one of the radical scavengers Cl_2, HBr or Br_2. In each case, 20 Torr BCF plus 1 Torr O_2 plus various pressures of scavenger were photolyzed at 248 nm in vessel A. After photolysis, the contents were transferred to several traps in series (all at -196 °C). Residual O_2 was then pumped away. The residues were transferred to an IR cell which was tailored to fit the tapering beam of the IR spectrometer. This puts all absorbing molecules into the IR beam and gives greater sensitivity than when vessel B was used. The yield of CF_2O was obtained from the IR spectrum. In the initial experiments with Cl_2 or HBr, the contents of the IR cell were then analysed using GLC to measure the yield of CF_2Cl_2 or CF_2ClH as appropriate.

6.1. CF_2Cl–O_2–Cl_2 mixtures

If BCF is photolyzed in the presence of Cl_2, the only organic product is CF_2Cl_2 [1], formed by the reaction

$$CF_2Cl + Cl_2 \longrightarrow CF_2Cl_2 + Cl \tag{11}$$

If O_2 is also present, reaction (5) competes with reaction (11) and, since reaction (5) ultimately leads to CF_2O, a mixture of CF_2Cl_2 and CF_2O is produced. The rate of reaction (5) is measured by the rate of formation of CF_2O so that

$$\frac{\phi(CF_2O)}{\phi(CF_2Cl_2)} = \frac{k_5[O_2]}{k_{11}[Cl_2]}$$

Hence k_5/k_{11} can be calculated from the measured $\phi(CF_2O)$ and $\phi(CF_2Cl_2)$. The results obtained using various BCF–O_2–Cl_2 mixtures are given in Table 2. The values k_5/k_{11} are clearly independent of the pressure of Cl_2 in the range 3 - 30 Torr. The mean value of k_5/k_{11} is

$$\frac{k_5}{k_{11}} = 39 \pm 3 \text{ at } 20 \text{ °C}$$

The error limits are one standard deviation.

If the primary quantum yield for loss of BCF is unity, then the value $\phi(CF_2O) + \phi(CF_2Cl_2)$ should equal 1 for all runs. In fact, the sum increases

TABLE 2

Photolysis of CF$_2$ClBr in the presence of O$_2$ plus Cl$_2$ at 20 °C

Pressure (Torr)			Quantum yield		k_5/k_{11}
CF$_2$ClBr	O$_2$	Cl$_2$	CF$_2$O	CF$_2$Cl$_2$	
20.4	0.96	3.14	0.80	0.063	42
20.4	0.90	3.18	0.79	0.067	41
20.6	0.86	4.90	0.81	0.11	43
20.0	0.98	5.05	0.86	0.12	40
20.4	0.94	5.08	0.86	0.13	37
20.3	0.96	8.09	0.79	0.18	37
20.3	0.93	8.21	0.71	0.15	43
20.5	0.91	15.3	0.74	0.34	36
21.3	0.97	19.5	0.56	0.32	36
19.8	0.96	30.3	0.63	0.52	39

Photolysis time, 30 min.

steadily from about 0.86 with 3 Torr of Cl$_2$ to unity (within experimental error) with 30 Torr Cl$_2$. The lower values could be caused by the back reaction (10) in which BCF is re-formed and its apparent decomposition is reduced. The Br$_2$ is formed by reaction (9). Reaction (10) competes with reaction (11) and the lower the pressure of added Cl$_2$ the more significant becomes reaction (10). This explains the decrease in $\{\phi(CF_2O) + \phi(CF_2Cl_2)\}$. Of course, if Cl$_2$ is initially present, virtually all the Br formed by reaction (2a) will be converted to BrCl but the reaction

$$CF_2Cl + BrCl \longrightarrow CF_2ClBr + Cl$$
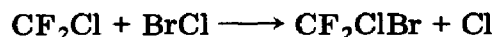
is expected [18] to be almost as efficient as reaction (10) in reforming BCF.

6.2. CF$_2$Cl–O$_2$–HBr mixtures

When BCF is photolyzed with HBr, the only organic product is CF$_2$ClH [1], formed by

$$CF_2Cl + HBr \longrightarrow CF_2ClH + Br \qquad (12)$$

If O$_2$ is also present, CF$_2$O is formed by reaction (5). Hence

$$\frac{\phi(CF_2O)}{\phi(CF_2ClH)} = \frac{k_5[O_2]}{k_{12}[HBr]} \qquad (13)$$

Equation (13) was tested using various BCF–O$_2$–HBr mixtures and the results are given in Table 3. It is clear that the values of k_5/k_{12} are independent of [O$_2$]/[HBr]. The mean value is

$$\frac{k_5}{k_{12}} = 147 \pm 20 \text{ at } 20 \text{ °C}$$

As in Section 6.1, the sum $\{\phi(CF_2O) + \phi(CF_2ClH)\}$ is slightly less than unity, probably because of back reaction (10).

TABLE 3

Photolysis of CF_2ClBr in the presence of O_2 plus HBr at 20 °C

Pressure (Torr)			Quantum yield		k_5/k_{12}
CF_2ClBr	O_2	HBr	CF_2O	CF_2ClH	
20.4	1.00	7.09	0.78	0.045	123
20.3	1.00	9.98	0.77	0.044	176
20.1	0.99	12.3	0.78	0.069	140
20.3	1.09	16.0	0.76	0.066	170
20.0	1.07	18.0	0.75	0.086	146
20.5	1.13	20.6	0.74	0.105	129

Photolysis time, 30 min.

6.3. $CF_2Cl-O_2-Br_2$ mixtures

If BCF is photolyzed with O_2 plus Br_2, reaction (10) competes with reaction (5). However, reaction (10) produces BCF so we cannot monitor its rate directly. We therefore assume that the primary quantum yield for loss of BCF on photolysis at 248 nm is unity (see Section 4). It then follows that the quantum yield of BCF formed in reaction (10) is $1 - \phi(CF_2O)$. Hence

$$\frac{\phi(CF_2O)}{\{1 - \phi(CF_2O)\}} = \frac{k_5[O_2]}{k_{10}[Br_2]} \tag{14}$$

The results of photolysis of $BCF-O_2-Br_2$ mixtures are given in Table 4. The values of k_5/k_{10} are independent of a tenfold variation in the Br_2 pressure and of a twofold variation in O_2 pressure. The mean result is

$$\frac{k_5}{k_{10}} = 1.4 \pm 0.1 \text{ at } 20 \text{ °C}$$

TABLE 4

Photolysis of CF_2ClBr in the presence of O_2 plus Br_2 at 20 °C

Pressure (Torr)			Quantum yield		k_5/k_{10}
CF_2ClBr	O_2	Br_2	CF_2O	CF_2ClBr[a]	
20.3	2.17	1.06	0.73	0.27	1.33
20.4	0.99	1.09	0.54	0.46	1.28
20.3	0.96	1.43	0.50	0.50	1.51
20.4	0.96	2.04	0.41	0.59	1.49
20.4	1.14	3.04	0.36	0.64	1.49
19.6	1.04	5.04	0.24	0.76	1.50
20.2	1.15	10.2	0.13	0.87	1.31

Photolysis time, 60 min.
[a]Calculated from $\phi(CF_2ClBr) = 1 - \phi(CF_2O)$; see text.

The fact that the sum of the quantum yields of the products in Sections 6.1 and 6.2 is a little less than unity does not invalidate eqn. (14) since we propose that these discrepancies arise from contributions from reaction (10). In the Br_2–O_2 system, we expect that *all* CF_2Cl radicals are converted to either CF_2O or CF_2ClBr.

6.4. Discussion of competitive results

There are no published rate constants for the reactions of CF_2Cl with O_2, Cl_2, Br_2 or HBr. However, Shanahan and Sidebottom [19] recently photolyzed CF_2Cl_2 with O_2 plus Br_2 and obtained $k_5/k_{10} = 2.1$ at 20 °C. Unpublished work in our laboratory [20] on the photolysis of $(CF_2ClCO)_2O$ in the presence of O_2 plus Br_2 gives $k_5/k_{10} = 2.5$. The results of the three studies are in good agreement.

The reactions

$$CF_3 + O_2 + M \longrightarrow CF_3OO + M \tag{15}$$

$$CF_3 + Br_2 \longrightarrow CF_3Br + Br \tag{16}$$

were studied by Vedeneev *et al.* [21]. They obtained $k_{15}^{\infty}/k_{16} = 3.1$. Shanahan and Sidebottom [19] studied the same reactions using a different system and obtained $k_{15}^{\infty}/k_{16} = 3.6 \pm 0.1$. These are close to the corresponding value for CF_2Cl radicals.

The ratios of rate constants obtained in Sections 6.1, 6.2 and 6.3 can be combined to give

$$\frac{k_{Br_2}}{k_{Cl_2}} = \frac{k_{10}}{k_{11}} = 28 \qquad \frac{k_{Br_2}}{k_{HBr}} = \frac{k_{10}}{k_{12}} = 105$$

The analogues of reactions (10) and (11) involving CF_3 radicals were studied by Amphlett and Whittle [22] who obtained $k_{Br_2}/k_{Cl_2} = 46$ at 20 °C which is close to the value given above for CF_2Cl radicals. Taylor and Whittle [23] studied the thermal bromination of CF_2ClH inhibited by HBr over the range 334 - 435 °C. Their Arrhenius plot for k_{10}/k_{12} yields a value of 197 at 20 °C. In view of the long extrapolation to 20 °C, this is in satisfactory agreement with the value of 105 above. The analogous reactions of CF_3 radicals with Br_2 and HBr were discussed by Amphlett and Whittle [22]. Their data for CF_3 give $k_{Br_2}/k_{HBr} = 147$. We conclude therefore that the competitive results in Sections 6.1, 6.2 and 6.3 are consistent and plausible.

We next attempted to obtain an absolute value for k_5 for the reaction between CF_2Cl and O_2. The rate constants for reaction of CF_2Cl with Cl_2, Br_2 and HBr are unknown, hence we cannot obtain k_5 directly from our competitive results. However, there have been two determinations of the rate constant for reaction (16). Rossi *et al.* [24] used the very low pressure pyrolysis technique to get $k_{16} = 7.8 \times 10^{11} \, cm^3 \, mol^{-1} \, s^{-1}$ whereas Whittle and coworkers [22, 25] obtained $4.6 \times 10^{11} \, cm^3 \, mol^{-1} \, s^{-1}$ (both at 20 °C). We have used the mean value.

The reactions of simple radicals with Br_2 are fast with activation energies close to zero. It is therefore reasonable to assume that the reactions of the similar radicals CF_3 and CF_2Cl with Br_2 have the same rate constant. Hence we take $k_{10} = 6.2 \times 10^{11}\,cm^3\,mol^{-1}\,s^{-1}$. Combining this with our present competitive data, we have

$$k_5 = k(CF_2Cl + O_2) = 8.7 \times 10^{11}\,cm^3\,mol^{-1}\,s^{-1}\ \text{at}\ 20\ °C$$

This estimate for k_5 is probably reliable to within a factor of 3.

Before discussing this result further, we consider the possible pressure dependence of reaction (5). The rate constant ratios given in Tables 2, 3 and 4 show no dependence on total pressure but the pressure range covered, $i.e.$ 23 - 51 Torr, was not large. However, other work in our laboratory [20] on the $CF_2Cl–Br_2–O_2$ system showed no evidence of a pressure effect on addition of up to 80 Torr perfluoromethylcyclohexane which is a very efficient quencher. The source of CF_2Cl radicals was $(CF_2ClCO)_2O$. Shanahan and Sidebottom [19] generated CF_2Cl radicals by photolysis of CF_2Cl_2 in the presence of O_2 plus Br_2. The addition of up to 500 Torr N_2 had no effect on k_5/k_{10}. Thus there is no evidence of a pressure dependence for k_5 at pressures above 23 Torr. In contrast, Shanahan and Sidebottom [19] found that the reaction between CF_3 and O_2 does show a weak pressure dependence below 300 Torr. Thus, as the total pressure was reduced from 300 to 50 Torr by reducing the pressure of added nitrogen, $k(CF_3 + O_2)/k(CF_3 + Br_2)$ fell from 3.8 to 2.6. Vedeneev $et\ al.$ [21] observed a similar change. The reaction between CF_2Cl and O_2 should become third order in a lower pressure range than CF_3 plus O_2 which could explain why no pressure dependence was observed in the various studies discussed above.

Our value of k_5 for the reaction of CF_2Cl with O_2 may be compared with k^∞ for $CF_3 + O_2$ and $CCl_3 + O_2$. Cooper $et\ al.$ [26] obtained $k^\infty(CF_3 + O_2) = 6.0 \times 10^{12}\,cm^3\,mol^{-1}\,s^{-1}$ using pressures up to about 700 Torr. Ryan and Plumb [10] measured $k(CF_3 + O_2)$ at pressures up to 8 Torr (most of the gas being helium) and obtained $k^\infty = 5.0 \times 10^{12}\,cm^3\,mol^{-1}\,s^{-1}$ using an RRKM treatment of their data. Cooper $et\ al.$ [26] obtained $k^\infty(CCl_3 + O_2) = 3.1 \times 10^{12}\,cm^3\,mol^{-1}\,s^{-1}$ whereas Ryan and Plumb [10] recently found a value of $1.5 \times 10^{12}\,cm^3\,mol^{-1}\,s^{-1}$ for this rate constant. It thus appears that the rate constants for the reaction of O_2 with CF_3, CF_2Cl and CCl_3 radicals are of similar magnitude.

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