GAS PHASE PHOTOLYSIS OF CF_2Cl_2, $CFCl_3$ AND CCl_4 IN THE PRESENCE OF BROMINE AT 213.9, 163.3, 147.0 AND 123.6 nm

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Summary

CF_2Cl_2–Br_2, $CFCl_3$–Br_2 and CCl_4–Br_2 mixtures were photolyzed at 213.9, 163.3 and 147.0 nm. The first two mixtures were also photolyzed at 123.6 nm. In the CF_2Cl_2–Br_2 system the quantum yields for the formation of CF_2Cl radicals (as determined by the formation of CF_2ClBr) were 1.0 ± 0.1, 0.67 ± 0.07, 0.05 ± 0.02 and not more than 0.02 respectively. For the $CFCl_3$–Br_2 system the quantum yields of formation of $CFCl_2$ radicals (as $CFCl_2Br$) were 1.0 ± 0.1, 0.53 ± 0.05, 0.02 ± 0.01 and 0.03 ± 0.02 respectively. In the CCl_4–Br_2 experiments the quantum yields of formation of CCl_3 radicals (as CCl_3Br) were 1.0 ± 0.1, 0.41 ± 0.04 and 0.02 ± 0.01 at the wavelengths 213.9, 163.3 and 147.0 nm respectively. These results are in excellent agreement with some earlier determinations which utilized a different technique. In all such cases the quantum yields, determined by the bromine addition technique for such fragments as CF_2, $CFCl$, CCl_2, CF and CCl, can only be used to set lower limits for the quantum yields of formation of these radicals. There are complications in this method for these fragments which cannot at present be taken entirely into account.

Introduction

In two previous studies [1, 2] on the photolysis of CF_2Cl_2, $CFCl_3$ and CCl_4 evidence was presented to show that in each case the main primary process occurring at 213.9 nm (5.8 eV) is the loss of one chlorine atom and the concomitant formation of a trihalomethyl radical. At shorter wavelengths (163.3 nm or 7.6 eV) the loss of two chlorine atoms and the formation of a halocarbene radical becomes more important. Actually, this process may be considered as a sequence of two steps in which the internally excited trihalomethyl radical or the chlorine molecule formed in the primary step undergoes further decomposition. At even shorter wavelengths (not more than 147.0 nm or not less than 8.4 eV) there was evidence of further fragmentation to form CF or CCl in the case of $CFCl_3$ or

CCl_4 respectively. In both these studies methane and/or ethane and sometimes HCl and HBr were used as radical interceptors to help elucidate the primary processes occurring in the system at the different wavelengths used in the photolysis.

More recently, Hautecloque and Bernas [3] have investigated the photolysis of CF_2Cl_2 and $CFCl_3$ at wavelengths greater than 180.0 nm (6.9 eV), also in the presence of methane and ethane as well as in the presence of hydrogen, diethyl ether and bromine. They essentially substantiated our earlier work except that they preferred the formation of molecular chlorine rather than of two chlorine atoms. They base their argument on the formation of small amounts of $CFClBr_2$ which is produced when bromine is added to $CFCl_3$ at wavelengths greater than or equal to 230.0 nm (5.4 eV). There is not enough energy at this wavelength to produce two chlorine atoms. This process would require about 5.6 eV.

Earlier Davis et al. [4] introduced bromine into the system in the photolysis of CCl_4 at various wavelengths. They found CCl_3Br with a quantum yield of approximately unity at 253.7 nm, while at wavelengths less than or equal to 184.9 nm CCl_2Br_2 was produced and at wavelengths less than or equal to 147.0 nm $CClBr_3$ was produced in addition to the monobromide. Since this bromine technique seemed so straightforward, it was decided to extend and further to quantify the results of Davis et al. by adding bromine as a radical scavenger in the photolysis of CF_2Cl_2, $CFCl_3$ and CCl_4 at varius wavelengths from 213.9 to 123.6 nm. In this way it was hoped that a measure of the quantum yield of formation of the various bromohalomethanes produced would also be a measure of the different primary processes occurring in each system. As a check on this method, these results could then be compared with the quantum yields of the various photofragments determined in the aforementioned articles [1, 2].

2. Experimental procedure

The experimental procedure is essentially identical to that described in the previous publications dealing with halomethanes [1, 2, 5]. Reagent grade ACS bromine was used after the usual degassing procedure. Identification and determination of relative sensitivities of CF_2ClBr, CF_2Br_2, CCl_3Br, $CFBr_3$ and CF_2BrCF_2Br were carried out by injecting known samples into one of two different gas chromatographs which were equipped with either a squalane or a silicone rubber (SE-30) column and flame ionization detectors. From our experience with these and many other halocarbons injected into the same chromatographs and columns, a reasonable estimate of retention time and sensitivity could be made for the remaining products for which no authentic samples could be obtained.

Chemical actinometry was performed by measuring the yield of acetylene formed in the photolysis of ethylene using identical photolysis conditions. The quantum yield of acetylene formation was taken as unity at 123.6

TABLE 1

Absorption coefficients (atm^{-1} cm^{-1}) of CF_2Cl_2, $CFCl_3$ and CCl_4 at 296 K

	213.9 nm	163.3 nm	147.0 nm	123.6 nm
CF_2Cl_2	0.073 0.074[a] 0.079[b] 0.077[c]	14.0[c]	21.2 ± 0.5	1140 ± 40 1240[d]
$CFCl_3$	1.90 1.98[a] 1.93[b] 1.87[c]	120[c]	183 ± 6	2570 ± 80 2480[d]
CCl_4	8.15[a]	—	714 ± 20	1760 ± 50

[a] From ref. 7. [b] From ref. 9. [c] From ref. 8. [d] Estimated from graphs of ref. 14.

and 147.0 nm and as 0.66 at 163.3 nm [6]. At 213.9 nm quantum yields were calculated from secondary intercomparison, utilizing the published absorption coefficients [7 - 10] and the results from the earlier work [1, 2] on halomethanes. Thus the quantum yields for CCl_4 photolysis at 213.9 nm were calculated by accepting the value of 0.98 for the quantum yield for $CFCl_2$ (as $CFCl_2Br$) from $CFCl_3$ given in ref. 1 and then taking into account the difference in the extinction coefficients for $CFCl_3$ and CCl_4. Likewise the quantum yields for CF_2Cl_2 photolysis at the same wavelength were calculated by accepting a value of unity for the quantum yield of CH_3Br in the photolysis of CH_3Cl.

The absorption coefficients of all three compounds have been measured in this work and are listed in Table 1. For each compound the absorption increases drastically as the wavelength of the photolytic light decreases. It is also seen in this table that, in general, the absorption coefficient at any given wavelength increases with the number of chlorine atoms present in the molecule. This is not true at the shortest wavelength.

3. Results and discussion

3.1. Photolysis of CF_2Cl_2–Br_2 mixtures

From the previous investigation [1] it may be concluded that the following primary processes occur in the photolysis of CF_2Cl_2:

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

$$\longrightarrow CF_2 + 2Cl \tag{2}$$

TABLE 2

Photolysis of CF_2Cl_2–Br_2 mixtures at 296 K

Wavelength (nm)	Pressure (Torr)			Quantum yields			
	CF_2Cl_2	Br_2	Additive	CF_2ClBr	CF_2Br_2	$CFClBr_2$	CF_2BrCF_2Br
213.9	19.9[a]	1.4		1.0	0.04	—	—
163.3	48.1	2.4		0.71	0.22	—	—
	32.0	3.0		0.63	0.19	—	—
	32.2[b]	1.7		0.68	0.23	—	—
	32.0	1.7		0.68	0.22	—	—
	32.0	0.7		0.66	0.23	—	—
	16.4	0.9		0.69	0.23	—	—
147.0	45.7	2.1		0.054	0.54	—	n.d.
	25.0	1.0		0.01	0.53	—	0.005
	22.5	1.1		0.037	0.61	—	n.d.
	11.9[a]	0.8		0.050	0.51	—	n.d.
	5.8[a]	~0.1		0.049	0.37	—	0.092
123.6	45.2	0.4		0.012	0.60	n.d.	0.005
	15.0	1.3		0.034	0.57	n.d.	0.012
	14.5	0.4		0.024	0.51	n.d.	0.023
	14.7	~0.1		0.015	0.60	n.d.	0.015
	4.5	0.4		0.037	0.26	0.057	0.11
	3.6	0.25		0.035	0.29	n.d.	0.12
	3.2	~0.1		0.020	0.13	n.d.	0.25
	3.4	<0.1		0.021	0.092	n.d.	0.29
	1.5	0.4		0.065	0.17	0.063	0.21
	0.6	~0.1		0.036	0.028	n.d.	0.34
	14.6	0.4	Xe 750	0.021	0.58	0.073	0.003
	15.1	1.1	O_2 0.5	0.013	0.33	n.d.	0.006
	4.8	1.2	O_2 0.2	0.028	0.43	n.d.	0.013

n.d., not determined.
[a]Corrected for incomplete absorption.
[b]Conversion for this run is about three times larger than for the following one.

The relative importance of these two processes changes with wavelength. At shorter wavelengths reaction (2) becomes more important while reaction (1) diminishes in importance. The earlier work clearly shows that molecular chlorine formation is not an important reaction at wavelength less than or equal to 184.9 nm and that even at 213.9 nm the previous results do not support a mechanism producing molecular chlorine. There is enough energy to produce two chlorine atoms even at 213.9 nm. However, a small yield of molecular chlorine formation, especially at wavelengths greater than or equal to 230.0 nm (*i.e.* near the absorption threshold), cannot be entirely ruled out.

With the addition of bromine, the following reactions are expected to occur:

$$CF_2Cl + Br_2 \longrightarrow CF_2ClBr + Br \qquad (3)$$

$$CF_2 + Br_2 \longrightarrow CF_2Br_2^* \qquad (4)$$

$$CF_2Br_2^* + M \longrightarrow CF_2Br_2 + M \qquad (5)$$

$$CF_2Br_2^* \longrightarrow CF_2Br + Br \qquad (6)$$

$$CF_2Br + Br_2 \longrightarrow CF_2Br_2 + Br \qquad (7)$$

$$2CF_2Br \longrightarrow CF_2BrCF_2Br \qquad (8)$$
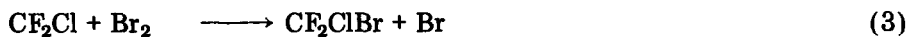
In addition the following two reactions would *a priori* also be expected to occur:

$$2CF_2Cl \longrightarrow CF_2ClCF_2Cl \qquad (9)$$

$$CF_2Cl + CF_2Br \longrightarrow CF_2ClCF_2Br \qquad (10)$$

However, neither combination product was observed under any of the conditions used in this investigation. Tentatively, we assume that the chlorine and bromine atoms produced in this system will combine and do not react further. Again from the previous study there is no evidence that CF_2Cl or CF_2 radicals react with the parent compound. Thus, if reactions (1) - (8) are the only ones occurring, then $\phi(CF_2Cl) = \phi(CF_2ClBr)$ and $\phi(CF_2) = \phi(CF_2Br_2) + 2\phi(CF_2BrCF_2Br)$.

Table 2 gives the results of the photolysis of CF_2Cl_2–Br_2 mixtures at 213.9, 163.3, 147.0 and 123.6 nm. Conversions were usually around 0.1% or less, but increases in conversion by a factor of about 3 did not cause any noticeable change in the yields of products. In general, quantum yields of product formation, especially at the longer wavelengths, are independent of total pressure or of bromine concentration. However, it is to be noted that at 123.6 nm the quantum yield of CF_2Br_2 decreases while the quantum yield of CF_2BrCF_2Br increases when the total pressure is reduced. This pressure effect is most noticeable below 15 Torr. At higher pressures the quantum yield of CF_2BrCF_2Br is very small while the quantum yield of CF_2Br_2 remains constant. The following relation between these two products is observed:

$$\phi(CF_2Br_2) + 2\phi(CF_2BrCF_2Br) = 0.60 \pm 0.06$$

This is exactly the type of behavior that is expected from reactions (4) - (8). Walton [11] reported a similar pressure effect on the quantum yield of dimer (CF_2BrCF_2Br) formation in the direct photolysis of CF_2Br_2 at 265.0 nm in the same pressure region. He interpreted his results on the existence of a long lived excited state for CF_2Br_2. In the low pressure region at a constant pressure of CF_2Cl_2 the ratio $\phi(CF_2Br_2)/\phi(CF_2BrCF_2Br)$ increases with an increase in bromine concentration (see the three experiments at 3.4 Torr in Table 2 at 123.6 nm). This is also to be expected from the above mechanism as reaction (7) becomes more important than reaction (8) at the higher bromine concentration.

Although at 123.6 nm the quantum yield of CF_2ClBr is small, its value seems to depend on the concentration of bromine (note the three experi-

ments at 15 Torr and also those at 3.4 Torr in Table 2). This is not the case at longer wavelengths where the yield of CF_2ClBr is independent of bromine concentration. The extinction coefficient of bromine at this wavelength is not negligible. It is about 1/4 to 1/5 of the extinction coefficient of CF_2Cl_2 itself. Perhaps some "hot" bromine atoms are produced which react with the parent compound to give additional CF_2Cl radicals by the reaction

$$Br^* + CF_2Cl_2 \longrightarrow CF_2Cl + BrCl \tag{11}$$

Since bromine concentration has no effect on the formation of any products at the longer wavelengths (greater than 123.6 nm), this reaction or similar ones do not occur at such wavelengths.

The formation of $CFClBr_2$ was unexpected. This product certainly indicates that the following primary process occurs at 123.6 nm (10.0 eV):
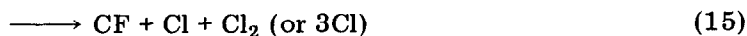
$$CF_2Cl_2 + h\nu \longrightarrow CFCl + F + Cl \tag{12}$$

There is enough energy at this wavelength for this reaction which requires approximately 7.2 eV [12]. The quantum yield of formation of $CFClBr_2$ is independent of pressure even down to 1.5 Torr (see the three experiments given at 123.6 nm in Table 2). In view of the pressure effect on the yield of CF_2Br_2, it must be concluded that the excited $CFClBr_2$ molecule is very easily stabilized. Further evidence for this conclusion will be discussed in Section 3.2 where the results of the photolysis of $CFCl_3$–Br_2 mixtures is presented.

In Table 3 are listed the quantum yields of the various radicals formed in the primary processes for CF_2Cl_2 at the different wavelengths as determined by the bromine technique. Also listed in parentheses are the quantum yields of formation for the same radicals determined in ref. 1. In general there is very good agreement between the two methods for the quantum yields of formation of CF_2Cl, but for CF_2 radicals the bromine technique always gives a smaller value (by a factor of about 2) than the technique used in ref. 1. Before discussing this further the photolysis of the other two compounds will be presented.

3.2. Photolysis of $CFCl_3$–Br_2 mixtures

Again from the earlier studies, it may be taken that the following primary processes occur in the photolysis of $CFCl_3$:

$$CFCl_3 + h\nu \longrightarrow CFCl_2 + Cl \tag{13}$$

$$\longrightarrow CFCl + 2Cl \tag{14}$$

$$\longrightarrow CF + Cl + Cl_2 \text{ (or 3Cl)} \tag{15}$$

When bromine is added we may also expect the following reactions to occur:

$$CFCl_2 + Br_2 \longrightarrow CFCl_2Br + Br \tag{16}$$

$$CFCl + Br_2 \longrightarrow CFClBr_2^* \tag{17}$$

TABLE 3

Quantum yields of photofragments derived from the photolysis of halomethane–Br_2 mixtures at 296 K

		213.9 nm	163.3 nm	147.0 nm	123.6 nm
CF_2Cl_2					
	CF_2Cl	1.0 ± 0.1 (0.91 ± 0.01)[a]	0.67 ± 0.07 (0.56 ± 0.04)	0.05 ± 0.02 (<0.1)	<0.02
	CF_2	0.04 ± 0.02 (0.07 ± 0.02)	0.22 ± 0.03 (0.40 ± 0.05)	0.55 ± 0.06 (>0.8)	0.60 ± 0.06
	$CFCl$	<0.01 (<0.005)	<0.01 (<0.005)	<0.01 (<0.005)	0.06 ± 0.02
$CFCl_3$					
	$CFCl_2$	1.0 ± 0.1 (0.98 ± 0.01)	0.53 ± 0.05 (0.50 ± 0.06)	0.02 ± 0.01 (<0.1)	0.03 ± 0.02
	$CFCl$	0.02 ± 0.01 (0.03 ± 0.02)	0.20 ± 0.02 (0.45 ± 0.07)	0.33 ± 0.03 (>0.87)	0.20 ± 0.02
	CF	<0.001 (<0.001)	<0.001 (<0.01)	<0.004 (~0.03)	0.04 ± 0.02
CCl_4					
	CCl_3	1.0 ± 0.1 (0.9 ± 0.1)	0.41 ± 0.04 (0.25 ± 0.05)	0.02 ± 0.01 (0.04 ± 0.02)	
	CCl_2	0.01 ± 0.01 (0.05 ± 0.03)	0.40 ± 0.04 (0.76 ± 0.2)	0.49 ± 0.05 (0.6 ± 0.2)	
	CCl	<0.01	<0.01	<0.02	

[a]Values in parentheses are taken from refs. 1 and 2.

TABLE 4

Photolysis of $CFCl_3$–Br_2 mixtures at 296 K

Wavelength (nm)	Pressure (Torr)		Quantum yields			
	$CFCl_3$	Br_2	$CFCl_2Br$	$CFClBr_2$	$CFBr_3$	$CFClBrCFClBr$
213.9	23.9[a]	0.9	0.98	0.02	—	—
163.3	32.0	1.5	0.54	0.20	—	—
	11.0	0.5	0.52	0.19	—	—
147.0	47.6	1.9	0.015	0.32	~0.001	—
	25.8	1.3	n.d.	0.34	~0.001	—
	12.6	0.9	0.014	0.34	~0.001	—
	12.1[b]	1.0	0.025	0.26	~0.004	—
123.6	24.9	~0.1	n.d.	0.18	0.046	0.017
	14.8	~0.1	n.d.	0.26	0.054	0.013
	4.5	~0.1	0.052	0.18	0.043	0.012
	0.6	~0.1	0.014	0.19	0.044	0.010

n.d., not determined.
[a]Corrected for incomplete absorption.
[b]Conversion for this run is about four times larger than for the previous run.

$$CFClBr_2^* + M \longrightarrow CFClBr_2 + M \qquad (18)$$

$$CFClBr_2^* \longrightarrow CFClBr + Br \qquad (19)$$

$$2CFClBr \longrightarrow CFClBrCFClBr \qquad (20)$$

In addition the CF radical may be expected to react with bromine to produce $CFBr_3$ by a series of consecutive reactions. Initially we assume, as before, that in the presence of bromine the determination of the quantum yields of $CFCl_2Br$, $CFClBr_2$, $CFClBrCFClBr$ and $CFBr_3$ gives a measure of the quantum yield of formation of the radicals $CFCl_2$, $CFCl$ and CF formed in the primary process.

Table 4 gives the results of the photolysis of $CFCl_3$–Br_2 mixtures at 213.9, 163.3, 147.0 and 123.6 nm. The quantum yields of all products are independent of total pressure. Notice in particular that, even at 123.6 nm at pressures of $CFCl_3$ from 0.6 to 25 Torr, the quantum yield of $CFClBr_2$ formation is constant and there is very little $CFClBrCFClBr$ formed. Consequently, as noted above, the excited $CFClBr_2$ formed in reaction (17) must be very easily quenched by reaction (18), compared with decomposition by reaction (19).

Again it can be seen from Table 3 that there is good agreement between the values determined for the quantum yields of the trihalomethyl radical by the two different methods, but for the dihalomethylene fragments the values determined by the bromine technique are somewhat less than one-half of those given in ref. 1. For the halomethylidyne radicals the bromine system also gives a value which is much too low (compare the results in
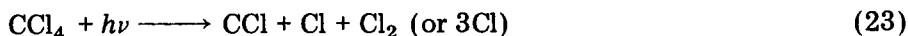
Table 3 for $CFCl_3$ at 147.0 nm which is the only wavelength in which both techniques give measurable results).

3.3. Photolysis of CCl_4–Br_2 mixtures

In the photolysis of CCl_4 the following primary processes have been determined to occur [2] :

$$CCl_4 + h\nu \longrightarrow CCl_3 + Cl \qquad (21)$$

$$\longrightarrow CCl_2 + 2Cl \qquad (22)$$

At shorter wavelengths it may be expected that the reaction

$$CCl_4 + h\nu \longrightarrow CCl + Cl + Cl_2 \text{ (or 3Cl)} \qquad (23)$$

is also one of the primary processes. As before we assume *a priori* that in the presence of bromine the amount of CCl_3Br, CCl_2Br_2 and $CClBr_3$ is a measure of the quantum yield of the primary fragments CCl_3, CCl_2 and CCl by reactions analogous to reactions (3), (4), (16) and (17) which were shown above. Table 5 lists the results of these experiments at 213.9, 163.3 and

TABLE 5

Photolysis of CCl_4–Br_2 mixtures at 296 K

Wavelength (nm)	Pressure (Torr)		Quantum yields		
	CCl_4	Br_2	CCl_3Br	CCl_2Br_2	$CClBr_3$
213.9	24.1[a]	0.4	1.13	0.004	—
	20.9[a]	1.1	0.98	0.005	—
	10.9[a]	0.7	0.93	0.011	—
163.3	20.7	0.9	0.44	0.41	—
	11.9	0.5	0.39	0.40	—
147.0	15.5	1.7	0.02	0.52	n.d.
	7.3	1.6	0.01	0.49	n.d.
	7.3	0.9	0.01	0.46	n.d.
	7.3	0.8	0.03	0.48	≤0.02
	7.3	0.4	0.02	0.48	n.d.

n.d., not determined.
[a] Corrected for incomplete absorption.

147.0 nm. As in the previous results the yields of products are independent of the total pressure or the concentration of bromine added. The values of the quantum yields of the different photofragments formed in the primary process are given in Table 3. The values in parentheses are taken from ref. 2. Again, the agreement between the two methods is reasonable for CCl_3, but with bromine the quantum yields determined for CCl_2 are much smaller than those determined in ref. 2.

3.4. Reactions of CX_2 and CX

It seems clear from the above that the bromine addition technique is well suited for the determination of the quantum yields of simple halomethyl radicals in various systems. However, it is also evident that this method is not quantitatively usable in determining the quantum yields of the dihalomethylene radicals or of the halomethylidyne radicals.

At this time it is not possible to give a complete explanation for the lack of efficiency of the added bromine in scavenging all of the dihalomethylene radicals, but it may conceivably be connected with the formation of both triplet and singlet CX_2 radicals. There is some evidence [13] that, like the CH_2 radical, both singlet and triplet states of CF_2 can be produced but unlike CH_2 the ground state is believed to be a singlet. The addition of 1 atm xenon to the CF_2Cl_2–Br_2 mixture at 123.6 nm produced no change in the quantum yield of CF_2Br_2 (see Table 2). Thus we are led to believe that the ground state CF_2 radical is responsible for the observed product. Moreover, it can be seen in Table 2 that the addition of small amounts (0.5 Torr) of oxygen to 15 Torr CF_2Cl_2 diminishes but does not eliminate the formation of CF_2Br_2.

The formation of $CFBr_3$ and $CClBr_3$ at 123.6 nm is evidence that CF and CCl are formed in the $CFCl_3$–Br_2 and CCl_4–Br_2 systems respectively. It is obvious that these products must be formed by at least a two-step mechanism such as

$$CX + Br_2 \longrightarrow CXBr_2 \tag{24}$$

$$CXBr_2 + Br_2 \longrightarrow CFBr_3 + Br \tag{25}$$

Because other competing reactions may occur, the quantum yields of $CFBr_3$ and $CClBr_3$ should be considered only as lower limits for a measure of CF and CCl.

Acknowledgments

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