

## PHOTOCHEMICAL REACTION OF CHLOROFORM

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**Abstract** – The photochemical reactions of the neat chloroform and the aqueous chloroform in the absence (saturated with argon) and presence of O<sub>2</sub> (saturated with air or oxygen) have been investigated using 184.9 nm UV light. The irradiation of the deoxygenated neat chloroform causes the formation of hexachloroethane, pentachloroethane, and 1,1,2,2-tetrachloroethane. The initial quantum yields of the products were determined to be  $6.37 \times 10^{-4}$ ,  $4.04 \times 10^{-4}$  and  $1.76 \times 10^{-4}$ , respectively. In the irradiation of aqueous chloroform, chloride ion was also formed along with the products listed above and 1,1,2,2-tetrachloroethane was the predominant product among the chlorinated organic products, which contrasts to the case of the neat chloroform. The presence of oxygen during the irradiation of aqueous chloroform had an effect on the yield of the products. With increasing the concentration of oxygen, the formation of the products was decreased. Probable reaction mechanisms for the photochemical reaction were presented on the basis of products analysis.

### INTRODUCTION

Photochemical reactions of chlorinated organic compounds have recently attracted considerable renewed attention.<sup>1–4</sup> Specifically, they are important in incineration of waste products, and in the production of hydrocarbons by oxidative pyrolysis and in atmospheric chemistry as well. Harris *et al.* reported that the near ultraviolet photolysis of halomethanes formed  $\cdot\text{CH}_3$  and  $\cdot\text{X}$  ( $\cdot\text{X} = \cdot\text{Cl}, \cdot\text{Br}, \cdot\text{I}$ ) radicals.<sup>5</sup> Some studies on the photolysis of chloroform in gas phase were reported that the electronically excited chloroform is splitted mainly into  $\cdot\text{CHCl}_2$  and  $\cdot\text{Cl}$  radicals.<sup>6</sup> In the irradiation of neat chloroform, it was only deduced that  $\cdot\text{Cl}$  radical might be abstracted from the excited neat chloroform on the basis of the results from the irradiation of halogenated methanes such as  $\text{CHI}_3$  and  $\text{CH}_2\text{Cl}_2$ ; iodine and chlorine radicals were abstracted from  $\text{CHI}_3$  and  $\text{CH}_2\text{Cl}_2$ , respectively.<sup>6,7</sup> Particularly,  $\cdot\text{Cl}$  radical abstraction from the chloroform was observed in the irradiation of chloroform containing the other chemicals.<sup>8</sup> However, the photochemical reaction of neat chloroform solution have not been studied so extensively to date and much less information is available on the quantitative investigation of the photochemical reactions of the neat chloroform and the aqueous chloroform solution. Herein, we report the results of the photochemical reactions of the neat chloroform and the aqueous chloroform solution in the absence and the presence of oxygen using vacuum UV light of 184.9 nm to suggest the mechanism of the

photochemical reaction. Particularly, oxygen may affect the consecutive photochemical reaction during the irradiation of aqueous chloroform solution.

### MATERIALS AND METHODS

*Lightsources and Actinometry.* Osram low pressure mercury resonance lamp (HNS 12/oz) was used as the light source, which emitted the two monochromatic lights of 184.9 nm and 253.7 nm. The lamp was mounted in a quartz tube which was surrounded by the solution to be irradiated. Actinometry of the lamp has been described in detail in the previous work.<sup>9</sup> The lamp intensity was found to be  $5.51 \times 10^{17}$  quanta  $\cdot\text{mL}^{-1} \cdot\text{min}^{-1}$  at 25°C. It corresponds to about 25% of the number of quanta at 253.7 nm. The intensity of the lamp was not changed over the period of the experiment.

*Reagents and General.* Chloroform (99.9% A.C.S. HPLC grade) was purchased from Aldrich Chemical Co. and purified by fractional distillation after washing with water to remove the ethanol, drying with  $\text{CaCl}_2$ , and refluxing with  $\text{CaCl}_2$ . No significant amount of impurities from chloroform was detected by gas chromatography with a flame-ionization detector. All other chemicals were reagent grade and used without further purification. Aqueous chloroform solution was prepared using quadruply distilled water, which was obtained by passing the distilled water through Barnstead (U.S.A.) Nonopure II deionization system. In cases of irradiating air-free aqueous chloroform, the distilled water and chloroform were first deaerated by bubbling high purity argon (99.999%) for about 60 min and then 0.04 M aqueous

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chloroform solution was prepared (solubility in water: 0.5 ml in 100 ml). The freshly prepared solution (100 mL) was transferred into the irradiation vessel and bubbled again for about 3 min before the irradiation. The solution was then irradiated using low pressure Hg lamp. During the irradiation, the temperature was kept at  $25.0 \pm 0.1^\circ\text{C}$  by a waterbath circulator. The UV spectrum of aqueous chloroform was recorded on a Hitachi Model 557 UV-spectrophotometer. The molar extinction coefficient ( $\epsilon$ ) of aqueous chloroform solution at 184.9 nm was obtained  $18.4 \text{ M}^{-1}\text{cm}^{-1}$  by extrapolation. Aqueous chloroform solution did not absorb the simultaneously emitted light at 253.7 nm.

**Products analysis.** The irradiated aqueous chloroform solution was extracted with chloroform and then analyzed using a GC-MS system (HP 5890II GC and 5988 MS, ultra-2 capillary column,  $50 \text{ m} \times 0.33 \mu\text{m}$ , EI method); [product: m/z (relative intensity)]. hexachloroethane: 47(32), 94(30), 117(100), 164(35), 166(40), 201(85). 1,1,2,2-tetrachloroethane: 35(10), 83(100), 85(60), 131(15), 168(10). pentachloroethane: 35(20), 60(35), 83(45), 117(100), 130(30), 165(75), 167(90). 1,1,2,2,3,3-hexachloropropane: 73(10), 85(47), 130(100), 167(40), 179(10). 1,1,1,2,2,3,3-heptachloropropane: 83(100), 85(80), 119(50), 166(80), 201(30), 249(10). carbontetrachloride: 47(13), 82(20), 117(100). 1,1,2,3,3-pentachloropropane: 49(10), 83(70), 85(50), 96(100), 143(85), 145(70), 147(20), 181(2). The identifications were made by comparison with fragmentation patterns of known amounts of the pure substances. The identified products from the Mass spectra were reconfirmed by comparison with retention time of the separated GC peaks of the standard chemicals using a Varian Model 3700 gas chromatography (DB-624 capillary column  $50 \text{ m} \times 0.24 \mu\text{m}$ ). Qualitative analysis was performed by estimating the area ratio of the products and chlorobenzene as an internal standard. The amount of the chloride ion was determined by spectrophotometric method.<sup>10</sup> An aliquot (1 mL) of the irradiated solution was treated with ferric nitrate and mercury (II) thiocyanate as a complexing reagent. The molar extinction coefficient ( $\epsilon$ ) of colored complex was determined to be  $66700 \text{ M}^{-1}\text{cm}^{-1}$  at 440 nm in these experiments and it was not interfered by the presence of the other chlorinated organic compounds. Spectrophotometric determination of hydrogen peroxide was carried out by treating with acidic  $\text{TiCl}_4$  solution.<sup>11</sup> Absorbance maximum of the formed color was shown at 414 nm and its molar extinction coefficient ( $\epsilon$ ) at this wavelength was calculated to be  $4430 \text{ M}^{-1}\text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

The photolysis of deoxygenated liquid chloroform was studied as a function of the number of quanta. During the irradiation of the solution, hexachloroethane 1,1,2,2-tetrachloroethane and pentachloroethane were produced as major products. No products were observed during the irradiation at 253.7 nm. As shown in Fig. 1,

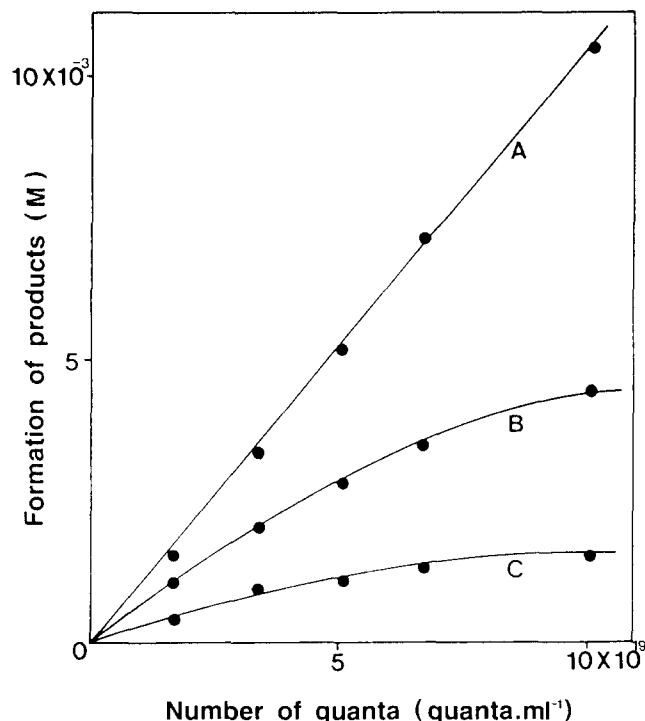
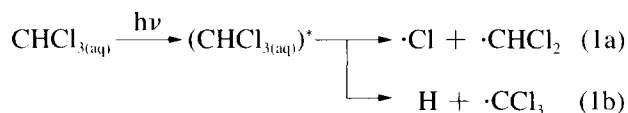


Figure 1. Formation of the products after irradiation of the deoxygenated liquid  $\text{CHCl}_3$  as a function of the number of quanta; A: hexachloroethane, B: pentachloroethane, C: 1,1,2,2-tetrachloroethane.

the formation of the products depends on the number of quanta in all cases. The tendency of the formation of the products was not linearly proportional to the increase of the number of quanta, indicating that a back reaction which contributes to the decomposition of the products occurred in the system by direct absorption of the UV light or by attack of the radicals formed during the photochemical reaction. Therefore, the initial quantum yields ( $Q_i$ ) were determined and summarized in Table I.

The formation of the products mentioned above indicates that the electronically excited chloroform by the absorption of 184.9 nm is splitted mainly into either  $\cdot\text{Cl}$  and  $\cdot\text{CHCl}_2$  radicals or  $\text{H}$  and  $\cdot\text{CCl}_3$  radicals as presented in process (1).

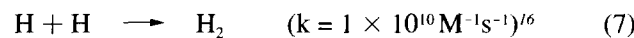
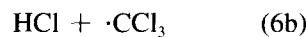
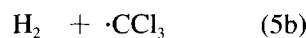
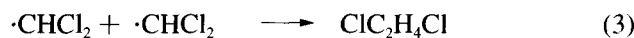


The primary radicals produced by reaction (1) react with each other to form hexachloroethane 1,1,2,2-tetrachloroethane and pentachloroethane as in reaction (2)-(4). Furthermore, the  $\text{H}$  and  $\cdot\text{Cl}$  radicals produced by the reaction (1) can attack chloroform as in reaction (5)-(6). This reaction facilitates the decomposition of chloroform and thereby much more  $\cdot\text{CHCl}_2$  and  $\cdot\text{CCl}_3$  radicals are reproduced. The hydrogen radical can react

Table 1. Initial quantum yield ( $Q_i$ ) of the products after irradiation of the deoxygenated neat  $\text{CHCl}_3$  at 184.9 nm

Products	Initial quantum yield ( $Q_i$ )
Hexachloroethane	$6.37 \times 10^{-4}$
Pentachloroethane	$4.04 \times 10^{-4}$
1,1,2,2-tetrachloroethane	$1.76 \times 10^{-4}$

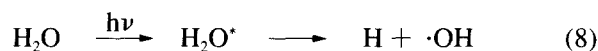
with each other to produce hydrogen molecule as in reaction (7). However, it can predominantly react with chloroform producing  $\cdot\text{CHCl}_2$  and  $\cdot\text{CCl}_3$  radicals in reactions (5) because the reaction probability of the reactions (5), defined by product of concentration and rate constant, is greater than that of the reaction (7). To test this hypothesis, we attempted to detect hydrogen molecules produced by the irradiation, but the yield of hydrogen molecules formation was so small that it could be negligible. This result supports that the hypothesis described above is reasonable. In the same manner, the formation of chlorine can also be negligible.



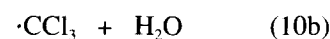
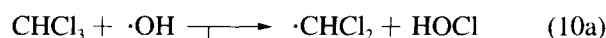
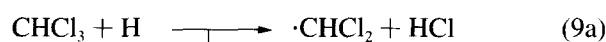
However, the initial quantum yield of hexachloroethane is greater than that of 1,1,2,2-tetrachloroethane in the irradiation of neat chloroform at 184.9 nm as shown in Table 1. It means that  $\cdot\text{CCl}_3$  radical is produced much more than  $\cdot\text{CHCl}_2$  radical in the irradiation of neat chloroform at 184.9 nm. The similar abstraction was observed in the radiolysis<sup>12</sup> and in the pyrolysis of chloroform,<sup>13</sup> although the C-Cl bond has a weak bond dissociation energy in chloroform. This result is quite different from the literature data, which deduced a halogen radical was abstracted in the near ultraviolet photolysis of halomethanes.<sup>6,7</sup>

In the irradiation of 0.04 M deoxygenated aqueous chloroform solution, chloride ion was also produced as major product in addition to hexachloroethane, pentachloroethane and 1,1,2,2-tetrachloroethane, although it was not detected in the irradiation of neat chloroform. In deoxygenated aqueous chloroform solution,  $\text{CHCl}_3$  and  $\text{H}_2\text{O}$  species absorb 184.9 nm light. The molar

extinction coefficient ( $\epsilon$ ) of  $\text{CHCl}_3$  at 184.9 nm was calculated to be  $18.4 \text{ M}^{-1}\text{cm}^{-1}$  by extrapolation and  $\epsilon$  of  $\text{H}_2\text{O}$  was reported<sup>14</sup> to be  $0.032 \text{ M}^{-1}\text{cm}^{-1}$ . From the calculation using these values, it was found that ca 70% of the 184.9 nm light was absorbed by water and ca 30% of the light was absorbed by chloroform in case of 0.04 M aqueous chloroform solution. It appears that the photochemical decomposition of aqueous chloroform solution was mainly initiated by an attack of the primary radicals formed during the photolysis of water under the given initial concentration of aqueous chloroform. Getoff *et al.* reported<sup>15</sup> that the electronically excited water by the absorption of 184.9 nm light (ca 6.70 eV) is splitted mainly into H and  $\cdot\text{OH}$  radicals as presented in the process (8).



The H and  $\cdot\text{OH}$  radical produced by the process (8) can attack chloroform, leading to form either  $\cdot\text{CCl}_3$  radical or  $\cdot\text{CHCl}_2$  radical as in reactions (9) and (10).



However, in the irradiation of aqueous chloroform solution, the initial quantum yield of 1,1,2,2-tetrachloroethane is greater than that of hexachloroethane as shown in Table 2. It means that H and  $\cdot\text{OH}$  radical produced by the reaction (8) can attack chloroform to form the  $\cdot\text{CHCl}_2$  radical rather than  $\cdot\text{CCl}_3$  radical, which contrasts to the case of neat chloroform. The  $\cdot\text{CHCl}_2$  and  $\text{CCl}_3$  radicals may react with each other to form 1,1,2,2-tetrachloroethane, hexachloroethane, and pentachloroethane as in reactions (2)-(4). The formation of chloride ion can be rationalized by attack of H radical on chloroform as in reaction (9a). The HCl molecule produced by the irradiation of aqueous chloroform solution was dissociated in the aqueous solution. Besides, hyperchlorite can be obtained in the photochemical reaction, but its formation was not investigated further in this study. In addition to water, chloroform also absorbs the 184.9 nm light. Therefore, it is expected that the  $\cdot\text{CHCl}_2$  and  $\cdot\text{CCl}_3$  radicals produced by direct photolysis of chloroform also take part in the formation of the products.

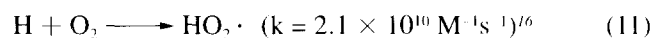
H and  $\cdot\text{OH}$  radical attack both chloroform and products formed during the irradiation as the number of quanta increases. As a result, the products are decomposed to produce some secondary radicals such as  $\cdot\text{CHClCCl}_2\text{H}$ ,  $\cdot\text{CCl}_2\text{CCl}_2\text{H}$ ,  $\cdot\text{CCl}_2\text{CCl}_3$  and  $\cdot\text{CHClCCl}_3$  radicals. This is the reason why the formation of the

Table 2. Initial quantum yield( $Q_i$ ) of the products after irradiation at 184.9 nm of 0.04 M  $\text{CHCl}_3$  aqueous solution in the absence and presence of  $\text{O}_2$ .

Products	$Q_i$ when saturated with		
	Ar	Air	$\text{O}_2$
Chloride ion	$3.28 \times 10^{-3}$	$3.91 \times 10^{-3}$	$4.52 \times 10^{-3}$
Hexachloroethane	$1.84 \times 10^{-3}$	$9.65 \times 10^{-4}$	$6.64 \times 10^{-4}$
Pentachloroethane	$3.04 \times 10^{-3}$	$2.21 \times 10^{-3}$	$1.16 \times 10^{-3}$
1,1,2,2-tetrachloroethane	$5.62 \times 10^{-3}$	$2.61 \times 10^{-3}$	$1.54 \times 10^{-3}$
1,1,2,2,3,3-hexachloropropane	$4.11 \times 10^{-4}$	$< 10^{-4}$	$< 10^{-4}$
1,1,1,2,2,3,3-heptachloropropane	$1.52 \times 10^{-4}$	$< 10^{-4}$	$< 10^{-4}$
Carbontetrachloride	$< 10^{-4}$	$< 10^{-4}$	$< 10^{-4}$
1,1,2,3,3-pentachloropropane	$< 10^{-4}$	$< 10^{-4}$	$< 10^{-4}$

products was not linearly proportional to the number of quanta. Although the initial quantum yields of these products are very small as shown in Table 2, 1,1,2,2,3,3-hexachloropropane, 1,1,1,2,2,3,3-heptachloropropane, carbontetrachloride, and 1,1,2,3,3-pentachloropropane can be formed by the combination of these secondary radicals. These secondary radicals combined not only with each other but also attacked the chloroform.

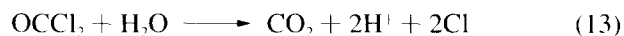
The formation of the chlorinated organic compounds was less in the irradiation of 0.04 M aqueous chloroform saturated with air than air-free aqueous chloroform as shown in Table 1. These behaviors can be interpreted as oxygen affects the photochemical process of aqueous chloroform. In the presence of oxygen, the produced H atoms may participate not only in the reaction (9) but also in the combination with oxygen very rapidly as in reaction (11). Therefore, in the aqueous chloroform solution saturated with air, chloroform was attacked by H atom less in the aqueous chloroform solution saturated with air than in the air-free solution.



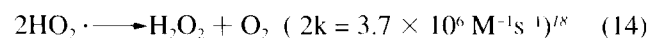
Since reactions (9) and (11) are competitive, the more  $\text{HO}_2 \cdot$  radical was produced, the less  $\cdot\text{CHCl}_2$  and  $\cdot\text{CCl}_3$  radicals were formed. On the other hand, the  $\cdot\text{CHCl}_2$  and  $\cdot\text{CCl}_3$  radicals can also react with oxygen very rapidly to produce chloromethylperoxide radicals such as  $\text{CHCl}_2\text{OO}\cdot$  and  $\text{CCl}_3\text{OO}\cdot$  because oxygen reacts generally with radicals very well.<sup>6</sup> As results, 1,1,2-tetrachloroethane, pentachloroethane, and hexachloroethane give lower yields in the irradiation of aqueous chloroform solution saturated with air. Especially, these chlorinated organic compounds in the presence of oxygen were the least produced as shown in Table 1. This result supports that the hypothesis described above is reasonable.

Koltzenburg *et al.* reported<sup>17</sup> that peroxide radicals are so unstable in aqueous solution that they are hydrolyzed. Recently, we suggested that  $\text{CHCl}_2\text{OO}\cdot$  radicals converted into  $\text{Cl}^-$  ion as in reaction (12)-(13).<sup>1</sup> The forma-

tion of chloride ion in the irradiation of aqueous chloroform saturated with air or oxygen greater than in the irradiation of air-free aqueous chloroform as shown in Table 1 can be explained by these reactions.



The  $\text{HO}_2 \cdot$  radical formed in reaction (11) is so unstable that it converted into hydrogen peroxide and oxygen *via* a disproportionation process as shown in reaction (14).



To prove this, the amount of hydrogen peroxide formed by the irradiation of aqueous chloroform was analyzed by the spectrophotometric method. In the irradiation of aqueous chloroform saturated with air and oxygen, hydrogen peroxide was detected. However, in the irradiation of air-free aqueous chloroform, it was not detected by the analytical method used in this study. These results indicate that oxygen plays an important role in the photochemical reactions.

In conclusion, in the irradiation of neat chloroform using 184.9 nm UV light, hexachloroethane, pentachloroethane and 1,1,2,2-tetrachloroethane were produced as major products. The fact that hexachloroethane was the predominant product among the chlorinated organic products implies that the electronically excited chloroform splitted into H and  $\cdot\text{CCl}_3$  radical rather than  $\cdot\text{Cl}$  and  $\cdot\text{CHCl}_2$  radical. However, in the irradiation of 0.04 M deoxygenated aqueous chloroform solution, chloride ion was also produced as major product in addition to hexachloroethane, pentachloroethane, and 1,1,2,2-tetrachloroethane. The fact that 1,1,2,2-tetrachloroethane was the predominant product among the chlorinated organic products indicates that the formation of  $\cdot\text{CHCl}_2$  radical is faster than that of  $\cdot\text{CCl}_3$  radical by attack of H

atom and  $\cdot\text{OH}$  radicals, contrasting to the case of the neat chloroform. In the presence of oxygen, the formation of the chlorinated organic products decreased, while the formation of chloride ion increased with increasing the concentration of oxygen. This is because the primary radicals, formed during the photolysis of aqueous chloroform solution, combined competitively with oxygen.

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