THE PHOTOLYSIS OF CHLOROFLUOROMETHANES IN THE PRESENCE OF O_2 OR O_3 AT 213.9 nm AND THEIR REACTIONS WITH $O(^1D)$

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Summary

The photolysis of $CFCl_3$ at 213.9 nm and 25 °C in the presence of O_2 or O_3 gives CFClO and Cl_2 as products with $\Phi\{CFClO\} = 0.90 \pm 0.15$ and $\Phi\{Cl_2\} = 0.50 - 0.63$. In the O_3 system, $-\Phi\{O_3\}$ increases from 2.75 at high total pressures to 4.6 at low total pressures. With CF_2Cl_2 the photolysis was done only in the presence of O_2; $\Phi\{CF_2O\} = 1.0 \pm 0.2$ and $\Phi\{Cl_2\} = 0.52 - 0.66$. These results indicate that the dominant photochemical process is chlorine atom ejection with a quantum yield near 1.0.

For the reactions of the chlorofluoromethanes with $O(^1D)$, prepared from the photolysis of O_3 at 253.7 nm and 25 °C, the same products are obtained as in the photo-oxidation, and with the same yields. The quantum yields of O_3 removal are 5.7 ± 1 and 6.3 ± 1, respectively for the $CFCl_3$ and CF_2Cl_2 systems. Thus the indicated dominant reaction path is chlorine atom abstraction by $O(^1D)$, with other paths (O^1D deactivation or direct molecular formation of products) being negligible.

Rate coefficients were obtained for the $O(^1D)$ reactions with O_3, CO_2, $CFCl_3$, CF_2Cl_2, CF_3Cl, and CCl_4 relative to N_2O. The relative rate coefficients are: O_3, 2.5; CO_2, 0.65; $CFCl_3$, 1.5; CF_2Cl_2, 1.2; CF_3Cl, 0.52; CCl_4, 2.1. The rate coefficients were also measured for the first five gases in the presence of He to remove the excess translational energy of the $O(^1D)$ atom. Except for O_3, the same results were obtained in the presence and absence of He. However, for O_3 in the presence of He, the relative rate coefficient was 1.6.

As a check on the reactivities of $O(^1D)$ with the chlorofluoromethanes, the competition with O_2, rather than N_2O, was studied in the O_3-O_2-chlorofluoromethane system. By monitoring O_3 decay the relative rate coefficients for $CFCl_3$, CF_2Cl_2, and CCl_4 relative to O_2 were found to be 4.04, 2.78, and 5.3 respectively. These results are consistent with those obtained from the N_2O competition.

Introduction

Recent suggestions [1] that the chlorofluoromethanes may have adverse effects upon the earth's O_3 shield has made an understanding of the oxidation processes of these compounds of great importance.

Very few studies of the photolysis of the chlorofluoromethanes have been reported in the literature. Marsh and Heicklen [2] studied the photolysis of $CFCl_3$ at 213.9 nm in the presence of NO and O_2 scavengers. As far as we know no photolysis studies of CF_2Cl_2 have been published, except for the qualitative observation that flash photolysis in the quartz u.v. produces a weak absorption due to the CF_2 radical [3].

The reactions of $O(^1D)$ atoms with the dichlorofluoromethanes have also not been extensively studied. Clerc [4] has observed ClO production in the flash photolysis of O_3-CF_3Cl mixtures, indicating that $O(^1D)$ abstracts the Cl atom. Recently, since our work was completed, a report by Pitts *et al.* [5] was published which gives rate coefficients for several chlorofluoromethanes, including CF_2Cl_2 and $CFCl_3$, obtained by competitive methods relative to the reaction with N_2O.

This paper presents results of a study of the photolysis of $CFCl_3$ and CF_2Cl_2 in the presence of O_2 and O_3 at 213.9 nm, and the reactions of $O(^1D)$ atoms, produced from O_3 photolysis at 253.7 nm, with the homologous series $CFCl_3$, CF_2CL_2, and CF_3Cl as part of our continuing program of halocarbon oxidation studies. A previous paper presented results for CCl_4 [6], and additional information is given here on the $O(^1D)-CCl_4$ reaction which corroborates the earlier results.

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. Extra Dry grade O_2 from the Matheson Co. was used without further purification. The O_3 was distilled at 87 K before use. The $CFCl_3$, CF_2Cl_2, CF_3Cl, N_2O and CO_2 were obtained from the Matheson Co. and were purified by degassing at 77 K. In a few experiments the CF_2Cl_2 was purified by distillation from a trap maintained at 87 K to one at 153 K. The CCl_4 was "Baker Analyzed" reagent and was purified by distillation from a trap maintained at 210 to one at 177 K. The chlorofluoromethane pressures were measured with a H_2SO_4 manometer, and the O_2, CO_2 and N_2O pressures were measured with an Alphatron gauge calibrated against a H_2SO_4 manometer. The O_3 pressure was measured spectrophotometrically at 253.7 nm and could be monitored continuously.

The 213.9 nm radiation for the photolysis of these compounds was provided by a Phillips (93109E) low pressure Zn resonance lamp. For the $O(^1D)$ 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 Cl_2 gas and Corning CS 7-54 filters before entering the reaction cell.

The actinometry for the photolysis experiments at 213.9 nm was done by measuring the rate of N_2 production from N_2O photolysis. For this system $\Phi\{N_2\} = 1.41$ [7]. The actinometry at 253.7 nm was done by either measuring the O_3 removal in pure $O_3 (-\Phi\{O_3\} = 5.5$ [8]), or by measuring $\Phi\{N_2\}$ 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 [7].

Analysis for CFClO and CF_2O was made with a thermal conductivity gas chromatograph equipped with a copper column (10 ft. $\times$ ¼ in.) containing silica gel. On this column the CFClO and CF_2O are quantitatively converted to CO_2 [2], and it is actually the yield of CO_2 that is measured. For N_2 analysis the column used was a 20 ft. $\times$ ¼ in. column containing 5 Å molecular sieves. Analysis for Cl_2 was made by u.v. absorption with a Cary 14 spectrophotometer.

Results

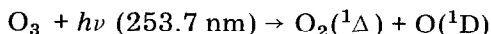### Photolysis of CFCl₃ and CF₂Cl₂

Photolysis of $CFCl_3$ in the presence of O_2 at 213.9 nm and 25 °C leads to the production of CFClO and Cl_2. Photolysis in the presence of O_3 leads to the consumption of O_3 and CFClO production. Presumably Cl_2 is also produced; however, because of the low yields, it was not determined. The photolysis of CF_2Cl_2 in the presence of O_2 at the same conditions as for $CFCl_3$ leads to CF_2O and Cl_2 production. Photolysis of CF_2Cl_2 in the presence of O_3 could not be studied because it absorbs weakly at 213.9 nm, and the light absorption by O_3 accounts for a significant fraction of the photodecomposition products. Measurements of CO production in the presence of O_2 were made but CO was insignificant; $\Phi\{CO\} < 0.01$. The results for $CFCl_3$ are presented in Tables 1 and 2 and for CF_2Cl_2 in Table 3. Experiments were done at different pressures of $CFCl_3$ and CF_2Cl_2 ranging from ~ 10 to 48 Torr. The O_2 pressure varied from 14 to 676 Torr, a factor of 48, for the $CFCl_3-O_2$ system and from 41 to 567 Torr, a factor of 13, for the $CF_2Cl_2-O_2$ system. In both systems the absorbed intensity, I_a was varied by about a factor of 4. From the results it can be seen that the quantum yields of CFClO and CF_2O are 0.9 ± 0.15 and 1.0 ± 0.2, respectively, invariant to the pressures of the reactants or absorbed light intensity. The Cl_2 quantum yields are significantly below one; 0.50 - 0.63 for the $CFCl_3$ system and 0.52 - 0.66 for the CF_2Cl_2 system.

Reactions of O(¹D) atoms with CFCl₃, CF₂Cl₂, CF₃Cl and CCl₄

The $O(^1D)$ atoms are produced by the photolysis of O_3 at 253.7 nm:

$$O_3 + h\nu \ (253.7 \text{ nm}) \rightarrow O_2(^1\Delta) + O(^1D)$$

Irradiation of O_3 at 253.7 nm in the presence of $CFCl_3$ and CF_2Cl_2 leads to

TABLE 1

Photolysis of $CFCl_3-O_2$ mixtures at 213.9 nm and 25 °C

$\dfrac{[O_2]}{[CFCl_3]}$	$[CFCl_3]$ (Torr)	$[O_2]$ (Torr)	I_a (mTorr/min)	$\Phi\{CFClO\}$	$\Phi\{Cl_2\}$
1.32	11.0	14.6	4.8	0.96	—
2.94	22.0	64.7	9.6	0.94	—
3.04	21.6	65.6	9.6	—	0.63
3.05	21.6	66.0	9.6	—	0.62
4.20	22.0	92.4[a]	9.6	1.04	—
5.73	46.6	267.0	19.2	0.8	—
6.24	10.8	67.4	4.8	0.83	—
6.24	10.8	67.0	4.8	0.77	—
6.24	10.8	67.0	4.8	0.85	—
7.32	46.3	339.0	19.2	0.75	—
7.41	10.8	80.0	4.8	—	0.50
13.00	21.6	281.0	9.6	—	0.62
15.78	21.6	341.0	9.6	—	0.51
18.00	22.0	396.0	9.6	1.06	—
21.52	21.0	452.0	9.6	0.88	—
26.0	22.0	572.0	9.6	0.75	—
62.64	10.8	676.5	4.8	0.77	—

[a] $[N_2] = 348$ Torr.

TABLE 2

Photolysis of $CFCl_3-O_3$ mixtures at 213.9 nm and 25 °C

$[CFCl_3]$ (Torr)	$[O_3]$ (mTorr)	I_a (mTorr/min)	$\Phi\{CFClO\}$	$-\Phi\{O_3\}$
10.8	276	4.8	—	3.8
10.8	285	4.8	0.89	4.56
11.0	266	4.8	0.84	4.54
11.2	306	4.8	—	3.64
11.6	241	4.8	—	4.10
13.5	266	4.8	—	4.54
23.2	249	9.6	0.94	3.64
23.5	233	9.6	0.94	3.26
23.5	233	9.6	—	3.8
31.3	258	14.4	—	3.26
44.8	276	19.2	—	2.75
47.5	249	19.2	—	2.80

the consumption of O_3 and the production of CFClO and Cl_2 in the $CFCl_3-O_3$ system and CF_2O and Cl_2 in the $CF_2Cl_2-O_3$ system. Quantum yields for CFClO and CF_2O formation and O_3 removal are presented in Tables 4 and 5, respectively, for the $CFCl_3$ and CF_2Cl_2 systems. The average quantum yields of CFClO and CF_2O formation are 0.90 ± 0.05 and $1.0 \pm$

TABLE 3

Photolysis of $CF_2Cl_2-O_2$ mixtures at 213.9 nm and 25 °C

$\dfrac{[O_2]}{[CF_2Cl_2]}$	$[CF_2Cl_2]$ (Torr)	$[O_2]$ (Torr)	I_a (mTorr/min)	$\Phi\{CF_2O\}$	$\Phi\{Cl_2\}$
0.85	48.2	41.0	1.2	—	0.66
1.06	46.6	49.3	1.2	—	0.66
2.58	22.1	57.1	0.64	—	0.52
6.02	10.8	65.0	0.32	0.80	—
6.76	10.8	73.0	0.32	0.88	—
7.60	48.6	369.0	1.20	1.10	—
9.38	48.7	·457.0	1.20	1.03	—
11.20	48.6	545.0	1.20	1.20	—
11.57	49.0	567.0	1.20	1.13	—
30.27	10.9	330.0	0.32	0.75	—
36.66	10.8	396.0	0.32	0.75	—

TABLE 4

Photolysis of O_3-CFCl_3 mixtures at 253.7 nm and 25 °C

$\dfrac{[O_2]}{[CFCl_3]}$	$[CFCl_3]$ (Torr)	$[O_2]$ (Torr)	$[O_3]$ (mTorr)	I_a (mTorr/min)	$-\Phi\{O_3\}$	$\Phi\{CFClO\}$
—	9.72	—	423	11.3	6.2	—
—	10.50	—	309	4.9	5.56	0.84
—	11.0	—	309	5.01	5.5	0.90
—	19.3	—	423	5.18	5.9	0.89
—	23.9	—	423	5.65	5.8	—
—	24.4	—	318	4.9	5.64	0.92
—	37.9	—	309	5.05	5.27	0.95
0.81	47.25	38.45	423	5.73	2.71	—
0.96	19.30	18.5	420	12.0	4.14	—
2.55	45.10	115.0	400	11.8	2.21	—
2.90	19.40	56.4	453	5.3	2.44	—
3.47	19.00	66.0	109	5.01	2.03	—
3.83	9.20	35.2	396	4.84	2.48	—
6.20	11.90	73.8	396	5.65	1.54	—
7.00	9.45	66.4	420	12.60	1.80	—
8.30	9.20	75.7	423	5.30	1.36	—
9.77	10.40	101.6	450	5.10	1.27	—
13.60	8.80	119.0	423	5.20	1.09	—
17.00	9.30	159.0	437	5.41	0.76	—
19.0	10.40	197.6	423	5.41	0.66	—
19.6	9.30	183.0	423	5.01	0.64	—
19.6	9.70	190.0	420	14.29	0.70	—
20.2	9.30	188.0	423	5.01	0.61	—
22.0	9.70	214.3	400	13.30	0.63	—

TABLE 5

Photolysis of $O_3-CF_2Cl_2$ mixtures at 253.7 nm and 25 °C

$\dfrac{[O_2]}{[CF_2Cl_2]}$	$[CF_2Cl_2]$ (Torr)	$[O_2]$ (Torr)	$[O_3]$ (mTorr)	I_a (mTorr/min)	$-\Phi\{O_3\}$	$\Phi\{CF_2O\}$
—	24.3	—	309	5.2	6.3	1.0
—	24.3	—	309	5.2	6.25	1.05
—	24.7	—	309	5.3	6.30	0.94
1.77	23.5	41.7	437	5.27	2.77	—
8.5	11.10	93.8	437	5.27	1.61	—
9.38	11.50	108.0	437	5.36	1.0	—
9.90	18.10	179.0	423	5.30	0.70	—
10.07	10.20	104.0	423	5.30	0.90	—
12.80	12.10	156.0	423	5.20	0.69	—
15.64	10.50	164.7	423	5.2	0.60	—
20.90	10.70	223.0	423	5.48	0.44	—

0.05, respectively. The average $-\Phi\{O_3\}$ = 5.7 in the $CFCl_3-O_3$ system and $-\Phi\{O_3\}$ = 6.3 in the $CF_2Cl_2-O_3$ system. Quantitative measurements of $\Phi\{Cl_2\}$ were not made, because of analysis difficulties at low Cl_2 concentrations. Product formation in the CF_3Cl-O_3 system was not determined. Presumably CF_2O and Cl_2 are the products in this system.

Also included in Tables 4 and 5 are results when O_2 was added initially to the chlorofluorocarbon–O_3 system. As expected the product yields and O_3 consumption are reduced as the $[O_2]$/[chlorofluoromethane] ratio increases because the O_2 is scavenging some of the $O(^1D)$ atoms.

To check the CCl_4 system studied earlier [6], $O_3-O_2-CCl_4$ mixtures were irradiated at 253.7 nm, and the results are presented in Table 6. In the absence of O_3, $-\Phi\{O_3\}$ = 6.0 ± 0.2, but this value drops as $[O_2]$/[CCl_4] increases.

In order to determine the rate coefficients for the $O(^1D)$ and chlorofluoromethane reactions, competitive experiments with added N_2O were done. Mixtures of O_3-N_2O–chlorofluoromethane were irradiated at 253.7 nm and the rate of N_2 production, $R\{N_2\}$, as a function of the [chlorofluoromethane]/[N_2O] was determined. These results are presented in Table 7.

The O_3 pressure was always sufficiently high that 100% of the light was absorbed, thus changes in the initial $[O_3]$ or change in $[O_3]$ due to O_3 consumption did not affect the rate of N_2 production. There was always some N_2 produced in the dark for which a small (≤ 10%) correction was applied.

The $O(^1D)$ atoms produced from O_3 photolysis may possess up to 14 kcal/mol excess translational energy [7]. In order to determine the effect of this excess energy experiments were done in the presence of excess helium. It is known that helium will not deactivate the $O(^1D)$ state of the oxygen atom [7], but it will remove the excess translational energy. These results are also presented in Table 7.

TABLE 6

Photolysis of O_3-CCl_4 mixtures at 253.7 nm and 25 °C

$\dfrac{[O_2]}{[CCl_4]}$	$[CCl_4]$ (Torr)	$[O_2]$ (Torr)	$[O_3]$ (mTorr)	Average I_a (mTorr/min)	$-\Phi\{O_3\}$
—	45.0	—	567	14.30	6.0
—	44.4	—	567	14.30	5.8
—	21.5	—	567	14.30	6.3
—	6.7	—	567	14.30	5.8
0.44	44.8	20	520	12.4	3.76
0.78	44.8	35	520	12.57	3.09
1.24	44.8	55.5	567	13.95	3.10
1.50	19.2	28.7	567	5.83	3.67
2.40	44.3	106.0	520	6.03	2.44
2.62	44.3	116	567	12.20	2.09
3.25	44.0	143	160	6.70	2.44
3.50	44.3	155	524	13.56	2.10
5.0	21.6	108	567	12.57	1.85
5.5	6.9	38	312	1.27	1.80
6.3	45.0	283	504	13.40	1.77
6.6	21.6	142	567	13.90	1.85
7.0	45.0	315	567	11.90	1.42
8.35	8.7	73	545	13.75	1.43
10.0	18.0	180	238	1.29	1.41
11.6	44.7	518	524	13.00	1.20
12.5	20.4	254	520	13.20	1.15
14.0	6.34	89	520	13.0	1.40
16.70	5.70	95	504	5.84	1.07
17.60	6.60	116	520	13.20	1.10
21.7	6.60	143	567	12.74	0.94
26.3	7.30	192	285	10.35	0.70

To test our method for rate coefficient determination the well known relative rate coefficients for $O(^1D)$ reactions with CO_2 and N_2O were measured in an analogous manner. Mixtures of $O_3-N_2O-CO_2$ were irradiated and $R\{N_2\}$ as a function of the $[CO_2]/[N_2O]$ ratio was determined. Again these results are presented in Table 7.

The relative rate coefficients for the reaction of $O(^1D)$ atoms with O_3 and N_2O enter as a small correction in the determination of the coefficients for the chlorofluoromethanes and CO_2. For this reason the competition of $O(^1D)$ for O_3 and N_2O was also studied. Mixtures of O_3-N_2O were irradiated and $R\{N_2\}$ was determined as a function of the $[O_3]/[N_2O]$ ratio. The results are presented in Table 8. In order to produce sufficient N_2 for an accurate measurement a significant amount of O_3 ($\sim$ 30%) was consumed. The average value was used in calculating the $[O_3]/[N_2O]$ ratio.

TABLE 7

Photolysis of O_3 in the presence of N_2O and reactant gas (X) at 253.7 nm and 25 °C

$\dfrac{[X]}{[N_2O]}$	[X] (Torr)	$[N_2O]$ (Torr)	$[O_3]$ (Torr)	[He] (Torr)	$R\{N_2\}$ (mTorr/min)
X = CFCl$_3$					
—	—	50	2.83	—	6.50
0.64	8.7	13.6	2.97	—	3.25
0.81	14.5	17.8	2.02	—	3.30
1.02	12.5	12.3	2.97	—	2.57
1.20	15.1	12.6	2.83	438	2.57
1.60	18.3	11.5	2.97	548	1.92
1.73	21.0	12.1	2.83	568	1.75
2.06	24.5	11.9	2.97	—	1.67
2.20	26.4	11.9	2.83	—	1.42
2.31	28.5	12.3	2.83	—	1.42
2.84	34.3	12.1	2.97	396	1.42
3.08	32.8	10.7	2.97	375	1.08
3.15	42.3	13.4	2.97	—	1.15
3.80	41.6	10.9	2.83	—	1.00
X = CF$_2$Cl$_2$					
—	—	50	2.83	—	6.5
0.83	9.7	11.7	2.7	—	3.05
1.25	15.2	12.1	2.7	—	2.70
1.55	18.0	11.6	2.83	75	2.00
1.60	18.5	11.6	2.83	420	1.75
1.68	19.3	11.5	2.63	—	2.05
2.63	30.8	11.7	2.56	—	1.50
2.72	34.0	12.5	3.10	400	1.42
3.10	35.6	11.5	2.70	—	1.38
3.30	40.3	12.3	2.83	—	1.42
3.40	57.8	17.0	2.83	—	1.25
X = CF$_3$Cl					
—	—	66	2.22	—	7.10
0.30	19.65	64.4	2.22	—	6.50
1.20	53.70	45.5	1.75	—	5.00
1.52	32.80	21.5	2.29	—	3.70
2.34	28.50	12.2	2.97	—	2.75
2.75	34.10	12.4	2.97	400	2.53
2.90	76.30	26.3	1.89	—	2.60
3.52	66.20	18.8	2.50	—	2.70
4.90	72.40	14.8	2.23	—	2.00
5.80	77.50	13.4	2.29	—	1.70
6.40	68.30	10.7	2.29	—	1.60
X = CCl$_4$					
—	—	57.65	2.83	—	6.0
0.66	9.42	14.30	2.83	—	2.58
1.05	11.47	11.30	2.97	—	1.83

TABLE 7 *(continued)*

$\dfrac{[X]}{[N_2O]}$	[X] (Torr)	[N$_2$O] (Torr)	[O$_3$] (Torr)	[He] (Torr)	$R\{N_2\}$ (mTorr/min)
1.44	17.55	12.10	2.97	—	1.41
1.75	19.60	11.20	2.97	—	1.25
2.01	25.00	12.40	2.97	—	1.33
2.07	25.20	12.10	2.83	—	1.25
2.49	30.50	12.25	3.00	—	1.00
3.31	37.10	11.21	2.83	—	0.77
X = CO$_2$					
—	—	56	2.97	—	6.50
0.43	5.94	13.90	2.97	—	4.25
0.94	14.50	15.45	2.83	—	3.50
1.10	13.10	11.60	2.97	—	3.33
1.30	16.97	13.00	2.97	390	3.33
1.40	18.80	13.20	2.70	—	3.40
1.71	20.50	12.0	2.83	390	2.91
2.09	24.60	11.8	2.83	385	2.08
2.50	33.70	13.5	2.70	—	2.20
2.80	29.30	10.4	2.97	—	2.17
3.10	33.60	10.9	2.97	350	2.00
3.15	36.60	11.6	2.83	385	2.00
4.06	51.60	12.7	2.70	—	1.70

Discussion

Photolysis of CFCl$_3$

The photolysis data for CFCl$_3$ in the presence of O$_2$ are consistent with the mechanism:

$$CFCl_3 + h\nu \text{ (213.9 nm)} \rightarrow CFCl_2 + Cl \tag{1a}$$

$$\rightarrow CFCl + Cl_2 \tag{1b}$$

$$CFCl_2 + O_2 \rightarrow CFCl_2O_2 \tag{2}$$

$$2CFCl_2O_2 \rightarrow 2CFCl_2O + O_2 \tag{3}$$

$$CFCl_2O \rightarrow CFClO + Cl \tag{4}$$

$$^1CFCl + CFCl_3 \rightarrow 2CFCl_2 \tag{5}$$

$$^3CFCl + O_2 \rightarrow Cl + CO + FO \tag{6}$$

$$2CFClO_2 \rightarrow 2CFClO + O_2 \tag{7}$$

$$2Cl \rightarrow Cl_2 \tag{8}$$
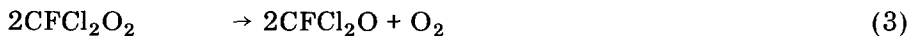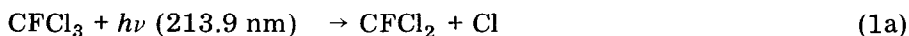
In the presence of O$_3$ reactions (2), (6) and (8) must be replaced by:

$$CFCl_2 + O_3 \rightarrow CFCl_2O + O_2 \tag{9}$$

$$CFCl + O_3 \rightarrow CFClO + O_2 \tag{10}$$

TABLE 8

Photolysis of O_3–N_2O mixtures at 253.7 nm and 25 °C

$\dfrac{[O_3]_0}{[N_2O]}$	$[O_3]_0$ (Torr)	$[N_2O]$ (Torr)	$[He]$ (Torr)	$R\{N_2\}$ (mTorr/min)
0.030	1.89	62.2	—	6.60
0.032	1.89	59.3	400	6.25
0.0517	2.77	53.5	355	6.90
0.0525	2.97	56.5	—	6.60
0.184	1.89	10.3	450	6.00
0.194	1.89	9.7	—	4.75
0.232	1.35	5.8	—	4.63
0.253	1.48	5.87	550	5.50
0.40	1.89	4.72	450	4.25
0.41	1.89	4.60	—	3.37
0.52	1.89	3.64	400	4.38
0.56	1.89	3.37	—	3.50
0.76	1.75	2.30	400	3.63
0.90	1.89	2.09	—	2.50
0.90	1.89	2.09	550	3.75
1.08	1.89	1.75	—	2.25
1.08	1.89	1.75	550	2.70

$$Cl + O_3 \quad\rightarrow ClO + O_2 \tag{11}$$

$$2ClO \quad\rightarrow 2Cl + O_2 \tag{12a}$$

$$\rightarrow Cl_2 + O_2 \tag{12b}$$

In the mechanism the formation of F or FCl in the primary process is not considered, since the bond energy of the C—F bond is much greater than that of the C—Cl bond. Studies of other halomethanes show that for the atom elimination process the bond broken is always the weakest one [9], and for halomethanes containing more than one F atom the stable CF_2 radical is produced [10]. By analogy it seems likely that, if carbene is produced from $CFCl_3$, it would be CFCl rather than CCl_2.

First, let us consider the reactions of CFCl. If the singlet CFCl, [1]CFCl, is produced, as expected from spin conservation rules, then reaction (5) would be expected by analogy to the [1]Cl_2–CCl_4 system [6]. On the other hand, if triplet CFCl, [3]CFCl, is produced it reacts with O_2, but not to give CFClO [11]. Thus the production of [1]CFCl would tend to promote CFClO production, whereas production of [3]CFCl would diminish CFClO production. It is possible that both spin states are produced, and their reaction processes just balance. However, as we shall see the results in the presence of O_3 are inconsistent with reaction (1b) being an important process.

The reaction of $CFCl_2$ with O_2 to give CFClO can proceed *via* the sequence of reactions (2) - (4) or *via*

$$CFCl_2 + O_2 \rightarrow CFClO + ClO$$
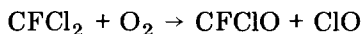
We favor the former path by analogy with the reaction of CCl_3 radicals with O_2 which has been shown to proceed by a sequence analogous to reactions (2) - (4) [12, 13]. In the presence of O_2 the Cl atoms will recombine, but in the presence of O_3 they will be removed by reaction (11) (k_{11} = 2 × 10^{-19} cm^3/s [14]). The ClO radicals produced in reaction (11) will be removed by either reactions (12a) or (12b), depending on the total pressure. The bimolecular reaction of ClO radicals at low pressures ($\leqslant$ 8 Torr argon) is known to proceed predominantly, if not exclusively, by reaction (12a) [15]. At higher pressures ($\geqslant$ 70 Torr argon) reaction (12b) is the exclusive reaction [16, 17]. In the present experiments reaction (12a) could occur at the low $CFCl_3$ pressures (~ 10 Torr), but for experiments in which the $CFCl_3$ pressure is ~ 50 Torr it should be negligible. The reaction:

$$ClO + O_3 \rightarrow Cl + 2O_2 \text{ or } ClO_2 + O_2$$
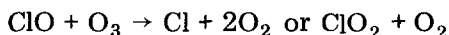
can be neglected, because it is very slow (k = 2 - 7 × 10^{-19} cm^3/s [18]).

The mechanism in the presence of O_3 requires that $-\Phi\{O_3\}$ = 3 at high pressures and $-\Phi\{O_3\} \geqslant$ 3 at low pressures if primary process (1a) is the exclusive reaction path. On the other hand, if reaction (1b) is the exclusive reaction path, then one of three situations must occur: (1) all the CFCl reacts with $CFCl_3$ and $-\Phi\{O_3\} \geqslant$ 4, but $\Phi\{CFClO\}$ should be 2.0; (2) all the CFCl reacts with O_3, $\Phi\{CFClO\}$ and $-\Phi\{O_3\}$ = 1; (3) the CFCl reacts with both $CFCl_3$ and O_3 (surely ^{1}CFCl will react with both species) and there should be a dependence of $-\Phi\{O_3\}$ and $\Phi\{CFClO\}$ on the $[CFCl_3]/[O_3]$ ratio.

The measured values of $-\Phi\{O_3\}$ range from 2.75 at high $CFCl_3$ pressures to 4.6 at low $CFCl_3$ pressures, but $\Phi\{CFClO\}$ = 0.90 ± 0.15 under all conditions. This clearly indicates that primary process (1a) is dominant and that at low total pressure (~ 10 Torr) reaction (12a) is not negligible. Based on the mechanism the rate law for O_3 removal is:

$$-\Phi\{O_3\} = 3 + 2k_{12a}/k_{12b}$$

Since at 10 Torr $-\Phi\{O_3\}$ = 4 - 4.5, $k_{12a}/k_{12b} \simeq$ 0.5 - 0.75.

The present conclusion that reaction (1a) is the dominant primary process is consistent with the earlier work of Marsh and Heicklen [2] who observed the formation of $CFCl_2NO$ when $CFCl_3$ was irradiated in the presence of NO indicating the formation of $CFCl_2$ radicals in the primary process.

If we ignore reaction (1b), then the mechanism requires that $\Phi\{CFClO\}$ = $\Phi\{Cl_2\}$ in the presence of O_2 or O_3. $\Phi\{CFClO\}$ is 1 to within the experimental uncertainty, but $\Phi\{Cl_2\}$ < 1. The reason for the low Cl_2 yield is not known, but perhaps other chlorine oxides are formed. The same Cl_2 deficiency was found in the CCl_4 photo-oxidation [6] and there was some evidence for other unidentified products in that system. In addition, $\Phi\{CFClO\}$ could be as low as 0.75, and the presence of undetected products containing carbon and chlorine is also possible.

Photolysis of CF_2Cl_2

The photolysis of CF_2Cl_2 in the presence of O_2 can be discussed in terms of an entirely analogous mechanism to that for $CFCl_3$ (experiments in the presence of O_3 were not done, because of experimental difficulties). The question of interest is whether primary process (1a') or (1b') or both are important:
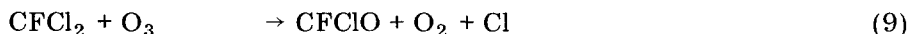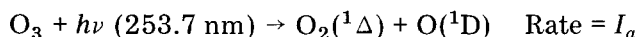
$$CF_2Cl_2 + h\nu \ (213.9 \ nm) \ \rightarrow CF_2Cl + Cl \tag{1a'}$$

$$\rightarrow CF_2 + Cl_2 \tag{1b'}$$
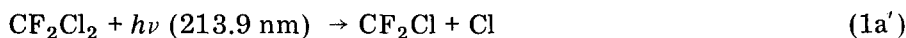
Since experiments in the presence of O_3 could not be done, our data cannot provide a definitive answer. The qualitative flash photolysis experiments of Simons and Yarwood [3] in the quartz u.v. showed a weak absorption due to CF_2 (by contrast CF_2Br produced a strong absorption); however, it is not clear whether this was due to the low primary efficiency of the primary process or simply reflects the lower absorption coefficient of CF_2Cl_2. Nevertheless the participation of process (1b') to some extent is indicated.

Singlet CF_2 does not react with O_2 at room temperature [19]. However, it may react with CF_2Cl_2. Dependent on the fate of CF_2, $\Phi\{CF_2O\}$ could vary anywhere from 0 to 2. In fact $\Phi\{CF_2O\} = 1.0 \pm 0.1$ invariant to conditions, exactly as would be expected if reaction (1a') were the dominant process. Both reaction paths lead to the expectation that $\Phi\{CF_2O\} = \Phi\{Cl_2\}$. Again as was the case for $CFCl_3$, $\Phi\{Cl_2\} < \Phi\{CF_2O\}$, but the reason for this is not known.

Reactions of $O(^1D)$ atoms with chlorofluoromethanes

The photolysis of O_3 at 253.7 nm in the presence of excess CF_2Cl_2 or $CFCl_3$ can be discussed by considering the following mechanism for $CFCl_3$ (a completely analogous mechanism is applicable to CF_2Cl_2):

$$O_3 + h\nu \ (253.7 \ nm) \rightarrow O_2(^1\Delta) + O(^1D) \quad Rate = I_a$$

$$O_2(^1\Delta) + O_3 \quad \rightarrow O_2 + O(^3P) \tag{13}$$

$$O(^3P) + O_3 \quad \rightarrow 2O_2 \tag{14}$$

$$O(^1D) + CFCl_3 \quad \rightarrow CFCl_2 + ClO \tag{15a}$$

$$\rightarrow CFClO + Cl_2 \tag{15b}$$

$$\rightarrow O(^3P) + CFCl_3 \tag{15c}$$

$$CFCl_2 + O_3 \quad \rightarrow CFClO + O_2 + Cl \tag{9}$$

$$Cl + O_3 \quad \rightarrow ClO + O_2 \tag{11}$$

$$2ClO \quad \rightarrow 2Cl + O_2 \tag{12a}$$

$$\rightarrow Cl_2 + O_2 \tag{12b}$$

The primary process giving $O_2(^1\Delta)$ and $O(^1D)$ as well as reactions (13) and (14) are firmly established and need not be discussed here. There are three reaction channels by which $O(^1D)$ atoms may react with the chloro-

fluoromethane, *i.e.* (15a) - (15c) for $CFCl_3$ and analogous reactions for the others. The ClO and trihalomethyl radicals will react as in the photolysis experiments already discussed. The reaction:

$$O(^1D) + O_3 \rightarrow O_2 + 2O(^3P) \tag{16a}$$

$$\rightarrow 2O_2 \tag{16b}$$

is neglected, because the $[O_3]/[\text{fluorocarbon}]$ is low ($\leqslant 0.03$) and the rate coefficient ratio $k_{15}/k_{16} \sim 1$ (see below).

The mechanism requires that for $CFCl_3$:

$$\Phi\{CClFO\} = \phi\{15a\} + \phi\{15b\}$$

and for CF_2Cl_2:

$$\Phi\{CF_2O\} = \phi\{15a\} + \phi\{15b\}$$

Since $\Phi\{CClFO\} = 0.90 \pm 0.05$ and $\Phi\{CF_2O\} = 1.0 \pm 0.05$, $\phi\{15c\} \leqslant 0.15$ and $\leqslant 0.05$ for $CFCl_3$ and CF_2Cl_2, respectively. The mechanism also requires that $-\Phi\{O_3\} = 5.0$ if process (15a) is dominant and reaction (12a) is negligible, and $-\Phi\{O_3\} > 5$ if reaction (12a) is important. However, if primary process (15b) is dominant then $-\Phi\{O_3\} = 3.0$. Since $-\Phi\{O_3\} = 5.7 \pm 1$ and 6.3 ± 1 for $CFCl_3$ and CF_2Cl_2, respectively, it follows that primary process (15a) is the dominant, if not exclusive, process.

We have shown in a previous paper [6] that $O(^1D)$ atoms also predominantly abstract a Cl atom from CCl_4, and Clerc [4] has qualitatively observed abstraction of a Cl atom from CF_3Cl. Thus for the homologous series CCl_4, $CFCl_3$, CF_2Cl_2 and CF_3Cl the abstraction of a Cl atom is the dominant and probably the exclusive reaction.

Determination of rate coefficients for the $O(^1D)$-chlorofluoromethane reactions

The photolysis of O_3–N_2O–X mixtures involves the competition:

$$O(^1D) + X \rightarrow \text{not } N_2 \tag{x}$$

$$O(^1D) + N_2O \rightarrow N_2 + O_2 \tag{17a}$$

$$\rightarrow 2NO \tag{17b}$$

where $X = O_3$, CO_2, $CFCl_3$, CF_2Cl_2, CF_3Cl, or CCl_4. When $X = O_3$ the mechanism consisting of reactions (13), (14), (16) and (17) describes the photolysis at 253.7 nm. The rate law for N_2 formation is given by:

$$R\{N_2\}^{-1}/(R_\circ\{N_2\}^{-1} - \alpha_\circ) = 1 + k_{16}[O_3]/k_{17}[N_2O] \tag{a}$$

where $R\{N_2\}$ is the rate of N_2 formation and $\alpha_\circ = k_{16}[O_3]_\circ/I_a k_{17a}[N_2O]_\circ$. The subscript $_\circ$ refers to the highest value of $[N_2O]/[O_3]$ used. When X is other than O_3, the photolysis is described by the mechanism consisting of reactions (13), (14), (17) and reaction (x). For the fluorocarbons reaction (x) is reaction (15) and for CO_2 it is reaction (18):

$$O(^1D) + CO_2 \rightarrow O(^3P) + CO_2 \tag{18}$$

The rate law for N_2 formation in the presence of X other than O_3 is given by:

$$(R\{N_2\}^{-1} - \alpha)/(R_o\{N_2\}^{-1} - \alpha_o) = 1 + k_x[X]/k_{17}[N_2O] \qquad (b)$$

Plots of the left-hand sides of equations (a) and (b) vs. $[O_3]/[N_2O]$ or $[X]/[N_2O]$, respectively, should be linear with slopes of k_{16}/k_{17} and k_x/k_{17}, respectively.

The plot of equation (a) for O_3–N_2O mixtures is shown in Fig. 1 and plots of equation (b) for O_3–N_2O–X mixtures are shown in Fig. 2. All the plots are reasonably linear as predicted by equations (a) and (b). The slopes of the plots are given in Table 9.

The value of k_{16}/k_{17} obtained in the presence of helium is about 30% lower than in its absence. Since helium removes the excess translational energy in the $O(^1D)$ atoms, this difference may be attributed to the excess translational energy of the $O(^1D)$ atom. This result is in agreement with other measurements from our laboratory. Goldman et al. [20] in O_3 photolysis experiments at 253.7 and 228.8 nm found k_{16}/k_{17} dependent upon the wavelength used to produce the $O(^1D)$ atoms. Thus k_{16}/k_{17} = 2.6 at 253.7 nm but k_{16}/k_{17} = 4.1 at 228.8 nm. Lissi and Heicklen [8] in O_3 photolysis experiments at 280.0 and 228.8 nm found k_{16}/k_{17} = 4.0 at 228.8 nm and k_{16}/k_{17} = 1.5 at 280.0 nm. The present value of 1.6 in the presence of helium is in excellent agreement with Lissi and Heicklen's value at 280.0 nm; under these conditions the $O(^1D)$ atoms should have nearly the equilibrium thermal energy. The present value of 2.5 in the absence of helium is in good agreement with the value of 2.6 measured by Goldman et al. at 253.7 nm and is intermediate, as expected, to the values of 1.5 and 4.0 measured by Lissi and Heicklen at 280.0 and 228.8 nm, respectively.

The value of k_{16}/k_{17} = 0.65 agrees well with the recommended value of 0.82 [21] and is in good agreement with the values of 0.55 [22] and 0.80 [23] measured by Cvetanović and coworkers.

Our values of k_x/k_{17} for the chlorofluoromethanes differ by nearly a factor of 2 from the values measured by Pitts et al. [5]. At first we thought that this difference could be due to the different amounts of translational energy of the $O(^1D)$ atoms. Pitts et al. [5] used the photolysis of NO_2 at 228.8 nm as a source of $O(^1D)$, and these are nearly thermal. However, the $O(^1D)$ atoms from O_3 photolysis at 253.7 nm could contain up to 14 kcal/mol translational energy. Thus experiments in the presence and absence of helium were done. For the $CFCl_3$ and CF_3Cl systems, the results in the presence and absence of helium are the same. For CF_2Cl_2, there appears to be a small effect, but this is not statistically significant. Thus excess translational energy does not affect k_{15}/k_{17}, and the reason for the discrepancy between our measurements and those of Pitts et al. is not known.

In an earlier study we found that the branching ratio for reaction (17), i.e. k_{17a}/k_{17b}, was slightly dependent upon the excess translational energy of the $O(^1D)$ atom [7]. Thus k_{17a}/k_{17b} = 0.69 for $O(^1D)$ atoms produced from N_2O photolysis at 213.9 nm in the absence of helium, but k_{17a}/k_{17b} =
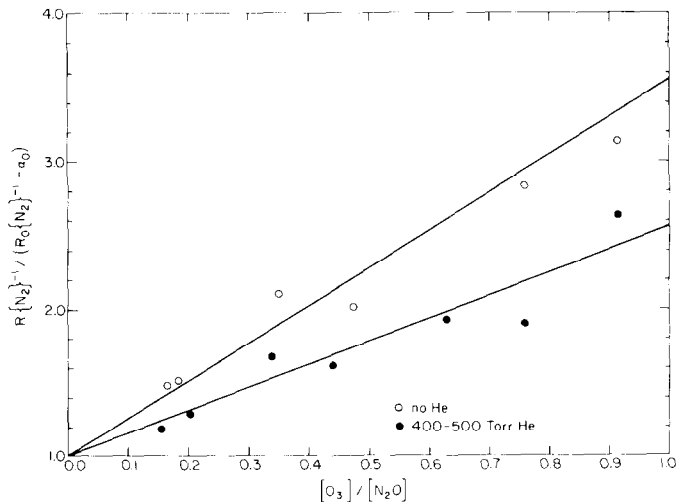
Fig. 1. Plot of $R\{N_2\}^{-1}/(R_o\{N_2\}^{-1} - \alpha_o)$ vs. $[O_3]/[N_2O]$ for photolysis of O_3–N_2O mixtures at 253.7 nm and 25 °C.
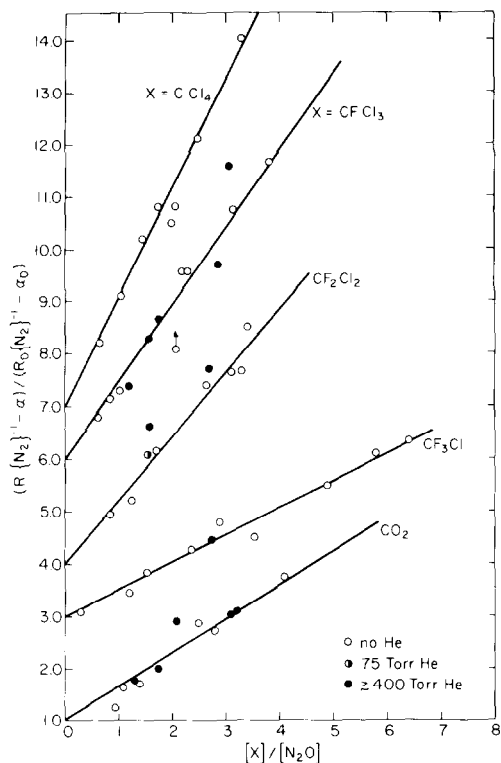

Fig. 2. Plot of $(R\{N_2\}^{-1} - \alpha)/(R_o\{N_2\}^{-1} - \alpha_o)$ vs. $[X]/[N_2O]$ for photolysis of O_3–N_2O–X mixtures at 253.7 nm and 25 °C. The ordinate scales are displaced for clarity. The intercept of each plot is 1.0.
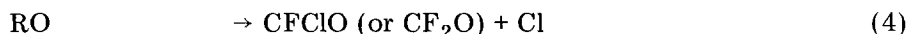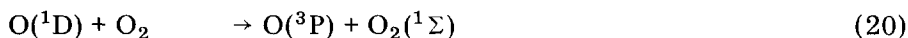
TABLE 9

Summary of measured and literature values of k_x/k_{17}

X	He (Torr)	k_x/k_{17} This work	Literature
O_3	—	2.5	2 - 3 [8]; 2.6 [20]; 2.2 [21]
O_3	400 - 500	1.6	—
CO_2	—	0.65	0.82 [21]; 0.55 [22]; 0.80 [23]
CO_2	400	0.65	—
$CFCl_3$	—	1.5	2.6 ± 0.5 [5]
$CFCl_3$	400 - 550	1.5	—
CF_2Cl_2	—	1.2	2.4 ± 0.5 [5]
CF_2Cl_2	75 - 420	~1.4	—
CF_3Cl	—	0.52	—
CF_3Cl	500	0.52[a]	—
CCl_4	—	2.1	—

[a] Based on one point.

0.83 in the presence of helium. This small difference was detectable, because a very sensitive chemical titration technique was employed. The present experiments show that $R_o\{N_2\}$ (note that $\Phi_o\{N_2\} \simeq k_{17a}/k_{17}$) is not affected by addition of excess helium, but such a small effect ($\sim 10\%$) would not be easily detectable by the present technique. Furthermore in the present system the $O(^1D)$ atoms are produced from O_3 photolysis at 253.7 nm giving only about 14 kcal/mol excess energy [7], whereas $O(^1D)$ atoms produced from N_2O photolysis at 213.9 nm could possess up to 32 kcal/mol excess energy [7]. Thus the difference in k_{17a}/k_{17b} in the present system in the presence and absence of helium is probably not more than about 5%, which is well within the experimental uncertainty.

As a check on the rate coefficients for $O(^1D)$ atom reactions, O_2 was used as a competitive gas rather than N_2O. In this system reactions (17a) and (17b) are replaced by:

$$O(^3P) + O_2 + M \rightarrow O_3 + M \tag{19}$$

$$O(^1D) + O_2 \rightarrow O(^3P) + O_2(^1\Sigma) \tag{20}$$

$$O_2(^1\Sigma) + O_3 \rightarrow 2O_2 + O(^3P) \tag{21}$$

$$CFCl_2 \text{ (or } CF_2Cl) + O_2 \rightarrow RO_2 \tag{2}$$

$$2RO_2 \rightarrow 2RO + O_2 \tag{3}$$

$$RO \rightarrow CFClO \text{ (or } CF_2O) + Cl \tag{4}$$

The rate law for O_3 removal is complex, but if reactions (14), (15b), (15c) and (16) are unimportant, the rate law reduces to:

$$-\Phi\{O_3\}^{-1} = 1/\beta + k_{20}[O_2]/\beta k_{15}[X] \tag{c}$$

where $\beta = 2$ if all the ClO are removed by reaction (12b), but $\beta > 2$ if reaction (12a) plays a role or O_3 is removed by ClO in some other way. Figure 3
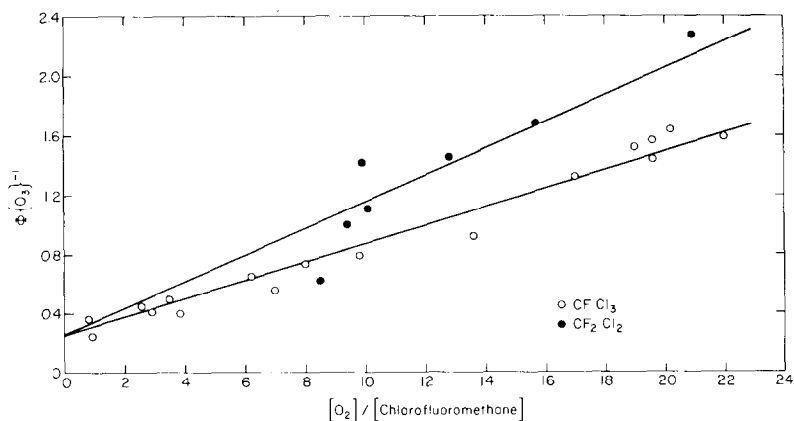
Fig. 3. Plots of $-\Phi\{O_3\}^{-1}$ vs. $[O_2]/$[chlorofluoromethane] for the photolysis of O_3–O_2–$CFCl_3$ and O_3–O_2–CF_2Cl_2 mixtures at 253.7 nm and 25 °C.
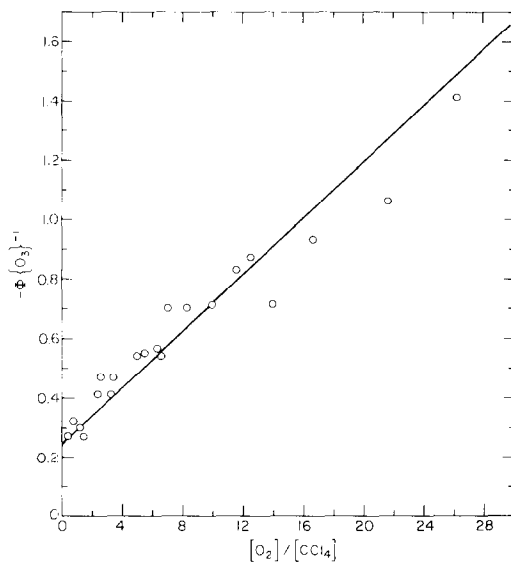

Fig. 4. Plot of $-\Phi\{O_3\}^{-1}$ vs. $[O_2]/[CCl_4]$ for the photolysis of O_3–O_2–CCl_4 mixtures at 253.7 nm and 25 °C.

gives plots of $-\Phi\{O_3\}$ vs. $[O_2]/[CFCl_3]$ and $[O_2]/[CF_2Cl_2]$, and Fig. 4 gives a similar plot for CCl_4. The data are well fitted by straight lines with intercepts of 0.25. The respective slopes are 0.062, 0.090, and 0.047. Thus k_{15}/k_{20} = 4.04 for $CFCl_3$, 2.78 for CF_2Cl_2, and 5.3 for CCl_4. The last value is slightly higher than the value of 4.0 found by us previously [6] by measuring $\Phi\{CCl_2O\}$. The currently accepted values for k_{17} and k_{20} are k_{17} = 2.2×10^{-10} cm^3/s and k_{20} = 0.74×10^{-10} cm^3/s [21]. When these values are combined with the values found here for k_{15}/k_{20}, k_{15}/k_{17} can be

computed to be 1.36, 1.02, and 1.79, respectively for $CFCl_3$, CF_2Cl_2, and CCl_4, which are 10 - 15% smaller than the respective values of 1.5, 1.2, and 2.1 found directly.

For $CFCl_3$, CF_2Cl_2 and CCl_4, the value of β was found to be 4 in each case, thus indicating that reaction (12b) is not the sole fate of ClO radicals in this system. Other reactions which ultimately lead to additional O_3 removal must be occurring.

Acknowledgements

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