

## THE PHOTOLYSIS OF $\text{CCl}_4$ IN THE PRESENCE OF $\text{O}_2$ OR $\text{O}_3$ AT 213.9 nm, AND THE REACTION OF $\text{O}(^1\text{D})$ WITH $\text{CCl}_4$

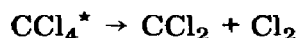
R. K. M. JAYANTY, R. SIMONAITIS and JULIAN HEICKLEN

*Department of Chemistry and Ionosphere Research Laboratory, The Pennsylvania State University, University Park, Pa. 16802 (U.S.A.)*

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### Summary

When  $\text{CCl}_4$  is photolyzed at 25 °C with 213.9 nm radiation in either the presence of  $\text{O}_2$  or  $\text{O}_3$  the products are  $\text{CCl}_2\text{O}$ ,  $\text{Cl}_2$ , and an unidentified compound. At low total pressure,  $\Phi\{\text{CCl}_2\text{O}\} = 2.0$ , but this value drops to 1.0 for  $[\text{CCl}_4] \sim 50$  Torr and  $[\text{O}_2]$  or  $[\text{N}_2] = 700$  Torr.  $\Phi\{\text{Cl}_2\}$  is reasonably invariant to pressure at  $\sim 1.3 - 1.4$ . The results are interpreted in terms of an excited molecule mechanism which proceeds entirely by:



at low pressures, with singlet  $\text{CCl}_2$  being produced. At higher pressures  $\text{CCl}_4^*$  is quenched and  $\text{CCl}_2$  production is inhibited, though it may (and probably is) replaced by production of  $\text{CCl}_3 + \text{Cl}$ .

The  $\text{O}(^1\text{D})$  reaction with  $\text{CCl}_4$  at 25 °C gives  $\text{CCl}_2\text{O}$  and  $\text{Cl}_2$  as the exclusive products. The  $\text{O}(^1\text{D})$  was produced from  $\text{O}_3$  photolysis at 253.7 nm. The quantum yields are invariant to reaction conditions and are  $\Phi\{\text{CCl}_2\text{O}\} = 0.87 \pm 0.2$  and  $\Phi\{\text{Cl}_2\} = 1.1 \pm 0.2$ . The  $\text{O}_3$  consumption is the same, or slightly higher than in the absence of  $\text{CCl}_4$ . The three possible reaction paths are:



Reaction (13a) was shown to be an important, and possibly the exclusive path, whereas reaction (13c) is unimportant and proceeds  $< 20\%$  of the time. The overall reaction rate coefficient for reaction (13) was measured by studying the decrease in  $\Phi\{\text{CCl}_2\text{O}\}$  in the presence of  $\text{O}_2$ . The rate coefficient for the  $\text{O}(^1\text{D})\text{-CCl}_4$  reaction relative to the  $\text{O}(^1\text{D})\text{-O}_2$  reaction is 4.0 with about a  $\pm 10\%$  uncertainty.

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## Introduction

The current interest in the atmospheric effects of anthropogenically released halocarbons has prompted us to initiate a program of halocarbon oxidation studies. In the present paper, results are presented for the photolysis of  $\text{CCl}_4$  in the presence of  $\text{O}_2$  or  $\text{O}_3$  and the reaction of  $\text{CCl}_4$  with  $\text{O}(^1\text{D})$  atoms.

The earliest works on the photochemistry of  $\text{CCl}_4$  were done in the liquid phase [1, 2]. In the vapor  $\text{CCl}_4$  has been used as a source of  $\text{CCl}_3$  radicals [3]. The only detailed study of the pure compound in the vapor phase was recently reported by Davis *et al.* [4] who photolyzed  $\text{CCl}_4$  at 25 °C with radiation at 253.7, 184.9, 147.0, and 106.7 nm. At 253.7 nm the only products were  $\text{Cl}_2$  and  $\text{C}_2\text{Cl}_6$  and the results indicated that  $\text{Cl}$  and  $\text{CCl}_3$  were produced with unit quantum efficiency. At 184.9 nm,  $\text{C}_2\text{Cl}_4$  was also produced and evidence for  $\text{CCl}_2$  production was indicated. As far as we know the photo-oxidation of  $\text{CCl}_4$  has not been studied previously.

The only report of the  $\text{O}(^1\text{D})$ - $\text{CCl}_4$  reaction was by Meaburn *et al.* [5]. They examined the gas-phase radiolysis of  $\text{CO}_2$ - $\text{O}_2$ - $\text{CCl}_4$  mixtures and concluded that singlet oxygen atoms react with  $\text{CCl}_4$  to give  $\text{ClO}$  radicals.

## Experimental

Mixtures of  $\text{CCl}_4$  with  $\text{O}_2$  or  $\text{O}_3$  or both were irradiated in a cylindrical quartz reaction cell 10 cm long and 5 cm in diameter. The cell was attached to a conventional Hg-free glass vacuum line equipped with Teflon stopcocks with Viton "O" rings. Extra dry grade  $\text{O}_2$  from the Matheson Co. was used without further purification. The  $\text{O}_3$  was prepared from a Tesla coil discharge through  $\text{O}_2$  and was distilled at 87 K before use. The  $\text{CCl}_4$  was "Baker Analyzed" reagent and was purified by distillation from a trap maintained at 210 to one at 177 K. The  $\text{CCl}_4$  pressure was measured with an  $\text{H}_2\text{SO}_4$  manometer, and the  $\text{O}_2$  pressure was measured with an alphasatron gauge calibrated against an  $\text{H}_2\text{SO}_4$  manometer. The  $\text{O}_3$  pressure was measured spectrophotometrically and could be monitored continuously.

The 213.9 nm radiation for the photolysis of  $\text{CCl}_4$  was provided by a Phillips (93109E) low-pressure zinc resonance lamp. For the  $\text{O}(^1\text{D})$ -atom study, the 253.7 nm radiation was obtained from a Hanovia "spiral" low pressure Hg resonance lamp. The 253.7 nm line was isolated by passing the radiation through  $\text{Cl}_2$  gas and a Corning CS 7-54 filter before entering the reaction cell. Actinometry at both wavelengths was done by measuring  $\text{H}_2$  production from HBr photolysis where the quantum yield of  $\text{H}_2$  production,  $\Phi\{\text{H}_2\}$ , is 1.0 [6].

Analysis for  $\text{COCl}_2$  was performed mainly by gas chromatography and in a few experiments by infra-red analysis. Chromatography was done with a stainless steel column 10 ft.  $\times$  ¼ in. containing 10% silicone oil (SP2100) on 80 - 100 mesh Supelcoport (Supelco Inc., Bellefonte, Pa.). Analysis for  $\text{Cl}_2$  was made in the photolysis experiments by chromatography in the same

column as for  $\text{COCl}_2$  and by ultra-violet absorption spectroscopy in a Cary 14 spectrometer. For the  $\text{O}(^1\text{D})$  experiments the analysis for  $\text{Cl}_2$  was made with a dual beam spectrophotometer [7] at 366.0 nm in order to obtain greater sensitivity. It was assumed that the increase in absorption at 366.0 nm was due entirely to  $\text{Cl}_2$ . For CO analysis the column used was 10 ft.  $\times$   $\frac{1}{4}$  in. containing 5 Å molecular sieves. For  $\text{C}_2\text{Cl}_6$  analysis a flame ionization chromatograph was used equipped with a 10 ft.  $\times$   $\frac{1}{4}$  in. column containing 3% SE 30 on Supelcoport.

## Results

### *Photolysis of $\text{CCl}_4$*

Irradiation of  $\text{CCl}_4$  at 213.9 nm and 25 °C in the presence of  $\text{O}_2$  or  $\text{O}_3$  leads to the production of  $\text{CCl}_2\text{O}$  and  $\text{Cl}_2$ . A careful search for CO and  $\text{C}_2\text{Cl}_6$  was made but these compounds were not detected. The upper limit for their quantum yields was 0.01. An examination of the u.v. spectrum of the reaction mixture in the range 220 - 500 nm showed the presence of an additional product with marked vibrational structure and a maximum at 260.0 nm. The identity of this product could not be established, nor could a systematic kinetic study be made because the yield was very irreproducible. This irreproducibility may have been related to the low volatility of the product making collection difficult.

The quantum yields of  $\text{Cl}_2$  and  $\text{COCl}_2$  formation in the presence of  $\text{O}_2$  and  $\text{O}_3$  are presented in Tables 1 and 2, respectively. Table 2 also gives some initial  $\text{O}_3$  removal quantum yields for the  $\text{CCl}_4$ - $\text{O}_3$  system, and they range from 1.9 to 4.9 with a slight downward trend with increasing pressure. Experiments were done at  $\text{CCl}_4$  pressures of  $\sim 10$  and 48 Torr, respectively. The  $\text{O}_2$  pressure varied from 22 to 640 Torr, a factor of 32, and the  $\text{O}_3$  pressure varied from 388 mTorr to 2.7 Torr, a factor of seven. In some runs up to 700 Torr  $\text{N}_2$  was added. The more extensive  $\text{COCl}_2$  data are presented in graphical form in Fig. 1. From the Figure it is evident that in spite of the considerable scatter of the data  $\Phi\{\text{COCl}_2\}$  is subject to a pressure effect in both the  $\text{CCl}_4$ - $\text{O}_2$  and  $\text{CCl}_4$ - $\text{O}_3$  systems.  $\Phi\{\text{COCl}_2\}$  falls from about 2.0 at low total pressure to  $\sim 1.0$  at high total pressure;  $\text{CCl}_4$  is much more efficient than  $\text{O}_2$  or  $\text{N}_2$  in reducing the yield. The  $\text{Cl}_2$  quantum yields are about 1.3 - 1.4 in both the  $\text{CCl}_4$ - $\text{O}_2$  and  $\text{CCl}_4$ - $\text{O}_3$  systems, and do not show a clear pressure dependence in the range 0 - 300 Torr  $\text{O}_2$  or  $\text{N}_2$  and 10 - 48 Torr  $\text{CCl}_4$ .

### *Reaction of $\text{O}(^1\text{D})$ with $\text{CCl}_4$*

Irradiation of  $\text{O}_3$  at 253.7 nm in the presence of  $\text{CCl}_4$  leads to the consumption of  $\text{O}_3$  and the production of  $\text{COCl}_2$  and  $\text{Cl}_2$ . A search for CO was made but none could be detected. The quantum yields of  $\text{COCl}_2$  and  $\text{Cl}_2$  formation, and  $\text{O}_3$  removal are presented in Table 3. These quantum yields of  $\text{O}_3$  removal are reported relative to the quantum yields of disappearance in the absence of  $\text{CCl}_4$ ,  $-\Phi_{\text{O}}\{\text{O}_3\}$ . Earlier work has shown that

TABLE 1

Photolysis of  $\text{CCl}_4\text{-O}_2$  mixtures at 213.9 nm and 25 °C

$\frac{[\text{O}_2]}{[\text{CCl}_4]}$	$[\text{CCl}_4]$ (Torr)	$[\text{O}_2]$ (Torr)	$I_a$ (mTorr/min)	$\Phi\{\text{CCl}_2\text{O}\}$	$\Phi\{\text{Cl}_2\}$
0.47	46.8	21.8	11.8	1.50	—
0.94	45.9	43.0	11.8	1.26	—
2.30	48.0	110.2 <sup>a</sup>	11.8	1.11	—
2.32	49.3	114.5	11.8	1.10	—
2.50	10.8	27.0	4.2	2.18	1.35
2.72	47.1	128.0	11.8	1.47	—
2.90	48.0	139.0	11.8	—	1.37 <sup>d</sup>
3.11	10.5	32.7	4.2	2.03	1.32
3.62	48.0	174.0	11.8	1.25	—
3.93	48.6	191.0	11.8	1.50	—
3.93	48.6	191.0	11.8	1.50 <sup>c</sup>	—
4.08	49.0	200.0	11.8	1.60 <sup>c</sup>	—
4.14	47.8	198.0	11.8	1.34	—
4.33	48.0	209.0	11.8	—	1.37 <sup>d</sup>
4.40	11.0	48.4	4.2	1.72	—
5.49	46.8	257.0	11.8	1.27	1.22
6.60	10.6	70.0	11.8	2.14	—
7.66	46.6	357.0	11.8	1.26	—
7.92	9.7	77.0	4.2	1.66	—
10.55	10.5	110.7 <sup>a</sup>	4.2	1.53	—
11.72	10.80	126.6 <sup>b</sup>	4.2	0.98	—
11.78	47.60	561	11.8	1.07	—
13.54	47.50	643	11.8	1.15	—
18.70	10.70	200	4.2	—	1.30 <sup>d</sup>
21.76	10.80	235	4.2	1.94	—
22.30	10.50	234	4.2	1.60	1.40
23.30	10.60	247	4.2	1.74	—
57.55	10.60	610	4.2	1.44	0.85

<sup>a</sup>  $[\text{N}_2] = 415$  Torr.<sup>b</sup>  $[\text{N}_2] = 476$  Torr.<sup>c</sup> I.r. analysis.<sup>d</sup> U.v. analysis.

TABLE 2

Photolysis of  $\text{CCl}_4\text{-O}_3$  mixtures at 213.9 nm and 25 °C

$[\text{CCl}_4]$ (Torr)	$[\text{O}_3]$ (mTorr)	$I_a$ (mTorr/min)	$\Phi\{\text{Cl}_2\}$ <sup>a</sup>	$\Phi\{\text{COCl}_2\}$	$-\Phi\{\text{O}_3\}$
8.3	2700	4.2	—	2.4	—
10.8	2700	4.2	1.44	—	—
10.8	357 <sup>b</sup>	4.2	—	1.31	3.45
11.0	388	4.2	—	2.2	4.90
45.6	388	11.8	—	1.35	3.39
45.6	357	11.8	—	1.46	—
46.8	2700	11.8	1.28	—	—
47.5	412	11.8	—	1.42	1.9

<sup>a</sup> U.v. analysis.<sup>b</sup>  $[\text{N}_2] = 700$  Torr.

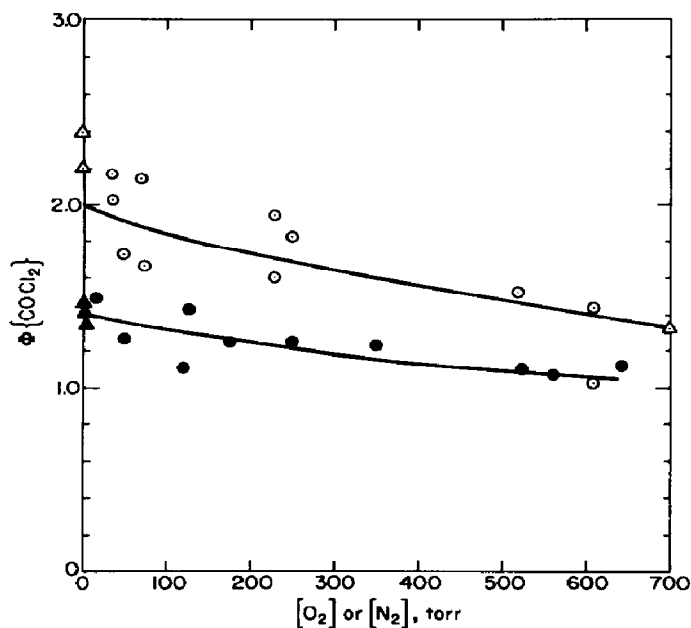


Fig. 1. Plot of  $\Phi\{\text{COCl}_2\}$  vs.  $[\text{N}_2]$  or  $[\text{O}_2]$  for  $\text{CCl}_4$  photolysis at 213.9 nm in the presence of  $\text{O}_2$  or  $\text{O}_3$  at 25 °C.  $\circ$ ,  $[\text{CCl}_4] \sim 10$  Torr in the presence of  $\text{O}_2$ ;  $\triangle$ ,  $[\text{CCl}_4] \sim 10$  Torr in the presence of  $\text{O}_3$ ;  $\bullet$ ,  $[\text{CCl}_4] \sim 50$  Torr in the presence of  $\text{O}_2$ ;  $\blacktriangle$ ,  $[\text{CCl}_4] \sim 50$  Torr in the presence of  $\text{O}_3$ . All analyses by gas chromatography.

-- $\Phi_0\{\text{O}_3\} = 5.5 \pm 0.5$  [8]. However, in this system we found that -- $\Phi_0\{\text{O}_3\}$  was consistently  $8.0 \pm 0.1$ , indicating some impurity or wall effect. For this reason the ratio is reported, and its average value is  $1.11 \pm 0.10$ .

The average quantum yields of  $\text{COCl}_2$  and  $\text{Cl}_2$  formation are  $0.87 \pm 0.2$  and  $1.1 \pm 0.2$  respectively. Results in the presence of  $\text{O}_2$  are shown in Table 4. Addition of  $\text{O}_2$  to the  $\text{CCl}_4\text{-O}_3$  system does not, as far as could be determined, lead to additional products but the formation of  $\text{COCl}_2$  and  $\text{Cl}_2$  and  $\text{O}_3$  removal are suppressed. A systematic study of the effect of  $\text{O}_2$  was performed only on the phosgene yield. The data in Table 4 show that  $\Phi\{\text{COCl}_2\}$  declines as the  $[\text{O}_2]/[\text{CCl}_4]$  ratio increases.

## Discussion

### Photolysis of $\text{CCl}_4$

At low pressures the photolysis data for  $\text{CCl}_4$  in the presence of  $\text{O}_2$  are consistent with the scheme:

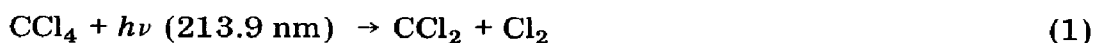


TABLE 3

Reaction of O(<sup>1</sup>D) with CCl<sub>4</sub> at 25 °C

[CCl <sub>4</sub> ] (Torr)	[O <sub>3</sub> ] (mTorr)	I <sub>a</sub> (mTorr/min)	Φ{COCl <sub>2</sub> }	Φ{Cl <sub>2</sub> }	$\frac{\Phi\{O_3\}}{\Phi_0\{O_3\}}$
9.45	150	2.04	0.67	—	—
10.00	150	2.04	0.87	—	—
10.4	183	2.70	0.84	—	1.10
10.8	377	5.78	0.65	—	0.94
16	2300	11.5	—	0.93	—
16	2650	11.5	—	1.1	—
20	880	9.5	—	1.2	—
20	1400	11.5	—	1.2	—
21	2300	11.5	—	1.0	—
21	2400	11.5	—	0.97	—
21.0	150	2.04	1.2	—	—
21.0	150	2.04	1.2	—	—
22	2800	11.5	—	1.2	—
23	2400	11.5	—	0.93	—
23	2700	11.5	—	1.1	—
24	1100	11.5	—	1.2	—
26.3	411	5.30	0.74	—	1.24
28.5	424	5.30	0.84	—	1.17
41.0	173	2.70	0.84	—	1.02
44.3	411	5.30	0.88	—	1.22

TABLE 4

Reaction of O(<sup>1</sup>D) with CCl<sub>4</sub> and O<sub>2</sub> at 25 °C<sup>a</sup>

$\frac{[O_2]}{[CCl_4]}$	[CCl <sub>4</sub> ] (Torr)	[O <sub>2</sub> ] (Torr)	Φ{COCl <sub>2</sub> }	$\frac{\Phi\{O_3\}}{\Phi_0\{O_3\}}$
0.78	46.8	36.7	0.83	0.69
0.86	46.8	40.4	0.61	1.02
1.75	46.9	81.9	0.83	0.82
4.10	46.0	189	0.46	0.40
6.06	46.4	281	0.40	0.58
7.30	20.5	149	0.37	0.51
9.74	21.9	214	0.26	0.42
10.0	21.0	210	0.26	0.42
11.5	46.8	538	0.26	0.38
12.1	22.3	270	0.26	0.39
17.0	20.1	343	0.19	0.28
13.5	20.8	260	0.154	0.35

<sup>a</sup> [O<sub>3</sub>] = 150 mTorr, I<sub>a</sub> = 2.04 mTorr/min.



In the presence of  $\text{O}_3$  reactions (3), (4) and (6) must be replaced by:



Primary process (1) followed by reaction (2) is suggested because the photolysis at low pressures leads to 2 molecules of phosgene per photon absorbed and therefore 2 molecules of  $\text{CCl}_4$  must be removed per photon. The only fragment which could decompose a second molecule of  $\text{CCl}_4$  appears to be  $\text{CCl}_2$ . Cl,  $\text{CCl}_3$  or any of the oxygenated radicals are unlikely to react with  $\text{CCl}_4$ .

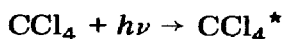
The  $\text{CCl}_2$  produced would be expected to be in a singlet state, from spin conservation rules. This is supported by the fact that the  $\text{CCl}_2$  fragment does not react with  $\text{O}_2$ . Triplet  $\text{CCl}_2$  reacts readily with  $\text{O}_2$  to produce CO [9], but no CO was not found in this system.

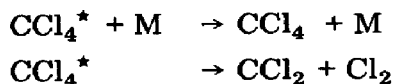
The fate of  $\text{CCl}_3$  in the presence of  $\text{O}_2$  is given by reactions (3) - (5) as first suggested by Huybrechts *et al.* [10] and confirmed by Mathias *et al.* [11]. The quantum yield of phosgene in the presence of  $\text{O}_3$  is the same as in the presence of  $\text{O}_2$ ; consequently the reactions of  $\text{CCl}_3$  with  $\text{O}_2$  and  $\text{O}_3$  must ultimately lead to a common precursor of  $\text{COCl}_2$ . Therefore reaction (7) must be the principle reaction between  $\text{CCl}_3$  and  $\text{O}_3$ . In the presence of  $\text{O}_3$  the Cl atoms will be removed by reaction (8) ( $k_8 = 2 \times 10^{-11} \text{ cm}^3/\text{s}$ ) [12]. The ClO radicals produced in reaction (8) will be removed by reactions (9a) or (9b), depending upon the total pressure. The bimolecular reaction of ClO radicals at low pressures ( $\leq 8$  Torr argon) is known to proceed exclusively by reaction 9a [13]. At higher pressures ( $\geq 70$  Torr argon) reaction (9b) is the exclusive reaction [14, 15]. In the present experiments reaction (9a) could occur at the lowest pressures used ( $\sim 10$  Torr  $\text{CCl}_4$ ), though for experiments for which  $\text{CCl}_4 \sim 50$  Torr reaction (9a) is negligible. The reaction:



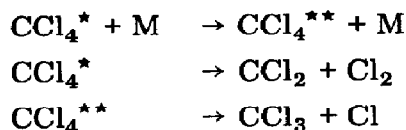
can be neglected because it is very slow ( $k_{10} = (2 - 7) \times 10^{-19} \text{ cm}^3/\text{s}$ ) [16].

At higher total pressures  $\Phi\{\text{COCl}_2\}$  declines and reaches a value of about 1.0 at 600 - 700 Torr  $\text{N}_2$  or  $\text{O}_2$  and  $\sim 50$  Torr  $\text{CCl}_4$ . The data are shown graphically in Fig. 1. A readily apparent explanation of this pressure effect, which is consistent with all the data, is the participation of a relatively long-lived excited state of  $\text{CCl}_4$ . Thus the following paths are possible:





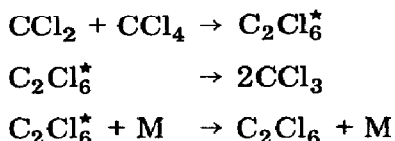
or



where \* and \*\* are excited states of  $\text{CCl}_4$  and these could be different electronic states, or the same electronic state with different vibrational energies.

The difficulty of postulating a long lived excited state for  $\text{CCl}_4$  is that spectral studies of other halomethanes suggest that the broad band observed from about 160 - 250 nm can be attributed to a  $n-\sigma^*$  transition which is not likely to lead to a stable excited state [17, 18]. However, the fact that the primary process appears to be molecular  $\text{Cl}_2$  elimination implies that the transition does not lead to a simple repulsive potential curve along the C-Cl bond reaction coordinate, but must involve considerable electronic rearrangement.

The most reasonable explanation of the pressure effect would be:



but a careful search for  $\text{C}_2\text{Cl}_6$  production was negative. The failure to stabilize  $\text{C}_2\text{Cl}_6$  (providing it is formed) even at 1 atm  $\text{O}_2$  or  $\text{N}_2$  is not impossible since the A factor for  $\text{C}_2\text{Cl}_6$  decomposition is very large ( $10^{17.7} \text{ s}^{-1}$ ) [19]. Furthermore primary process (1) is exothermic by  $\sim 50$  kcal/mol at 213.9 nm, and the  $\text{CCl}_2$  may be produced with excess energy.

In the mechanism, we have neglected the reaction of  $\text{CCl}_2$  with  $\text{O}_2$  at high  $\text{O}_2$  pressures, because addition of  $\text{O}_2$  has the same effect as the addition of  $\text{N}_2$ . Consequently the reaction of  $\text{CCl}_2$  with  $\text{O}_2$  cannot compete with reaction (2); the rate coefficient is  $\leq 10^{-13} \text{ cm}^3/\text{s}$ , and  $\text{CCl}_2$  cannot be in its triplet state.

The first of the excited-state mechanisms predicts that  $\Phi\{\text{COCl}_2\} = \Phi\{\text{Cl}_2\}$  goes from 2  $\rightarrow$  0 as  $[\text{M}]$  goes from 0  $\rightarrow$   $\infty$ ; whereas the second mechanism predicts that  $\Phi\{\text{COCl}_2\} = \Phi\{\text{Cl}_2\}$  goes from 2  $\rightarrow$  1 as  $[\text{M}]$  goes from 0  $\rightarrow$   $\infty$ . The highest total pressures used were not sufficiently high to determine if the quantum yields of  $\text{COCl}_2$  drop below 1. Thus if either of the two mechanisms is operative the present data cannot distinguish between them. However, since at longer wavelengths the primary process:



becomes dominant [3, 4], the second mechanism is more attractive, because it provides for the formation of  $\text{CCl}_3 + \text{Cl}$  within the same electronic



transition; \* and \*\* now would refer to different vibrational levels of the same electronic state.

The  $\text{Cl}_2$  quantum yield is substantially below 2 (1.2 - 1.4) at low pressures and is insensitive to total pressure, contrary to expectation. The reason for this is not known, but stable oxides of chlorine may have been formed which were not detected. The previously mentioned product observed in the u.v. spectrum of the reaction mixture does not correspond to that of any of the known chlorine oxides. Both mechanisms predict that in the presence of  $\text{O}_3$  at low pressures  $-\Phi\{\text{O}_3\}$  should be 4 and decline to either 3 or zero as  $M \rightarrow \infty$ . The data for  $\text{O}_3$  are very limited, but they do show a slight downward trend with increasing pressure (Table 2).

The present results can be compared to the only other study of  $\text{CCl}_4$  photolysis at shorter wavelengths by Davis *et al.* [4]. This group studied the photolysis at 253.7, 184.9, 147.0 and 106.7 nm. In that study, using  $\text{Br}_2$  scavenging experiments, it was concluded that at 253.7 nm the dominant primary process is:



in agreement with other studies [3]. However, at 184.9 nm process (1) becomes important with  $\phi\{1\} = 0.6$  and  $\phi\{1'\} = 0.4$ . From the large amounts of  $\text{Br}_2$  necessary to scavenge the  $\text{CCl}_2$  radicals it was concluded that reaction (2) is very efficient, though no direct evidence for reaction (2) was presented.  $\text{C}_2\text{Cl}_6$  formation *via* reaction (2) was suggested but its presence was not determined.

The present results show that  $\phi\{1\} = 1$  and  $\phi\{1'\} \sim 0$  at low pressures. These results are not necessarily in conflict with those of Davis *et al.* if an excited state mechanism is operative, according to which the relative importance of process (1) and (1') could vary with conditions.

The production of carbene in the photolysis of  $\text{CCl}_4$  is not unique for halomethanes. The photolysis of  $\text{CH}_2\text{I}_2$ , (20),  $\text{CF}_2\text{Br}_2$  and  $\text{CF}_2\text{HBr}$  [21] have been shown to undergo molecular elimination reactions at around 200 nm.

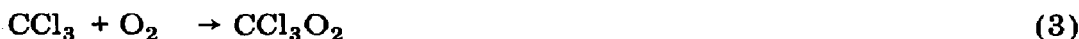
#### Reaction of $\text{O}(^1\text{D})$ with $\text{CCl}_4$

The photolysis of  $\text{O}_3$  at 253.7 nm in the presence of excess  $\text{CCl}_4$  can be discussed by considering the following mechanisms:





In the presence of  $\text{O}_2$  the additional reactions are:



The primary process giving  $\text{O}_2({}^1\Delta)$  and  $\text{O}({}^1\text{D})$  as well as reactions (11) and (12) are so well known that they need not be discussed here [8]. The reactions of  $\text{O}({}^1\text{D})$  with  $\text{CCl}_4$  may proceed by way of 3 channels. The resulting  $\text{ClO}$  and  $\text{CCl}_3$  will react as in the photolysis experiments already discussed. The reaction of  $\text{O}({}^1\text{D})$  with  $\text{O}_3$ :



is neglected and this is justified below.

The mechanism predicts that in the absence of  $\text{O}_2$ :

$$\Phi\{\text{COCl}_2\} = \Phi\{\text{Cl}_2\} = \phi\{13a\} + \phi\{13b\} \quad (I)$$

Since  $\Phi\{\text{COCl}_2\} = 0.87 \pm 0.2$  and  $\Phi\{\text{Cl}_2\} = 1.1 \pm 0.2$ ,  $\phi\{13a\} + \phi\{13b\} = 1.0 \pm 0.2$ ; thus  $\phi\{13c\} \leq 0.20$ . The mechanism also predicts that  $-\Phi\{\text{O}_3\} = 3$  if reaction (13b) is the exclusive primary process. If reaction (13a) is the exclusive primary process,  $-\Phi\{\text{O}_3\} = 5$  when reaction (9a) is negligible, and  $-\Phi\{\text{O}_3\} > 5$  when reaction (9a) is important. The measured value of  $\Phi\{\text{O}_3\}/\Phi_0\{\text{O}_3\} = 1.11 \pm 0.01$  indicates that  $-\Phi\{\text{O}_3\} \geq 6$ . Consequently process (13a) is dominant. This agrees with the direct observation of  $\text{ClO}$  production in the  $\text{O}({}^1\text{D})$ - $\text{CCl}_4$  system [5].

In the presence of  $\text{O}_2$  the rate law for  $\text{COCl}_2$  formation is:

$$\Phi\{\text{COCl}_2\}^{-1} = 1 + k_{14}[\text{O}_2]/k_{13}[\text{CCl}_4] \quad (II)$$

A plot of  $\Phi\{\text{COCl}_2\}^{-1}$  vs.  $[\text{O}_2]/[\text{CCl}_4]$  is shown in Fig. 2. The plot obeys equation (II) reasonably well. From the slope  $k_{14}/k_{13} = 0.25 \pm 0.03$ , and, since  $k_{14} = 7.4 \times 10^{-11}$  cm<sup>3</sup>/s [22],  $k_{13} = 3.0 \times 10^{-10}$  cm<sup>3</sup>/s. Also since  $k_{15} = (5.3 \pm 0.3) \times 10^{-10}$  cm<sup>3</sup>/s [22], and the  $\text{O}_3$  pressures were very much lower than the pressures for the other reactants, the neglect of reaction (15) in the mechanism is justified.

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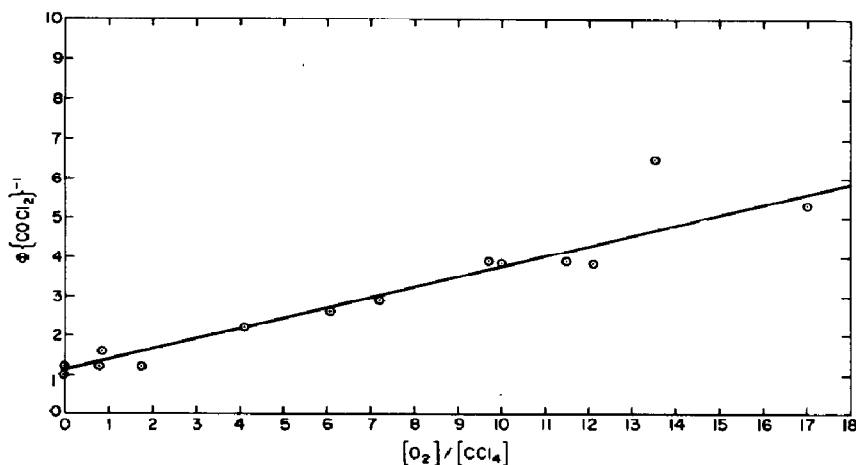


Fig. 2. Plot of  $\Phi[COCl_2]^{-1}$  vs.  $[O_2]/[CCl_4]$  for  $O_3$  photolysis at 253.7 nm in the presence of  $CCl_4$  at 25 °C.

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