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# THE PHOTOCHEMISTRY OF METHYL CHLORIDE

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## Summary

Methyl chloride and $CH_3Cl$–$CD_3Cl$, $CH_3Cl$–$Br_2$ and $CD_3Cl$–HI mixtures have been photolyzed at 163.3, 147.0 and 123.6 nm in the gas phase and methyl chloride has also been photolyzed at 147.0 nm in the liquid phase. Over this range of wavelengths, there are four principal primary processes:

$$CH_3Cl + h\nu \rightarrow CH_3 + Cl \quad (1)$$

$$\rightarrow CH_2Cl + H \quad (2)$$

$$\rightarrow CH_2 + HCl \quad \text{(or H + Cl)} \quad (3)$$

$$\rightarrow CHCl + H_2 \quad \text{(or 2H)} \quad (4)$$

At 163.3 nm, process (1) is almost exclusively responsible for the photodecomposition. However, at shorter wavelengths processes (2), (3) and (4) increase while process (1) decreases in importance. At all wavelengths these four processes account for a total quantum yield of 0.75 - 1.0.

## 1. Introduction

The recent concern that the presence of chlorine atoms in the stratosphere, arising from the photochemical decomposition of chloromethanes, might affect the stratospheric ozone layer prompted research in this laboratory to determine the modes of decomposition of $CFCl_3$, $CF_2Cl_2$ [1] and $CCl_4$ [2]. However, it has been suggested [3] that a major source of chlorine in the stratosphere at the present time may be methyl chloride which is produced from natural sources. Until now there has been to our knowledge only one quantitative investigation of the gas phase photochemistry of this important compound. Takacs and Willard [4] irradiated methyl chloride in the gas phase at 184.9 nm and found that chlorine atom elimination was the most

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important process, resulting in methane formation (via hydrogen abstraction by $CH_3$) with a quantum yield of 0.79. They were unable to detect more than a trace of any products which could arise from either HCl elimination to produce $CH_2$ or combinations of methyl and $CH_2Cl$ radicals to form ethane or ethylene.

The purpose of this research is to provide a firm understanding of the primary photochemical processes which methyl chloride undergoes at several wavelengths in the vacuum UV from 163.3 to 123.6 nm. The use of NO, HI and bromine as radical traps and of $CD_3Cl$ for isotopic distribution studies has permitted a rather complete analysis of the photochemistry of methyl chloride as a function of exciting wavelength.

## 2. Experimental procedure

### *2.1. Materials*

Methyl chloride was purified by trapping with liquid nitrogen the effluent from a gas chromatograph equipped with a squalane column. The major impurity in the chloride was determined from its retention time to be either methyl bromide or n-butane. This impurity was reduced after purification to a level of $4 \times 10^{-3}$%. No other impurities were observed (detection limit estimated at $2 \times 10^{-4}$%). Methane was purified as described in an earlier publication [5]. $CD_3Cl$ was determined to have an isotopic purity of 98.7 mol.%-$d_3$ and was used without further purification except for the usual low temperature degassing procedures. ACS reagent grade bromine was used.

### *2.2. Product analysis*

Gas chromatographs were equipped with flame ionization detectors and squalane or silicone rubber columns of various lengths. Identification of products was made by comparison of retention times with those of authentic samples. Mass spectral analysis of products and isotopic distribution patterns were determined on a high resolution mass spectrometer. Results are corrected for the isotopic purity of the $CD_3Cl$.

### *2.3. Light sources and actinometry*

163.3, 147.0 and 123.6 nm radiation was obtained from microwave-operated bromine, xenon and krypton resonance lamps, respectively. The construction and operation of these lamps has been described previously [6]. The reaction vessels were approximately 300 ml in volume and were designed to fit directly over the windows of the lamps by means of standard taper joints.

A saturation-ion-current technique [6] was used to determine the absorption coefficients of methyl chloride at 147 and 123.6 nm and at 297 K. The following values were obtained:

| | | |
|---|---|---|
| $CH_3Cl$ | 123.6 nm | $342 \pm 10$ atm$^{-1}$ cm$^{-1}$ |
| | 147.0 nm | $29.2 \pm 0.5$ atm$^{-1}$ cm$^{-1}$ |
| $CD_3Cl$ | 123.6 nm | $247 \pm 8$ atm$^{-1}$ cm$^{-1}$ |
| | 147.0 nm | $13.2 \pm 0.3$ atm$^{-1}$ cm$^{-1}$ |

The absorption coefficient of $CH_3Cl$ at 163.3 nm has recently been reported to be 26.3 atm$^{-1}$ cm$^{-1}$ [7]. The absorption coefficient is defined by the equation $I/I_0 = \exp(-\epsilon P l)$, where $I/I_0$ is the fraction of incident light transmitted through $l$ cm of gas at $P$ atm pressure.

The photolysis of ethylene to form acetylene was used as an actinometer. The quantum yield for the actinometric reaction is unity at 123.6 and 147.0 nm, but 0.66 at 163.3 nm [8]. The light flux used in these experiments was between $5 \times 10^{13}$ and $4 \times 10^{14}$ photons s$^{-1}$. Total conversions were generally not more than 0.1% in order to minimize secondary reactions.

Errors in the quantum yields are difficult to assess, but examination of the scatter in the data suggests that the results are reproducible to within 20% from run to run. The ratios of the quantum yields of the various products, as compared between one run and another, are usually more accurate. The accuracy of the mass spectral data presented here is estimated to be ± 10%.

## 3. Results

The yields of the major products from the photolysis of chloromethane in the gas phase at one typical pressure and in the liquid phase are presented in Table 1. In contrast to the results of Takacs and Willard [4], there are several products formed with quantum yields greater than 0.006. These major products are methane, ethylene, ethane, vinyl chloride, ethyl chloride, dichloromethane and 1,2-dichloroethane. A minor product was acetylene which was present with a quantum yield of 0.004 - 0.03, increasing with an increase in wavelength. Some of the products, particularly chloroethane, vinyl chloride and 1,2-dichloroethane, exhibited variations in quantum yield with pressure as did ethylene to a less noticeable extent. The liquid phase experiment at 147.0 nm is also presented in Table 1 for comparison. In this experiment $C_2H_4$ and $C_2H_3Cl$ are essentially absent.

In the gas phase most of the quantum yields were drastically reduced in the presence of NO. Quantum yields in the photolysis of 50 Torr of methyl chloride in the presence of 1 Torr of NO at 123.6 nm were reduced from the values given in Table 1 to 0.013 for methane and to 0.010 for ethylene. The yields for all the other products were reduced to unobservably small yields with two exceptions. The quantum yield for acetylene formation was 0.0035 with or without the presence of NO. The formation of hydrogen (see below) was reduced only by a factor of 2.

The results of irradiation of equimolar mixtures of $CH_3Cl$ and $CD_3Cl$ are shown in Table 2 where the relative isotopic abundances of hydrogen,

TABLE 1

Quantum yields of products in photolysis of $CH_3Cl$ at 296 K

| Wavelength (nm) | $CH_3Cl$ pressure (Torr) | Quantum yields | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $CH_4$ | $C_2H_2$ | $C_2H_4$ | $C_2H_6$ | $C_2H_3Cl$ | $C_2H_5Cl$ | $CH_2Cl_2$ | $(CH_2Cl)_2$ | $\phi(CH_3)$[a] | $\phi(CH_2Cl)$[a] |
| 163.3 | 25 | 0.475 | 0.027 | 0.254 | 0.041 | 0.146 | 0.0069 | 0.014 | 0.121 | 0.86 | 1.10 |
| 147.0 | 25 | 0.231 | 0.0052 | 0.208 | 0.063 | 0.088 | 0.037 | n.d. | 0.132 | 0.60 | 0.84 |
| | Liquid[b] | 1.00 | <0.001 | 0.0012 | 0.006 | <0.001 | 0.145 | 0.222 | 1.31 | – | – |
| 123.6 | 25 | 0.277 | 0.0035 | 0.108 | 0.028 | 0.075 | 0.0061 | n.d. | 0.122 | 0.50 | 0.62 |

[a]Calculated from eqns. (I) and (II) and averaged over several experiments.
[b]Relative yields only, based on $[CH_4] = 1.00$.

TABLE 2

Photolysis of $CH_3Cl$–$CD_3Cl$ (1:1) mixtures at 295 K

| Wavelength (nm) | Quantum yields | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $H_2$ | HD | $D_2$ | $CH_4$ | $CH_3D$ | $CH_2D_2$ | $CD_3H$ | $CD_4$ | $C_2H_4$ | $C_2H_3D$ | $CH_2CD_2$ | $C_2D_3H$ | $C_2D_4$ |
| 163.3 | 0.031 | 0.025 | 0.013 | 0.242 | 0.017 | 0.0021 | 0.206 | 0.0089 | 0.124 | 0.0013 | 0.090 | 0.0027 | 0.033 |
| 147.0 | 0.043 | 0.018 | 0.010 | 0.153 | 0.0048 | 0.0049 | 0.066 | 0.0019 | 0.082 | 0.010 | 0.051 | 0.0023 | 0.030 |
| 123.6 | 0.103 | 0.032 | 0.032 | 0.147 | 0.011 | 0.012 | 0.111 | 0.0034 | 0.067 | 0.0092 | 0.046 | 0.0046 | 0.011 |

Total pressure, 50 Torr.

TABLE 3

Photolysis of $CD_3Cl$–HI (50:1) mixtures at 295 K

| Wavelength (nm) | Quantum yields | | | | |
|---|---|---|---|---|---|
| | HD | $D_2$ | $CH_2D_2$ | $CD_3H$ | $CD_4$ |
| 163.3 | 0.031 | 0.014 | 0.0039 | 1.0 | 0.013 |
| 147.0 | 0.124 | 0.071 | 0.025 | 0.47 | 0.014 |
| 123.6 | 0.153 | 0.093 | 0.059 | 0.31 | 0.0077 |

These quantum yields are based on the quantum yields of methyl bromide formation given in Table 4.

methane and ethylene are expressed in terms of quantum yields. The total quantum yield for hydrogen in these experiments is 0.069 at 163.3 nm, 0.071 at 147.0 nm and 0.168 at 123.6 nm. The isotopic distribution of the methane produced shows that the yield of $CH_2D_2$ increases at the higher energies. The analysis of the ethylene shows that only a small fraction of these molecules have mixed hydrogen and deuterium atoms on the same carbon atom. (The amount of $CH_2CD_2$ was calculated assuming the yield of CHDCHD to be negligible.) The results from a similar analysis of the ethanes, not presented here, reveals that in this case $C_2D_6$, $CH_3CD_3$ and $C_2H_6$ account for over 80% of the ethane formed.

Results from experiments involving scavenging of radicals by HI in the photolysis of $CD_3Cl$ are presented in Table 3. The quantum yields of $C_2$ products were less than 0.005. Small amounts ($\phi \approx 0.05$) of methyl iodide were also observed as well as an unknown product which on the basis of its retention time was assumed to be choroiodomethane. The mass spectral analysis of the products of these experiments shows that the methane consists primarily of $CD_3H$ with significant contributions from $CH_2D_2$ at the shorter wavelengths.

Results from the gas chromatographic analysis of the irradiation of methyl chloride in the presence of bromine at the three wavelengths are shown in Table 4. There is no apparent trend with pressure in the quantum yields of either $CH_3Cl$ or bromine. The major product at each wavelength is $CH_3Br$ which comprises about 85% of the products at 163.3 nm. At 147.0 and 123.6 nm the quantum yield of $CH_2ClBr$ has doubled and $CH_2Br_2$ has become an important product, accompanied by a reduction in the quantum yield of methyl bromide. At 123.6 nm small amounts of $CHClBr_2$ and $CH_2BrCH_2Br$ are also formed.

## 4. Discussion

There are several paths available for the decomposition of the photoexcited methyl chloride. Each of the following plausible primary processes is energetically allowed at the lowest photon energy (7.6 eV at 163.3. nm) used in this study:

TABLE 4

Photolysis of $CH_3Cl$ in the presence of bromine at 295 K

| Wavelength (nm) | Pressure (Torr) | | Quantum yields | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $CH_3Cl$ | $Br_2$ | $CH_4$ | $CH_3Br$ | $CH_2ClBr$ | $CH_2Br_2$ | $CHClBr_2$ | $(CH_2Br)_2$ |
| 163.3 | 20.7 | 1.1 | 0.010 | 1.02 | 0.11 | | | |
| | 31.9 | 2.9 | 0.010 | 0.95 | 0.13 | | | |
| | 32.0 | 0.3 | 0.010 | 0.96 | 0.20 | | | |
| | 40.8 | 2.0 | 0.010 | 1.01 | 0.13 | | | |
| | 81.8 | 4.1 | 0.010 | 1.12 | 0.19 | | | |
| 147.0 | 10.8 | 0.5 | 0.012 | 0.42 | 0.31 | 0.037 | | |
| | 21.5 | 2.0 | 0.012 | 0.44 | 0.35 | 0.038 | | |
| | 21.8 | 0.6 | 0.014 | 0.49 | 0.37 | 0.035 | | |
| | 22.1 | 1.0 | 0.015 | 0.56 | 0.40 | 0.039 | | |
| | 41.9 | 2.1 | 0.012 | 0.44 | 0.32 | 0.040 | | |
| | 62.8 | 2.8 | 0.012 | 0.49 | 0.32 | 0.024 | | |
| 123.6 | 5.4 | 0.7 | 0.009 | 0.30 | 0.28 | 0.091 | 0.026 | 0.011 |
| | 16.4 | 2.5 | 0.008 | 0.31 | 0.29 | 0.089 | 0.026 | 0.011 |
| | 16.4 | 0.5 | 0.009 | 0.33 | 0.31 | 0.081 | 0.041 | 0.015 |
| | 30.0 | 1.7 | 0.009 | 0.29 | 0.27 | 0.086 | 0.033 | 0.015 |
| | 49.5 | 2.7 | 0.008 | 0.32 | 0.29 | 0.086 | 0.033 | 0.015 |

$$CH_3Cl + h\nu \rightarrow CH_3 + Cl \quad (1)$$

$$\rightarrow CH_2Cl + H \quad (2)$$

$$\rightarrow CH_2 + HCl \text{ (or } H + Cl) \quad (3)$$

$$\rightarrow CHCl + H_2 \text{ (or } 2H) \quad (4)$$

The atom products in reactions (3) and (4) are energetically possible only at the highest photon energy used in this work, 10.0 eV (123.6 nm). The determination of the relative importance of these reactions and the eludication of the secondary reactions which the resulting fragments undergo is the primary goal of this research.

In the photolysis of pure methyl chloride the following secondary reactions may tentatively be assumed to occur after the initial primary processes:

$$Cl + CH_3Cl \rightarrow HCl + CH_2Cl \quad (5)$$

$$CH_3 + CH_3Cl \rightarrow CH_4 + CH_2Cl \quad (6)$$

$$CH_3 + HCl \rightarrow CH_4 + Cl \quad (7)$$

$$2CH_2Cl \rightarrow CH_2Cl_2 + CH_2 \quad (8a)$$

$$\rightarrow CH_3Cl + CHCl \quad (8b)$$

$$\rightarrow CH_2ClCH_2Cl^* \quad (9)$$

$$CH_2ClCH_2Cl^* \rightarrow CH_2CHCl + HCl \quad (10)$$

$$CH_2ClCH_2Cl^* + M \rightarrow CH_2ClCH_2Cl + M \quad (11)$$

$$CH_3 + CH_2Cl \rightarrow CH_3Cl + CH_2 \quad (12a)$$

$$\rightarrow CH_4 + CHCl \quad (12b)$$

$$\rightarrow C_2H_5Cl^* \quad (13)$$

$$C_2H_5Cl^* \rightarrow C_2H_4 + HCl \quad (14)$$

$$C_2H_5Cl^* + M \rightarrow C_2H_5Cl + M \quad (15)$$

$$2CH_3 \rightarrow C_2H_6 \quad (16)$$

$$CH_2 + CH_3Cl \rightarrow CH_3 + CH_2Cl \quad (17)$$

$$CH_2 + CH_3 \rightarrow C_2H_4 + H \quad (18)$$

$$CH_2 + CH_2Cl \rightarrow C_2H_4 + Cl \quad (19)$$

$$CHCl + CH_3Cl \rightarrow 2CH_2Cl \quad (20a)$$

$$\rightarrow CHCl_2 + CH_3 \quad (20b)$$

$$CHCl + CH_3 \rightarrow C_2H_4 + Cl \quad (21)$$

$$CHCl + CH_2Cl \rightarrow C_2H_3Cl + Cl \quad (22)$$

$$2CH_2 \rightarrow C_2H_4 \quad (23)$$

$$2CHCl \rightarrow CHClCHCl \quad (24)$$

$$CH_2 + CHCl \rightarrow C_2H_3Cl \quad (25)$$

From the product analysis which is given in Table 1 for the photolysis of pure methyl chloride at various wavelengths, it seems clear that many, if not all, of the above reactions do occur. However, because of the large number and complexity of these reactions it is difficult to assign quantitative values unambiguously even to the four possible primary processes without further information. For instance, ethylene, which is an important product, could result from the further reactions of $CH_3$, $CH_2Cl$, $CH_2$ and CHCl with each other (see for instance reactions (13), (14), (18), (19), (21) and (23)). Therefore, in order to determine the quantum yields of the primary processes at the various wavelengths, several different experimental techniques have been used. These techniques, which are described in detail below, enable us to assign quantitative values to the different primary processes. Then it is possible to use these values to help unravel all the reactions which occur in the photolysis of pure methyl chloride. It is assumed that the scavengers used do not quench the excited state of methyl chloride formed by light absorption. The results reported here give evidence that this assumption is correct. The overall quantum yield is near unity and is not affected by pressure changes.

*4.1. HI and bromine scavenging experiments*

Both bromine [9, 10] and HI [11] have been used successfully as radical scavengers when small amounts are added to the primary system of interest. In each case characteristic products result which may then be identified. In the case of HI, deuterated methyl chloride was used. Thus, the initially formed deuterated radicals will abstract hydrogen from HI to produce labelled products. In this way the normal secondary reactions are prevented and only the primary radicals are revealed. Experimentally, the photolysis of $CD_3Cl$–HI mixtures produces HD and deuterium as major products (see Table 3). This implies that processes (2) and (4) are indeed primary processes which apparently are responsible for all of the hydrogen production. The amount of hydrogen produced increases with an increase in energy, and the increase in deuterium relative to HD at shorter wavelengths implies that process (4) becomes relatively more important. Processes (2) and (4) together account for quantum yields of 0.045, 0.20 and 0.25 at wavelengths of 163.3, 147.0 and 123.6 nm, respectively.

In addition to hydrogen, methane is formed in these experiments. Its analysis, which is also reported in Table 3, reveals that at 163.3 nm essentially all of the methane is $CD_3H$ with only 0.4% $CD_2H_2$. The $CD_3H$ arises from the H abstraction reaction of $CD_3$ with HI, while the $CH_2D_2$ comes from the reactions of methylene ($CD_2$). However, for the 147.0 and 123.6 nm irradiations increasing amounts of $CH_2D_2$ are formed which are about 5% and 16% of the total methane yield respectively. Therefore in these experiments a significant fraction of the excited $CD_3Cl$ decays by step (3) to form $CD_2$ and DCl. The importance of methylene formation may be somewhat greater than indicated here since $CD_2$ may react with HI to produce $CD_2HI$ which was not measured in this mass spectroscopic analysis. Chromatographic analysis of similar mixtures, using $CH_3Cl$, shows that significant amounts of $CH_3I$ are formed. The quantum yields obtained suggest that the total quantum yield for methylene formation is about 0.08 ± 0.01 for both the 147.0 and 123.6 nm wavelengths. As we shall see later, this value still seems too low, especially at 123.6 nm. The quantum yields of hydrogen and methane formation given in Table 3 are based on the quantum yields of methyl bromide formation from the photolysis of $CH_3Cl$–$Br_2$ mixtures given in Table 4.

In the bromine scavenging experiments the methyl radicals react efficiently with bromine to form methyl bromide. Table 4 shows the results of the analysis for methyl bromide. Since bromine should prevent other secondary reactions from occurring, the quantum yield of methyl bromide formation can be equated with the quantum yield of methyl radicals or of process (1). Thus the quantum yields for process (1) (from Table 4) are 1.01 ± 0.05, 0.47 ± 0.04 and 0.31 ± 0.02 for 163.3, 147.0 and 123.6 nm respectively.

Chlorine atoms are produced along with methyl radicals by process (1). The fate of most of these atoms must be to react with bromine to form ClBr. This scavenging is apparently not complete, since some $CH_2ClBr$ forms even

with the 163.3 nm light where the quantum yield of methyl radical formation is essentially unity. It is reasonable to suppose that the $CH_2Cl$ radical which reacts with bromine to form $CH_2ClBr$ arises from the hydrogen abstraction reaction (5).

Of course, process (2) would also produce $CH_2Cl$ radicals, but the results of the $CD_3Cl$–HI photolysis indicate that the quantum yield for this process is at most 0.03 at 163.3 nm (Table 3, HD production). Thus, about 12 - 15% of the chlorine atoms produced in the presence of bromine react in this fashion (*i.e.* by process (5)) at 163.3 nm. At the shorter wavelengths it is necessary to attribute a larger fraction of the chlorine atoms to this reaction in order to explain the larger yield of $CH_2ClBr$ even though the yield of $CH_3Br$ is smaller. The hydrogen results of Table 3 show that the quantum yields of process (2) are 0.124 and 0.153 at 147.0 and 123.6 nm respectively. These results indicate that about 50% of the chlorine atoms react in this way at these two wavelengths. Perhaps at the shorter wavelengths more energy goes into the chlorine atom when process (1) occurs and under these conditions bromine is less efficient as a chlorine atom scavenger.

The formation of methylene in primary process (3) is reflected in the products $CH_2Br_2$ and $CH_2BrCH_2Br$. Neither of these products is observed with light at 163.3 nm (see Table 4). The yield of $CH_2Br_2$ at 147.0 nm is 0.036 and at 123.6 nm the total yield of $CH_2Br_2$ + $2CH_2BrCH_2Br$ is approximately 0.11. These values must be multiplied by a correction factor of 2.44 (see Appendix). The corrected quantum yields of process (3) determined by the bromine scavenging experiments are 0.09 and 0.27 at 147.0 and 123.6 nm respectively. The product which results from the formation of CHCl by process (4) is $CHClBr_2$. This product is only formed in the photolysis at 123.6 nm where its quantum yield was determined to be 0.032. However, this value also must be multiplied by a correction factor. This correction factor for CHCl is not known, but is probably close to the value determined in the Appendix for $CH_2$, namely 2.44. This would make the quantum yield determined for process (4) by the bromine technique (0.08) very close to that obtained from $D_2$ production in the $CD_3Cl$–HI photolytic experiments (0.09 in Table 3).

### *4.2. $CH_3Cl$–$CD_3Cl$ experiments*

Results from the irradiation of 1:1 mixtures of $CH_3Cl$–$CD_3Cl$ confirm the trends observed above and provide some additional information. The first fact to be observed is the formation of hydrogen at every wavelength (see Table 2). The total hydrogen quantum yield in these experiments (determined by comparing the methane yield with that in Table 1) increases from 0.069 at 163.3 nm to 0.071 at 147 nm and to 0.167 at 123.6 nm. Process (3), methylene formation, also occurs at all wavelengths. One of the products formed by $CH_2$ or $CD_2$ from a 1:1 mixture of $CH_3Cl$–$CD_3Cl$ is $CH_2D_2$ (Table 2). This compound forms in increasing amounts at shorter wavelengths, reaching 4% of the total methane formed at 123.6 nm. Obviously the total quantum yield of methylene formation is greater than this

since various other products will also be produced. Moreover a considerable fraction of the methylene would be expected to exist in the triplet state (see Appendix) and thus it would be unreactive. Thus, process (3) must be even more significant, particularly at the shorter wavelength. This observation is in qualitative agreement with the results from the bromine and HI scavenging experiments.

It must be noted that the quantum yields of $CD_3$ and $CD_2$ formation are not precisely expressed in the isotopic distribution of the methanes formed. First, the optical densities of $CH_3Cl$ and $CD_3Cl$ are not identical. However, the ratios of the optical densities at different wavelengths can be approximated by the ratios of the yields of $CH_4$ and $CD_3H$, since the amount of $CH_3$ or $CD_3$ formed should be proportional to the extinction coefficients of $CH_3Cl$ or $CD_3Cl$ and both $CH_3$ and $CD_3$ abstract hydrogen with similar efficiency [12]. The $[CH_4]/[CD_3H]$ ratios at the relevant wavelengths are as follows: 1.17 at 163.3 nm; 2.33 at 147.0 nm; 1.34 at 123.6 nm. These values are in excellent agreement with the ratios of the extinction coefficients which were determined at 147.0 nm (2.21) and 123.6 nm (1.38) (see Section 3). Even after correcting for differences in absorption of $CH_3Cl$ and $CD_3Cl$, certain peculiarities remain in the isotopic distributions. The excess of hydrogen over deuterium in the hydrogen analysis is more than can be accounted for by differences in absorption characteristics. Furthermore, the ratios $[CH_4]/[CH_3D]$ and $[CD_3H]/[CD_4]$ are unusually large (typically about 30:1). It appears that some process is removing deuterium atoms from the system which results in an overabundance of hydrogen. This can be explained by considering HCl as a reaction intermediate. Chlorine atoms which are produced from the primary process (1) will abstract a hydrogen atom from methyl chloride and produce $CH_2Cl$ and HCl as in reaction (5). Now abstraction of hydrogen from HCl by a methyl radical has an activation energy of only 2.3 kcal $mol^{-1}$ in contrast to 9.4 kcal $mol^{-1}$ for the same abstraction from $CH_3Cl$ [13]. Thus it is clear that HCl, particularly under conditions of high conversion, is an important source of hydrogen abstraction since the rate constant for this reaction is about $10^3$ times the rate constant for the same reaction with methyl chloride. Since HCl or DCl has a tendency to become adsorbed onto Pyrex and may exchange its H or D for a proton on the wall of the reaction cell, it is quite likely that any DCl formed exchanges its D for a H in this manner and thus produces an abnormally large amount of protonated product $CH_4$, $CD_3H$, $H_2$ or HD.

Although the determination of quantitative results from experiments of this kind ($CH_3Cl$–$CD_3Cl$) is difficult, they do serve to confirm the results obtained in the earlier scavenging experiments. For instance, it is possible to estimate from these experiments the quantum yields of molecular and atomic hydrogen formation and to compare these values with those deduced earlier from the HI scavenging experiments. Since there is very little DCl in the system available for reaction with D atoms to form $D_2$, the assumption is made that essentially all of the $D_2$ formed in the equimolar mixtures arises via molecular deuterium elimination by process (4). The ratios of the extinc-

TABLE 5

Quantum yields for atomic and molecular hydrogen formation

| Wavelength (nm) | Process (2) | | Process (4) | |
|---|---|---|---|---|
| | $CD_3Cl$–HI | $CD_3Cl$–$CH_3Cl$ | $CD_3Cl$–HI | $CD_3Cl$–$CH_3Cl$ |
| 163.3 | 0.031 | 0.040 | 0.014 | 0.028 |
| 147.0 | 0.12 | 0.038 | 0.071 | 0.033 |
| 123.6 | 0.15 | 0.091 | 0.093 | 0.076 |

tion coefficients of $CH_3Cl$ to $CD_3Cl$, as measured above, can then be used to estimate the amount of molecular $H_2$ formed. The excess $H_2$ and HD may be attributed then to the abstraction of a H atom by either H or D. The results which are reported in Table 5 show an approximate agreement in most cases with the values determined by the HI scavenging experiments. The simplistic assumptions which were necessary for this analysis of the isotopic mixture experiments can probably account for most of the discrepancies.

The isotopic labelling patterns of ethylene (Table 2) and ethane (see Section 3) show that most carbon atoms are bonded to only one type of hydrogen. About one ethane molecule in four contains one isotopically mixed methyl group. This indicates that the majority of the methyl radicals which form ethane arise from process (1), as has been assumed. A still smaller fraction of the ethylene has both a H and a D atom on a single carbon. About one molecule in sixteen has a carbon atom with both isotopes. This result gives strong evidence that most of the ethylene found at all wavelengths comes from reaction (14) rather than from reaction (21), which would result in mixed isotopes on the same carbon in ethylene. However, it is evident that this or a similar reaction is taking place, especially at the shorter wavelengths.

### *4.3. Quantum yield of primary processes*

From the above information from all the different techniques it is possible to assign quantum yields within certain limits to the four processes (1) - (4). These are given in Table 6 and have been determined with the following considerations in mind. The results of the $CH_3Cl$–bromine mixtures gives strong evidence that the quantum yield of $CH_3Br$ formation can be equated with the quantum yield of process (1). Qualitatively these results are substantiated by the results given in Table 1 in which the $\phi(CH_3)$ are calculated by eqn. (I) which is given later in this discussion. Because of the complex mechanisms and assumptions involved, these measurements of $\phi(CH_3)$ are less reliable than those calculated from the bromine addition experiments. Moreover, if we accept the results for the quantum yields of hydrogen from the $CD_3Cl$–HI experiments (see Table 5), then the quantum yields for processes (2) and (4) can be estimated. In general these results are partially substantiated by the results from the $CH_3Cl$–$CD_3Cl$ and $CH_3Cl$–bromine experiments. Finally, the quantum yield for process (3) can be estimated from the

TABLE 6

Summary of the quantum yields for primary processes

| Wavelength (nm) | $CH_3$ + Cl Process (1) | $CH_2Cl$ + H Process (2) | $CH_2$ + HCl Process (3) | CHCl + $H_2$ Process (4) | Total |
|---|---|---|---|---|---|
| 163.3 | 0.86 - 1.01 | 0.00 - 0.03 | $<$ 0.02 | $\approx$ 0.02 | 0.90 - 1.08 |
| 147.0 | 0.47 - 0.60 | 0.12 - 0.27 | $\approx$ 0.09 | $\approx$ 0.07 | 0.75 - 1.03 |
| 123.6 | 0.31 - 0.50 | 0.15 - 0.24 | $\approx$ 0.27 | $\approx$ 0.09 | 0.82 - 1.10 |

formation of $CH_2Br_2$ and $CH_2BrCH_2Br$ in the bromine addition experiments using the correction factor of 2.44 mentioned earlier and explained in the Appendix. Again the results of the $CD_3Cl$–HI experiments are in qualitative agreement with these values if we consider the quantum yields of $CD_2H_2$ (Table 2) as a relative measure of process (3).

### *4.4. Secondary reactions*

Since the nature of the primary photochemical processes is reasonably well understood, there remains the determination of the reactions of the primary fragments which lead eventually to the observed product distributions in the photolytic experiments. Because process (1) is the most important reaction, the fate of methyl radicals and chlorine atoms will be examined first. Methane is an important product in every case. Apparently, the methyl radicals abstract hydrogen atoms from some source. That source, as mentioned previously, may be either a second molecule of $CH_3Cl$ (reaction (6)) or a molecule of HCl (reaction (7)) which itself may be formed by the abstraction of a hydrogen atom by chlorine (reaction (5)). It should be noted that the concentration of HCl will increase with time. Thus the abstraction of hydrogen from HCl will predominate as the reaction progresses and will compete more favorably with radical recombination reactions such as (13) and (16). In any case the result is the same, *i.e.* the formation of one molecule of methane and two $CH_2Cl$ radicals. The only pathway for reaction of $CH_2Cl$ radicals at room temperature is with another radical, such as reactions (8) - (15), (19) and (22). The final products derived from these radical–radical reactions are given in Table 1. The quantum yields for most of these products are independent of pressure. However, the quantum yields of vinyl chloride and 1,2-dichloroethane vary in a complementary fashion, which suggests that the production of these species is mechanistically related. Reactions (9) - (11) satisfy such a relation in which an increase in pressure results in a decrease in formation of vinyl chloride and an increase in the dimer $CH_2ClCH_2Cl$. This relation is verified by a Stern–Volmer plot of $\phi(C_2H_3Cl)/\phi(CH_2ClCH_2Cl)$ *versus* the reciprocal pressure which is shown in Fig. 1. Included in this graph are the results from Setser and Siefert [14] for the combination reaction of thermalized $CH_2Cl$ radicals. The fact that the experimental data all fall on the same line indicates that the above mechanism adequately accounts for the results at all wavelengths and pressures examined.

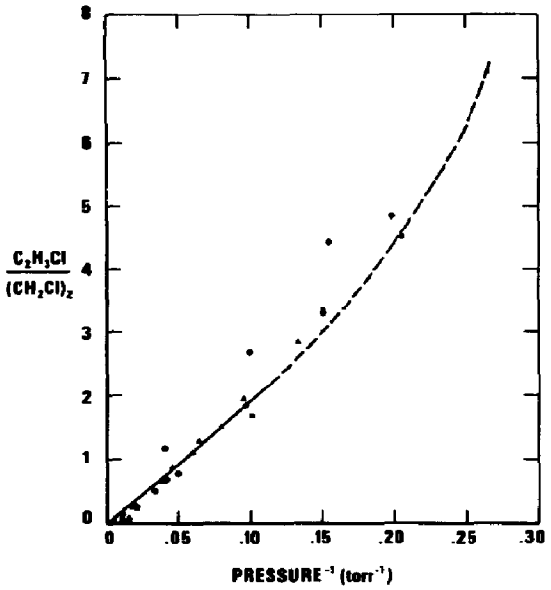


**Fig. 1. Variation of the $[C_2H_3Cl]/[(CH_2Cl)_2]$ ratio with reciprocal pressure: ●, 163.3 nm; ■, 147.0 nm; ◆, 123.6 nm; ▲, data from ref. 14.**

The slight upward curvature at low pressures may result from a stepwise deactivation of vibrationally excited $CH_2ClCH_2Cl$, as was suggested by Setser and Siefert.

A second pair of products which exhibit a similar relation are ethylene and chloroethane. Reactions (13) - (15) describe their formation. However, a graph similar to Fig. 1 can only be made for high pressures since only small amounts of chloroethane are produced, particularly at low pressures, and our measurements under these conditions are inaccurate. Some of the high pressure data are plotted in Fig. 2 together with some of the data of Clark *et al.* [15]. The data on this plot are not precise enough to reveal curvature clearly, but stepwise deactivation would be expected. Owing to the limited accuracy of these data it is impossible to exclude formation of ethylene from other mechanisms and some is apparently formed by other processes such as reactions (18), (19), (21) and (23).

Further support for the occurrence of these combination and decomposition processes may be obtained by examining the results from the liquid phase experiment at 147.0 nm. In this experiment the major reaction of methyl radicals is hydrogen abstraction from the solvent or HCl, since the relative quantum yield of ethane in the liquid phase is reduced by a factor of about 40 from the gas phase value. The resulting $CH_2Cl$ radicals combine to form 1,2-dichloroethane which is stabilized immediately and so does not produce any vinyl chloride. Similarly, a small amount of chloroethane is formed, while the formation of ethylene is almost completely quenched. Thus the rapid quenching of vibrationally excited molecules in the liquid phase prevents the formation of vinyl chloride and ethylene.

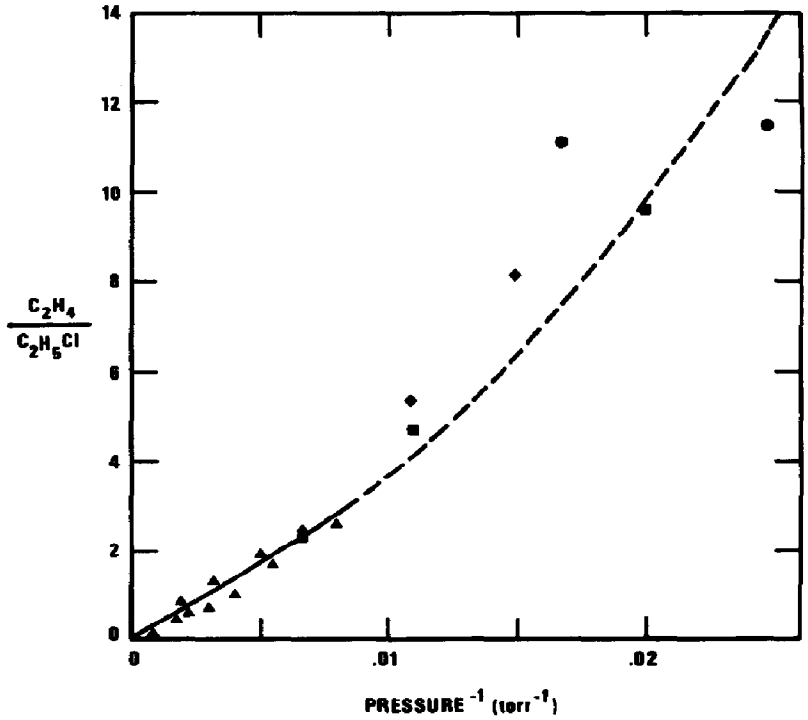


Fig. 2. Variation of the $[C_2H_4]/[C_2H_5Cl]$ ratio with reciprocal pressure: ●, 163.3 nm; ■, 147.0 nm; ◆, 123.6 nm; ▲, data from ref. 15.

Besides radical combinations, radical disproportionations (reactions (8) and (12)) may also occur and may compete with the combination reactions. The presence of $CH_2Cl_2$ as a product is diagnostic for the disproportionation reaction (8a). The ratio $\phi(CH_2Cl_2)/\{\phi(C_2H_3Cl) + \phi(CH_2ClCH_2Cl)\}$ should give an accurate measure of the disproportionation combination ratio $k_{8a}/k_9$ for $CH_2Cl$ radicals. The average value obtained for this ratio from both liquid and gas phase experiments from 213.9 to 123.6 nm is 0.16 ± 0.03. (Data for this calculation are not given in the tables.) It is not possible from the available data to determine the corresponding ratio for reactions (12 a) - (13). However, since a statistical factor of $\frac{1}{2}$ should apply, $k_{12a}/k_{13} \approx 0.08$ may be tentatively assumed.

The chemistry of methylene is more complex. Singlet $CH_2$ is known to insert into methane to produce $C_2H_6^*$ [16]. Neither $CH_2$ nor CHCl inserts significantly into methyl chloride, since the resulting products, chloroethane in one case and vinyl chloride and dichloroethane in the other, are not formed in the presence of NO. Small amounts of ethylene are formed in presence of NO to the extent of about 10% of that formed in absence of NO. The reaction of singlet $CH_2$ (and presumably CHCl) with NO is slow [16]. Thus singlet $CH_2$ must either undergo an intersystem crossing to the triplet and/or abstract a hydrogen or a chlorine atom from the bulk methyl chloride. The abstraction of a chlorine atom by CHCl from $CH_3Cl$ (reaction (20b)) forms a $CHCl_2$ radical which might further react to give $CH_2Cl_2$. The ratio $k_{8a}/k_9$

calculated above remains nearly constant, however, even at different wavelengths, suggesting that the amount of $CH_2Cl_2$ formed by this process is small. Hydrogen abstraction by CHCl from methyl chloride would simply result in the formation of two $CH_2Cl$ radicals. Setser *et al.* [17] have concluded that the methylene generated from ketene or diazomethane photolysis does not insert into methyl chloride but rather abstracts a chlorine or hydrogen atom. This observation together with the lack of chloroethane formation in the presence of NO in our experiments strongly suggests that reaction (17) is the predominant process for $CH_2$ in our system. Radical–radical reactions such as (18), (19), (21) and (22) may also occur to some extent.

It seems probable that the 10% of ethylene ($\phi$ = 0.01) which is not quenched by NO addition at 123.6 nm arises from the insertion of CH into $CH_3Cl$ with the subsequent loss of a chlorine atom. A similar process occurs in the photolysis of methane [18] at the same wavelength. In a similar way the small amounts of acetylene ($\phi$ = 0.004) formed at 123.6 nm and unchanged by the addition of NO may arise from carbon atom insertion into $CH_3Cl$ and the subsequent HCl elimination. However, the larger yields of acetylene ($\phi$ = 0.03) formed at the longer wavelengths cannot result in this way since there is not enough energy to form carbon atoms. It seems probable at these wavelengths that the vinyl chloride formed by reactions (10), (22) or (25) is still vibrationally excited and may decay further to acetylene and HCl. The yields of acetylene at these longer wavelengths do seem to decrease with an increase in pressure. The methane yield in the presence of NO is reduced to 5.8% of its unscavenged value. This suggests that a small fraction of the methyl radicals produced are "hot" enough to abstract a hydrogen from $CH_3Cl$ in the presence of a radical scavenger such as NO. The hydrogen yield was reduced to only about half of its unscavenged value and the isotopic distribution was essentially unchanged. Thus, most of the hydrogen produced is either molecular or "hot" enough to form hydrogen without interference from NO.

As a final check on the reliability of the mechanistic analysis of the photolysis of methyl chloride, the total quantum yields for methyl radicals and chloromethyl radicals can be calculated from the quantum yields of final products and the mechanism assumed above. The total quantum yield of methyl radicals is given by

$$\phi(CH_3) = \phi(CH_4) + 2\phi(C_2H_6) + \frac{1.00}{0.92}\{\phi(C_2H_4) + \phi(C_2H_5Cl)\} \qquad \text{(I)}$$

and the total quantum yield of chloromethyl radicals is given by

$$\phi(CH_2Cl) = \frac{1.00}{0.92}\{\phi(C_2H_4) + \phi(C_2H_5Cl)\} + 2\,\frac{1.00}{0.84}\{\phi(C_2H_4Cl_2) + \phi(C_2H_3Cl)\} \qquad \text{(II)}$$

In the derivation of the above equations it was assumed for simplicity that reactions (8b) and (12b) are not important and that the reactions of $CH_2$ and CHCl are not critical in the calculations. At the shorter wavelengths in particular this is not true and the calculated quantum yield for methyl radicals will be larger than expected from process (1) exclusively. The values calculated from eqns. (I) and (II) are given in Table 1. They are certainly in qualitative agreement with the bromine and HI addition experiments. In all cases the quantum yields of methyl radicals show a decrease with decreasing wavelength. Also the quantum yield of chloromethyl radicals is larger than that of methyl radicals. This is in agreement with the hypothesis that each methane molecule formed results in the formation of a second chloromethyl radical. There is a deficiency of $CH_2Cl$, however, since in general $\phi(CH_2Cl) < \phi(CH_3) + \phi(CH_4)$. In view of the simplifying assumptions which were made, the disagreement is not severe.

As seen in Table 6, the quantum yield for process (1) decreases with a decrease in wavelength, while processes (2), (3) and (4) all increase. However, there seems to be a slight overall decrease in the total quantum yield at the shorter wavelengths. It is at these wavelengths that the methylene-type radicals are becoming more important. Perhaps the corrections which were applied are not accurate enough. This is especially true for the CHCl radical.

## 5. Conclusions

The results in Table 6 show that there is a distinct change in the primary photochemistry of chloromethane as the energy of the exciting photon increases. At 163.3 nm more than 86% of the photoexcited molecules react by simple chlorine atom elimination as shown in process (1). At the shorter wavelengths the processes involving loss of hydrogen or HCl become more important, so that at 123.6 nm all four major primary processes occur with approximately comparable probability. These changes in photochemistry may be associated with the different regions of the spectrum which are involved in the excitation process. The 163.3 nm irradiation falls within the lowest band of the absorption spectrum. This broad band has its maximum at about 172 nm and it has been assigned to the $\sigma^* \leftarrow n$ transition of an electron in the C—Cl bond [19]. It is therefore gratifying to find that most of the chemistry occurring at this wavelength involves simple C—Cl bond cleavage.

At shorter wavelengths the absorption spectrum becomes more complex. Light at 147.0 nm excites a region of the spectrum which is thought partially to involve the $4S \leftarrow n$ Rydberg transition of chlorine and light at 123.6 nm is thought to excite the $5P \leftarrow n$ transition [19]. This region of the spectrum, at least in the case of the unsubstituted methane, also involves excitation of electrons in the C—H bonding orbitals [19]. Thus, it may be speculated that some C—H excitation also occurs in this same region for chloromethane and dissociation is immediate, *i.e.* before most of the internal energy flows into the C—Cl bond. In any case the results in this work do attest to

the fact that at these shorter wavelengths a large fraction of the chemistry involves the C—H bonds. While more detailed speculation about the possible correlations between the photochemistry and spectroscopy of this molecule is not warranted at this time, it is clear that these results represent a significant step forward toward the goal of correlating the results of photochemistry with those of spectroscopy. It remains to be seen whether similar correlations can be made on related molecules. Work on this problem is in progress at this laboratory.

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## Appendix

The factor of 2.44 which was applied to the experiments noted in the text in order to account for the inefficiency in scavenging of $CH_2$ by bromine was determined by performing several related experiments involving the photolysis of methane in the presence of bromine at 123.6 nm. The results of these experiments are given in Table AI. Previously, it was determined that the quantum yield of $CH_2$ formation from the photolysis of methane at 123.6 nm is 0.80 [A1]. Presumably the remainder consists largely of $CH_3$, *i.e.* $\phi(CH_3) = 0.2$. Any methyl radicals which are formed will react with bromine to produce methyl bromide. The methylene is assumed to be produced initially in the singlet state so as to conserve spin. This singlet methylene reacts very rapidly with methane ($k = 1.9 \times 10^{-12}$) [A2] by insertion to produce vibrationally excited ethane which mainly dissociates at the pressures used to form two methyl radicals. Experimentally only traces of $C_2H_6$ and $C_2H_5Br$ ($\phi \leqslant 0.008$) were observed. However, not all of the singlet methylene undergoes this insertion reaction. The remainder is deactivated by collision with methane to give the triplet methylene. Thus, we have

$$^1CH_2 + CH_4 \rightarrow C_2H_6^* \quad \text{(A1)}$$

$$C_2H_6^* \rightarrow 2CH_3 \quad \text{(A2)}$$

$$^1CH_2 + CH_4 \rightarrow {}^3CH_2 + CH_4 \quad \text{(A3)}$$

These two reactions, insertion and deactivation, are assumed to be rapid enough to preclude reaction of singlet methylene with bromine. The triplet methylene above therefore reacts with bromine to give $CH_2Br_2$ and $CH_2BrCH_2Br$ by the following reactions:

$$^3CH_2 + Br_2 \rightarrow CH_2Br_2^* \quad \text{(A4)}$$

$$CH_2Br_2^* \rightarrow CH_2Br + Br \quad \text{(A5)}$$

$$CH_2Br_2^* + M \rightarrow CH_2Br_2 + M \quad \text{(A6)}$$

$$CH_2Br + Br_2 \rightarrow CH_2Br_2 + Br \quad \text{(A7)}$$

$$2CH_2Br \rightarrow CH_2BrCH_2Br \quad \text{(A8)}$$

Evidence for the non-reactivity of the singlet methylene with bromine under the conditions used is found by observing the reaction in the presence of an inert gas such as xenon. Collisions with xenon deactivate the singlet to triplet methylene. Thus the methyl bromide yield decreases while the yields of $CH_2Br_2$ and $CH_2BrCH_2Br$ increase, as is to be expected when xenon is added to the $CH_4$–$Br_2$ mixtures.

If we accept from the previous study [AI] that in the photolysis of methane at 123.6 nm $\phi(CH_2) = 0.80$, then in the presence of bromine this same value should be obtained. However, as is seen in Table A1 this is not the case. For each experiment $\phi(CH_2)$ is considerably below 0.80. This value has been calculated by the following equation:

TABLE A1

Photolysis of $CH_4$–$Br_2$ mixtures at 123.6 nm and 295 K

| Pressure (torr) | | | Quantum yields | | | $\phi(CH_2)$[a] | Correction factor[b] |
|---|---|---|---|---|---|---|---|
| $CH_4$ | $Br_2$ | Xe | $CH_3Br$ | $CH_2Br_2$ | $(CH_2Br)_2$ | | |
| 7.2 | 0.7 | | 0.58 | 0.22 | 0.014 | 0.435 | 2.48 |
| 18.7 | 1.4 | | 0.60 | 0.21 | 0.015 | 0.435 | 2.55 |
| 29.9 | 0.5 | | 0.74 | 0.18 | 0.021 | 0.493 | 2.38 |
| 29.9 | 3.9 | | 0.51 | 0.22 | 0.010 | 0.408 | 2.71 |
| 108 | 5.2 | | 0.59 | 0.20 | 0.018 | 0.436 | 2.52 |
| 30 | 0.6 | 317 | 0.42 | 0.32 | 0.017 | 0.460 | 1.97 |
| 7.2 | 0.6 | 725 | 0.32 | 0.28 | 0.011 | 0.340 | 2.46 |

[a]See eqn. (A1).
[b]See Appendix.

$$\phi(CH_2) = \{\phi(CH_3Br) - 0.2\}/2 + \phi(CH_2Br_2) + 2\phi(CH_2BrCH_2Br) \quad \text{(AI)}$$

Since the reaction of bromine with methyl radicals produced from the singlet methylene should be straightforward [9], there must be a significant inefficiency in the scavenging of triplet methylene by bromine. Although the cause of this inefficiency is unknown, perhaps involving wall reactions, a multiplication factor can be calculated which can be applied to the observed $^3CH_2$ product yields in order to bring the observed total methylene yield to 0.80. These calculated correction factors are listed in Table A1. They have been calculated according to the following equation:

$$\text{correction factor} = \frac{0.80 - \phi(^1CH_2)}{\phi(^3CH_2)}$$

where

$$\phi(^1CH_2) = \frac{\phi(CH_3Br) - 0.2}{2}$$

and

$$\phi(^3CH_2) = \phi(CH_2Br_2) + 2\phi(CH_2BrCH_2Br)$$

The average value is 2.44 ± 0.09. This correction factor has been applied to the observed yields of $CH_2Br_2$ and $CH_2BrCH_2Br$ in the methyl chloride experiments.

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