

## REACTION OF O( $2^1D_2$ ) WITH HALOMETHANES

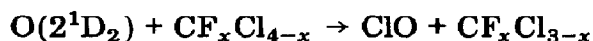
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### Summary

The reactions of O( $2^1D_2$ ) with the halomethanes CFCl<sub>3</sub>, CF<sub>2</sub>Cl<sub>2</sub>, CF<sub>3</sub>Cl, CF<sub>2</sub>HCl, CFHCl<sub>2</sub> and CF<sub>3</sub>Br have been studied using flash photolysis with kinetic spectroscopy (O( $2^1D_2$ ) atoms were generated by photolysis of O<sub>3</sub> or N<sub>2</sub>O in the ultraviolet). Formation of ClO has been observed and lower limits for the branching ratio into the channel



relative to the total cross section for removal of O( $2^1D_2$ ) were determined as 0.39, 0.47, 0.39, 0.27 and 0.36 for the molecules CF<sub>3</sub>Cl, CF<sub>2</sub>Cl<sub>2</sub>, CFCl<sub>3</sub>, CF<sub>2</sub>HCl and CFHCl<sub>2</sub>, respectively. The secondary yields of ClO following the reaction of CF<sub>x</sub>Cl<sub>3-x</sub> radicals with O<sub>2</sub> are also reported.

The reaction of O( $2^1D_2$ ) with CF<sub>3</sub>Br is shown to yield BrO as a primary product. The photolysis of CCl<sub>3</sub>Br in the presence of O<sub>2</sub> is also shown to yield BrO, but in this case via secondary reactions.

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### 1. Introduction

There is considerable current interest [1, 2] in the ClO<sub>x</sub> cycle which is one of the catalytic processes leading to removal of odd oxygen (O<sub>3</sub> and O) in the stratosphere:

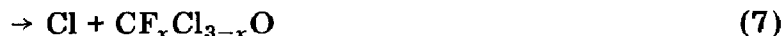
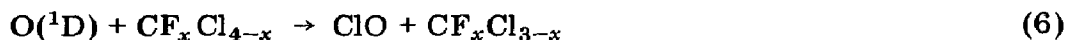


( $k_1 = 1.25 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [3, 4],  $k_2 = 5.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [5] at 300 K). Injection of ClO<sub>x</sub> into the stratosphere by reactions of both naturally occurring and synthetic halogenated alkanes (the latter including in particular the commercially important CF<sub>2</sub>Cl<sub>2</sub> and CFCl<sub>3</sub>) has been considered [1, 2]. Photolysis by solar UV radiation and reaction with electronically excited oxygen atoms O( $2^1D_2$ ) may each release ClO<sub>x</sub>:



There may be further release of  $\text{ClO}_x$  in subsequent reactions of the fragment R and in photolysis or reactions of products of other channels (5). Several studies of the photo-oxidation of haloalkanes employing end product analysis [6 - 8] indicate that a carbonyl halide is the main and possibly the only oxidation product; however, the complete mechanism has not been established unambiguously and there is a clear need for more direct studies of the reactions of halomethyl radicals with  $\text{O}_2$  and of the contribution of the various possible channels in the reaction of  $\text{O}(^1\text{D})$  atoms with halomethanes.

The complexity of the reaction of  $\text{O}(^1\text{D})$  atoms with  $\text{CH}_4$  is now reasonably well understood [9] and studies by Lin [10] of HCl and HF chemical laser emission following the reaction of  $\text{O}(^1\text{D})$  atoms with various hydrogen-containing chlorofluoromethanes have provided some information on the occurrence of insertion-elimination reactions with these molecules. Given this background, a number of possible channels in the reaction of  $\text{O}(^1\text{D})$  with a molecule  $\text{CF}_x\text{Cl}_{4-x}$  merit consideration:



There is no reason to discount reaction (7) *a priori*, although its analogue has not been observed for  $\text{O}(^1\text{D}) + \text{CH}_4$ . Equation (7) is more exothermic than eqn. (6) (with  $\text{CF}_3\text{Cl}$ ,  $\Delta H_{298}^\circ$  (eqn. (6)) =  $-98 \text{ kJ mol}^{-1}$  and  $\Delta H_{298}^\circ$  (eqn. (7))  $\cong -239 \text{ kJ mol}^{-1}$ )\*. Since it appears that certain reactions of  $\text{O}(^1\text{D})$  atoms occur by insertion followed by fragmentation in a statistical manner governed by the volume of phase space available for different channels [13], reaction (7) appears quite plausible. It should be noted that the molecule  $\text{CF}_3\text{OCl}$  is well characterised [14] and might be stabilised at very high pressures if the reaction proceeds via  $\text{CF}_3\text{OCl}$ . Furthermore, hypochlorites are known to be useful reagents for producing alkoxy radicals and the photolysis and thermal reactions of  $\text{CF}_3\text{OCl}$  are thought to proceed through the formation of  $\text{CF}_3\text{O}$ , thus supporting our suggestion that channel (7) deserves serious consideration. Direct abstraction, on the other hand, would favour reaction (6). Evidence for reactions of the type shown in

\*Thermochemical data have been taken from ref. 11, with the exceptions of  $\text{CF}_3\text{O}$  [6] and  $\text{ClO}$  [12].

eqns. (9) and (10) has been obtained [15] by employing flash photolysis in a fast flow system with nozzle beam mass spectrometric sampling. Heicklen and coworkers [7] have concluded from steady photolysis experiments that deactivation of  $O(^1D)$  to  $O(^3P)$  by  $CCl_4$ ,  $CFCl_3$  and  $CF_2Cl_2$  is negligible. Pitts *et al.* [16] have come to a similar conclusion but no direct measure of any contribution from this channel has been reported.

In a preliminary report [17] we described measurements of a lower limit to the branching ratio for ClO formation in the reaction of  $O(^1D)$  with  $CF_3Cl$ ,  $CF_2Cl_2$  and  $CFCl_3$ , employing  $O_3$  as the source of  $O(^1D)$  atoms. However, these experiments are open to the possible objection that ClO could be produced indirectly via



The possible involvement of reaction (7) has been mentioned; under the conditions of our experiments [17] the half-life of a Cl atom with respect to reaction (1) is about  $5 \mu s$ , so that a large contribution from reactions (7) and (1) would not be readily distinguishable from the occurrence of reaction (6) alone. For this reason we have carried out further studies employing  $N_2O$  as the source of  $O(^1D)$ . We also describe some experiments on the oxidation of halomethyl radicals.

## 2. Experimental

The apparatus for flash photolysis with time-resolved absorption spectroscopy in the ultraviolet ( $\lambda > 200 \text{ nm}$ ) has been described [17]. During work where measurements were made on the  $NO \gamma(0,0)$  and  $\delta(0,4)$  bands it was found that the spectral intensity in the region below 230 nm fell quite rapidly owing to the deposition of powdered silica on the window of the spectroscopic flashlamp when this was discharged at 15 kV as in previous experiments. Reducing the voltage to 13 kV did not significantly alter the output of the lamp but greatly prolonged the useful life of the window.

The concentration of ozone in mixtures was measured by recording the UV absorption around 250 nm on a spectrophotometer (Perkin-Elmer model 402); absorption coefficients were taken from the work of Griggs [18]. Pressures of other gases were measured with a glass spiral gauge backed by a mercury manometer. Gases were handled in a conventional greaseless glass vacuum system.

Photographic plates were developed under standard conditions and optical density tracings obtained using a Joyce-Loebl double beam recording microdensitometer. The concentration of ClO was determined from the optical density in the (8,0) or (11,0) bands of the  $A^2\Pi \leftarrow X^2\Pi$  system. The contrast at the wavelength of these bands was determined for the

majority of plates and remained constant throughout this work at about 1.2. Extinction coefficients (base 10) of  $\epsilon(11,0) = 3 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  and  $\epsilon(8,0) = 2.5 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  were employed (see below). The Beer-Lambert law was obeyed in the concentration range of these experiments ( $[\text{ClO}] \leq 5 \times 10^{14} \text{ molecule cm}^{-3}$ ). The concentration of  $\text{NO}(v'' = 0)$  was calibrated directly using standard mixtures of NO in the presence of the same pressure of  $\text{N}_2\text{O}$  or  $\text{N}_2\text{O} + \text{CF}_3\text{Cl}$ , as used in kinetic experiments. Because of the low plate density at the wavelengths of the various  $\text{NO}(v'' \leq 4)$  transitions employed, the contrast was not constant and was determined for the wavelength of each band; plots of  $D$  versus  $\log E$  were approximately linear for small optical density changes in this region, the contrast falling to about 0.6 at 227 nm. Concentrations of vibrationally excited NO were normalised to the  $\text{NO}(v'' = 0)$  calibration using Franck-Condon factors from the compilations of Jain and Sahni [19] ( $\gamma$  bands) and Ory [20] ( $\delta$  bands) together with a value for the relative oscillator strength  $f_{00}^{\gamma}/f_{00}^{\delta} = 0.08$  calculated as the mean of several reported values for these two quantities [21 - 25].

### 2.1. Materials

$\text{O}_3$  was prepared by passing dried  $\text{O}_2$  through an ozonizer and trapping the product on silica gel at 195 K. After pumping to remove  $\text{O}_2$ , the  $\text{O}_3$  was allowed to expand into a large blackened bulb.  $\text{N}_2\text{O}$  of B.O.C. medical grade ( $\geq 99\%$ ) was thoroughly degassed and used directly. NO (Matheson) was fractionally distilled several times from 90 K to a trap held at 77 K, retaining the middle fraction.  $\text{CF}_2\text{Cl}_2$  and  $\text{CFCl}_3$  (given by I.C.I.) were degassed and used without further purification.  $\text{CF}_3\text{Cl}$ ,  $\text{CF}_3\text{Br}$  (Matheson) and  $\text{CF}_2\text{HCl}$ ,  $\text{CFHCl}_2$  (I.C.I. Arcton) were taken from cylinders, degassed by repeated freeze-pump-thaw cycles and used directly.

## 3. Results and discussion

### 3.1. Branching ratio for ClO formation using $\text{O}_3$

The determination of a lower limit to the branching ratio for ClO formation,  $k_4/(k_4 + k_5)$ , for  $\text{CF}_3\text{Cl}$ ,  $\text{CF}_2\text{Cl}_2$  and  $\text{CFCl}_3$  has been described [17]. In these experiments,  $\text{O}_3$  was photolysed in the presence of a large excess ( $10.7 \text{ kN m}^{-2}$ ) of chlorofluoromethane. Under such conditions the half-life for removal of  $\text{O}(^1\text{D})$  is about 1 ns, so that the early appearance of ClO followed the integrated profile of the photolysis flash. Branching ratios for ClO formation were estimated by comparison of the extent of  $\text{O}_3$  removal at  $10 \mu\text{s}$  with the amount of ClO produced. An improved measurement of the relative extinction coefficients of  $\text{ClO}(\text{A}^2\Pi \leftarrow \text{X}^2\Pi)$  bands and continuum has now been carried out, using the photolysis of  $\text{N}_2\text{O}$  in the presence of  $\text{CF}_3\text{Cl}$  to produce ClO in the absence of other absorbers in the spectral region of interest (250 - 290 nm). Extinction coefficients relative to the ClO continuum at 257.7 nm, which was taken as unity, in the (8,0)

TABLE 1

Lower limits to the branching ratio for ClO formation in removal of  $O(2^1D_2)$  atoms by chlorofluoromethanes using  $O_3$

Molecule	$k_4/(k_4 + k_5)$
$CF_3Cl$	$\geq 0.39$
$CF_2Cl_2$	$\geq 0.47$
$CFCl_3$	$\geq 0.39$
$CF_2HCl$	$\geq 0.27$
$CFHCl_2$	$\geq 0.36$

and (11,0) bands were found to be 1.25 and 1.46, respectively. Clyne and Coxon [26] determined absolute extinction coefficients at 298 K of  $\epsilon(257.7 \text{ nm}) = (2.11 \pm 0.07) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  and  $\epsilon(11,0) = (3.15 \pm 0.10) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ ; Basco and Dogra [27] have obtained  $\epsilon(257.7 \text{ nm}) = 1.91 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  and  $\epsilon(11,0) = 2.82 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ \*. Combining these results, we have used  $\epsilon(11,0) = 3 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  and  $\epsilon(8,0) = 2.5 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ . The (11,0) band was employed for concentration measurements in experiments using  $N_2O$  as the source of excited atoms, while the (8,0) band was used in experiments with  $O_3$ , the intensity of absorption by  $O_3$  being less at the wavelength of the latter band, 285.2 nm.

Results for  $CF_3Cl$ ,  $CF_2Cl_2$  and  $CFCl_3$ , modified in the light of the above determination of the ClO extinction coefficient and of a small systematic error in  $O_3$  concentration measurement, are listed in Table 1. Also included are lower limits for the ClO formation branching ratio for  $CF_2HCl$  and  $CFHCl_2$ . It is emphasised that these results represent lower limits only, since it appears that removal of ClO may be important even at a very early stage of the reaction. In contrast, secondary formation of ClO is fairly slow in the cases where it is possible. Since these experiments involved a rather imprecise measurement of reduction in  $O_3$  concentration using plate photometry, it was not possible to circumvent this problem by calculating ClO formation and  $O_3$  removal for delays less than 10  $\mu\text{s}$ .

### 3.2. Secondary reactions in the presence of $O_3$ and $O_2$

The kinetic behaviour of ClO subsequent to the initial rapid formation is of interest; results for  $CF_3Cl$ ,  $CF_2Cl_2$  and  $CFCl_3$  appear in Fig. 1. For  $CF_3Cl$ , the disappearance of ClO may be divided into two distinct regions. Immediately after the photolysis flash, ClO removal is rapid and cannot be explained solely by the bimolecular reaction of ClO

\*The vibrational numbering in the A state has recently been revised [28] and differs from that given in refs. 26 and 27; the revised values are lower by unity.

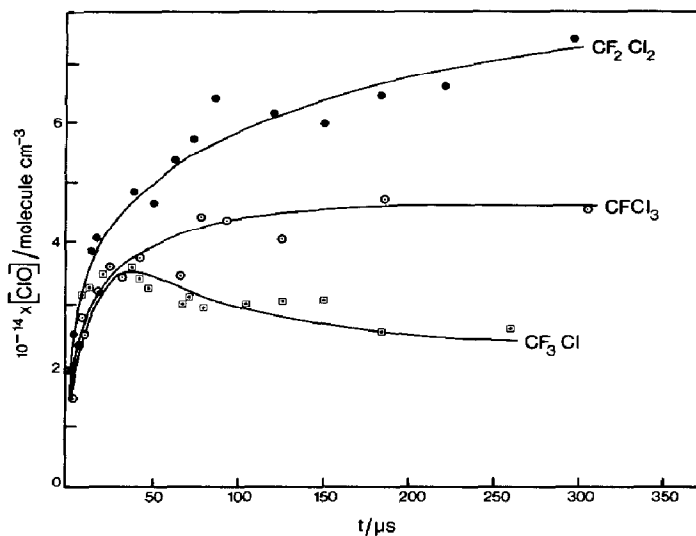
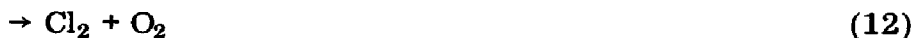


Fig. 1. Formation and decay of ClO after the photolysis of  $O_3$  ( $14.9 \text{ N m}^{-2}$ ) in the presence of  $CF_3Cl$ ,  $CF_2Cl_2$  or  $CFCl_3$  ( $10.7 \text{ kN m}^{-2}$ ).



The mechanism of removal of ClO at higher pressures is subject to some disagreement [12, 29, 30]; recent work by Jaffee and DeMore [30] suggests that at pressures around 1 atm reactions (11) and (12) have approximately equal rates. However, the rate of ClO removal at  $50 \mu\text{s}$  in the  $O_3/CF_3Cl$  system is at least a factor of ten faster than the rate of mutual reaction of ClO radicals and must therefore be due to reaction of ClO with some other radical; the most plausible process is the reaction of ClO with  $CF_3$ . Reaction between ClO and  $O(^3P)$  can be discounted as the Cl atom formed would regenerate ClO by reaction (1).

Any similar rapid removal of ClO for  $CF_2Cl_2$  and  $CFCl_3$  is obscured by secondary formation of ClO in reactions of the radicals  $CF_2Cl$  and  $CFCl_2$ . This secondary growth is most pronounced for  $CF_2Cl_2$ , the total yield of ClO in this case being approximately twice that actually formed during the flash. However, it cannot be concluded (although it seems probable) that there is a more rapid secondary reaction for  $CF_2Cl$ , since competing formation and removal processes might be occurring to different extents.

Possible sources of secondary ClO are reactions with  $O_3$  and with  $O_2$  (some  $O_2$  is always present with the  $O_3$ ), *e.g.*

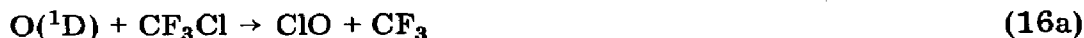


This mechanism requires removal of two ozone molecules for each ClO molecule formed; this is at variance with our observation that the removal of O<sub>3</sub> subsequent to the flash is rather slow. Thus we are forced to conclude that secondary formation of ClO must be attributed to the reaction of halomethyl radicals with O<sub>2</sub>. These reactions are discussed further in Section 3.5.

### 3.3. Photolysis of N<sub>2</sub>O in the presence of CF<sub>3</sub>Cl

The thermal reaction of Cl atoms with N<sub>2</sub>O is known to be extremely slow [31]. This was confirmed in the present work by photolysis of Cl<sub>2</sub> in the presence of excess N<sub>2</sub>O using radiation filtered through Pyrex to prevent any photolysis of the N<sub>2</sub>O; no ClO was detected. Thus all the initial ClO formation observed during the photolysis of N<sub>2</sub>O with CF<sub>3</sub>Cl present must arise from a reaction of the type shown in eqn. (6).

With photolysis restricted to  $\lambda > 200$  nm, and with the available flash energy, mixtures of 33.3 kN m<sup>-2</sup> N<sub>2</sub>O and 33.3 kN m<sup>-2</sup> CF<sub>3</sub>Cl were required to give sufficient absorption by NO and ClO for plate photometry. The behaviour early in the reaction may be considered in terms of the simplified mechanism



NO production (reaction (15b)) provides a measure of O(<sup>1</sup>D) formation when N<sub>2</sub>O is photolysed alone; there have been a number of recent determinations of the ratio  $k_{15a}/k_{15b}$ , values reported being  $0.70 \pm 0.02$  [32],  $0.83 \pm 0.06$  [33],  $1.01 \pm 0.06$  [34] and  $1.0 \pm 0.17$  [35]. Heicklen has suggested [33] that these discrepancies, lying well outside the quoted error limits, reflect a dependence on the translational energy of the O(<sup>1</sup>D) atom, but other workers [35] have found no evidence for such an effect. For the present purpose,  $k_{15a}$  has been set equal to  $k_{15b}$ ; any reduction in the ratio  $k_{15a}/k_{15b}$  would increase the derived branching ratio. Comparison of NO production on photolysis of N<sub>2</sub>O (33.3 kN m<sup>-2</sup>) and mixtures of N<sub>2</sub>O and CF<sub>3</sub>Cl (33.3 kN m<sup>-2</sup> of each) gave the ratio of overall rate constants  $k_{15}/k_{16} \approx 1$ , in reasonable agreement with reported values [36].

It may readily be shown that, for photolysis of an equimolar N<sub>2</sub>O/CF<sub>3</sub>Cl mixture, the branching ratio for ClO formation,  $k_{16a}/(k_{16a} + k_{16b})$ , is related to the ratio [ClO]/[NO], extrapolated to zero time to allow for the effect of differing rates of removal of those species, by

$$\frac{k_{16a}}{k_{16a} + k_{16b}} = \lim_{t \rightarrow 0} \frac{[\text{ClO}]}{[\text{NO}]} \frac{k_{15}}{k_{16}}$$

Calculation in this manner is made difficult by the fact that the reaction of  $O(^1D)$  with  $N_2O$  releases a substantial part of the available excess energy in channel (15b) as vibrational excitation of  $NO(v'' \leq 6)$  [37]. In the present work the (0,0), (0,1) and (0,2) bands in the  $\gamma$  system could be monitored, together with the (0,4)  $\delta$  band, but measurement by plate photometry of the very small concentrations of  $NO(v'' > 0)$  near  $t = 0$  was imprecise. The ratio of vibrationally excited to ground vibrational state  $NO$  in the early stages of reaction of the  $N_2O/CF_3Cl$  system was estimated to be 0.3 and the branching ratio for  $ClO$  formation to be greater than 0.27. This does not improve upon the limit determined using  $O_3$  (Section 3.1) which is therefore to be preferred. While these results confirm that formation of  $ClO$  is by the direct reaction of  $O(^1D)$  with  $CF_3Cl$ , this does not appear to be a promising method for precise determination of the branching ratio into reaction (4) because of the relatively imprecise nature of plate photometry measurements and the difficulty of making due allowance for the contribution of vibrationally excited  $NO$  formation.

The production of  $ClO$  in a primary step suggests that the reaction proceeds via direct dynamics; one would expect the product  $CF_3O$  to be favoured if the insertion complex  $CF_3OCl$  were formed (see Section 1). There is, however, an alternative structure for the collision complex which has the geometry  $CF_3ClO$  (analogous to iodoso compounds). This type of complex, while probably less stable than the hypochlorite ( $CF_3OCl$ ) structure, would be more likely to yield  $ClO$  and  $CF_3$ . Observations on the energy distribution in  $ClO$  are needed before more detailed conclusions can be drawn about the dynamics of this reaction.

#### 3.4. Reaction of $O(^1D)$ with $CF_3Br$

Formation of  $BrO$  has been observed from the reaction



using both  $N_2O$  and  $O_3$  as the source of  $O(^1D)$  atoms. Concentrations were measured at the (4,0) band head at 316.9 nm in the  $A^2\Pi \leftarrow X^2\Pi$  system. When  $O_3$  was employed, the photolysis radiation was filtered ( $\lambda > 240$  nm) so that no appreciable photolysis of the  $CF_3Br$  occurred. The reaction



is slower than that of the chlorine analogue ( $k_{19} = (1.2 \pm 0.2) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [38]) so that in this case all the initial rapid  $BrO$  formation must be due to reaction (18). This conclusion is confirmed by the observation of  $BrO$  following the photolysis of  $N_2O$  in the presence of  $CF_3Br$ . Rapid disappearance of  $BrO$  was observed during the tail of the flash (Fig. 2) so that no useful estimate of the branching ratio for reaction (18) could be made. This disappearance might be attributable to the occurrence of an appreciable degree of quenching of  $O(^1D)$  to  $O(^3P)$ , followed by the rapid reaction ( $k_{20} = (5 \pm 2) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [38])





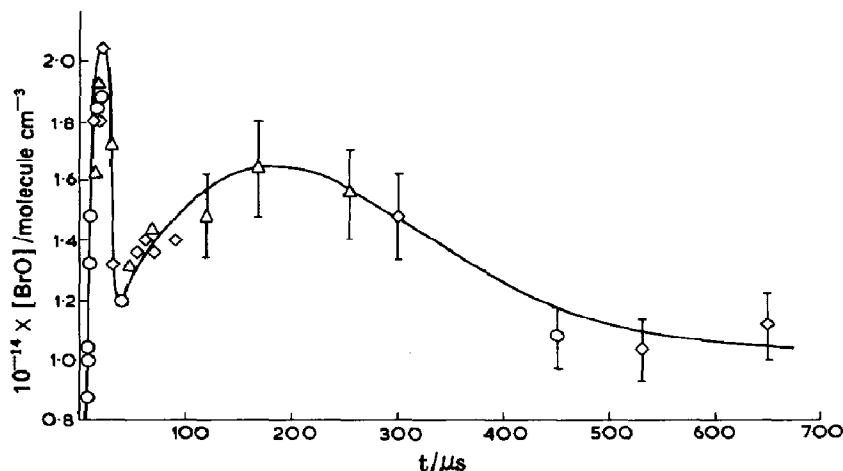


Fig. 2. Formation and decay of BrO after the photolysis of  $\text{O}_3$  in the presence of  $\text{CF}_3\text{Br}$ . The various symbols used indicate the scatter in data obtained from three independent experimental runs. The same experimental conditions were used for all three runs:  $P_{\text{O}_3} = 40.0 \text{ N m}^{-2}$ ;  $P_{\text{CF}_3\text{Br}} = 0.56 \text{ kN m}^{-2}$ ;  $P_{\text{He}} = 2.27 \text{ kN m}^{-2}$ .

until the  $\text{O}(^3\text{P})$  atoms are substantially depleted. The rise in BrO concentration in the range  $40 - 100 \mu\text{s}$  is consistent with the known rate of reaction (19). At longer times, when most of the  $\text{O}_3$  has been removed, the BrO decay was found to be second order in  $[\text{BrO}]$ ; using the extinction coefficient  $\epsilon(4,0) = (8.0 \pm 0.8) \times 10^{-38} \text{ cm}^2 \text{ molecule}^{-1}$  obtained by Clyne and Cruse [39], a second order rate constant for BrO disappearance,  $k_{21} = (4 \pm 2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , was obtained. Clyne and Watson [38] have determined  $k_{21} = (6.4 \pm 1.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reaction



### 3.5. Oxidation of halomethyl radicals

Reactions of radicals  $\text{CF}_x\text{Cl}_{3-x}$  with other species which are present in systems where photo-oxidation is occurring are not well understood. Milstein and Rowland [8] have photolysed  $\text{CF}_2\text{Cl}_2$  in the presence of  $\text{O}_2$  and deduced a quantum yield of 2 for the formation of  $(\text{Cl} + \text{ClO})$ . Heicklen and coworkers [7] have investigated the photolysis of  $\text{CCl}_4$  and chlorofluoromethanes in the presence of  $\text{O}_2$  and  $\text{O}_3$  using static photolysis with end product analysis. The points of interest for the present discussion are that the following mechanism of oxidation of the radical  $\text{CCl}_3$  by  $\text{O}_2$  was proposed:



Also it was concluded that the contribution of the following reaction, earlier favoured by Heicklen [6], is negligible:



Reactions analogous to eqns. (22) - (24) were proposed for  $\text{CF}_2\text{Cl}$  and  $\text{CFCl}_2$ .

We have observed ClO formation following photolysis of  $\text{CFCl}_3$  ( $5.33 \text{ kN m}^{-2}$ ) in the presence of  $\text{O}_2$  ( $4.67 \text{ kN m}^{-2}$ ). However, this might arise solely from the  $\text{Cl/O}_2$  reaction and provides no definitive information on the reaction of  $\text{CFCl}_2$  with  $\text{O}_2$ . Studies of the reaction  $\text{CCl}_3 + \text{O}_2$ , using photolysis of  $\text{CCl}_3\text{Br}$  to produce the  $\text{CCl}_3$  radical, are more revealing. Our observations are consistent with dissociation to give  $\text{CCl}_3 + \text{Br}$  in the first continuum ( $\lambda_{\text{max}} \approx 236 \text{ nm}$ ) with dissociation giving Cl atoms at shorter wavelength. Photolysis of  $\text{CCl}_3\text{Br}$  ( $133 \text{ N m}^{-2}$ ) in the presence of  $\text{O}_2$  ( $3.87 \text{ kN m}^{-2}$ ) using unfiltered radiation ( $\lambda > 200 \text{ nm}$ ) gave both BrO and ClO. BrO, which has a larger rate constant for removal, passed through a maximum concentration at about  $50 \mu\text{s}$ ; ClO continued to increase until about  $300 \mu\text{s}$ . The reaction of Br with  $\text{O}_2$  is very slow [39] and cannot be responsible for the observed rapid formation of BrO. Nevertheless, Br and Cl atoms are responsible for the production of BrO and ClO, as the following observations indicate.

(1) With photolysis down to  $200 \text{ nm}$ , the addition of  $4.2 \text{ kN m}^{-2}$  of  $\text{C}_2\text{H}_6$  to intercept Cl atoms reduced the ClO yield to an undetectable level, while the BrO yield was only slightly reduced.

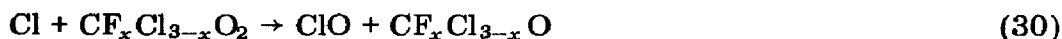
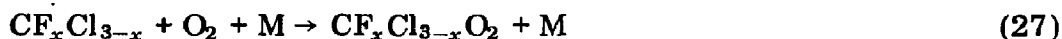
(2) With filtered photolysis radiation ( $\lambda > 223 \text{ nm}$ ), so that the formation of Cl atoms in photolysis of  $\text{CCl}_3\text{Br}$  was reduced, the ratio BrO/ClO increased fivefold.

These observations demonstrate that reaction (25) is indeed negligible, but that reactions (22) - (24), while they may occur, do not constitute a complete mechanism since OX radicals are also present as intermediates. Reaction (22) is expected to be rapid (by analogy with  $\text{CH}_3 + \text{O}_2$ ) and might be followed by abstraction reactions such as



The inclusion of such reactions is consistent with the end products which have been observed.

The secondary formation of ClO from reaction of  $\text{CF}_2\text{Cl}$  and  $\text{CFCl}_2$  with  $\text{O}_2$ , referred to in Section 3.2, can now be accounted for by the sequence of reactions



Further study of these systems is clearly warranted.

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