# PHOTODECOMPOSITION OF $CFCl_3$ AND CF_2Cl_2

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Summary

The photochemical decomposition of $CFCl_3$ and CF_2Cl_2 has been investigated, using added CH_4 and C_2H_6 as chlorine atom interceptors. From the quantum yields of the stable products formed at 213.9, 184.9, 163.3 and 147 nm, quantum yields of the primary photofragments $CFCl_2$, CF_2Cl, $CFCl$, CF_2, CF and Cl, were derived. At wavelengths close to the absorption threshold, detachment of one chlorine atom from $CFCl_3$ and CF_2Cl_2 occurs with a quantum yield of 0.95 ± 0.05. As the photon energy is increased, there is a rapidly increasing probability that absorption of a photon will lead to the release of two chlorine atoms:

$$CFCl_3 + h\nu \rightarrow CFCl + 2Cl$$

$$CF_2Cl_2 + h\nu \rightarrow CF_2 + 2Cl$$
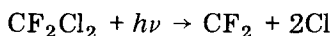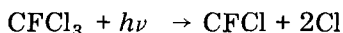
The $CFCl$ or CF_2 formed in these processes (which are most likely in the ground singlet state) are unreactive towards the parent halocarbons, or alkanes. They combine with other free radicals to form stable products. No evidence was found for the cleavage of C–F bonds, or the elimination of stable chlorine molecules.

In the vicinity of the absorption threshold, the absorption cross-sections of CF_2Cl_2 and $CFCl_3$ diminish sharply with a decrease in temperature.

Introduction

Recently considerable concern has been expressed that the photochemical decomposition of CF_2Cl_2 and $CFCl_3$ in the stratosphere might lead to the formation of chlorine atoms whose reactions would deplete the earth's ozone layer [1]. In fact, however, until now there has been little concrete information available about the modes of decomposition of $CFCl_3$ and CF_2Cl_2 excited by photons in the wavelength range which is important in the stratosphere (~ 215 to 190 nm).

In 1965, Marsh and Heicklen [2] reported on the photolysis of $CFCl_3$ and CF_2Cl_2 at 213.9 nm in presence of oxygen and of nitric oxide,

respectively. They observed absorption bands due to CFClO in $CFCl_3-O_2$ mixtures, and bands which they ascribed to CF_2ClNO in CF_2Cl_2-NO mixtures. More recently, Jayanty et al. [3] attempted to determine the quantum yields of products formed in the photolysis of these molecules in the presence of added oxygen at the same photon energy. They reported the formation of Cl_2 with a quantum yield of 0.5 in $CFCl_3-O_2$ and with a quantum yield of 0.52 - 0.66 in $CF_2Cl_2-O_2$. In the photolysis of both these mixtures, CO_2 was observed, with a quantum yield of 0.90 ± 0.15 in $CFCl_3$ and 1.0 ± 0.2 in CF_2Cl_2; the CO_2 was assumed to result from the conversion of CFClO or CF_2O to CO_2 on the silica gel column used in the analyses. Milstein and Rowland [4] studied the photolysis of $CF_2Cl_2-O_2$ mixtures at 184.9 nm, and reported that the quantum yield of CO_2 was 1.11 ± 0.05 and the quantum yield for the removal of CF_2Cl_2 was 1.12 ± 0.09. Since spectroscopic evidence suggests [5] that the cleavage of a C—Cl bond rather than the stronger C—F bond is to be expected in the photolysis of these molecules, the results of these three studies were interpreted to mean that the predominant primary process in the photolysis of both $CFCl_3$ and CF_2Cl_2 is the elimination of one chlorine atom from the halocarbon molecule. However, other results have been reported which indicate the need for more detailed results. An earlier study [6] of the flash photolysis of CF_2Cl_2 showed the presence of CF_2, and it has recently been reported [7] that CCl_2 plays an important role in the photolysis of CCl_4 at wavelengths shorter than 253.7 nm.

The present investigation was undertaken with the intention of providing definitive experimental determinations of the photodissociation fragments, and thereby arriving at a detailed picture of the photochemical decomposition processes of CCl_2F_2 and $CFCl_3$. In order to do this, a somewhat different approach from that of the earlier studies has been used. Since it is known [8] that Cl or F atoms abstract H atoms from alkanes (RH) with a high rate constant, the photolysis was carried out in the presence of ethane or methane, added to scavenge halogen atoms. (The abstraction of a hydrogen atom from C_2H_6 by a chlorine atom occurs with an activation energy of only 0.043 eV.) The product alkyl radicals, R, combine or disproportionate with other radicals in the system such as $CFCl_2$, CF_2Cl, CF_2, CFCl, etc., to form products which can be quantitatively analyzed by gas chromatography. It will be demonstrated that the quantum yields of the photofragments can be obtained with reasonable precision from an analysis of the quantum yields of all the products formed via such radical—radical reactions.

Experimental

CF_2Cl_2 and C_2H_6 were purified by gas chromatography. The CF_2ClH, which was the major detectable impurity in CF_2Cl_2, could be removed entirely in this manner. Because no impurities could be detected in $CFCl_3$, this compound was used as such after the usual low-temperature degassing

procedure. Methane was purified in the same fashion as described in an earlier publication [9].

Gas chromatographs equipped with flame ionization detectors and squalane or activated alumina columns of various lengths were used in the quantitative analysis of all products. Identification of the products was carried out by injecting known samples of CH_2CF_2, C_2F_4, $C_2F_2Cl_2$, $C_2F_4Cl_2$, $C_2F_2Cl_4$, CF_2ClH, $CFCl_2H$, CF_2H_2, CF_2Cl_2, CH_3Cl, C_2H_5Cl, and the various hydrocarbons. Furthermore, most products were collected separately in a low temperature trap at the exit of a thermal conductivity chromatograph. Analysis of trapped material was then carried out on a high resolution mass spectrometer. Although standard mass spectral cracking patterns of some of the products have not been reported in the literature, identification was usually based on the identities of the major fragment ions.

Light sources and actinometry

The 147 nm (8.4 eV) experiments were carried out with a microwave operated xenon resonance lamp the construction of which has been described in an earlier report [10]. A bromine lamp similar in design to that described by Loucks and Cvetanović [11] was used to obtain 163.3 nm (7.4 eV) radiation. A 0.1 cm thick Suprasil quartz window was used which effectively removed the shorter wavelength lines at 158.2 and 157.5 nm. The microwave-operated lamp was filled with 1 Torr of argon and the bromine was maintained at constant pressure by cooling the lamp to 195 K. Approximately 80% of the ultra-violet light transmitted through the window consists of 163.3 nm radiation. A microwave-operated low pressure (1 Torr) mercury−argon lamp provided with a sapphire window was used to obtain the 184.9 nm (6.7 eV) mercury resonance line. In some experiments an 185 nm interference filter was used to eliminate the 253.7 nm resonance line. A zinc arc provided the 213.9 nm (5.8 eV) line. An attempt was made to eliminate the two neighboring resonance lines located at 202.5 and 206.2 nm. These lines which usually account for about 20% of the total radiation from a zinc discharge could be removed in part by an interference filter.

The xenon, bromine, and mercury light sources were inserted into a spherical (500 ml) reaction vessel *via* a tapered joint to which temperature-resistant epoxy cement was applied. A cylindrical (10 cm long) quartz reaction vessel was used in conjunction with the zinc discharge lamp. An interference filter and a photomultiplier were used to monitor the intensity of the lamp as well as to determine the light absorbed by CF_2Cl_2 or $CFCl_3$. Chemical actinometry was performed by measuring the yield of nitrogen formed in the photolysis of N_2O and the yield of acetylene formed in the photolysis of ethylene. The quantum yield for nitrogen formation was assumed to be 1.4 at all wavelengths [12].

At 163.3 and 184.9 nm, where the extinction coefficients are relatively high, all incident photons are absorbed at the halocarbon pressures used in this study. At 147 nm, absorption by CF_2Cl_2 in excess of 95% was

only achieved at pressures around 35 Torr. The absorption cross-sections recently determined by Huebner *et al.* [13] were used to calculate the extent of light absorbed at lower pressures. In the case of $CFCl_3$, light absorption at 147 nm was in excess of 95% at the lowest pressure used in this study.

Because at 213.9 nm, we found the absorption cross-section to be a sensitive function of the temperature, literature data could not be used to calculate the fraction of light absorbed by either CF_2Cl_2 or $CFCl_3$ at any particular temperature.

The 213.9 nm absorption cross-sections obtained for CF_2Cl_2 at temperatures ranging from 234 to 442 K are given in Table 1. The value obtained at 295 K is in good agreement with the value of 0.30×10^{-20} cm^2 molecule^{-1} measured by Rowland and Molina at room temperature. The sharp increase of σ with increasing temperature close to the absorption threshold is not unexpected. Other investigators have observed similar effects for molecules such as N_2O [14], OCS [15], CO_2 [16] and CCl_4 [17]. In the case of CCl_4 an eight-fold increase in σ (250 nm) was observed when the temperature was raised from 293 to 453 K. The magnitude of such temperature effects on absorption cross-section is expected to be smaller at wavelengths farther from threshold. In the case of $CFCl_3$, whose absorption threshold is shifted about 20 nm towards longer wavelengths as compared to that of CF_2Cl_2, there is only a two-fold decrease in σ when the temperature is reduced from 295 to 234 K at 213.9 nm (the wavelength of the results of Table 1). Additional measurements of absorption cross-sections of the halocarbons at the relatively low temperatures ($\sim$ 190 - 275 K) [18] prevailing in the upper atmosphere would seem to be indicated.

The light flux of all lamps used in this investigation was generally maintained between 5×10^{13} and 10^{14} quanta/s. All experiments listed in Tables 2 to 4 were carried out at constant conversion (0.02%) of the halocarbon. If the conversion is increased above this level, secondary reactions involving the unsaturated products, complicate the interpretation of the experimental results. The accuracy of the quantum yields of the stable products given in the Tables is difficult to evaluate. However, considering the various experimental manipulations involved, the accuracy should be better than 10%. The reproducibility of the analytical procedure is better than 5%.

Results and discussion

On the basis of spectroscopic evidence and energetic considerations, the most likely primary dissociative processes in the photolysis of CF_2Cl_2 are as follows:

$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl \tag{1}$$

$$\rightarrow CF_2 + Cl_2 \tag{2}$$

TABLE 1

Effect of temperature on the absorption cross-section of CF_2Cl_2 at 213.9 nm

T (K)	Cross-section, $\sigma \times 10^{-20}$ (cm^2)
442	1.1
378	0.67
343	0.41
295	0.27
274	0.20
249	0.15
234	0.08

The primary fragments CF_2Cl and Cl_2 may dissociate further, depending on their internal energy content. In that case the photodecomposition can be written as follows:

$$CF_2Cl_2 + h\nu \rightarrow CF_2 + 2Cl \tag{3}$$

The energy requirement for process (3) is approximately 5.6 eV, which is close to the absorption threshold energy ($\sim$ 5.5 eV) [1d, 13] and 0.2 eV below the energy of the main zinc discharge resonance line at 213.9 nm.

Accepting a value of 2.8 eV for $\Delta H_f(CF_2Cl)$ [19] and -1.9 eV for $\Delta H_f(CF_2)$ [20] cleavage of the C–Cl bond in process (1) requires 3.4 eV, while 2.2 eV is needed to break the C–Cl bond in the CF_2Cl radical.

On the same basis, the most plausible photodissociative processes in the case of $CFCl_3$ can be depicted as follows:

$$CFCl_3 + h\nu \rightarrow CFCl_2 + Cl \tag{4}$$

$$\rightarrow CFCl + Cl_2 \tag{5}$$

$$\rightarrow CFCl + 2Cl \tag{6}$$

The Cl atoms formed in the various dissociative processes can either be in the ground state, $^2P_{3/2}$, or in an excited state. The experimental results obtained in this study do not reveal any information concerning the electronic or kinetic energy of the chlorine atoms.

Although the C–F bond is nearly 2 eV stronger than the C–Cl bond [21], the occurrence of a primary process such as:
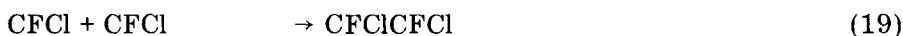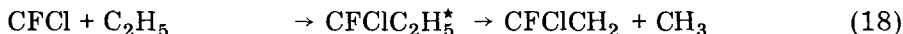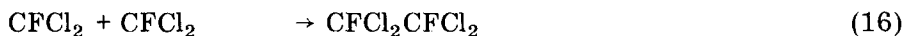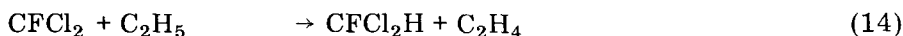
$$CF_2Cl_2 + h\nu \rightarrow CFCl_2 + F \tag{7}$$

possibly followed by decomposition of $CFCl_2$ cannot be dismissed on an *a priori* basis. In the next section we will, however, show that the quantum yield of process (7) is negligibly small, even at the highest photon energy (8.4 eV) used in this study.

In the following discussion of the photolysis of CF_2Cl_2 and $CFCl_3$ in the presence of CH_4 and C_2H_6, we will attempt to derive the quantum yields of all photofragments. Reliable estimates will strongly depend on the

reactions which the CF_2 and $CFCl$ species undergo. Because little is known about the kinetics of these intermediates, all energetically allowed reactions will have to be considered.

Photolysis of $CFCl_3-C_2H_6$ mixtures

Table 2 gives the quantum yields of the products formed in the photolysis of $CFCl_3-C_2H_6$ mixtures at 213.9, 184.9 and 163.3 nm. The formation of most of these products can be accounted for by photo-dissociation processes (4), (5) and (6), followed by the reactions:

$$Cl + C_2H_6 \rightarrow HCl + C_2H_5 \tag{8}$$

$$C_2H_5 + C_2H_5 \rightarrow n\text{-}C_4H_{10} \tag{9}$$

$$\rightarrow C_2H_4 + C_2H_6 \tag{10}$$

$$CFCl_2 + C_2H_5 \rightarrow CH_3CH_2CFCl_2^\star \tag{11}$$

$$CH_3CH_2CFCl_2^\star \rightarrow CH_3CHCFCl + HCl \tag{12}$$

$$CH_3CH_2CFCl_2^\star + M \rightarrow CH_3CH_2CFCl_2 + M \tag{13}$$

$$CFCl_2 + C_2H_5 \rightarrow CFCl_2H + C_2H_4 \tag{14}$$

$$\rightarrow CFCl + C_2H_5Cl \tag{15}$$

$$CFCl_2 + CFCl_2 \rightarrow CFCl_2CFCl_2 \tag{16}$$

$$\rightarrow CFCl_3 + CFCl \tag{17}$$

$$CFCl + C_2H_5 \rightarrow CFClC_2H_5^\star \rightarrow CFClCH_2 + CH_3 \tag{18}$$

$$CFCl + CFCl \rightarrow CFClCFCl \tag{19}$$

$$CH_3 + C_2H_5 \rightarrow C_3H_8 \tag{20}$$

$$CH_3 + HCl \rightarrow CH_4 + Cl \tag{21}$$
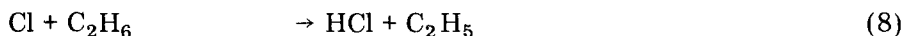
Reaction (12) is included to account for the pressure-dependent yield of $CH_3CHCFCl$ (Table 2). Elimination of HCl from chemically activated chlorinated hydrocarbon molecules is well established [22]. The disproportionation reaction (14) is included to account for the C_2H_4 product in excess of that which can be accounted for by reaction (10). Taking the accepted [8] value for k_{10}/k_9 of 0.13, we can estimate the excess ethylene yield (*i.e.*, reaction 14) from the butane yield. In all the experiments listed in Table 2, the quantum yield of $CFCl_2H$, the other product of reaction (14), is in reasonably good agreement with the calculated "excess" ethylene which is attributed to this reaction. (In most cases the yield of $CFCl_2H$ exceeds that of the excess ethylene by 10 - 20%, which probably indicates that a small fraction of the $CFCl_2$ radicals abstract a hydrogen from ethane.) From the excess ethylene yield, as well as the yields of $CH_3CH_2CFCl_2$ and $CH_3CHCFCl$, we can estimate that $k_{14}/k_{11} = 0.17 \pm 0.015$. Assuming that the yield of reaction (15) is represented by the yield of C_2H_5Cl, $(k_{14} + k_{15})/k_{11} = 0.20 \pm 0.02$. This estimate for the value of the disproportionation-recombination ratio for the $CFCl_2-C_2H_5$ radical pair is in good agreement with the values of about 0.2 - 0.25 found [23] for the analogous

TABLE 2

Quantum yields of products formed in the photolysis of $CFCl_3$–C_2H_6 mixtures

		213.9*nm		184.9 nm	163.3 nm			
Pressure (Torr[†]):	$CFCl_3$	10.5	91.5	30.6	10.6	30.6	31.1	94.5
	C_2H_6	5.3	44.8	15.5	5.5	15.5	61.0	45.7
CH_4		0.006	0.006	0.11	0.130	0.150	0.127	0.121
$CFCl_2H$		0.084	0.089	0.075	0.051	0.057	0.060	0.062
$CFClCFCl$		0.018	0.013	0.070	0.100	0.095	0.095	0.097
CH_2CFCl		0.048	0.036	0.20	0.294	0.326	0.290	0.292
C_2H_4		0.107	0.102	0.114	0.102	0.110	0.101	0.105
C_2H_5Cl		0.015	0.013	0.010	0.101	0.007	0.008	0.008
$CFCl_2CFCl_2$		0.176	0.196	0.100	0.049	0.045	0.046	0.040
$CH_3CHCFCl$		0.070	0.012	0.04	0.051	0.036	0.017	0.011
$CH_3CH_2CFCl_2$		0.397	0.418	0.32	0.246	0.247	0.252	0.268
C_3H_8		0.003	0.003	0.08	0.095	0.111	0.097	0.109
n-C_4H_{10}		0.231	0.235	0.33	0.406	0.469	0.410	0.459
$k_{11}/(k_9^{1/2} \cdot k_{16}^{1/2})$ =		2.3	2.3	2.1	2.1	1.95	2.0	2.0
Derived quantum yields:								
$C_2H_5 \cdot$		1.12	1.09	1.46	1.67	1.83	1.64	1.76
$CFCl_2 \cdot$		0.97	0.97	0.67	0.47	0.44	0.43	0.43
		(0.99)	(0.98)	(0.74)	(0.57)	(0.54)	(0.54)	(0.53)
$CFCl$		0.074	0.052	0.34	0.49	0.52	0.48	0.49
		(0.056)	(0.039)	(0.27)	(0.39)	(0.42)	(0.39)	(0.39)

Values in parentheses are based on the assumption that $CFClCFCl$ is formed entirely by reaction (23). Temperature: $298 \pm 2K$.
*There is approximately a 10% contribution from 202.5 and from 206.2 nm.
[†] 1 Torr = 133.3 pascals.

ratios for the CCl_3–C_2H_5 or CCl_3–CH_3CHCl radicals. Also, the results given in Table 2 lead to a value of 2.15 ± 0.15 at every wavelength for the ratio $k_{11}/k_9^{1/2} k_{16}^{1/2} = [CH_3CH_2CFCl_2 + CH_3CHCFCl]/[C_4H_{10}]^{1/2}[CFCl_2CFCl_2]^{1/2}$. A value of 2 has been reported for the analogous expression for the CCl_3–C_2H_5 reaction pair [23].

We will tentatively assume that k_{17}/k_{16} is ~ 0.17, as recently determined [24] for the analogous disproportionation reactions of CF_2Cl. Finally, reactions (18) - (21) are included in the reaction scheme to account for the products $CFClCH_2$, $CFClCFCl$, C_3H_8 and CH_4. The justification for writing reaction (21) to explain the formation of methane is that the methane yield increases with conversion, as it should if formed in a fast reaction [8] with a product molecule, HCl. It is true that CH_3 may also react with C_2H_6 to give a methane product, and this reaction may well occur also. However, the exact pathway for methane formation will not influence the overall chemistry occurring in the system since each Cl atom formed in reaction (21) will generate an ethyl radical (reaction 8), as will each CH_3 reacting directly with ethane.

The CFCl radicals do not react with C_2H_6 or $CFCl_3$ under our experimental conditions. This we know because the products which would be expected from a reaction with C_2H_6 could not be detected in any experiment. Reaction with $CFCl_3$ can be rejected since under conditions (147 nm, see discussion in next section) in which photodissociation process (6) accounts for over 90% of the photofragmentation (*i.e.*, initial fragmentation results in the formation of CFCl in high yield, but essentially no $CFCl_2$), there is no evidence for the presence of $CFCl_2$ (*i.e.*, its reaction products are below the detection limit) which would result from the reaction:

$$CFCl + CFCl_3 \rightarrow CFCl_2CFCl_2^* \rightarrow 2CFCl_2 \qquad (22)$$

There is one other reaction which might plausibly occur, but for which no firm evidence was obtained:

$$CFCl + CFCl_2 \rightarrow CFClCFCl + Cl \qquad (23)$$

Taking into account reactions (8) - (21), we can derive the following expressions for the yields of the $CFCl_2$, CFCl, and C_2H_5 radicals:

$$\Phi(C_2H_5) = 2.26\ \Phi(C_4H_{10}) + 1.2\ [\Phi(C_2H_5CFCl_2) + \Phi(CH_3CHCFCl)] +$$
$$\Phi(C_3H_8) + \Phi(CH_2CFCl)$$

$$\Phi(CFCl_2) = 2.34\ \Phi(CFCl_2CFCl_2) + 1.2\ [\Phi(C_2H_5CFCl_2) + \Phi(CH_3CHCFCl)]$$

$$\Phi(CFCl) = \Phi(CH_2CFCl) + 2\Phi(CFClCFCl)$$

The quantum yields of these radicals derived from these expressions are given in Table 2. Since each ethyl radical results from the reaction of one chlorine atom, the ethyl radical yield can be equated to the yield of Cl, and it is evident from the radical yields listed in Table 2 that at 213.9 nm the quantum yield which can be attributed to the primary photodissociation process (4) is well above 0.9. Some CFCl radicals are produced, but some of these ($\Phi \sim 0.02$) may be formed in reaction (17). However, the fact that $\Phi(C_2H_5)$ (*i.e.*, $\Phi(Cl)$) is higher than $\Phi(CFCl_2)$ and is also slightly higher than unity points to the occurrence of process (6). A reasonable estimate of Φ(process 6) is 0.05 ± 0.03 at a total pressure of 15.8 Torr. (The wide uncertainty limits cited for this estimate are chosen because of the quantitative uncertainties in the yields of the radicals due to the estimates of the relative importances of different reaction channels.) In the 213.9 nm photolysis, the quantum yield obtained for CFCl is lower at the higher pressure, possibly because of partial collisional deactivation of the internally excited $CFCl_2$ radical formed in process (4). It is evident from the yields of these three radicals at 213.9 nm, that elimination of a chlorine molecule from electronically excited $CFCl_3$ (process 5) is of negligible importance at this wavelength.

The product distribution obtained at 184.9 and 163.3 nm as well as the derived yields of C_2H_5, $CFCl_2$ and CFCl differ considerably from those found at 213.9 nm. In these experiments, where reaction (21) is presumed to occur to a more significant extent, the quantum yield of Cl atoms formed

through a primary dissociation is equal to the difference between the C_2H_5 and the methane quantum yields. It can be seen that:

$$\Phi(C_2H_5) - \Phi(CH_4) = \Phi(CF_2Cl) + 2\Phi(CFCl)$$

which indicates that processes (4) and (6) adequately account for the observed product distribution. In the 184.9 nm experiment, $[\Phi(CFCl_2) + \Phi(CFCl)]$ is unity, while at the higher energy, 163.3 nm, this total is somewhat lower, 0.91 - 0.96, a difference which is probably not significant in view of some of the uncertainties in the ratios of the competing reaction channels in the mechanism from which the radical yields were derived. It is encouraging to note that in the experiments at 163.3 nm, the derived values for $\Phi(CFCl_2)$ and $\Phi(CFCl)$ are, within experimental error, independent of pressure or the relative concentration of $CFCl_3$ and C_2H_6.

It should be pointed out that if reaction (23) were included in the reaction scheme, the quantum yields for CFCl would have to be revised. Making the extreme assumption that all CFClCFCl is formed in reaction (23), then the value for $\Phi(CFCl)$ must be revised downward by approximately 20%, while $\Phi(CFCl_2)$ must be increased from 2 to 20%, depending on the wavelength; these revised quantum yield values are given in parentheses in the Table. Because one additional Cl atom is formed in reaction (23), this change in the reaction mechanism would not affect the material balance between C_2H_5 and the other intermediates. It will be shown in the discussion of the 147 nm experiments that recombination of CFCl (reaction 19) does compete with other recombination reactions. Therefore, the actual quantum yields of CFCl and $CFCl_2$ probably lie somewhere between the two limiting values given in Table 2.

Photolysis of $CF_2Cl_2-C_2H_6$ mixtures

A reaction mechanism analogous to that proposed for the photolysis of $CFCl_3-C_2H_6$ mixtures can be written to account for the quantum yields of the products formed in the photolysis of $CF_2Cl_2-C_2H_6$ mixtures, which are listed in Table 3. Reactions (11) to (19) are replaced by their counterparts:
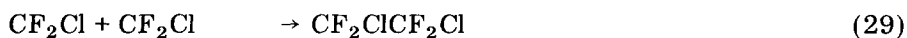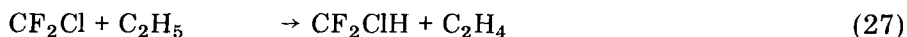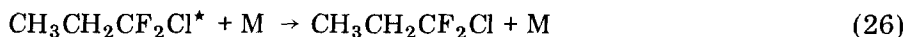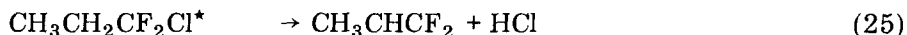
$$CF_2Cl + C_2H_5 \rightarrow CH_3CH_2CF_2Cl^\star \tag{24}$$

$$CH_3CH_2CF_2Cl^\star \rightarrow CH_3CHCF_2 + HCl \tag{25}$$

$$CH_3CH_2CF_2Cl^\star + M \rightarrow CH_3CH_2CF_2Cl + M \tag{26}$$

$$CF_2Cl + C_2H_5 \rightarrow CF_2ClH + C_2H_4 \tag{27}$$

$$\rightarrow CF_2 + C_2H_5Cl \tag{28}$$

$$CF_2Cl + CF_2Cl \rightarrow CF_2ClCF_2Cl \tag{29}$$

$$\rightarrow CF_2Cl_2 + CF_2 \tag{30}$$

$$CF_2 + C_2H_5 \rightarrow CF_2C_2H_5^\star \rightarrow CF_2CH_2 + CH_3 \tag{31}$$

$$CF_2 + CF_2 \rightarrow CF_2CF_2 \tag{32}$$
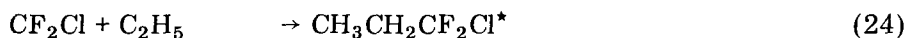
TABLE 3

Quantum yields of products formed in the photolysis of $CF_2Cl_2-C_2H_6$ mixtures

		213.9* nm	184.9 nm	163.3 nm
Pressure (Torr):	CF_2Cl_2	20	20	20
	C_2H_6	10	10	10
CH_4		0.025	0.150	0.146
CF_2ClH		0.063	0.049	0.049
C_2F_4		0.026	0.070	0.078
CF_2CH_2		0.059	0.247	0.28
C_2H_4		0.091	0.089	0.090
$C_2F_4Cl_2$		0.170	0.070	0.050
C_2H_5Cl		0.006	0.0017	0.002
C_3H_8		0.011	0.084	0.093
$C_2H_5CF_2Cl$		0.387	0.332	0.308
CH_3CHCF_2		0.055	0.053	0.042
$n\text{-}C_4H_{10}$		0.231	0.351	0.392
$k_{24}/(k_9^{1/2} \cdot k_{29}^{1/2})$		2.23	2.47	2.50
Derived quantum yields:				
C_2H_5		1.09	1.56	1.66
CF_2Cl		0.90(0.92)	0.60(0.68)	0.51(0.60)
CF_2		0.11(0.08)	0.39(0.32)	0.44(0.36)

Values in parentheses are based on the assumption that C_2F_4 is entirely formed by reaction (33). Temperature: $298 \pm 2K$.
*There is approximately a 10% contribution from 202.5 and from 206.2 nm.

Again calculating the "excess" ethylene yield from the total ethylene yield, the yield of n-butane, and the value of 0.13 for k_{10}/k_9, we obtain an estimate of the yield which can be attributed to reaction (27) which is in reasonably good agreement with the observed yield of CF_2ClH, the other product of reaction (27). The 3 - 25% excess of CF_2ClH probably originates from the small fraction of CF_2Cl radicals which abstract a H atom from ethane or HCl. The "excess" ethylene yield and the yields of $C_2H_5CF_2Cl$ and CH_3CHCF_2 lead to an estimate for k_{27}/k_{24} of 0.12 ± 0.015. Taking the yield of C_2H_5Cl as an estimate of the importance of reaction (28), we obtain $(k_{28} + k_{27})/k_{24} = 0.13 \pm 0.02$.

A value of 0.17 has been reported by Pritchard and Perona [24] for k_{30}/k_{29}. We then can say:

$$\Phi(C_2H_5) = 2.26 \; \Phi(C_4H_{10}) + 1.13 \; [\Phi(C_2H_5CF_2Cl) + \Phi(CH_3CHCF_2)] + \Phi(C_3H_8) + \Phi(CF_2CH_2)$$

$$\Phi(CF_2Cl) = 2.34 \; \Phi(CF_2ClCF_2Cl) + 1.13 \; [\Phi(C_2H_5CF_2Cl) + \Phi(CH_3CHCF_2)]$$

$$\Phi(CF_2) = \Phi(CF_2CH_2) + 2 \; \Phi(CF_2CF_2)$$

In deriving the quantum yield of CF_2 it is possible to make an alternative assumption, that CF_2CF_2 is entirely formed in the reaction:

$$CF_2 + CF_2Cl \rightarrow CF_2CF_2 + Cl \tag{33}$$

rather than reaction (32). The yields based on this assumption are given in parentheses in the Table.

The quantum yields derived for C_2H_5, CF_2Cl and CF_2 can be compared with those derived in Table 2 for the analogous radicals (C_2H_5, $CFCl_2$, and $CFCl$) in the photolysis of CCl_3F. In every case, the corresponding yields are comparable except for those of CF_2 and $CFCl$ in the 213.9 nm photolyses: $\Phi(CF_2)$ in CF_2Cl_2 is much greater than $\Phi(CFCl)$ in $CFCl_3$ at the same wavelength.

It is not possible to obtain an unambiguous answer as to whether CF_2 is produced in CF_2Cl_2 through process (2) or process (3) (in addition to disproportionation 28). If processes (2) and (28) were entirely responsible for CF_2 formation, then, since the quantum yield of Cl atoms formed through a primary dissociation is equal to the difference between the C_2H_5 and the methane quantum yield, we would see that:

$$\Phi(C_2H_5) - \Phi(CH_4) = \Phi(CF_2Cl)$$

However, since the yield which we can attribute to Cl atoms formed in a primary process always exceeds $\Phi(CF_2Cl)$, we must conclude that process (3) is indeed important under these conditions, (a contribution of process (2) to the production of CF_2, $\Phi \leqslant 0.04$, is not excluded) and we write:

$$\Phi(C_2H_5) - \Phi(CH_4) = \Phi(CF_2Cl) + 2\Phi(CF_2)$$

Especially at 184.9 and 163.3 nm, the product yields follow this relationship very well, indicating that processes (1) and (3) account for the formation of most of the intermediates.

There is no evidence for the formation of $CFCl_2$ or $CFCl$ in CF_2Cl_2 at 184.9 or 163.3 nm, even though the formation of these radicals is energetically possible.

Photolysis of CF_2Cl_2 and $CFCl_3$ in the presence of methane

Methane is the only hydrocarbon molecule which is transparent to 147 nm xenon resonance radiation. Therefore, unlike ethane, it can be used as a Cl atom interceptor at this wavelength (as well as at longer wavelengths).

The important products formed in the 147 nm photolysis of $CFCl_3$ – CH_4 and CF_2Cl_2–CH_4 mixtures are shown in Table 4. At this wavelength, the following reaction scheme accounts for over 90% of the observed products in the photolysis of CF_2Cl_2–CH_4 mixtures:

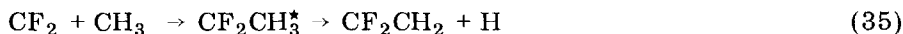$$Cl + CH_4 \rightarrow HCl + CH_3 \tag{34}$$

(In some of these experiments the temperature was raised to 125 °C to insure that all Cl atoms react with CH_4.)

TABLE 4

Photolysis of CF_2Cl_2 and $CFCl_3$ in the presence of methane

Pressure (Torr)		Temp. (K)	Quantum yields			
CF_2Cl_2	CH_4		C_2F_4	CF_2CH_2	C_2H_6	CH_3/CF_2
11.4	64	297	0.15	0.35	0.45	1.92
35.5	211	297	0.16	0.37	0.49	1.96
11.4	67	334	0.18	0.42	0.58	2.02
11.6	68	364	0.18	0.44	0.60	2.05
35.1	205	398	0.19	0.45	0.65	2.11
$CFCl_3$*	CH_4		$CFClCFCl$	$CFClCH_2$	C_2H_6	$CH_3/CFCl$
11.4	100	398	0.27	0.33	0.65	1.87

*CFCH was observed as a product.
 Xenon lamp (147 nm).

$$CF_2 + CF_2 \rightarrow C_2F_4 \tag{32}$$

$$CF_2 + CH_3 \rightarrow CF_2CH_3^* \rightarrow CF_2CH_2 + H \tag{35}$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{36}$$

In the case of $CFCl_3$, reactions (32) and (35) in the above reaction scheme have to be replaced by their counterparts:

$$CFCl + CFCl \rightarrow CFClCFCl \tag{19}$$

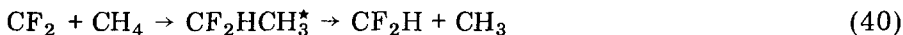$$CFCl + CH_3 \rightarrow CFClCH_3^* \rightarrow CFClCH_2 + H \tag{37}$$

Comparing this reaction scheme with those given above for photolysis of $CFCl_3$ and CF_2Cl_2 at longer wavelengths (*i.e.*, reactions (8) - (21) for $CFCl_3$ and reactions (8) - (10), (24) - (32), and (20) and (21) for CF_2Cl_2) it is immediately evident that reactions involving CF_2Cl and $CFCl_2$ are missing from the reaction scheme for the 147 nm experiments. At this energy the quantum yields of products which could be traced to reactions of these radicals are negligibly small (< 0.02).

It should be mentioned that there is no evidence for processes involving C–F bond cleavage at 147 nm. For instance, process (7) would lead to the formation of $CFCl_2$, or subsequently to $CFCl$ radicals, but the quantum yield of $CFClCH_2$, which would be formed in the reactions of these radicals with methyl radicals:

$$CFCl + CH_3 \rightarrow CFClCH_3^* \rightarrow CFClCH_2 + H \tag{38}$$

$$CFCl_2 + CH_3 \rightarrow CFCl_2CH_3^* \rightarrow CFClCH_2 + HCl \tag{39}$$

is lower than the detection limit (0.005) in all experiments on the 147 nm photolysis of CF_2Cl_2. We verified that $CFCl$ and $CFCl_2$ radicals do undergo reactions (38) and (39) by photolyzing $CFCl_3$ at 213.9 and 184.9 nm (where reactions (4) and (6) lead to the formation of $CFCl_2$ and $CFCl$) in the presence of CH_4.

There is no evidence that the CF_2 species undergoes any important reactions other than (32) and (35), *i.e.*, even though recombination of CF_2 radicals is relatively slow [25], we can rule out the occurrence of insertion or abstraction reactions involving CF_2Cl_2 or CH_4. It can be concluded that such reactions do not occur between CF_2 and CF_2Cl_2 because of the absence of CF_2ClCF_2Cl and CF_2ClH as products. Furthermore, in view of the low yield of CF_2HCH_3 ($\Phi \sim 0.01$), reactions such as:

$$CF_2 + CH_4 \rightarrow CF_2HCH_3^* \rightarrow CF_2H + CH_3 \tag{40}$$

or:

$$CF_2 + CH_4 \rightarrow CF_2H + CH_3 \tag{41}$$

are of negligible importance. A small fraction of the CF_2 radicals do combine with H atoms, as evidenced by the presence of a small amount of CF_2HCH_3:

$$CF_2 + H \quad \rightarrow CF_2H \tag{42}$$

$$CF_2H + CH_3 \rightarrow CF_2HCH_3 \tag{43}$$

Under the present experimental conditions (see Table 4), there is no evidence for the collisional stabilization of the excited $CH_3CF_2^*$ and CH_3CFCl^* intermediates formed in reactions (35) and (37), respectively. This is substantiated by the absence of C_3 products such as $CH_3CF_2CH_3$ and $CH_3CFClCH_3$ in low conversion experiments. At conversions exceeding 0.1%, C_3 products start to appear which are to be accounted for by the addition of Cl and H atoms to the two unsaturated products, C_2F_4 and CF_2CH_2, followed by combination of the resulting C_2 radicals with CH_3.

If one ignores the minor reactions (42) - (43) and makes the simplifying assumption that reactions (34), (32), (35) and (36) account for all of the C_2 products in CF_2Cl_2, it follows that:

$$\frac{CH_3}{CF_2} = \frac{2(C_2H_6) + (CF_2CH_2)}{2(C_2F_4) + (CF_2CH_2)}$$

The results shown in Table 4 show that the value obtained for this ratio is 2.0 ± 0.1, independent of the pressure of methane (64 to 205 Torr) or temperature (25 to 125 °C). Since each CH_3 results from the reaction of one Cl atom, the occurrence of process (3) to the exclusion of processes (1) and (2) would result in a $CH_3 : CF_2$ ratio of 2. If the quantum efficiency of process (3) is indeed equal to one, then $\Phi(CF_2)$ should also be unity.

$$\Phi(CF_2) = 2\Phi(C_2F_4) + \Phi(CF_2CH_2) = 0.91 \pm 0.06$$

This quantum yield is slightly less than unity, probably because we have ignored the combination of H atoms and CF_2 (reaction 42), as mentioned above. Similarly, the fact that (CH_3) as given by $[(CF_2CH_2) + 2(C_2H_6)]$ is lower than two can be accounted for by the occurrence of a reaction such as:

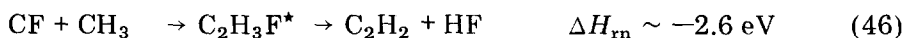$$CH_3 + H + M \rightarrow CH_4 + M \tag{44}$$

The results given in Table 4 show that the yields of CF_2CH_2 and C_2H_6 increase slightly with increasing temperature. This can most likely be ascribed

to the fact that the activation energy for abstraction of a H atom from methane by Cl is not entirely negligible.

It is of incidental interest that from the data given in Table 4 one can derive an estimate for k_{35}. If one accepts values of 7.2×10^{-14} and 5×10^{-11} cm^3/molecule s for k_{32} [25] and k_{36} [26], respectively, a value of 2.6 ± 0.1 $\times 10^{-12}$ cm^3/molecules is obtained for k_{35} independent of pressure or temperature.

It is of interest in the photolysis of $CFCl_3$–CH_4 mixtures at 147 nm, CHCH and $CFHCH_2$ are formed with quantum yields of ~ 0.02. The formation of these products, which are absent in the photolysis of CF_2Cl_2 or the 213.9 nm photolysis of $CFCl_3$, can tentatively be accounted for by the following mechanism:

$$CFCl_3 + h\nu \rightarrow CF + Cl_2 + Cl \tag{45}$$

$$CF + CH_3 \rightarrow C_2H_3F^* \rightarrow C_2H_2 + HF \qquad \Delta H_{rn} \sim -2.6 \text{ eV} \tag{46}$$

The photodissociation process (45) which requires 6.65 eV probably occurs through the loss of a Cl_2 molecule from an internally excited $CFCl_2$ radical formed in process (4).

Conclusions

The present results show that the photodissociation of both CF_2Cl_2 and $CFCl_3$ occurs with a quantum yield which is, within experimental error, equal to unity over the entire wavelength region covered in this study (213.9 · 147 nm). This region encompasses the band of wavelengths between 215 and 180 nm which brings about most of the photolysis which occurs in the stratosphere [1d]. The quantum yields of photodissociation products determined in this study are summarized in Table 5. At the long wavelength end of this "window" region, the probability of releasing one chlorine atom per quantum absorbed by either CF_2Cl_2 or $CFCl_3$ is 0.95 ± 0.05 as shown by the yields of CF_2Cl and CCl_2F, respectively. At the shorter wavelengths, the probability that two chlorine atoms will be detached increases to about 0.3 ± 0.1. The CF_2 and $CFCl$ radicals produced at these shorter wavelengths are unreactive towards alkanes and halocarbons; these radicals would therefore be expected to react with oxygen in the upper atmosphere. Reaction with oxygen is substantiated by the recent observation that in the 184.9 nm photolysis of CF_2Cl_2–O_2 mixtures, where $\Phi(CF_2) = 0.36 \pm 0.04$, the quantum yields of disappearance of CF_2Cl_2 and production of CO_2 (or CF_2O) were both found to be equal to 1.1 ± 0.1. The latter observation is not inconsistent with the occurrence of the reaction proposed earlier [25]:

$$CF_2 + O_2 \rightarrow CF_2O + O(^3P) \tag{47}$$

Acknowledgements

TABLE 5

Quantum yields of photofragments

	CF_2Cl_2				$CFCl_3$			
	213.9 nm	184.9 nm	163.3 nm	147.0 nm	213.9 nm	184.9 nm	163.3 nm	147.0 nm
Cl	1.09	1.41	1.51	>1.75	1.11	1.35	1.60	>1.6
CF_2Cl	0.91 ± 0.01	0.65 ± 0.04	0.56 ± 0.04	<0.1	—	—	—	—
$CFCl_2$	<0.01	<0.01	<0.01	<0.01	0.98 ± 0.01	0.70 ± 0.04	0.50 ± 0.06	<0.1
CFCl	<0.005	<0.005	<0.005	<0.005	0.03 ± 0.02	0.30 ± 0.03	0.45 ± 0.07	>0.87
CF_2	0.07 ± 0.02	0.34 ± 0.04	0.40 ± 0.047	>0.8	—	—	—	—
CF	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	~0.01	~0.03

Pressure: 15 Torr; temperature: 298 ± 2 K. The experimental accuracy is estimated to be ± 10%. The values for $\Phi(CF_2)$ and $\Phi(CFCl)$ have been corrected for contributions of disproportionation reactions. The limits cited reflect estimated variations which could result if different assumptions about reaction mechanisms were made.

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