

UV ABSORPTION SPECTRUM AND PHOTOCHEMISTRY OF CF₂ClBr

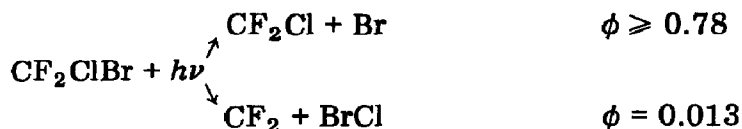
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Summary

The absorption spectrum of the vapour of CF₂ClBr (BCF) was measured over a wide range of pressures. Absorption cross sections in the range 190 - 340 nm are given. BCF vapour was photolysed at 248 nm and 20 °C, alone and with each of the radical scavengers HCl, HBr, Cl₂ and Br₂. Quantum yields of the products were measured. Two primary modes of photodecomposition are proposed:



The mechanism of the photolysis is discussed. Irradiation of BCF at 313 nm gave no detectable products with $\phi(-\text{BCF}) \leq 0.01$. However, BCF vapour is readily photodecomposed at 313 nm if liquid mercury is present. Results of the long-term exposure of BCF vapour to sunshine (up to 3 years) under various conditions are described.

1. Introduction

The compound bromochlorodifluoromethane (CF₂ClBr) is sold under various names, the most common being BCF. Some of its applications, *e.g.* as a flame retardant, involve its eventual release into the atmosphere. It is therefore one of the group of fluorocarbons whose photolysis in the stratosphere poses a threat to the stratospheric ozone layer. The annual world production of BCF is much less than the production of CFCl₃ and CF₂Cl₂ which have been widely studied in connection with the removal of ozone from the stratosphere. However, the photolysis and photo-oxidation of BCF are of interest, particularly as the presence of the C—Br bond means that BCF should be more photolabile than the chlorofluorocarbons (CFCs). It is even possible that, unlike the CFCs, the photolysis of BCF could occur in the troposphere if there were sufficient tail-end absorption of daylight by BCF.

We now report a detailed study of the UV photochemistry of BCF and also of its UV spectrum. There seems to be no published work on the photochemistry of BCF although Kagiya *et al.* [1] have briefly reported on its photo-oxidation. Giolando *et al.* [2] have recently published results on the absorption spectrum of BCF and they also refer to their unpublished work on the photochemistry of BCF.

2. Experimental details

2.1. Materials

BCF was used as supplied by I.C.I. Mond Division. Analysis by gas-liquid chromatography (GLC) and IR spectroscopy revealed traces of CF_2Cl_2 and CF_2ClH ($\leq 0.01\%$). The CF_2Cl_2 , $\text{CF}_2\text{ClCF}_2\text{Cl}$ and CF_2Br_2 were also obtained from I.C.I. No impurities could be detected. HCl and HBr (B.D.H. Ltd.) were purified by bulb-to-bulb distillations from -80 to -196 °C with a middle cut being retained each time. Bromine was obtained from a sample stored over KBr to remove chlorine. Chlorine (B.D.H.) was bubbled through aqueous KMnO_4 , water and concentrated H_2SO_4 and was then passed through P_2O_5 . It was collected at -80 °C. Bisperfluoroisopropyl ketone (Peninsular Chem-research) and perfluoropropionic anhydride (Fluorochem) were used as supplied. All the above reagents were degassed before use.

2.2. Apparatus

Unless otherwise stated, the light source was an A.E.G. Wotan 200 W HBO/W2 high pressure mercury lamp. A quartz lens was used to obtain a parallel beam. Details of filters, reaction vessels and actinometers are given later. The reactants were handled in a conventional vacuum line and the pressures were measured by a Bell and Howell transducer. The products were analysed mainly by GLC using a 5 m column of silicone oil on brick dust at 0 °C preceded by 10 cm of auramine on brick dust to scrub out halogens and hydrogen halides.

3. The UV absorption spectrum of BCF

The UV spectrum of BCF was measured mainly to obtain absorption cross sections for the tail-end absorption in the near-UV region. Accordingly, 13 spectra were run using progressively greater absorptions. The ranges of conditions used were as follows: path lengths, 1 - 8 cm; BCF pressures, 13 - 1621 Torr. Spectra were run on the following spectrophotometers: Unicam SP800, SP1800, SP8-100 and SP8-400 and Cary 17. Each instrument was calibrated using a holmium filter. Beer's law plots of the absorbance (normalized to 1 cm pathlength) *versus* the pressure were constructed at 10 nm intervals. The slopes of these plots are given in Table 1 together with corresponding absorption cross sections σ . The spectra gave $\lambda_{\text{max}} =$

TABLE 1

Photoabsorption cross sections σ for BCF from Beer's law plots at specific wavelengths and 18 °C

λ (nm)	Slope of Beer's law plot (absorbance) ^a (Torr ⁻¹)	σ (cm ²)
198	1.55×10^{-2}	1.07×10^{-18}
208	2.02×10^{-2}	1.40×10^{-18}
218	1.52×10^{-2}	1.05×10^{-18}
228	6.31×10^{-3}	4.38×10^{-19}
238	2.51×10^{-3}	1.74×10^{-19}
248	1.09×10^{-3}	7.56×10^{-20}
258	2.49×10^{-4}	1.73×10^{-20}
268	4.46×10^{-5}	3.10×10^{-21}
278	1.13×10^{-5}	7.82×10^{-22}
288	0.94 ^a	2.9×10^{-22}
298	0.20 ^a	6.0×10^{-23}

^a Absorbances for 1 cm of liquid BCF.

206 ± 0.5 nm. The spectrum of 1 cm of liquid BCF was also run. The results are also given in Table 1.

The σ values for the vapour were fed into the equation given by Herzberg [3]:

$$\log \sigma = a(\bar{\nu}_{\max} - \bar{\nu})^2 + b \quad (1)$$

A plot of $\log \sigma$ against $(\bar{\nu}_{\max} - \bar{\nu})^2$ was a good straight line for which a least-squares analysis gave

$$\log \sigma = -2.049 \times 10^{-8}(\bar{\nu}_{\max} - \bar{\nu})^2 - 17.855 \quad (2)$$

with $\bar{\nu}$ in reciprocal centimetres. The constant b in eqn. (1) corresponds to $\log \sigma_{\max}$ which can be converted to a decadic extinction coefficient of $365 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at $\lambda_{\max} = 206 \text{ nm}$.

Equation (2) yields smoothed $\log \sigma$ values of -21.77 at 288 nm and -22.46 at 298 nm for BCF vapour, whereas the corresponding values for BCF liquid from Table 1 are -21.54 and -22.22 respectively. Thus the ratio $\sigma_{\text{liq}}/\sigma_{\text{vap}} = 1.7$ at each wavelength, *i.e.* there is little significant difference in absorption by liquid and by vapour.

Equation (2) can be used to calculate absorption cross sections at wavelengths above those at which the absorption can be measured ($\lambda > \approx 280 \text{ nm}$). Such σ values are given in Table 2 which includes corresponding values obtained by Giolando *et al.* [2] (the wavelengths in Table 2 are those used in ref. 2). Table 2 also includes absorption cross sections for the experimentally accessible range 200 - 280 nm based on eqn. (2). These σ values differ slightly from those in Table 1 as they are smoothed.

The results of Giolando *et al.* [2] agree with ours. We obtain the same λ_{\max} , and the σ values in Table 2 agree to well within experimental error. We

TABLE 2

Smoothed absorption cross sections for BCF vapour at 18 °C

λ (nm)	$-\text{Log}(\sigma \text{ (cm}^2\text{)})$		λ (nm)	$-\text{Log}(\sigma \text{ (cm}^2\text{)})$	
	<i>This work</i>	<i>Ref. 2</i>		<i>This work</i>	<i>Ref. 2</i>
191	18.153	18.281	301	22.665	22.403
201	17.885	17.959	307	23.081	22.914
211	17.882	17.939	310	23.290	—
221	18.077	18.134	320	23.983	—
231	18.420	18.452	330	24.673	—
241	18.873	18.839	340	25.356	—
251	19.407	19.280			
261	19.999	19.810			
271	20.633	20.404			
281 ^a	21.295	21.081			
291 ^b	21.975 ^c	21.690			

^aLong wavelength limit of our experimental measurements.

^bApparent upper limit of measurements in ref. 2 as indicated by Fig. 1 in ref. 2. However, the text seems to indicate that a measurement was made at 307 nm.

^cValues at $\lambda > 291$ nm were extrapolated using eqn. (2) of the present work (see text).

feel that our use of the linear eqn. (2) yields somewhat more reliable σ values where absorption is weak. Extrapolation is certainly more reliable if eqn. (2) is used.

4. Photolysis of BCF vapour at room temperature

4.1. Optical arrangement for photolysis at 248 nm

The data in Section 3 indicate that, with pressures of up to 100 Torr of BCF in a vessel 10 cm long, the light absorption is very weak above 260 nm. We have therefore photolysed BCF using what is usually referred to as "the 254 nm mercury line". This was isolated by passing the parallel beam of light from the high pressure mercury lamp through a filter of aqueous cyanine perchlorate (1.25 g dm^{-3} ; path length, 2.5 cm) [4] preceded by 2.5 cm of aqueous sodium acetate solution (0.5 M) which cuts off wavelengths of 232 nm or less and thereby protects the cyanine perchlorate.

To establish the actual wavelengths used for photolysis, the light from the mercury lamp and the filters was monitored using a Jarrell-Ash monochromator and an IP28 photomultiplier. The system was calibrated using the 253.7 nm line from a low pressure mercury lamp. The profile of the emission around 254 nm is shown in Fig. 1. It is evident that the centre of emission is at 248 nm.

For photolysis of BCF, the parallel beam from the lamp and the filters was passed through a cylindrical quartz vessel of length 10 cm and internal diameter 5 cm. On leaving the vessel, the light passed through 4.5 cm of a

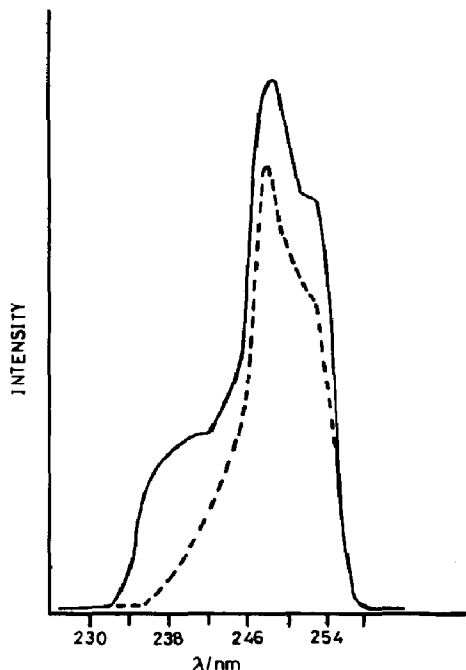


Fig. 1. Output of Wotan HBO W/2 high pressure mercury lamp around 248 nm: —, no filters (intensity scaled down by a factor of 3); ---, cyanine perchlorate plus sodium acetate filters (see text); the intensity is in arbitrary units.

solution containing $250 \text{ g NiSO}_4 \cdot 7\text{H}_2\text{O dm}^{-3}$ and $80 \text{ g CoSO}_4 \cdot 7\text{H}_2\text{O dm}^{-3}$ followed by a Chance-Pilkington OX7 filter. The intensity was then measured using a Rank-Cintel photocell (QVA39). The filters in front of the reaction vessel transmitted in the range 236 - 266 nm and also transmitted visible and UV light ($\lambda \geq 355 \text{ nm}$). However, the absorption at wavelengths above 300 nm by BCF under our conditions (100 Torr or less of BCF) was negligible, and hence the only wavelengths absorbed by BCF are those shown in Fig. 1. The wavelengths above 355 nm did not reach the photocell because of the filters between it and the rear of the reaction vessel. This was confirmed by the fact that on inserting a Pyrex plate in front of the reaction vessel the photocell output fell to 0.1% or less of the value without the plate.

The performance of the optical system was also checked by measuring I_t/I_0 for various BCF pressures. The Beer law plot was linear and a decadic extinction coefficient α of $17.5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ was calculated from its slope. The spectral data in Section 3 give an α value of $15.1 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at the mean wavelength of 248 nm. This agreement is very satisfactory since our optical system involves a spread of wavelengths around 248 nm (see Fig. 1) and hence will give less accurate results than a spectrophotometer will.

4.2. Photolysis of BCF vapour at 248 nm without added radical scavengers

The products of the photolysis of BCF vapour at 248 nm and 20°C were CF_2Cl_2 , $\text{CF}_2\text{ClCF}_2\text{Cl}$, CF_2Br_2 and Br_2 . There were also traces of C_2F_4

in non-reproducible amounts. The products were identified by their GLC retention times and the identities were confirmed by mass and IR spectra of separated components. Product yields (other than Br_2) were determined by GLC analysis. This was done by injecting all the contents of the reaction vessel onto the column after photolysis. It was difficult to obtain reproducible analyses of the reaction mixture owing to the fact that it consisted almost entirely of undecomposed BCF. The amount of BCF decomposed was never more than 0.1%. At first we determined sensitivities using a sample of a synthetic calibration mixture of products which followed an analysis of the photolysis sample. However, the sensitivities changed if excess BCF was present and so sufficient BCF to match that in the photolysed mixture was added to each calibration dose. Reproducible results were then obtained.

Quantum yields were generally measured using HBr ($P \approx 100$ Torr) as the actinometer (ref. 5, p. 782). The vapour of $(\text{C}_2\text{F}_5\text{CO})_2\text{O}$, for which Chamberlain and Whittle [6] obtained $\phi_{\text{CO}} = 0.24$ at 20°C and 254 nm , was used as the actinometer in a few runs. Both actinometers gave the same results. Typical values of the quantum yields are given in Table 3. It can be seen that the quantum yields are all small, lying in the range from about 2×10^{-3} to 2×10^{-2} . At 10 Torr BCF there is an indication that $\phi(\text{CF}_2\text{Cl}_2)$ and $\phi(\text{CF}_2\text{ClCF}_2\text{Cl})$ decrease as the photolysis time increases. This behaviour is not observed for $\phi(\text{CF}_2\text{Br}_2)$.

The obvious mechanism to explain qualitatively the formation of the products is as follows:



TABLE 3

Quantum yields of products from the photolysis of CF_2ClBr vapour at 248 nm and 20°C

CF_2ClBr pressure (Torr)	Photolysis time (min)	$\phi \times 10^3$		
		CF_2Cl_2	$\text{CF}_2\text{ClCF}_2\text{Cl}$	CF_2Br_2
10.1	60	2.8	7.6	16
10.0	120	2.6	6.0	16
9.7	180	1.7	3.7	15
50.2	30	4.8	6.3	19
50.7	30	4.4	5.6	15
49.7	60	5.1	6.2	19

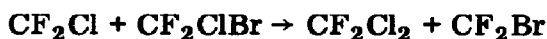


In this mechanism CF_2Cl_2 is formed by the disproportionation reaction (5) which has been shown to occur in several other systems where CF_2Cl radicals are present (see below). The observed traces of C_2F_4 could come from combination of the CF_2 radicals formed by reaction (5). The low overall quantum yields of the products are expected since reaction (8) will be fast and will occur readily when small amounts of Br_2 have been formed. Such back reactions are well known to give low quantum yields of products when organic halides are photolysed (ref. 5, p. 525).

While the above mechanism qualitatively explains the observed products, various objections to it emerge when the quantum yields are examined. Thus, even if all the CF_2 radicals formed by reaction (5) were removed by reaction (9), the quantum yield $\phi(\text{CF}_2\text{Br}_2)$ could never be greater than $\phi(\text{CF}_2\text{Cl}_2)$. However, inspection of Table 3 shows that $\phi(\text{CF}_2\text{Br}_2)/\phi(\text{CF}_2\text{Cl}_2)$ is in the range 4 - 8. Furthermore, for reactions (4) and (5),

$$\frac{\text{rate}(\text{CF}_2\text{ClCF}_2\text{Cl})}{\text{rate}(\text{CF}_2\text{Cl}_2)} = \frac{k_4}{k_5} = \frac{\phi(\text{CF}_2\text{ClCF}_2\text{Cl})}{\phi(\text{CF}_2\text{Cl}_2)}$$

where the ratio k_4/k_5 is the combination-to-disproportionation ratio for CF_2Cl radicals which has been determined in several photolytic systems as shown in Table 4. The data in Table 4 suggest that our yields of CF_2Cl_2 in Table 3 are anomalously high relative to $\text{CF}_2\text{ClCF}_2\text{Cl}$ which in turn suggests that there is another source of CF_2Cl_2 in the system as well as reaction (5). The reaction



can be excluded as it is likely to be far too slow at room temperature. Also it would produce CF_2Br radicals which might be expected to give $\text{CF}_2\text{BrCF}_2\text{Cl}$ as one final product. This was not detected in our system.

TABLE 4

Combination-to-disproportionation ratio k_4/k_5 for CF_2Cl radicals

Radical source	k_4/k_5	Reference
$\text{CF}_3\text{COCF}_2\text{Cl}$	$\approx 25 - 4^a$	[7]
$\text{CF}_2\text{ClCOCF}_2\text{Cl}$	$\approx 17 - 1.7^a$	[8]
$\text{CF}_2\text{ClH} + \text{Hg}^*$	> 2	[9]
$\text{CF}_2\text{ClCOCF}_2\text{H}$	5.9	[10]
$(\text{CF}_2\text{ClCO})_2\text{O}$	7.6	[11]

^aDecreases as the wavelength of photolysis decreases from 310 to 260 nm.

It is clear that reactions (3) - (9) do not adequately account for our product yields. Also the quantum yields in Table 3 should not be used to deduce the true primary quantum yield of decomposition of BCF in view of the occurrence of the efficient back reaction (8). To obtain further information on these problems we have photolysed BCF in the presence of various radical scavengers.

4.3. Photolysis of BCF in the presence of HCl

Mixtures of BCF (20 - 55 Torr) and HCl (0.3 - 26 Torr) were photolysed for various times. With HCl pressures of 1.6 Torr or more the only product was CF_2ClH . This is expected if the primary photolysis of BCF (reaction (3)) is followed by



Reaction (10) should be rapid by analogy with the corresponding reaction between CF_3 and HCl [12] and hence should suppress formation of $\text{CF}_2\text{ClCF}_2\text{Cl}$ and CF_2Cl_2 by reactions (4) and (5). The results of these photolyses are given in Table 5. It is evident that the $\phi(\text{CF}_2\text{ClH})$ are quite low, of the order of 0.05 - 0.1. This confirms that the primary value of $\phi(-\text{BCF})$ is greater than is indicated by the data in Table 3 but suggests that HCl is not a very efficient radical scavenger. The low values of $\phi(\text{CF}_2\text{ClH})$ probably arise from the fact that the back reaction (8) still competes efficiently with reaction (10).

In principle, the shorter the photolysis time, the less Br_2 will be formed and hence the nearer $\phi(\text{CF}_2\text{ClH})$ should be to the true value of $\phi(-\text{BCF})$. The effect of varying the photolysis time is shown in the first three runs in Table 5. There is some increase in $\phi(\text{CF}_2\text{ClH})$ as the photolysis time decreases but the change is small, confirming that HCl is not a very good radical scavenger compared with Br_2 . The last three runs in Table 5 show that with $P_{\text{HCl}} \leq 1.2$ Torr scavenging of CF_2Cl is now sufficiently slow that reactions (4) and (5) can occur. If CF_2ClH and $\text{CF}_2\text{ClCF}_2\text{Cl}$ are formed only by reactions (10) and (4), it follows that

TABLE 5

Quantum yields of products from the photolysis of CF_2ClBr vapour in the presence of HCl

Pressure (Torr)		Photolysis time (min)	ϕ		
CF_2ClBr	HCl		CF_2ClH	$\text{CF}_2\text{ClCF}_2\text{Cl}$	CF_2Cl_2
25	25	30	0.089	—	—
25	25	15	0.106	—	—
25	26	5	0.122	—	—
20	1.2	120	0.097	0.026	0.0088
19	0.57	120	0.046	0.014	0.0038
24	0.32	120	0.030	0.040	0.0078

$$\frac{\text{rate}(\text{CF}_2\text{ClH})}{\{\text{rate}(\text{CF}_2\text{ClCF}_2\text{Cl})\}^{1/2}} = \frac{k_{10}[\text{HCl}]}{k_4^{1/2}} \quad (11)$$

where rate denotes rate of formation. Applying eqn. (11) to the last three runs in Table 5, we obtain values of 19.4, 29.5 and 27.8 for $k_{10}/k_4^{1/2}$, the mean value being $25.6 \text{ cm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$ at 23°C . The analogue of reaction (10) involving CF_3



was studied by Amphlett and Whittle [12]. Their results yielded $k_{12}/k_c^{1/2} = 6.0 \text{ cm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$ at 23°C where k_c refers to CF_3 combination. It is likely that k_c is about the same for the combination of CF_2Cl and CF_3 radicals [13], and hence CF_2Cl apparently abstracts H more readily from HCl than CF_3 does. The reduced reactivity of CF_3 could well be caused by its greater polarity. A similar effect was observed by Tucker and Whittle [14] in a comparison of the rate constants for the reaction of CF_3 and CH_3 with HBr.

4.4. Photolysis of BCF in the presence of HBr

The results in Section 4.3 indicate that HCl does not compete effectively with Br_2 as a radical scavenger. It is known [12, 14] that CF_3 radicals react much faster with HBr than with HCl, so we next photolysed BCF with added HBr. The CF_2Cl radicals should be scavenged by the reaction



However, there is now the complication that HBr absorbs at the wavelengths (about 248 nm) used to photolyse the BCF. A comparison of extinction coefficients shows that in our reaction vessel a mixture of 25 Torr of BCF with 2 Torr of HBr irradiated at 248 nm would involve the absorption of 45% of the light by BCF and 0.5% by HBr. Hence there should be negligible photolysis of HBr. This was confirmed by an experiment in which 2 Torr of HBr was photolysed alone for 60 min; there was less than 0.9% decomposition. Even if traces of H_2 and Br_2 were formed from HBr when BCF is photolysed with HBr present, it would not matter since we have extrapolated $\phi(\text{CF}_2\text{ClH})$ from BCF to zero photolysis time (see below).

Mixtures of 25 Torr of BCF and 2 Torr of HBr were photolysed under standard conditions (constant I_0) for photolysis times in the range 0.5 - 10 min. The only product was CF_2ClH , and $\phi(\text{CF}_2\text{ClH})$ is plotted against the photolysis time in Fig. 2. The quantum yields of CF_2ClH are much higher than when HCl was used as scavenger with similar photolysis times which shows that HBr is a better scavenger than HCl is. This is confirmed by the fact that a run with 34 Torr of BCF and only 0.2 Torr of HBr still gave CF_2ClH as the only product (compare with the results for BCF and HCl in Table 5). The results of runs using 50 Torr of BCF with 2 Torr of HBr and 25 Torr of BCF with 5 Torr of HBr for various photolysis times are also

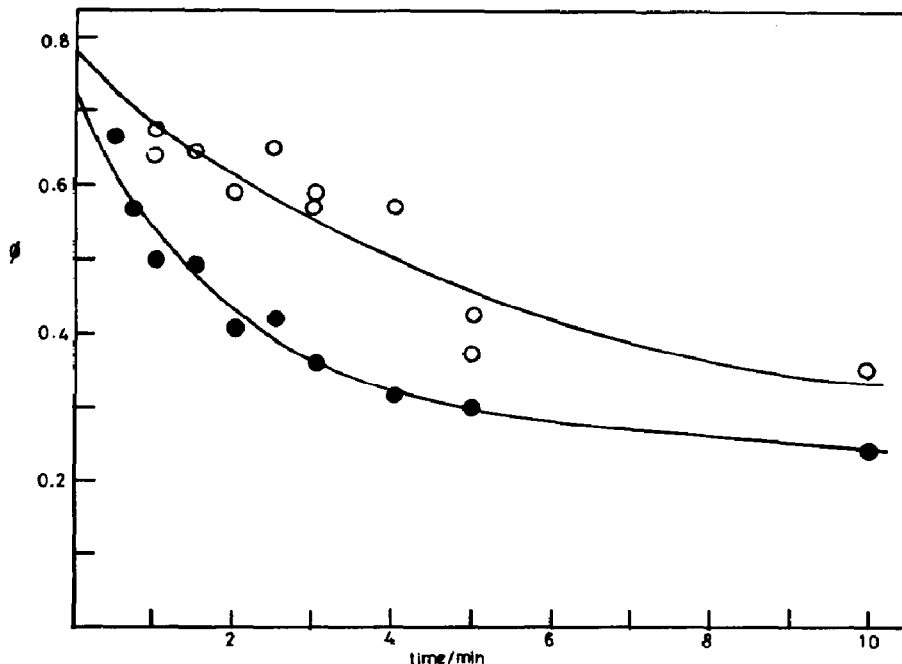


Fig. 2. Variation with the photolysis time of the quantum yield for removal of BCF: ●, HBr scavenger; ○, Cl₂ scavenger.

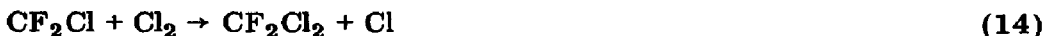
shown in Fig. 2. It is clear that $\phi(\text{CF}_2\text{ClH})$ is independent of the pressures of BCF or HBr. A computer curve fit to the data in Fig. 2 leads to

$$\phi(-\text{BCF}) = \phi(\text{CF}_2\text{ClH}) = 0.73 \pm 0.08$$

at zero photolysis time. The error limit is 1 standard deviation.

4.5. Photolysis of BCF in the presence of Cl₂

The primary quantum yield for the decomposition of BCF obtained in Section 4.4 was checked by the photolysis of BCF in the presence of Cl₂ when the expected scavenging reaction should be



We found that CF₂Cl₂ was the only product from all the runs using BCF and Cl₂. The absence of CF₂ClCF₂Cl indicates complete suppression of reactions, other than (14) and (8), involving CF₂Cl. Another possible route to CF₂Cl₂ is via the sequence



followed by reaction (14). Reaction (16) should be very slow at room temperature but as a check we photolysed a mixture of 25 Torr of BCF and 2 Torr of Cl₂ for 10 min with a Pyrex plate in front of the reaction vessel to remove wavelengths absorbed by BCF. No products were obtained.

Mixtures of 25 Torr of BCF and 2 Torr of Cl_2 were photolysed for various times and the values of $\phi(\text{CF}_2\text{Cl}_2)$ obtained are shown in Fig. 2. The results of other runs using 50 Torr of BCF and 2 Torr of Cl_2 or 10 Torr of BCF and 1 Torr of Cl_2 are also shown in Fig. 2. It is clear that $\phi(\text{CF}_2\text{Cl}_2)$ is independent of the pressures of BCF or Cl_2 . The fact that the quantum yields with a given photolysis time are higher for the BCF- Cl_2 mixture than for the BCF-HBr mixture indicates that Cl_2 is a more efficient scavenger of CF_2Cl than HBr is. Extrapolation of the line in Fig. 2 to zero photolysis time, as in Section 4.4, gave

$$\phi(-\text{BCF}) = \phi(\text{CF}_2\text{Cl}_2) = 0.78 \pm 0.08$$

4.6. Photolysis of BCF in the presence of Br_2

If reactions (3) - (9) correctly describe the photolysis of BCF alone, with reaction (8) acting as an efficient back reaction, then the photolysis of BCF to which a few torr of Br_2 are added initially should make reaction (8) so efficient as to lead to the trivial result that no detectable products should be formed at all provided that the products all involve the CF_2Cl radical as a precursor. The results of such photolyses are given in Table 6. As expected, no $\text{CF}_2\text{ClCF}_2\text{Cl}$ or CF_2Cl_2 (or C_2F_4) were formed but CF_2Br_2 was still obtained. Within experimental error, $\phi(\text{CF}_2\text{Br}_2)$ was independent of the photolysis time and was also the same as that of the photolysis of BCF alone (see Table 3). This strongly suggests that CF_2Br_2 is *not* formed via reactions involving CF_2Cl radicals, *e.g.* reaction (5) followed by reaction (9).

TABLE 6

Quantum yields of products from the photolysis of CF_2ClBr vapour in the presence of Br_2

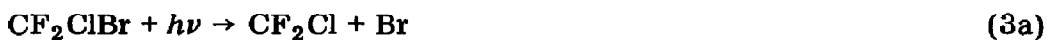
Pressure (Torr)		Photolysis time (min)	$\phi(\text{CF}_2\text{Br}_2) \times 10^3$
CF_2ClBr	Br_2		
10.3	0.54	60	13
10.0	0.50	120	13
10.2	0.53	180	10

5. Discussion of the mechanism of the BCF photolysis

The experiments on the photolysis of BCF-HBr and BCF- Cl_2 mixtures give primary quantum yields for the removal of BCF of 0.73 ± 0.08 and 0.78 ± 0.08 respectively after extrapolation to zero photolysis time. However, these results probably have larger error margins than are indicated by the standard deviations above since the quantum yield curves in Fig. 2 rise rapidly at short photolysis times. Ideally we need data obtained after a few

seconds photolysis but the product yields would be too small to measure. Figure 2 clearly illustrates how spurious values of $\phi(-\text{BCF})$ would be obtained if short photolysis times were not used. These remarks suggest that the values for $\phi(-\text{BCF})$ given above are quite compatible with a primary quantum yield of unity for loss of BCF (see also below). Quantum yields of unity have been obtained for the photolysis of related chlorofluorocarbons [15].

The results in Sections 4.2 - 4.6 help to explain some of the anomalies arising from the mechanism proposed in Section 4.2. The major weakness of reactions (3) - (9) is that they do not explain either the anomalously high yields of CF_2Cl_2 or the fact that CF_2Br_2 is formed in greater yield than any other product when BCF is photolysed alone. Also, CF_2Br_2 is the only product from the photolysis of $\text{BCF}-\text{Br}_2$ mixtures. To explain the formation of CF_2Br_2 , we propose that the photolysis of BCF involves two primary processes, one major and one minor:



The dominant route is (3a) for which we have already obtained $\phi_{3a} = 0.78 - 1$. If CF_2 is formed directly by step (3b) and is totally scavenged by reaction (9), then $\phi(\text{CF}_2\text{Br}_2)$ should be independent of the photolysis time and should be the same for the photolyses of BCF alone and with added Br_2 . A comparison of Tables 3 and 5 shows that this is the case within experimental error (the accuracy of measurement of CF_2Br_2 yields by GLC is reduced by the fact that CF_2Br_2 appears as a broadish peak on the tail of the massive BCF peak whereas CF_2Cl_2 and $\text{CF}_2\text{ClCF}_2\text{Cl}$ appear before BCF).

If all the CF_2 formed by reaction (3b) reacted with Br_2 , then $\phi(\text{CF}_2\text{Br}_2)$ would equal ϕ_{3b} . However, reaction (3b) also forms BrCl which would rapidly equilibrate by



Thus Cl_2 is formed so that CF_2Cl_2 could be produced by the reaction



This could explain the anomalously high yields of CF_2Cl_2 when BCF is photolysed alone (see Section 4.2). Thus

$$\phi_{3b} = \phi(\text{CF}_2\text{Br}_2) + \phi(\text{CF}_2\text{Cl}_2 \text{ from reaction (18)})$$

The second term can be calculated if a value of k_4/k_5 is assumed (Section 4.2), but it would have little effect on ϕ_{3b} since $\phi(\text{CF}_2\text{Br}_2)$ in Table 2 is considerably greater than $\phi(\text{total CF}_2\text{Cl}_2)$ and some of the latter yield comes from reaction (5). Furthermore, in runs with added Br_2 equilibrium (17) will lie well to the left so that little Cl_2 will be available. It therefore seems likely that in these runs $\phi(\text{CF}_2\text{Br}_2)$ measures the true $\phi_{3b} = 1.3 \times 10^{-2}$ (see Table 6).

It can be argued that CF_2Br_2 could be formed by the reactions



where (3c) is a primary process that has not so far been considered. Process (3c) seems unlikely because $D(\text{CF}_2\text{Cl}-\text{Cl})$ is 336 kJ mol^{-1} [16] whereas $D(\text{CF}_2\text{Cl}-\text{Br}) = 270 \pm 5 \text{ kJ mol}^{-1}$ [17]. Hence photolysis should cause almost exclusively C-Br bond breaking. Also process (3c) gives CF_2Br radicals and we found none of the products expected if these radicals are present (Section 4.2).

An alternative to reaction (3b) is



This process seems unlikely since it is more endothermic than (3b) by $D(\text{Cl}-\text{Br}) = 218 \text{ kJ mol}^{-1}$ [17].

The discussion above indicates that, for the major and minor routes involved in the photolysis of BCF, ϕ_{3a} is 0.78 or more and could well be close to unity and $\phi_{3b} = 0.013$. The fact that the photolysis of BCF alone leads to products derived mainly from route (3b) is readily explained by the facile back reaction (8) which almost completely prevents the formation of products from the CF_2Cl radicals produced by route (3a).

The occurrence of the analogues of reactions (3a) and (3b) is widely accepted in the photolysis of alkyl halides, *e.g.* in CH_3Br and in fluoro analogues of BCF such as CF_2Br_2 , CF_2Cl_2 and CFCl_3 . For example, CF_2Cl_2 has been the subject of much IR laser photolysis work where laser-induced fluorescence has convincingly demonstrated the formation of CF_2 [18, 19]. Much of the IR laser work gives information only about the carbene channel and hence provides no data regarding the relative contributions of the analogues of our channels (3a) and (3b). However, most workers accept that carbene formation is the minor channel. This is confirmed by recent studies by Grant and coworkers [20] of the IR laser photolysis of CF_2Cl_2 , CF_2Br_2 and CF_2ClBr using added Br_2 as a scavenger. They conclude that the decomposition of CF_2Cl_2 gives up to 10% of CF_2 while that of CF_2Br_2 gives up to 30% of CF_2 with the other channels yielding $\text{CF}_2\text{Cl} + \text{Cl}$ and $\text{CF}_2\text{Br} + \text{Br}$ respectively. In contrast, they find no more than 1% of CF_2 from CF_2ClBr . Folcher and Braun [21] obtained results for CF_2Cl_2 decomposition similar to those of Grant and coworkers. Ritter [22] also showed that CF_2 is formed by the IR laser photolysis of CF_2Cl_2 and CF_2Br_2 . The CF_2 was trapped using olefins.

More relevant to our work are the UV photolyses of mixed halides in which Wampler *et al.* [23] and Sam and Yardley [24] obtained CF_2 from CF_2Br_2 using laser photolysis at 248 and 193 nm.

Direct photolysis of fluoroalkyl halides using conventional sources of UV light also provides evidence of carbene formation. Some of the work gives quantum yields into channels analogous to (3a) and (3b). Thus

Hauteclouque [25] studied CHFCl_2 using $\lambda = 193$ nm and obtained $\phi(\text{CHFCl} + \text{Cl})/\phi(\text{CFCl} + \text{HCl}) \approx 10$ with $P > 50$ Torr whereas the ratio is closer to 100 with $P \approx 90$ Torr. Rebert [15] photolysed CF_2Cl_2 , CFCl_3 and CCl_4 with Br_2 present as a scavenger. The results for CF_2Cl_2 are typical, with $\phi(\text{CF}_2\text{ClBr}) = 1$ for channel (3a) and $\phi(\text{CF}_2\text{Br}_2) \approx 0.04$ using $\lambda = 214$ nm. Hauteclouque and Bernas [26] obtained similar values.

The photolysis of CF_2Br_2 at 265 nm was studied by Walton [27] who found the only products to be Br_2 and $(\text{CF}_2\text{Br})_2$. The values of $\phi(\text{CF}_2\text{Br})_2$ were small, e.g. at 67 °C ϕ decreased from 0.085 to 0.0045 as the pressure of CF_2Br_2 was increased from 3.3 to 34 Torr. Walton explained this decrease by suggesting that the initial excited state of CF_2Br_2 is quenchable. However, he took no account of a possible back reaction analogous to reaction (8) and the consequent possible dependence of $\phi(\text{CF}_2\text{Br})_2$ on the photolysis time. The low values of ϕ suggest that a back reaction was indeed occurring. An increase in initial CF_2Br_2 pressure would cause more light absorption and hence the production of more Br_2 in a given photolysis time. This in turn would reduce $\phi(\text{CF}_2\text{Br})_2$ as observed. Walton found no evidence of CF_2 production but this is not surprising as no radical scavengers were present. Mann and Thrush [28] and Simons and Yarwood [29] flash photolysed CF_2Br_2 and observed the absorption spectrum of CF_2 . However, they gave no information about the quantum yield for decomposition of CF_2Br_2 by the carbene channel.

The thermochemistry of the analogues of channels (3a) and (3b) has been considered by several workers, e.g. for CF_2Cl_2 and CF_2Br_2 . It is generally accepted that, despite the carbene channel (3b) being the minor primary photolytic process, it is slightly *less* endothermic than the C–X bond-breaking channel (3a). Thus King and Stephenson [19] used data from the *JANAF Thermochemical Tables* [30] to obtain for CF_2Cl_2



However, some of the bond energies and ΔH_f° values needed for this and similar calculations have been either estimated or calculated using data with large error limits. In our present work the thermochemical parameters are more reliable, as is shown below.

Recent studies in our laboratory of the kinetics and thermodynamics of the reaction



lead to $D(\text{CF}_2\text{Cl}-\text{Br}) = 270 \pm 5 \text{ kJ mol}^{-1}$ [17] which is equal to the endothermicity of channel (3a). To calculate ΔH° for channel (3b) we use

$$\Delta H_{3b}^\circ = \Delta H_f^\circ(\text{CF}_2) + \Delta H_f^\circ(\text{BrCl}) - \Delta H_f^\circ(\text{CF}_2\text{ClBr})$$

Our data for reaction (20) yield $\Delta H_f^\circ(\text{CF}_2\text{ClBr}) = 424 \text{ kJ mol}^{-1}$ which, together with other ΔH_f° values from ref. 30, leads to $\Delta H_{3b}^\circ = 257 \text{ kJ mol}^{-1}$.

Hence channel (3b) is less endothermic than channel (3a) by 13 kJ mol^{-1} . This difference is similar to those obtained for analogous processes, *e.g.* for CF_2Cl_2 [19], but is considerably more reliable.

6. Photolysis of BCF vapour at 313 nm

The absorption spectra of chlorofluorocarbons such as CF_2Cl_2 and CFCl_3 indicate that they will not be photodecomposed in the troposphere. However, this is less certain for BCF which contains the more photolabile C—Br bond. We have therefore tried to photolyse BCF at 313 nm.

The light source was as described in Section 2 and the 313 nm mercury line was isolated using filters [5]. The actinometers were potassium ferrioxalate [5] and $(i\text{-C}_3\text{F}_7)_2\text{CO}$. Stock and Whittle [31] showed that, for the latter, $\phi(\text{CO}) = 0.98$ at 313 nm. The data in Table 2 indicate that any absorption of light by BCF at 313 nm will be very weak. We therefore photolysed 600 Torr of BCF vapour at 20°C in a Pyrex reaction vessel of length 100 cm and internal diameter 5 cm. No products were detected after a 24 h photolysis which indicates that no more than $6 \times 10^{-4}\%$ of the BCF had decomposed. Using a collision cross section from Table 2, we estimate that $\phi(-\text{BCF})$ is 0.01 or less. A similar experiment with HCl added as a radical scavenger gave no detectable products from which we estimate that $\phi(-\text{BCF})$ is 0.02 or less.

7. Photolysis of BCF vapour in the presence of liquid mercury

Liquid mercury has frequently been used to scavenge halogens and hence to suppress back reactions such as (8). We therefore photolysed 100 Torr of BCF vapour in the reaction vessel (100 cm long) described in Section 6 which contained a pool of distilled mercury 1 cm wide along its length. After 6 h photolysis at 313 nm, CF_2Cl_2 (about $0.39 \mu\text{mol}$) and $(\text{CF}_2\text{Cl})_2$ (about $0.17 \mu\text{mol}$) were present. The ratio $[\text{CF}_2\text{Cl}_2]/[(\text{CF}_2\text{Cl})_2]$ was equal to 2.5 and $\phi(-\text{BCF})$ was about 0.1 - 0.2. Similar experiments carried out at 248 nm using a quartz cell 10 cm long containing a pool of mercury also gave CF_2Cl_2 and $(\text{CF}_2\text{Cl})_2$ with $[\text{CF}_2\text{Cl}_2]/[(\text{CF}_2\text{Cl})_2] = 0.23$ and $\phi(-\text{BCF}) = 0.24$, compared with $\phi(-\text{BCF}) \approx 0.01$ and $[\text{CF}_2\text{Cl}_2]/[(\text{CF}_2\text{Cl})_2]$ in the range 0.37 - 0.82 for BCF photolysed at 248 nm in the absence of mercury (see Table 3). In both series of experiments a dark grey deposit was formed on the mercury surface. The facts that (a) the ratio $[\text{CF}_2\text{Cl}_2]/[(\text{CF}_2\text{Cl})_2]$ was very different at the two wavelengths in the presence of mercury, (b) the ratio differed at 248 nm from that for BCF in the absence of mercury and (c) $\phi(-\text{BCF})$ was substantial at 313 nm suggest that the photodecomposition of BCF is readily catalysed by the presence of a liquid mercury surface. Boynton and Taylor [32] found that, on photolysis of CH_3Br vapour in the presence of liquid mercury, $\phi(-\text{CH}_3\text{Br})$ depended

strongly on the state of the mercury surface. Surface catalysis was also observed by Ausloos *et al.* [33] who showed that in the presence of silica powder CF_2Cl_2 , CFCl_3 and CCl_4 are photodecomposed by wavelengths much longer than those that they normally absorb. The following section gives further information on the mercury catalysis.

We recommend that liquid mercury is not used as a scavenger for halogens in photochemical systems even if the incident light is incapable of absorption by mercury vapour (*e.g.* 313 nm). This recommendation is reinforced by other work in our laboratory on the photolysis of CF_3CHClBr vapour (Halothane (Fluothane)) in the presence of liquid mercury where anomalous results were also obtained [34].

8. Effect of sunshine on BCF vapour

Long-term experiments to test the effect of sunshine on BCF vapour were carried out as follows. Six Pyrex spherical flasks of volume 1 dm^3 were each fitted with a Young grease-free tap with Teflon sealing rings. Each bulb contained 100 Torr of BCF under the following conditions: bulb 1, BCF alone; bulb 2, BCF alone, bulb blackened; bulb 3, BCF with a mercury pool 3 cm in diameter; bulb 4, as bulb 3 but with the bulb blackened; bulb 5, BCF plus 50 g clean dry fired Sahara Desert sand (supplied by Dr. G. S. Milne, I.C.I. Mond Division); bulb 6, BCF plus air to 1 atm.

The bulbs were mounted on the university roof in full daylight. About 0.3% of the contents of each bulb were removed at intervals of about 4 weeks for a total period of 60 weeks and the samples were analysed by GLC. Sampling was repeated after 3 years' exposure to sunshine. Analysis was again by GLC and an IR spectrum of a sample from bulb 6 was obtained. The results were as follows.

Bulbs 1, 2, 4, 5 and 6 contained no detectable products after 60 weeks. In bulb 3 (BCF plus liquid mercury) products were detectable after 1 week; by far the major product was $(\text{CF}_2\text{Cl})_2$. After 11 weeks 50% of the BCF in bulb 3 had reacted and many products were present. After exposure for 3 years the following GLC results were obtained. In bulb 1 a single peak X (apart from BCF) with the same appearance time as air or C_2F_4 was obtained. By using an estimated sensitivity and correcting for depletion by sampling, the partial pressure of X was determined to be about 1.3 Torr relative to the initial 100 Torr of BCF. Only product X, equivalent to 0.1 Torr, was produced in bulb 2. A variety of products was present in bulb 3 with the significant ones having the following partial pressures (Torr): X, 1; CF_2Cl_2 , 0.08; $(\text{CF}_2\text{Cl})_2$, 12; CF_2Br_2 or $\text{CF}_2\text{ClCF}_2\text{Br}$, 0.1; residual BCF, 0.3. Hence more than 99% of the BCF had disappeared. The inside of the bulb was coated with an extensive dark grey solid deposit. The tests in bulb 4 were stopped after 1 year when there were no detectable products. Bulb 5 contained 1 Torr of X, the only product, and 44 Torr of BCF. Hence 56 Torr of

the original BCF had disappeared. The tests in bulb 6 were stopped after 1 year when there were no detectable products or loss of BCF.

These observations lead to the following conclusions. There was slightly more decomposition of BCF in bulb 1 (BCF in daylight) than in bulb 2 (BCF in the dark). However, even after 3 years' exposure to daylight, no more than about 2% of the BCF had decomposed (assuming that peak X was C_2F_4 and that each C_2F_4 molecule comes from $2CF_2ClBr$ molecules). In complete contrast, bulb 3 (BCF plus mercury in daylight) contained no more than 1% of the original BCF and 50% had reacted after 11 weeks. No such reaction occurred with mercury present but daylight absent (bulb 4). The catalytic effect of mercury is again apparent, just as reported in Section 7. This must involve wavelengths above 290 nm as the bulbs were Pyrex. It is unlikely that the catalysis involves the formation of a BCF-Hg complex in the vapour phase since the partial pressure of mercury vapour should be greatly reduced by the halogens formed from BCF. This catalysis needs more study.

The results from bulb 5 (BCF plus sand in daylight) were novel in that no products were detected yet 56% of the BCF had reacted and the sand had become discoloured. The catalytic decomposition of chlorofluorocarbons by sand and by silica has been reported previously. The results from bulb 6 show that BCF is very stable in the presence of air in daylight.

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