

THE REACTION OF O(¹D) WITH CCl₂O, CFCIO AND CF₂O

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Summary

O(¹D) atoms, prepared from the photolysis of O₃ at 253.7 nm and 25 °C, were reacted with CCl₂O, CFCIO, or CF₂O. In each case some chemical reaction occurred, since the quantum yield of O₃ removal, $-\Phi\{O_3\}$, exceeded 4, the value expected if O(¹D) were deactivated to O(³P) by the carbonyl halides. The values for $-\Phi\{O_3\}$ were 5.6 ± 0.2 , 7.0 ± 0.5 , and 5.4 ± 0.4 , respectively. In the CCl₂O system, CO was formed with a quantum yield ranging from 0.4 to 0.8; at least 80% of the O(¹D) removal by CCl₂O is by chemical reaction. In addition there was evidence for the formation of chlorine oxides. No products were found with CFCIO or CF₂O, but we were unable to analyze for CO₂, which may be the major product. That chemical reaction actually occurs in the CF₂O system was substantiated by experiments in the presence of O₂. If no chemical reaction had occurred, $-\Phi\{O_3\}$ should have dropped to 0, but it only dropped to 1.1. The rate coefficients relative to the O(¹D)-N₂O reaction were obtained by adding N₂O to the system, and these were found to be 1.57, 0.96, and 0.41 with about a 10% uncertainty for the reaction of O(¹D) with CCl₂O, CFCIO and CF₂O, respectively.

Introduction

In previous publications [1, 2] we have reported on our studies of the photolysis of CCl₄ and the chlorofluoromethanes in the presence of O₂ and O₃ and their reactions with O(¹D) atoms. These studies have shown that photolysis and reaction with O(¹D) atoms gives rise to CCl₂O, CFCIO, or CF₂O as a major product. In the stratosphere these molecules will be subject to photolysis and may react with O(¹D) atoms (and perhaps with other atmospheric species); thus CCl₂O and CFCIO may release additional free chlorine atoms which will participate in O₃ destruction. Consequently a detailed understanding of the photolysis in the presence of O₂ and the reactions with O(¹D) atoms of these molecules is important.

In this paper we report on the reactions of $O(^1D)$ atoms produced from O_3 photolysis at 253.7 nm with CCl_2O , $CFCIO$ and CF_2O . As far as we know no previous studies of these reactions have been reported except for a preliminary measurement of the rate coefficient for the reaction of $O(^1D)$ with CF_2O relative to that for N_2O [3].

Experimental

The experiments were performed in a conventional Hg-free vacuum line equipped with Teflon stopcocks with Viton "O" rings. The cylindrical quartz reaction cell was 10 cm long and 5 cm in diameter. The O_3 was distilled at 87 °K before use. Extra dry grade O_2 from the Matheson Co. was used without further purification. The CCl_2O , $CFCIO$, CF_2O and N_2O were obtained from the Matheson Co. and were purified by degassing at 77 °K. In a few experiments CCl_2O was purified by degassing at 113 °K. All the pressures of the above-mentioned gases were measured with a H_2SO_4 manometer. The O_3 pressures was measured spectrophotometrically at 253.7 nm and could be monitored continuously during the reaction.

The $O(^1D)$ atoms were produced by O_3 photolysis with 253.7 nm radiation which was obtained from a Hanovia "spiral" low pressure Hg resonance lamp. The 253.7 nm line was isolated by passing the radiation through Cl_2 gas and Corning CS 7-54 filters before entering the reaction cell.

The actinometry at 253.7 nm was performed by either measuring the O_3 removal rate in pure O_3 ($-\Phi\{O_3\} = 5.5$ [4]) or by measuring the rate of N_2 production in the photolysis of O_3 in the presence of excess N_2O . For the latter system $\Phi\{N_2\} = 0.46$ for thermally equilibrated $O(^1D)$ atoms and $\Phi\{N_2\} = 0.41$ for $O(^1D)$ atoms possessing excess translational energy [5].

Analysis of CO and N_2 was made with a thermal conductivity gas chromatograph equipped with a copper column (20 ft \times ¼ in) containing 5Å molecular sieves. Analysis for CO_2 (a possible reaction product) was not possible owing to the fact that the $CFCIO$ and CF_2O decomposed to CO_2 on the chromatographic columns. With CCl_2O , a good separation did not result.

Attempts were made to detect other products by i.r. analysis of the reaction mixture with a Beckman Microspec infra-red spectrophotometer after photolysis of ~6 Torr O_3 , 5 - 10 Torr O_2 and excess substrate. The O_2 served to reduce the rate of O_3 consumption by regeneration *via* the reaction:

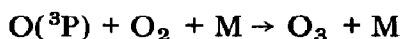


TABLE 1

Photolysis of O₃-X mixtures at 253.7 nm and 25 °C

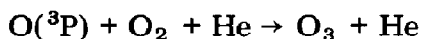
| [X] (Torr) | [O ₃] (Torr) | [He] (Torr) | [O ₂] (Torr) | <i>I</i> _α (mTorr/min) | -Φ{O ₃ } | Φ{CO} |
|----------------------------|-----------------------------|----------------|-----------------------------|--------------------------------------|---------------------|-------|
| [X] = [CCl ₂ O] | | | | | | |
| 9.2 | 2.97 | -- | -- | 16.2 | -- | 0.42 |
| 10.3 | 0.42 | -- | -- | 12.6 | 6.0 | 0.79 |
| 11.5 | 0.35 | -- | -- | 11.5 | 5.9 | -- |
| 18.2 | 3.64 | -- | -- | 16.2 | -- | 0.53 |
| 19.7 | 2.97 | -- | -- | 16.2 | -- | 0.57 |
| 22.5 | 0.35 | -- | -- | 11.5 | 5.5 | 0.61 |
| 28.9 | 2.97 | -- | -- | 16.2 | -- | 0.54 |
| 32.8 | 0.35 | -- | -- | 11.5 | 5.1 | 0.74 |
| 37.1 | 2.83 | -- | -- | 16.2 | -- | 0.76 |
| 38.0 | 0.35 | -- | -- | 11.5 | 5.7 | 0.74 |
| 43.0 | 2.97 | 250 | -- | 16.2 | -- | 0.67 |
| 43.2 | 0.42 | -- | -- | 12.6 | 5.6 | 0.79 |
| 46.5 | 0.35 | -- | -- | 11.5 | 5.4 | 0.78 |
| 56.0 | 2.97 | -- | -- | 16.2 | -- | 0.76 |
| [X] = [CFCIO] | | | | | | |
| 5.9 | 0.31 | -- | -- | 11.6 | 7.2 | -- |
| 11.7 | 0.31 | -- | -- | 11.6 | 6.9 | -- |
| 17.4 | 0.31 | -- | -- | 11.6 | 7.5 | -- |
| 23.5 | 0.31 | -- | 4.8 | 11.6 | 5.8 | -- |
| 27.1 | 0.42 | -- | -- | 12.6 | 7.4 | -- |
| [X] = [CF ₂ O] | | | | | | |
| 5.5 | 0.31 | -- | -- | 11.9 | 5.9 | -- |
| 7.3 | 0.11 | -- | -- | 5.0 | 4.5 | -- |
| 9.3 | 0.42 | -- | -- | 15.3 | 6.4 | -- |
| 9.7 | 0.31 | -- | -- | 11.9 | 5.3 | -- |
| 10.4 | 0.49 | -- | -- | 15.4 | 5.3 | -- |
| 15.4 | 0.31 | -- | -- | 11.9 | 5.4 | -- |
| 20.1 | 0.49 | 250 | 4.9 | 15.4 | 1.9 | -- |
| 22.1 | 0.11 | -- | -- | 5.0 | 5.1 | -- |
| 29.7 | 0.31 | -- | -- | 11.9 | 5.6 | -- |
| 30.5 | 0.31 | -- | -- | 11.9 | 5.1 | -- |
| 38.9 | 0.12 | 690 | 9.6 | 5.0 | 1.1 | -- |
| 40.0 | 0.47 | 530 | 4.1 | 15.5 | 1.7 | -- |
| 42.2 | 0.12 | 690 | 10.6 | 5.0 | 1.1 | -- |
| 48.9 | 0.47 | 400 | 3.6 | 15.5 | 2.1 | -- |

Results

The photolysis of O₃ at 253.7 nm in the presence of CCl₂O or CFCIO or CF₂O leads to the consumption of O₃. In the case of CFCIO or CF₂O they did not absorb any measurable fraction of the radiation under our

conditions. The CCl_2O absorbed up to 5% of the radiation. CO is produced in the $\text{O}_3\text{-CCl}_2\text{O}$ system, but not in the other two systems. No other products could be detected by i.r. analysis of the reaction mixtures even after extended irradiation times. However, in the $\text{O}_3\text{-CCl}_2\text{O}$ system after extended irradiation a brownish-red color could be observed in a trap of the frozen reaction mixture at 77 °K indicating the presence of chlorine oxides. CO_2 may have been produced in all systems, but analysis for it was not possible.

The average initial O_3 removal quantum yields ($-\Phi\{\text{O}_3\}$) for the $\text{O}_3\text{-CCl}_2\text{O}$, $\text{O}_3\text{-CFClO}$ and the $\text{O}_3\text{-CF}_2\text{O}$ systems are 5.6 ± 0.2 , 7.0 ± 0.5 , and 5.4 ± 0.4 , respectively, independent of total pressure. The results are presented in Table 1. In the case of the $\text{O}_3\text{-CF}_2\text{O}$ system, $-\Phi\{\text{O}_3\}$ was also measured in the presence of a few Torr of O_2 and excess He in order to establish whether there is a chemical reaction between $\text{O}(^1\text{D})$ and CF_2O . The O_2 and He pressures were adjusted such that $\text{O}(^1\text{D})$ deactivation by them was not important, but all the $\text{O}(^3\text{P})$ atoms were scavenged by O_2 via:



The limiting value of $-\Phi\{\text{O}_3\} = 1.1$ is obtained at ~ 10 Torr O_2 and 700 Torr He (Table 1). Under these conditions $>95\%$ of the $\text{O}(^3\text{P})$ atoms are scavenged, but $<30\%$ of the $\text{O}(^1\text{D})$ atoms are deactivated as can be shown by calculation with known rate coefficients [6].

The CO quantum yield for the $\text{O}_3\text{-CCl}_2\text{O}$ system is given in Table 1. It can be seen that $\Phi\{\text{CO}\}$ is clearly dependent on the CCl_2O pressure, going from about 0.4 at 10 Torr to about 0.7 - 0.8 at 40 - 60 Torr with ~ 3 Torr O_3 . Cl_2 formation was not determined owing to difficulties with Cl_2 analysis.

The rate coefficients for the $\text{O}(^1\text{D})$ atom reactions with CCl_2O , CFClO and CF_2O were determined by competitive experiments with added N_2O . The procedure is completely identical to our measurement of the rate coefficients for the reaction of $\text{O}(^1\text{D})$ atoms with the chlorofluoromethanes reported in an earlier paper [2], where the reliability and validity of this method was established. Briefly the method consists of irradiating mixtures of $\text{O}_3\text{-N}_2\text{O-X}$, where $\text{X} \equiv \text{CCl}_2\text{O}$, CFClO or CF_2O at 253.7 nm and determining the rate of N_2 production, $R\{\text{N}_2\}$, as a function of the $[\text{X}]/[\text{N}_2\text{O}]$ ratio. The results are presented in Table 2.

Discussion

The photolysis of O_3 at 253.7 nm proceeds as follows [4]:



In the CCl_2O system, $\leq 5\%$ of the photoreaction is due to CCl_2O absorption, but this is of no consequence since the ClO intermediate is produced regard-

TABLE 2

Photolysis of O_3-N_2O-X mixtures at 253.7 nm and 25 °C.

| $\frac{[X]}{[N_2O]}$ | [X] (Torr) | [N ₂ O] (Torr) | [O ₃] (Torr) | R{N ₂ } (mTorr/min) |
|------------------------|---------------|------------------------------|-----------------------------|-----------------------------------|
| X = CCl ₂ O | | | | |
| -- | -- | 55.6 | 2.97 | 6.00 |
| 0.32 | 4.2 | 13.2 | 2.83 | 4.16 |
| 0.65 | 8.2 | 12.7 | 2.83 | 3.33 |
| 0.98 | 12.9 | 13.1 | 2.83 | 2.50 |
| 1.24 | 15.1 | 12.2 | 2.83 | 1.92 |
| 1.62 | 21.1 | 13.0 | 2.83 | 1.66 |
| 2.42 | 31.9 | 13.2 | 2.83 | 1.25 |
| 2.95 | 32.8 | 11.1 | 2.83 | 1.00 |
| X = CFCIO | | | | |
| -- | -- | 66.0 | 2.83 | 6.00 |
| 0.85 | 10.3 | 12.1 | 2.83 | 3.25 |
| 1.49 | 18.5 | 12.4 | 2.97 | 2.50 |
| 1.73 | 20.6 | 11.9 | 2.97 | 2.17 |
| 1.82 | 24.7 | 13.6 | 2.97 | 2.04 |
| 2.50 | 32.5 | 13.0 | 2.97 | 1.64 |
| 2.62 | 29.6 | 11.3 | 2.97 | 1.58 |
| 2.77 | 33.2 | 12.0 | 2.97 | 1.54 |
| 3.82 | 45.8 | 12.0 | 2.83 | 1.33 |
| X = CF ₂ O | | | | |
| -- | -- | 55.6 | 2.97 | 6.00 |
| 0.50 | 6.3 | 12.7 | 2.83 | 4.25 |
| 0.77 | 9.8 | 12.7 | 2.83 | 3.83 |
| 1.85 | 25.0 | 13.5 | 2.83 | 3.17 |
| 2.63 | 33.2 | 12.6 | 2.83 | 2.50 |
| 2.69 | 32.3 | 12.0 | 2.83 | 2.67 |
| 3.47 | 39.6 | 11.4 | 2.97 | 2.20 |
| 4.28 | 47.5 | 11.1 | 2.83 | 2.17 |
| 4.63 | 51.8 | 11.2 | 2.83 | 2.00 |

less of whether the CCl₂O or O₃ absorbs the radiation (see below). If all of the O(¹D) atoms are only deactivated to O(³P) by the substrate (CCl₂O, CFCIO, or CF₂O), then $-\Phi\{O_3\}$ should be 4.0. In none of the three systems was this the case; $-\Phi\{O_3\} > 4$, and reaction must be occurring at least part of the time.

In the CCl₂O experiments, direct evidence for reaction comes from the fact that CO is produced, its quantum yield reaching 0.79 in one experiment. The only reasonable way to produce CO appears to be:



Reaction (5) occurs readily since $D\{Cl-CO\} = 6.3$ kcal/mol [7]. Presumably

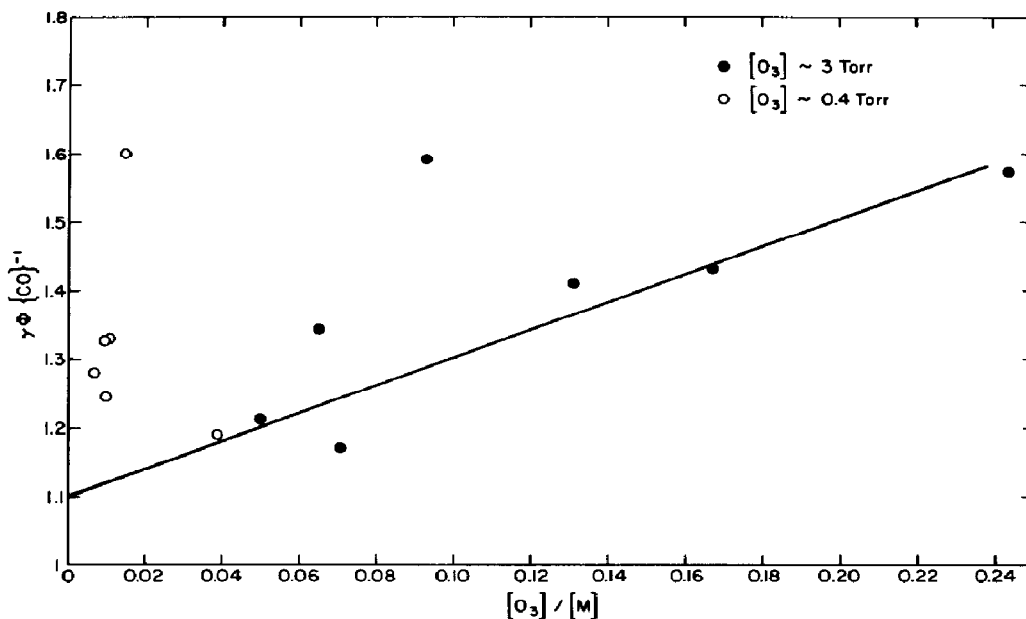


Fig. 1. Plot of $\gamma\Phi\{\text{CO}\}^{-1}$ vs. $[\text{O}_3]/[\text{M}]$ in the photolysis of $\text{O}_3\text{-CCl}_2\text{O}$ mixtures at 253.7 nm and 25 °C.

$\Phi\{\text{CO}\}$ varies with conditions because of the competition between reaction (5) and



The rate law for CO formation becomes:

$$\gamma\Phi\{\text{CO}\}^{-1} = \beta(1 + k_6[\text{O}_3]/k_5[\text{M}]) \quad (a)$$

where γ is a small correction due to the fact that some of the $\text{O}(^1\text{D})$ may react with O_3 :



so that

$$\gamma \equiv k_4[\text{CCl}_2\text{O}]/(k_4[\text{CCl}_2\text{O}] + k_7[\text{O}_3])$$

and β represents the ratio of the likelihood of all reaction paths in the $\text{O}(^1\text{D})\text{-CCl}_2\text{O}$ reaction to the likelihood of ClCO production.

Figure 1 is a plot of $\gamma\Phi\{\text{CO}\}^{-1}$ vs. $[\text{O}_3]/[\text{M}]$, where $[\text{M}]$ is taken as the total pressure. The data at high $[\text{O}_3]$ (~ 3 Torr) fall on a good straight line with the intercept = 1.1 ± 0.1 . However, the data at lower $[\text{O}_3]$ lie significantly above the line. The reason for this is not clear. The points at low $[\text{O}_3]$ are much less accurate (because less CO is produced) and may have systematic error associated with them. Alternatively CClO may be involved in other reactions at low O_3 , for example:



TABLE 3

Summary of measured and literature values of k_x/k_9

| X | k_x/k_9 | |
|--------------------|-------------------|-------------------|
| | This work | Literature |
| CCl ₂ O | 1.57 ^a | — |
| CFCIO | 0.96 ^a | — |
| CF ₂ O | 0.41 ^a | 0.27 ^b |

^aAbout 10% uncertainty in these values.

^bReference 3.

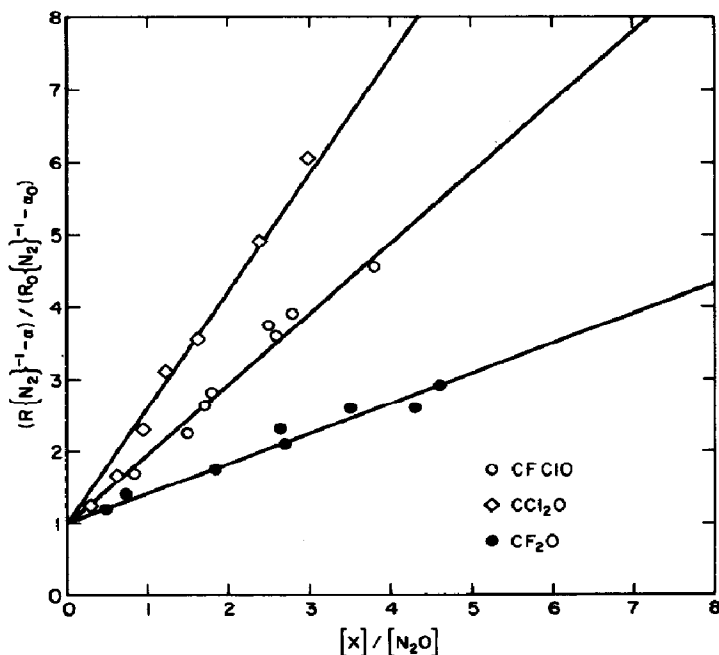
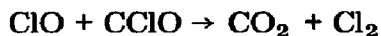


Fig. 2. Plots of $R[\text{N}_2]^{-1} - \alpha / (R_0[\text{N}_2]^{-1} - \alpha_0)$ vs. $[\text{X}] / [\text{N}_2\text{O}]$ in the photolysis of $\text{N}_2\text{O}-\text{O}_3-\text{X}$ mixtures at 253.7 nm and 25 °C.



With CFCIO, the chlorine abstraction reaction can, and presumably does, occur since $-\Phi\{\text{O}_3\} > 4$. However, with CF₂O, chlorine atom abstraction is not possible, yet some reaction [other than deactivation of O(¹D)] apparently does occur because $-\Phi\{\text{O}_3\} > 4$. To check this conclusion experiments were done with added O₂ to remove any O(³P) atoms that would be formed:



Under the conditions of the reaction, if the $O(^1D)$ - CF_2O reaction only deactivated $O(^1D)$, then $-\Phi\{O_3\}$ should approach 0 (actually ~ 0.03 for $[O_2] \sim 10$ Torr, $[He] = 700$ Torr). However, measurements gave $-\Phi\{O_3\} = 1.1$, indicating that some chemical reaction occurred.

Rate coefficients for the reactions of $O(^1D)$ atoms with CF_2O , $CFCIO$, and CCl_2O were determined relative to N_2O . The photolysis of O_3 - N_2O - X mixtures leads to the competition:



where $X = CF_2O$, $CFCIO$ or CCl_2O . The rate law for N_2 formation is given by:

$$(R\{N_2\}^{-1} - \alpha)/(R_0\{N_2\}^{-1} - \alpha_0) = 1 + k_x [X]/k_9 [N_2O] \quad (b)$$

where $R\{N_2\}$ is the rate of N_2 formation and $\alpha = k_7 [O_3]/I_a k_{9a} [N_2O]$. The subscript 0 refers to the highest value of $[N_2O]/[O_3]$ used. Only a small fraction of the $O(^1D)$ atoms are lost by reaction (7); thus α and α_0 are small. In computing α and α_0 , $k_7/k_9 = 2.5$ [2] and $k_{9a}/k_9 = 0.55$ were used [5]. Plots of the left hand side of equation (b) vs. $[X]/[N_2O]$ should be linear with a slope of k_x/k_9 .

Plots based on equation (b) are shown in Fig. 2. The plots are reasonably linear as predicted by equation (b). The slopes of the plots are given in Table 3. Literature values for $CFCIO$ and CCl_2O are not available. For CF_2O our value for k_x/k_9 differs from the value determined by Pitts *et al.* [3] by nearly a factor of 2. The reason for this discrepancy is not known.

Acknowledgements

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