

THE GAS PHASE PHOTOLYSIS OF CHFCl_2

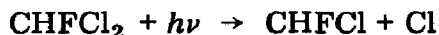
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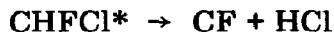
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Summary

The photolysis of CHFCl_2 at 300 K has been investigated at 213.9, 163.3 and 147 nm. Methane, Br_2 , HBr and HCl were added as free radical interceptors in order to unravel the primary photodecomposition processes. Analysis of the data shows that at 213.9 and 163.3 nm the photodissociative process



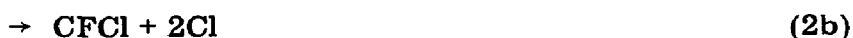
occurs with a quantum yield of 0.9 - 1.0, giving stable CHFCl radicals. At shorter wavelengths the quantum yield of CHFCl shows a drastic decrease with concurrent appearances of species such as CFCl , CHF and CF . The laboratory experiments indicate that CF is mainly formed via the dissociative process



The CF radicals react with CH_3 to yield C_2H_2 ($\text{CF} + \text{CH}_3 \rightarrow \text{C}_2\text{H}_2 + \text{HF}$) while the CHF species insert readily into HCl to yield CH_2FCl . In the presence of Br_2 , CF and CHF undergo reactions which result in the formation of CFBr_3 and CHFBr_2 respectively.

Introduction

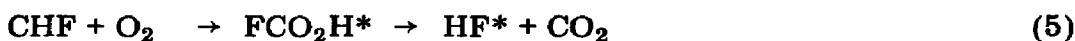
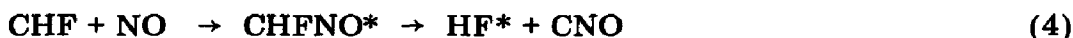
In a preceding study [1] on the photolysis of CF_2Cl_2 and CFCl_3 , evidence was presented for the occurrence of two major photodecomposition steps:



These processes may be considered as a sequence of two steps in which the internally excited halomethyl radicals (CF_2Cl or CFCl_2) formed in the primary step (1a and 2a) may undergo further decomposition. In the case of CFCl_3 a third overall photodecomposition step was suggested to occur at 163 and 147 nm [1]:



This study deals with the photodecomposition of a halocarbon molecule containing one H atom, namely CHFCl_2 . To our knowledge, the only previous investigations of the photodecomposition of CHFCl_2 are the flash photolysis studies [2, 3] ($\lambda \geq 165$ nm) of $\text{CHFCl}_2\text{-O}_2$ and $\text{CHFCl}_2\text{-NO}_2$ mixtures carried out with the purpose of inducing HF infrared stimulated laser emissions. The conclusion was reached that the principal laser pumping reaction involved CHF:



where it is suggested that CHF is formed in the photodecomposition process



Experimental

The experimental procedure is identical to that described in the previous publications dealing with halocarbons [1, 4].

The CHFCl_2 had to be rigorously purified, because the commercial sample contained various chemical impurities the retention times of which on a gas chromatograph coincide with some of the photochemical products.

The absorption cross section of CHFCl_2 was measured to be 0.054 ± 0.005 and $166 \pm 3 \text{ atm}^{-1} \text{ cm}^{-1}$ at 213.9 and 147 nm, respectively.

Results and discussion

Quantum yield of CHFCl

Table 1 gives the quantum yields of products which were identified in the photolysis of $\text{CH}_4\text{-CHFCl}_2$ mixtures with 213.9 nm (5.8 eV), 163.3 nm (7.6 eV) and 147.0 nm (8.4 eV) photons, respectively. Several additional products whose identities are unknown were observed, but the quantum yields of these products were very small (≤ 0.005) under all conditions; the combined quantum yield of all unidentified products was not more than 0.01 - 0.02. In the experiments at high conversions ($> 0.1\%$) there were small quantities of C_3H_8 and $\text{CH}_3\text{CH}_2\text{CHFCl}$ which originated from reactions of radicals with the product C_2H_6 . The combined quantum yields of these C_3 products never exceeded 0.01 for all the experiments listed in Tables 1 - 3.

TABLE 1

Quantum yields of products formed in the photolysis of $\text{CH}_4\text{-CHFCl}_2$ mixtures

Total pressure (Torr)	CHFCl_2 (%)	C_2H_2	$\text{C}_2\text{H}_3\text{F}$	C_2H_6	CH_2FCl	CH_2CFCl	CH_3CFClH	CH_3CFCl_2	CFClHCFClH
213.9 nm									
211	14	$< 10^{-3}$	0.34	0.19	0.0049	0.071	0.14	0.012	0.26
352	9	$< 10^{-3}$	0.27	0.21	0.0098	0.064	0.12	0.023	0.28
756	4	$< 10^{-3}$	0.19	0.30	0.0086	0.045	0.18	0.030	0.25
1456	2	$< 10^{-3}$	0.14	0.30	0.0092	0.034	0.27	0.059	0.23
163.3 nm									
120	4.1	0.019	0.32	0.22	0.048	0.034	0.057	-	0.25
140	3.8	0.016	0.40	0.30	0.017	0.025	0.085	-	0.29
210	4.9	0.009	0.31	0.24	0.017	0.030 (0.016)	0.084	0.003	0.22
410	2.5	0.007	0.25	0.26	0.017	0.025 (0.017)	0.13	0.006	0.19
620	1.6	0.007	0.23	0.25	0.015	0.018 (0.011)	0.17	0.006	0.21
925	1.1	0.006	0.19	0.26	0.013	0.012 (0.008)	0.22	0.007	0.21
147 nm									
140	3.7	0.084	0.048	0.26	0.15	0.043	0.007	-	-
315	3.2	0.10	0.063	0.30	0.20	0.048 (0.014)	0.023	0.004	0.006
320	9.6	0.11	0.065	0.31	0.24	0.054 (0.023)	0.025	0.007	-
410	2.5	0.11	0.066	0.34	0.22	0.048 (0.016)	0.034	0.006	0.007
610	1.7	0.081	0.054	0.30	0.20	0.040 (0.015)	0.041	0.008	0.009
900	1.1	0.072	0.047	0.30	0.21	0.035 (0.011)	0.054	0.009	-
1000	3.0	0.073	0.039	0.30	0.17	0.036 (0.013)	0.036	0.012	0.003

Values in parentheses are quantum yields of CH_2CFCl attributed to reaction (19).

TABLE 2

Quantum yields of radicals* derived from the photolysis of CHFCl₂-CH₄ mixtures (Table 1)

λ (nm)	Cl(CH ₃)	CHFCl	CFCl ₂	CHF	CFCl	CF
213.9	1.0 ± 0.1	1.0 ± 0.1	0.08	< 10 ⁻³	< 10 ⁻³	< 10 ⁻³
163.3	1 ± 0.1	0.9 ± 0.1	0.03 ± 0.01	0.015 ± 0.005	0.014 ± 0.004	0.01 ± 0.05
147	0.75 ± 0.05	0.09 ± 0.02	0.03 ± 0.01	0.20 ± 0.04	0.034 ± 0.005	0.1 ± 0.02

*Based on reactions (7) - (22) and (27) - (34) (see Discussion). The error limits are based on averaging of the experiments listed in Table 1.

TABLE 3

Photolysis of CHFCl₂ in the presence of bromine

λ (nm)	Pressure (Torr)		Quantum yields			
	CHFCl ₂	Br ₂	CHFClBr	CFCl ₂ Br	CHFBr ₂	CFBr ₃
213.9	26	1.0	1.0	≈ 0.01	< 0.02	< 0.01
163.3	10	0.9	0.84	≈ 0.02	< 0.02	< 0.02
	20	0.5	0.87	n.d.	< 0.02	< 0.02
	40	0.5	0.91	n.d.	< 0.02	< 0.02
	40	2.1	0.87	n.d.	< 0.02	< 0.02
147	11.2	0.9	0.10	n.d.	0.11	0.17
	22.5	0.9	0.12	≈ 0.025	0.12	0.21
	45	2.2	0.12	n.d.	0.09	0.17

n.d., not determined.

In view of the findings of the earlier study of the photolysis of chloro-fluoromethanes, one would expect that the most likely primary process in the photolysis of CHFCl₂ would be the cleavage of a C-Cl bond:



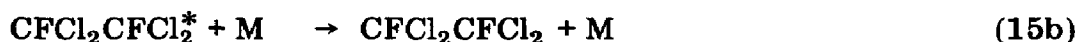
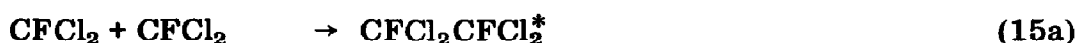
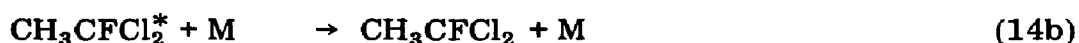
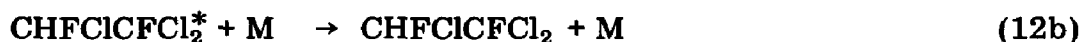
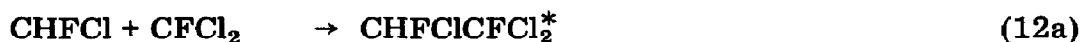
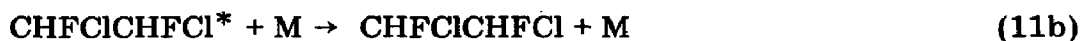
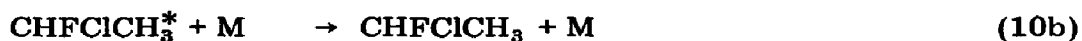
If this process occurs in the presence of methane (which will not absorb light at these wavelengths), the Cl atom will abstract an H atom from methane [1]:



In such a mixture, abstraction could also occur from CHFCl₂:



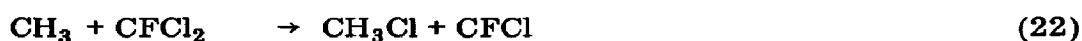
Reaction (9a) should not be important if methane is present in excess. Most products obtained at 213.9 and 163.3 nm result from the combination of the various radicals which would be formed in reactions (7) - (9):



In every case the combination products which have not been collisionally stabilized will dissociate in the following manner:



At the relatively high pressure ($\text{CH}_4 > 100$ Torr) and low temperature (300 K) used in this study, the unimolecular reactions (17) and (18) are of minor importance. This is confirmed by the fact that the quantum yields of CFCICHF and CFCICFCl are less than 0.01. In addition, disproportionation reactions among the various radicals can be written. For instance, one might expect



However, the disproportionation reactions (21) and (22) are unimportant, since CH_3Cl is not observed as a product. Furthermore, in the experiments carried out at 213.9 nm, where there is insufficient energy to form CFCl or CHF through dissociation of the CHFCI radical formed in process (7), the yields of products which can be attributed to CHF are negligibly small and the quantum yield of CH_2FCl which may also arise from reaction of CHF (as will be discussed later) is only about 0.009.

If primary process (7) were the only photolytic decomposition process occurring in a mixture of CHFCI_2 in an excess of methane there would be

one Cl atom for every CHFCl radical. According to the mechanism represented by reactions (8) - (19), the following material balance should then be observed:

$$\text{CHFCl} \equiv \text{CH}_3 + \text{CFCl}_2 \approx 1 \quad (\text{I})$$

where

$$\begin{aligned} \text{CHFCl} &\equiv (\text{CHFClCH}_3 + \text{CHFCH}_2) + 2(\text{CHFClCHFCl} + \text{CFCiCHF}) + \\ &\quad + (\text{CHFClCFCl}_2 + \text{CFCiCFCl}) \\ \text{CH}_3 &\equiv (\text{CHFClCH}_3 + \text{CHFCH}_2) + 2\text{C}_2\text{H}_6 + (\text{CH}_3\text{CFCl}_2 + \text{CH}_2\text{CFCl}) \\ \text{CFCl}_2 &\equiv (\text{CHFClCFCl}_2 + \text{CFCiCFCl}) + (\text{CH}_3\text{CFCl}_2 + \text{CH}_2\text{CFCl}) + \\ &\quad + 2(\text{CFCl}_2\text{CFCl}_2) \end{aligned} \quad (\text{II})$$

All of these products except CFCiCHF, CFCiCFCl, CHFClCFCl₂ and CFCl₂CFCl₂, the quantum yields of which are less than 0.005, have been measured in the experiments on the photolysis of CH₄-CHFCl₂ mixtures. Estimates of the quantum yields of CHFCl, CFCl₂ and CH₃ derived from the results in Table 1 are given in Table 2. It is evident that the equality (I) is observed at least approximately in the 213.9 and 163.3 nm experiments, but that in the 147.0 nm experiments the yield estimated in this way for CHFCl is much lower than the sum of the yields of CH₃ and CFCl₂. We tentatively conclude that most of the products formed in the 213.9 and 163.3 nm photolyses can be accounted for by the reaction mechanism (7) - (19).

Further verification of certain details of this mechanism can be obtained by examining the ratios of products as a function of pressure. For instance, since the mechanism postulates that CHFClCH₃* dissociates to give CHFCH₂ (process (16)) or is collisionally stabilized (reaction (10b)), we write

$$\frac{[\text{CH}_2\text{CHF}]}{[\text{CH}_3\text{CHFCl}]} = \frac{k_{16}}{k_{10b} [\text{M}]} \quad (\text{III})$$

Thus, a plot of the ratios of these two products as a function of the reciprocal of pressure should give a line with slope k_{16}/k_{10b} and zero intercept if all the CH₂CHF actually originates in process (16). Figure 1 shows such a plot of this ratio taken from the data given in Table 1 as well as from additional experiments. Figure 1 indicates that CH₂CHF does originate from decomposition of CH₃CHFCl, not only at the two lower energies but at 147.0 nm as well. From the slope of the plot we can estimate that the minimum dissociative lifetime of the CH₃CHFCl* formed in these experiments is about 0.5×10^{-10} s.

Values for the quantum yield of CHFCl were also obtained in a more direct fashion by measuring the quantum yield of CHFClBr in the photolysis of CHFCl₂-Br₂ mixtures (Table 3). If one CHFClBr molecule is produced for each CHFCl radical



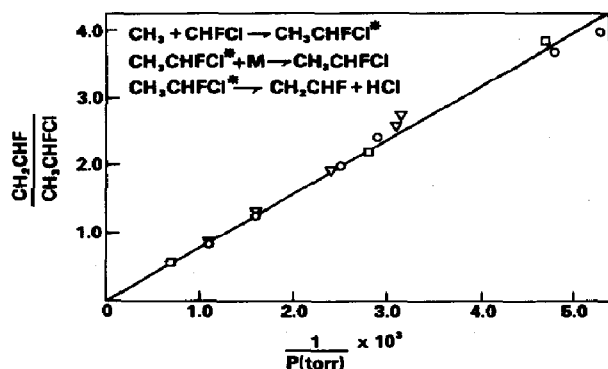


Fig. 1. Photolysis of CHFCl_2 (3 ± 1 Torr) in the presence of CH_4 (100 - 1000 Torr). Plot of $[\text{CH}_2\text{CHF}]/[\text{CH}_3\text{CHFC}]$ vs. $1/P$ (Torr): ∇ , 213.9 nm; \square , 163.3 nm; \circ , 147.0 nm.

TABLE 4

Photolysis of CHFCl_2 in the presence of HBr and HCl

λ (nm)	Pressure (Torr)		Quantum yield of CH_2FCl	
	CHFCl_2	Additives		
163.3	30.9	HCl 2.3	0.23	
		HCl 2.3	0.004	
	30.9	NO 1.5		
		HBr 1.0	0.9	
147	32.4	HCl 2.2	0.22	
		HCl 2.2	0.11	
	32.4	NO 1.5		
		HBr 1.0	0.09	

then there is good agreement between the quantum yields of CHFCl derived from the results of Table 1 and those of Table 3 at all wavelengths.

Similarly, in the photolysis of CHFCl_2 in the presence of HBr (Table 4) the quantum yield of CH_2FCl formed in the abstraction reaction



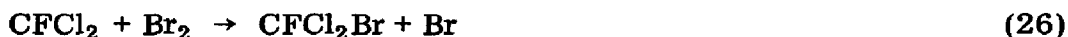
is consistent with the yields of CHFCl given in Table 2.

Quantum yield of CFCl_2

The presence of CH_3CFCl_2 among the products listed in Table 1 clearly shows that CFCl_2 radicals are produced in the photolysis of CHFCl_2 - CH_4 mixtures. Quantum yields of this product are given in Table 2. However, because CFCl_2 may be formed via reaction (9) as well as by the primary process



a series of experiments was carried out in which Br_2 was added as a free radical scavenger. The data obtained in these experiments (Table 3) do show the presence of small amounts of CFCl_2Br . Accepting that the latter product is exclusively formed via the reaction



one concludes that primary process (25) occurs with quantum yields ranging from 0.01 to 0.025 over the wavelength range 213.9 to 147 nm. Because a two-step mechanism for the formation of CFCl_2Br cannot be entirely ruled out, these estimates should be considered as upper limits. Furthermore, it is apparent that a fraction of the CFCl_2 radical yields derived from the $\text{CHFCl}_2\text{-CH}_4$ experiments originates from free radical reactions such as (9).

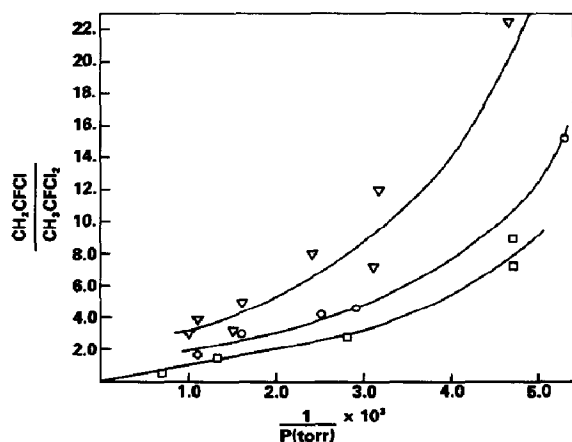


Fig. 2. Photolysis of CHFCl_2 (3 ± 1 Torr) in the presence of CH_4 (100 - 1000 Torr). Plot of $[\text{CH}_2\text{CFCl}]/[\text{CH}_3\text{CFCl}_2]$ vs. $1/P$ (Torr): \square , 213.9 nm; \circ , 163.3 nm; ∇ , 147.0 nm.

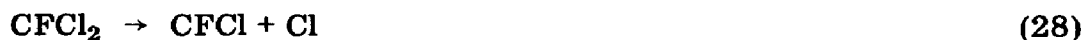
Quantum yield of CFCl

Figure 2 shows plots for the dissociation and collisional stabilization of $\text{CH}_3\text{CFCl}_2^*$ (reactions (19) and (14b)). These data show much more scatter than those presented in Fig. 1 because of the much smaller yields involved. In spite of this, it is obvious that the ratios $[\text{CH}_2\text{CFCl}]/[\text{CH}_3\text{CFCl}_2]$ observed at a given pressure are lowest for the 213.9 nm experiments and that the ratios for the 163.3 nm experiments are generally lower than those for the 147.0 nm experiments. This implies either that there are sources of CH_2CFCl in the 163.3 and 147.0 nm experiments in addition to dissociation process (19) or that k_{19} is higher in the higher energy experiments. The latter explanation is highly unlikely, because the CFCl_2 and CH_3 radicals which react to form the $\text{CH}_3\text{CFCl}_2^*$ undergo many collisions before combining. If there are additional sources of formation of CH_2CFCl at the higher energies, the plots should have positive intercepts (and concave upward curvature if the additional source is pressure dependent). At the lowest energy (213.9 nm) the plot

has an intercept close to zero. If we assume that at this energy process (19) is the only source of CH_2CFCl , we can then make estimates of the yields of the "excess" CH_2CFCl at the two higher energies from the $[\text{CH}_2\text{CFCl}]$ to $[\text{CH}_3\text{CFCl}_2]$ ratios observed at the low energy. At both energies the yield of "excess" CH_2CFCl diminishes with increasing pressure (indicating that it originates in a reaction of a decomposition product) and levels off to a constant value (about 0.034 at 147 nm, about 0.014 at 163.3 nm) at low pressures (see Table 1). A plausible source for this product is



where the CFCl originates in a secondary decomposition of a radical formed in a primary decomposition, most likely



and/or in the primary process



Quantum yield of CHF

We have already shown (Fig. 1) that a Stern–Volmer plot of the ratio $[\text{CH}_2\text{CHF}]/[\text{CH}_3\text{CHFCl}]$ has the same slope at all three energies and furthermore has an intercept of zero, indicating that the reaction



apparently does not occur since all CHFCH_2 originates in process (16). (In the 163.3 nm experiments the occurrence of reaction (30) might not be discernible in the Stern–Volmer plot if the yield of CHF is as small as that of CFCl ; however, in the 147.0 nm experiments the occurrence of process (30) should be noticeable.) Smail and Rowland [5] have reported that CHF reacts with hydrogen halides through a direct insertion reaction, *e.g.*

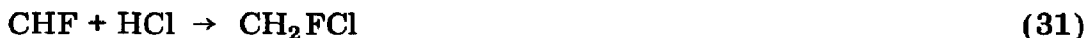


Table 4 shows the results of experiments in which HCl was added to CHFCl_2 at 163.3 nm and 147.0 nm. It is seen that CH_2FCl is indeed an important product in these experiments, and in fact is also a product in the experiments on CHFCl_2 – CH_4 mixtures in the absence of added HCl (Table 1). If this product is formed in reaction (31), the reactant HCl must be that formed as a product (reaction (8), reactions (16) - (19) etc.). The fact that a product compound (HCl) would be able quantitatively to intercept CHF implies that this carbene is very unreactive toward all the other molecules and radicals in the system*. However, a similar conclusion was arrived at in a study of the photolysis of CCl_4 – C_2H_6 mixtures [4] in which CHCl_3 was observed

*All experiments given in Table 1 were carried out at conversions ranging from 0.02 to 0.1%. The quantum yield of CH_2FCl was found to be independent of conversion over this range.

as a major product at wavelengths where CCl_2 is a major photofragment. Experiments carried out at 147 nm in which NO was added to the CHFCl_2 -HCl mixture indicate that reaction (31) is quite efficient (Table 4) since this free radical scavenger reduces the yield of CH_2FCl by only 50%. In contrast, addition of a similar amount of NO in an experiment at 163.3 nm reduces the yield of CH_2FCl essentially to zero. In the latter experiment CH_2FCl observed in the absence of NO can be ascribed to the abstraction reaction



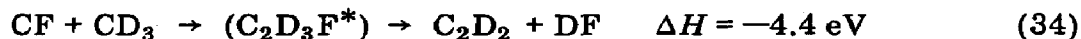
The question of whether the CFCl radical is also scavenged by HCl must be answered; a reaction analogous to (31) would lead to the formation of the starting material, CHFCl_2 . Small and Rowland [5] have shown that HCl scavenges CF_2 much less efficiently than CHF; perhaps the scavenging of CFCl by HCl



is inefficient compared with reaction (20) with CH_3 . This is actually indicated by a recent study on CCl_4 [4]. It is clear, however, that more information is needed about the kinetics of halocarbene radicals. The formation of CHF radicals at 147 nm is also evidenced by the observation of CHFBr_2 in the photolysis of CHFCl_2 -Br mixtures. However, the quantum yield of CHFBr_2 is lower than that of CHF given in Table 2. It will be shown in a subsequent study that the quantum yield of CX_2Br_2 (where X = F, Cl or H) is consistently more than a factor of 2 lower than the quantum yield which can be ascribed to CX_2 . Therefore, the values for the quantum yield of CHFBr_2 given in Table 3 should only be considered as lower limits for the quantum yield of CHF.

Quantum yield of CF

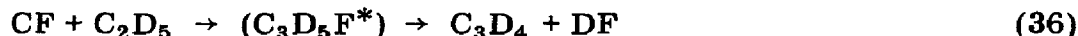
At 147 nm C_2H_2 appears as a major product. Some information about the mode of formation of this product was obtained in an experiment in which a CHFCl_2 - CD_4 mixture was photolyzed at 147.0 nm; the acetylene product was all fully deuterated. One plausible reaction which would account for the acetylene is



Little is known about the chemistry of CF, but the formation of acetylene in reaction (34) is more exothermic than the alternative possibility leading to the formation of C_2HF by 1.8 eV. A reaction of CF with CH_4 such as



is unfavorable on energetic grounds. In an experiment in which methane was replaced by C_2D_6 the acetylene product was not formed. Instead, equivalent yields of C_3D_4 (propyne and allene) were observed:



The formation of CF is also evidenced by the results of the experiments on $\text{CHFCl}_2\text{-Br}_2$ mixtures (Table 3) which show that CFBr_3 is formed with a quantum yield of 0.19 ± 0.02 independent of pressure. It is obvious that this product must be formed via a mechanism involving at least two consecutive reactions such as



Because other competing reactions may occur, the quantum yield of CFBr_3 should be considered as a lower limit for the quantum yield of CF. The same remark holds for the quantum yield of C_2H_2 in the experiments on $\text{CHFCl}_2\text{-CH}_4$ mixtures (*i.e.* the quantum yield of CF is greater than or equal to that of acetylene).

The formation of CF at 147.0 nm may come about through the process



which requires 5.8 eV, or through the process



which requires 7.7 eV. However, since a small amount of C_2H_2 is observed at 163.3 nm, where there is not enough energy to bring about the occurrence of process (40), process (39) is the most likely mode of formation of CF. The process



requires about 10 eV and cannot occur in these experiments.

The low quantum yield of CH_3 (Table 2) at 147 nm, which can be approximated to that of the Cl atoms, points to the importance of HCl elimination processes such as (29) and (39). It is clear, however, that our present knowledge of the kinetics of species such as CF, CHF and CFCl makes a quantitative assessment of the material balance at 147 nm or shorter wavelengths difficult. Work is at present in progress to gain a better insight into the reactivity of these species.

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