Journal of Photochemistry, *17* (1981) 405–412

PHOTOCHEMISTRY OF THE OZONE–HALOCARBON SYSTEM*

D.G. RALPH and R.P. WAYNE

Physical Chemistry Laboratory, Oxford University, South Parks Road, Oxford, Oxon. OX1 3QZ (Gt. Britain)

Summary

A photolytic flow system was used to study the primary and secondary steps in the reaction of $O(^1D)$ with chlorofluorocarbons. Concentrations of reactants and products were determined by quadrupole mass spectrometry; varying contact times were obtained by altering the distance between the photolysis lamp and the sampling orifice. "Intermediate" quantum yields for ozone loss and for ClO production were then analysed to provide kinetic information. Preliminary results with CF_2Cl_2 as the halocarbon suggest that $O(^1D)$, produced by ozone (O_3) photolysis, reacts to yield mainly CF_2Cl and ClO fragments. The CF_2Cl radicals then react with O_3, with a rate constant of the order of 10^{-14} molecule^{-1} cm^3 s^{-1}, to produce a further ClO radical, probably together with CF_2. CF_2O appears only at relatively long contact times, suggesting that it is not formed directly in a branch of the $O(^1D) + CF_2Cl_2$ reaction but rather in a secondary reaction between CF_2 and O_3.

1. Introduction

Direct photolysis in the stratosphere of the fluorocarbons CF_xCl_y can produce chlorine atoms that initiate a catalytic chain for ozone (O_3) destruction. Another initiation path involves the abstraction of a chlorine atom by $O(^1D)$, the $O(^1D)$ being formed by O_3 photolysis:

$$O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta_g) \qquad (1)$$

$$O(^1D) + CF_xCl_y \rightarrow CF_xCl_{y-1} + ClO \qquad (2)$$

Although the mechanism of reaction (2) has been studied, and rate constants established for some fluorocarbons [1 - 3], little seems known about the role that may be played by the CF_xCl_{y-1} radical. The end products CF_2O and CFClO have been observed with CF_2Cl_2 and $CFCl_3$ as the starting halocarbon [4 - 6]. Direct insertion of $O(^1D)$ has been suggested as a route to these products [7], but secondary radical reactions offer an alternative path [6].

---

* Paper presented at the Xth International Conference on Photochemistry, Iraklion, Crete, Greece, September 6 - 12, 1981.

0047-2670/81/0000-0000/$02.50

The experiments described in the present paper were intended to provide further information on the ozone–halocarbon system. The method of "intermediate quantum yields" [8, 9] was used, with a flow system to provide time resolution and with mass spectrometric detection of reactants and products. In the ideal form of the technique, concentrations and contact times are chosen to separate "fast" and "slow" reactions, the fast ones proceeding to completion and the slow ones not participating. In our experiments, the ideal conditions cannot conveniently be attained, and small corrections are applied, by computer modelling, for the finite rates of reaction.

2. Experimental details

A flow of carrier gas and reactants is passed through a fused silica photolysis tube of diameter 2.1 cm and length 100 cm. Flow velocities were in the range 7 - 10 m s^{-1} and total flow tube pressures were typically 0.7 - 0.9 Torr. A helical low pressure mercury discharge lamp, length 20 cm, with a reflecting enclosure, was arranged concentrically with the photolysis tube. The intensity of radiation at $\lambda = 253.7$ nm was maintained constant using an optical feedback system [8, 10]. At the downstream end of the flow tube, a pinhole permitted sampling, via a differential pumping system, to the ion source of a quadrupole mass spectrometer (poles of 0.75 in diameter and of length 9 in). The distance between the photolysis zone and the sampling pinhole could be altered in order to vary the contact time t_2 after photolysis, while both t_2 and the time t_1 in the photolysis region could be varied by changing the flow velocity.

The photolysis lamp was turned on and off repetitively for equal periods of about 12 s. Amplified and shaped pulses from the mass spectrometer detector (channel electron multiplier) were directed to one of two identical counters. The counters were gated by a precision timer that provided a delay (approximately 2 s) followed by a counting period (approximately 8 s) in a channel determined by whether the light was on or off.

Calibration of the mass spectrometer sensitivity for O_3 was achieved directly from the known partial pressure of O_3 in the flow tube. However, we noted that the response was non-linear in the presence of halocarbon, and allowance was made for the non-linearity when changes in O_3 concentration were calculated. The problem seems to be associated with the high pressures needed in the ion source for sufficient sensitivity to O_3. Improvements to the sampling system are in hand in an attempt to overcome the problem. For ClO, the sensitivity was assessed by adding a small flow of Cl_2, through which a microwave discharge had been passed, to a flow of O_3 in helium. The decrease in the $m/e = 48$ (O_3^+) signal was then compared with the increase in that at $m/e = 51$ (ClO^+), and a calibration factor was derived after making a small correction for the processes following bimolecular recombination of ClO.

Helium from a cylinder was dried by passing over P_2O_5 and then through a trap held at 99 K. Halocarbons were obtained from cylinders and dried by passing over P_2O_5. O_3 was prepared, and its purity measured, as described previously [11].

3. Results and discussion

In this section we present preliminary data obtained using CF_2Cl_2 as the halocarbon. The chemical processes not involving CF_2Cl reactions are assumed to be as in Table 1.

The parameter β represents a combination of incident light intensity, absorption cross section, primary quantum yield and geometrical factors. It is derived from experiments performed in the absence of CF_2Cl_2. Numerical integration of the rate equations yields a predicted value for the decrease $-\Delta[O_3]$ in O_3 concentration on photolysis which may be compared with the observed decrease. Iterative calculation then gives a best-fit value of β: the mean in these experiments was 0.73 s^{-1}. For the purposes of graphical display, we have plotted $-\Delta[O_3]$ against the function $[O_3]t_1$ in Fig. 1. Computer simulation shows that, for a fixed t_2, the relation between $-\Delta[O_3]$ and $[O_3]t_1$ is only weakly dependent on t_1 over the range of times employed. For the figures in the paper we use this device only for the convenience of graphical presentation. Figure 1 also indicates the extent of the "slow" reactions. The full line shows the values of $-\Delta[O_3]$ predicted for the full scheme of reactions, while the broken line is calculated using reactions (1) and (3) ("fast") alone.

Measured ClO concentrations produced by photolysis of O_3 in the presence of CF_2Cl_2 are appreciably higher than those explicable if reaction (2a) is the only source of the radicals. Some doubt exists about the branching ratio α ($= k_{2a}/k_2$) for the process, estimates ranging from a lower limit of 0.4 [13] to essentially unity [5, 7]. However, ratios of less than unity aggravate the shortfall between calculated and observed ClO concentrations. There must therefore be an additional source of ClO. For the time being we may write this source as

$$CF_2Cl + O_3 \rightarrow ClO + \text{other products} \qquad k_8 \qquad (8)$$

and return later to the nature of the process. Figure 2 shows some experimental results for fixed CF_2Cl_2 concentration and t_2. It is impossible to fit computed curves to the data with values of $\alpha < 0.7$, but for larger branching ratios good

TABLE 1

		Rate constants (units: molecule, cm^3, s)	
$O_3 + h\nu$	$\rightarrow O(^1D) + O_2(^1\Delta_g)$	β (see text)	(1)
$O(^1D) + CF_2Cl_2$	$\rightarrow ClO + CF_2Cl$	$k_{2a} + k_{2b} = k_2 = 1.4 \times 10^{-10}$	(2a)
	$\rightarrow O(^3P) + CF_2Cl_2$	$\alpha = k_{2a}/k_2$ (see text)	(2b)
$O(^1D) + O_3$	$\rightarrow 2O_2$	$k_{3a} = 1.2 \times 10^{-10}$	(3a)
	$\rightarrow 2O(^3P) + O_2$	$k_{3b} = 1.2 \times 10^{-10}$	(3b)
$O_2(^1\Delta_g) + O_3$	$\rightarrow 2O_2 + O(^3P)$	$k_4 = 3.8 \times 10^{-15}$	(4)
$O(^3P) + O_3$	$\rightarrow 2O_2$	$k_5 = 8.8 \times 10^{-15}$	(5)
$O(^3P) + ClO$	$\rightarrow O_2 + Cl$	$k_6 = 7.7 \times 10^{-11}$	(6)
$Cl + O_3$	$\rightarrow ClO + O_2$	$k_7 = 1.2 \times 10^{-11}$	(7)

Rate constants are taken from ref. 12.

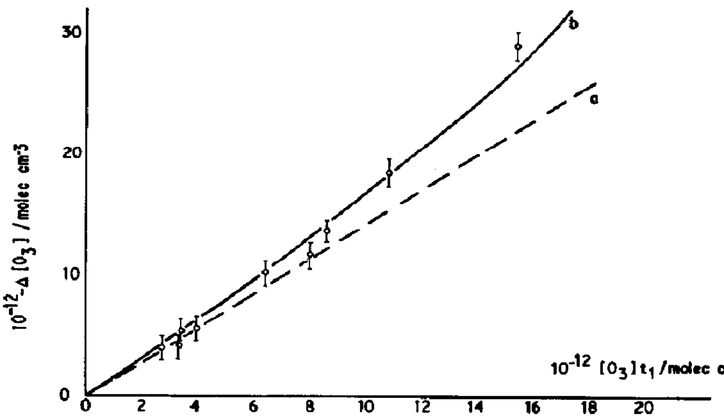

Fig. 1. Variation of $-\Delta[O_3]$ with $[O_3]t_1$ ($[CF_2Cl_2] = 0$; $t_1 = 17$ - 23 ms; $t_2 = 40$ ms; $P_{total} \approx$ 0.7 Torr; flow velocity, 8 m s^{-1}; carrier gas, helium): O, experimental data; curve a, - - -, computed results ($\beta = 0.73$ s^{-1}), reactions (1) and (3) only; curve b, ——, computed results ($\beta = 0.73$ s^{-1}), reactions (1) - (7).

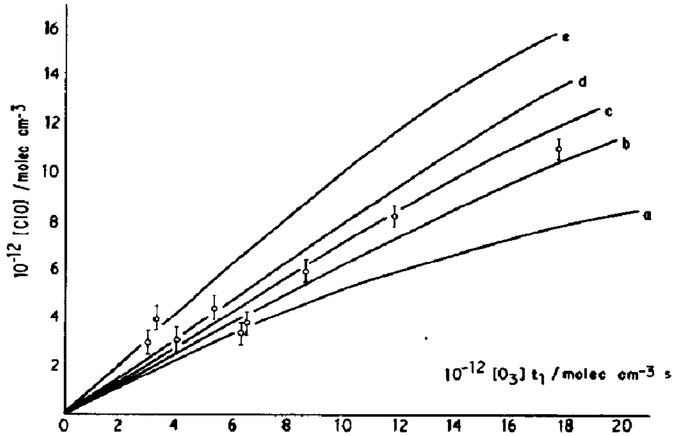

Fig. 2. Variation of [ClO] with $[O_3]t_1$ ($[CF_2Cl_2] = 3.2 \times 10^{15}$ molecule cm^{-3}; other parameters as for Fig. 1): O, experimental data; curves a - e, computed ($\alpha = 0.9$; $\beta = 0.73$ s^{-1}) for various values of k_8 (cm^3 $molecule^{-1}$ s^{-1}) (curve a, $k_8 = 0$; curve b, $k_8 = 1 \times 10^{-14}$; curve c, $k_8 = 2 \times 10^{-14}$; curve d, $k_8 = 3 \times 10^{-14}$; curve e, $k_8 = 10 \times 10^{-14}$).

agreements can be obtained by adjusting k_8. The figure shows a family of calculated curves for $\alpha = 0.9$, a value that we show later to be the most probable. The same values of α and k_8 also predict quite well the expected ClO concentration at other CF_2Cl_2 concentrations and contact times (Table 2).

The question now arises whether the measurements of $-\Delta[O_3]$ also require destruction of O_3 in reaction (8). Figure 3 gives experimental data for the $[CF_2Cl_2]$ and t_2 values used in the ClO concentration measurements. Curve a, for $k_8 = 0$ (and $\alpha = 0.9$), lies well below the observed $-\Delta[O_3]$ values, showing

TABLE 2

Observed and calculated [ClO] and $-\Delta[O_3]$

10^{-14} [O_3] (molecule cm^{-3})	10^{-14} [CF_2Cl_2] (molecule cm^{-3})	t_1 (ms)	t_2 (ms)	10^{-12} [ClO] (molecule cm^{-3}) *Observed*	*Predicted*	$10^{-12}\Delta[O_3]$ (molecule cm^{-3}) *Observed*	*Predicted*
5.8	17.4	18.7	39.2	7	—	18	19
3.6	34.7	34.6	72.7	14	11	22	19
11.9	37.6	34.9	73.3	34	33	95	94
7.8	77	17.1	35.5	16	12	—	21

For the calculations $k_8 = 2 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} and $\alpha = 0.9$.

that an additional source of O_3 destruction must indeed be found. By analogy with the proposal of Donovan *et al.* [6] we suggest that the reaction first forms vibrationally excited CF_2ClO^+.

$$CF_2Cl + O_3 \rightarrow CF_2ClO^+ + O_2 \tag{8a}$$

Dissociation of the excited molecule

$$CF_2ClO^+ \rightarrow CF_2O + Cl \tag{8b}$$

is then followed by the rapid reaction

$$Cl + O_3 \rightarrow ClO + O_2 \tag{7}$$

to destroy *two* O_3 molecules and produce one ClO. (The alternative path, to CF_2 + ClO, seems disfavoured on thermodynamic grounds.) The calculated

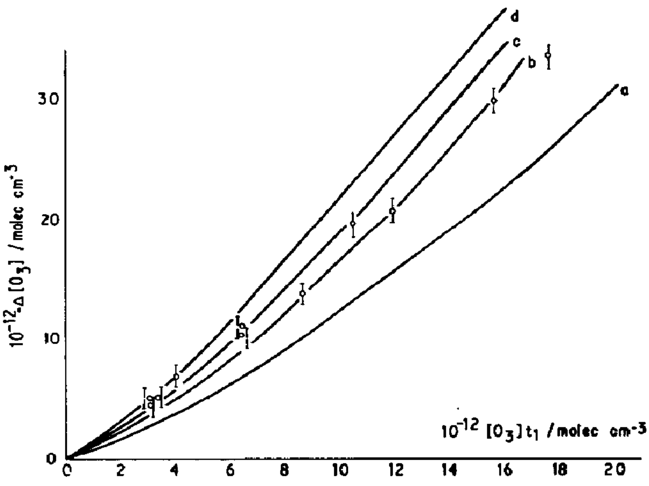

Fig. 3. Variation of $-\Delta[O_3]$ with $[O_3]t_1$ (experimental parameters as for Fig. 2): O, experimental data; curves a - d, computed ($\alpha = 0.9$; $\beta = 0.83$ s^{-1}) for various values of k_8 (cm^3 $molecule^{-1}$ s^{-1}) (curve a, $k_8 = 0$; curve b, $k_8 = 2 \times 10^{-14}$; curve c, $k_8 = 4 \times 10^{-14}$; curve d, $k_8 = 10 \times 10^{-14}$).

curves for $k_8 > 0$ in Fig. 3 are based on this stoichiometry. It is seen that the best fit with the experimental data is obtained, as in Fig. 2, with $k_8 \approx 2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} (for $\alpha = 0.9$).

We now consider the influence of the branching ratio α, for production of ClO and CF_2Cl in reaction (2), on the comparisons between prediction and experiment. As long as $\alpha > 0.7$, a value of k_8 may be found that allows the ClO concentration profile to match the experimental results. Fortunately, the $-\Delta[O_3]$ profiles allow the individual values of k_8 and α to be quite closely defined. Figure 4 reproduces the experimental points for O_3 loss, and the family of curves is calculated for the values of k_8 required to fit the ClO concentration data at a series of branching ratios. The most satisfactory agreement is obtained for $\alpha \approx 0.9$ and $k_2 \approx 2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. Such a magnitude for α is consistent with other reported results. A lower limit of $\alpha \not< 0.4$ is possible [13], although the consensus seems to be that reaction (2a) is the dominant channel [4, 5, 14]; some authors believe that it is the exclusive one [4, 7].

A modulated peak, coherent with the photolysis lamp period, appears in the mass spectrum at $m/e = 66$. It is probable that the signal is due to CF_2O^+, although there is a considerable (unmodulated) background signal resulting from $CFCl^+$, a fragment ion of CF_2Cl_2. We have not, so far, obtained an absolute calibration for sensitivity to CF_2O. Relative signals, however, behave kinetically as predicted by the source (8a) followed by (8b). Table 3 shows the computed and experimental results. The dependence of $[CF_2O]_{rel}$ on t_2 and on $[O_3]$ at least suggests that the major source of CF_2O in the system involves secondary reactions of CF_2Cl rather than a third branch of the $O(^1D) + CF_2Cl_2$ interaction

$$O(^1D) + CF_2Cl_2 \rightarrow CF_2O + Cl_2 \qquad (2c)$$

as previously suggested [6, 7]. Our value of $\alpha \approx 0.9$ allows a minor contribution

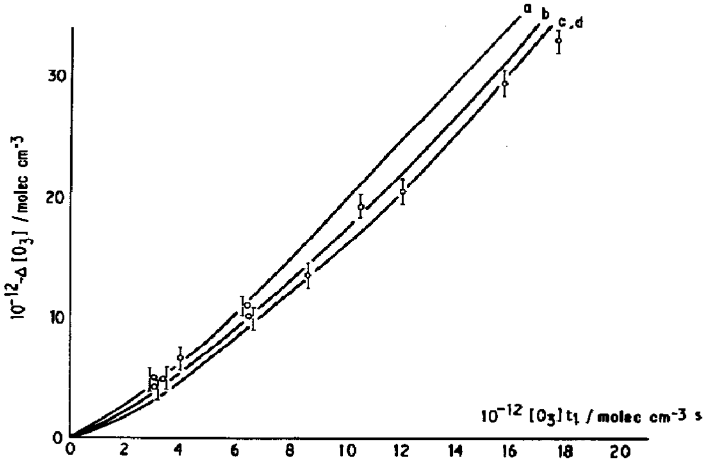

Fig. 4. Comparison of the computed O_3 loss profiles, for various values of α, with experimental results: ○, experimental data; curves a - d, computed ($\beta = 0.73$ s^{-1}) (curve a, $\alpha = 0.7$, $k_8 = 7 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}; curve b, $\alpha = 0.8$, $k_8 = 3 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}; curve c, $\alpha = 0.9$, $k_8 = 2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}; curve d, $\alpha = 1.0$, $k_8 = 1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}).

TABLE 3

Observed and calculated relative concentrations of CF_2O

10^{-14} $[O_3]$ (molecule cm^{-3})	*10^{-14}* $[CF_2Cl_2]$ (molecule cm^{-3})	t_1 (ms)	t_2 (ms)	$[CF_2O]_{rel}$	
				Observed	*Predicted*
7.2	21	33.0	118.0	1.0	1.0
6.7	20	25.0	89.5	0.6	0.6
4.2	20	25.0	55.3	0.2	0.3
2.6	20	25.0	104.9	0.2	0.2

For the calculations $k_8 = 2 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} and $\alpha = 0.9$. One CF_2O is assumed to be formed for every CF_2Cl radical that reacts with O_3.

from the channel (2c), and further quantitative measurements are obviously needed to establish a limit to the efficiency of the process.

4. Conclusions

The preliminary experiments reported here have shown that the photolytic flow method is capable of yielding kinetic and mechanistic information about the ozone–halocarbon system. Refinements in the technique will enable us to obtain more precise kinetic parameters. The results presented already suggest the following.

(i) Most of the reaction of $O(^1D)$ with CF_2Cl_2 yields ClO, the branching ratio for ClO production being approximately 0.9.

(ii) The reaction between CF_2Cl and O_3 proceeds with a rate constant of about 2×10^{-14} cm^3 $molecule^{-1}$ s^{-1}.

(iii) One ClO radical is formed, and two O_3 molecules are ultimately lost, in the reaction between CF_2Cl and O_3.

(iv) CF_2O is produced predominantly in reactions of CF_2Cl rather than in the reaction of $O(^1D)$ with CF_2Cl_2.

Acknowledgment

We wish to acknowledge with gratitude the financial support given to D.G.R. by the Gassiot Grants Committee of the Meteorological Office.

References

1 J.A. Davison, H.I. Schiff, T.J. Brown and C.J. Howard, *J. Chem. Phys., 69* (1978) 4277.
2 I.S. Fletcher and D. Husain, *J. Phys. Chem., 80* (1976) 1837.
3 NASA Panel for Data Evaluation, *JPL Publ. 81-3,* January 15, 1981.
4 J.N. Pitts, Jr., H.L. Sandoval and R. Atkinson, *Chem. Phys. Lett., 29* (1974) 31.
5 H.L. Sandoval, R. Atkinson and J.N. Pitts, Jr., *J. Photochem., 3* (1974) 325.

6 R.J. Donovan, K. Kaufmann and J. Wolfrum, *Nature (London), 262* (1976) 204.
7 R.K.M. Jayanty, R. Simonaitis and J. Heicklen, *J. Photochem., 4* (1975) 381.
8 D.J. Giachardi and R.P. Wayne, *Proc. R. Soc. London, Ser. A, 330* (1972) 131.
9 D. Biedenkapp and E.J. Bair, *J. Chem. Phys., 52* (1970) 6119.
10 D.N. Mitchell and R.P. Wayne, *J. Phys. E, 13* (1980) 494.
11 I.T.N. Jones, U.B. Kaczmar and R.P. Wayne, *Proc. R. Soc. London, Ser. A, 316* (1970) 431.
12 R.F. Hampson, *U.S. Dept. of Transportation Rep. FAA-EE-80-17,* April 1980.
13 H.M. Gillespie and R.J. Donovan, *Chem. Phys. Lett., 37* (1976) 468.
14 M.C. Addison, R.J. Donovan and J. Garraway, *Faraday Discuss. Chem. Soc., 67* (1979) 286.