Photochemical Reaction of Dichloromethane in Aqueous Solution

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Received July 1, 1996

The photochemical reaction of aqueous dichloromethane in the absence (saturated with argon) and the presence of O_2 (saturated with air or oxygen) has been investigated using 184.9 nm UV light. The irradiation of the solution causes the formation of 1,2-dichloroethane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane and chloride ion. The initial quantum yield of the products in the absence of oxygen was determined to be 8.6×10^{-3}, 7.3×10^{-3}, 4.4×10^{-3} and 2.3×10^{-2}, respectively. In addition to these main products, small amounts of 1,2,3-trichloropropane, 1,1,2,2,3-pentachloropropane, 1,1,2,3,3-penta- chloropropane, 1,3-dichloropropane and 1,1,2,2,3, 3-hexachloropropane were detected. In the presence of oxygen, hydrogen peroxide was also detected along with the products listed above. With increasing the concentration of oxygen, while formation of the chlorinated organic products diminished, formation of chloride ion increased. Probable reaction mechanisms for the photochemical reaction were presented on the basis of products analysis.

Introduction

Chlorinated organic chemicals released from the manufacturing process in electronic and food processing factories can cause a serious environmental pollution. It is interesting to study the photochemical and radiation-induced decomposition of such chlorinated compounds. In the present study, we choose dichloromethane as a model substance, one of the most frequently used organic solvents in laboratory. Harris *et al.* reported the near ultraviolet photolysis of halomethanes forming $\dot{C}H_3$ and $\dot{X}$ (X=Cl, Br, I) radicals.[1] Numerous studies on the photolysis of chloromethane and chloroform in gas phase were reported in order to understand the reaction mechanism.[2-9] Recently, Su *et al.* described the photochemical reaction of gaseous CH_2Cl_2 at high temperatures (468-1355 K).[10] To our knowledge, there has been no report to date on the quantitative investigation of the photochemical reaction of aqueous dichloromethane solution. Here we report photochemical reaction of aqueous dichloromethane solution in the absence and the presence of oxygen using vacuum UV light of 184.9 nm to investigate the mechanism of the photochemical reaction. Oxygen may affect the consecutive photochemical reaction during the irradiation of aqueous dichloromethane solution.

Experimental

Reagents and General. Dichloromethane (Aldrich Chemical Co., 99.9% A.C.S. HPLC grade) was used as received. All other chemicals were reagent grade and used without further purification. Aqueous dichloromethane 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 dichloromethane, the distilled water and dichloromethane were first deaerated by bubbling for about 60 minutes with high purity argon (99.999%) and then 0.15 M aqueous dichloromethane solution was prepared (solubility in water: 1.629 g in 100 g). 100 mL of the

fresh prepared solution was transfered into the irradiation vessel and bubbled again for about 3 minutes before the irradiation. The solution was then irradiated using low pressure Hg lamp (Osram HNS 12/oz). During the irradiation, the temperature was kept at 25.0 ± 0.1 °C using a waterbath circulator. Actinometry of the lamp was described in detail in the previous work.[11] The lamp intensity was found to be 5.51×10^{17} quanta·mL^{-1}·min^{-1} at 25 °C. It corresponds to about 25% of the number of quanta at 253.7 nm which is emitted simultaneously from the lamp. No change in the intensity of the lamp was observed over the period of the experiment.

Analysis. In order to obtain the mass spectra of the products in the irradiated aqueous dichloromethane solution, the sample was prepared by extraction of the irradiated solution using dichloromethane as an extractant. The sample was then analyzed using a GC-MS system (HP 5890II GC and 5988 MS, ultra-2 capillary column, 50 m × 0.33 μm, EI method); [product: m/z (relative intensity)]. 1,2-dichloroethane: 35 (5), 49 (20), 62 (100), 64 (40), 98 (10). 1,1, 2-trichloroethane: 49 (10), 61 (50), 83 (90), 85 (60), 97 (100), 99 (80), 132 (10). 1,1,2,2-tetrachloroethane: 60 (10), 83 (100), 85 (90), 131 (20), 168 (10). 1,2,3-trichloropropane: 49 (20), 61 (25), 75 (100), 97 (25), 110 (50), 148 (2). 1,1,2, 2,3-pentachloropropane: 49 (15), 83 (50), 96 (70), 131 (100), 133 (85), 167 (5). 1,1,2,3,3-pentachloropropane: 61 (5), 83 (70), 85 (50), 96 (100), 143 (85), 145 (70), 147 (20), 181 (2). 1,3-dichloropropane: 39 (20), 41 (40), 76 (100), 78 (30), 112 (3). 1,1,2,2,3,3-hexachloropropane: 32 (7), 60 (5), 83 (70), 85 (50), 130 (100), 167 (40). The identifications were made by comparison with fragmentation patterns of known amounts of the pure substances. The identified products from the MS spectra were reconfirmed by comparison with retention times of the separated GC peaks of the standard chemicals using a Varian Model 3700 gas chromatography (DB-624 capillary column 50 m × 0.24 μm). 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.[12] 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 (ε) of colored complex was determined to be 66700 $M^{-1}cm^{-1}$ 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 $TiCl_4$ solution.[13] The absorbance maximum of the formed color appeared at 414 nm and its molar extinction coefficient (ε) at this wavelength was calculated to be 4430 $M^{-1}cm^{-1}$.

Results and Discussion

The photolysis of 0.15 M deoxygenated aqueous dichloromethane solution was studied as a function of the number of quanta. During the irradiation of the solution, 1,2-dichloroethane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane and chloride ion were produced as major products. No products were observed during the irradiation at 253.7 nm. As shown in Figure 1, the formation of the products depends on the number of quanta in all cases. The tendency of the formation of the products was not linear with the number of quanta; therefore, the first order rate law is inadequate. It indicates that a back reaction occured in the system, which contributes to the decomposition of the formed products, by direct absorption of the UV light or by attack of the radicals formed during the photochemical reaction. Thereby we determined only the initial quantum yields (Q_i) and summarized them in Table 1.

In the absence of oxygen. In deoxygenated aqueous dichloromethane solution, CH_2Cl_2 and H_2O species absorb 184.9 nm light. The molar extinction coefficient (ε) of CH_2Cl_2 at 184.9 nm was calculated to be 2.29 $M^{-1}cm^{-1}$ by ex-

trapolation and of H_2O was reported[14] to be 0.032 $M^{-1}cm^{-1}$. These values indicate that *ca.* 82% of the 184.9 nm light was absorbed by water and *ca.* 18% of the light was absorbed by dichloromethane in case of 0.15 M aqueous dichloromethane solution. It appears that the photochemical decomposition of dichloromethane was mainly initiated by attack of the primary radicals formed during the photolysis of water under the given initial concentration of aqueous dichloromethane.
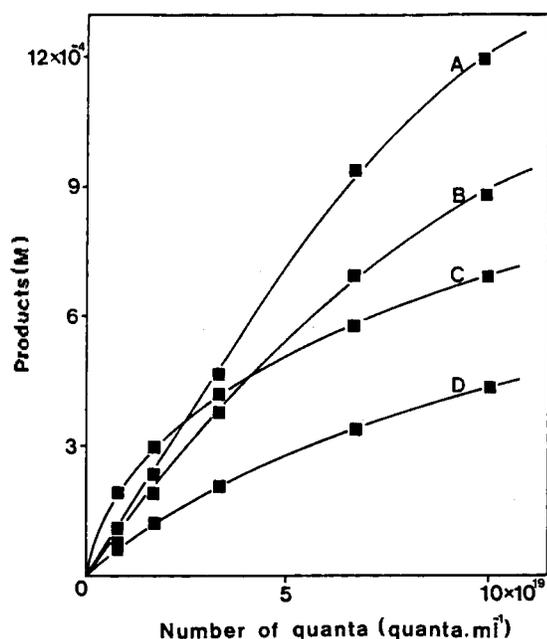
In the photolysis of water at 184.9 nm wavelength (*ca.* 6.70 eV), Getoff *et al.* reported[15] that the electronically excited water is splitted mainly into H and ȮH radicals as presented in the process (1).

$$H_2O \xrightarrow{\text{hv}} H_2O^* \longrightarrow H + \dot{O}H \qquad (1)$$
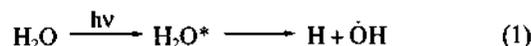
The hydrogen atom and ȮH radical produced by the process (1) can attack dichloromethane, leading to the formation of either $\dot{C}H_2Cl$ radical or $\dot{C}HCl_2$ radical as in reactions (2) and (3).

$$CH_2Cl_2 + H \longrightarrow \begin{cases} \dot{C}H_2Cl + HCl & (2a) \\ \dot{C}HCl_2 + H_2 & (2b) \end{cases}$$

$$CH_2Cl_2 + \dot{O}H \longrightarrow \begin{cases} \dot{C}H_2Cl + HOCl & (3a) \\ \dot{C}HCl_2 + H_2O & (3b) \end{cases}$$
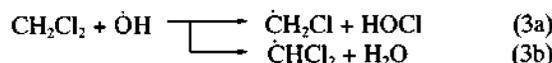
The $\dot{C}H_2Cl$ radicals produced by reactions (2) and (3) may react with each other to form 1,2-dichloroethane as in reaction (4). In the same manner, the $\dot{C}HCl_2$ radicals may react with each other to produce 1,1,2,2-tetrachloroethane as in reaction (5). Since the initial quantum yield of 1,2-dichloroethane is greater than that of 1,1,2,2-tetrachloroethane as shown in Table 1, it can be deduced that greater amount of $\dot{C}H_2Cl$ radical is produced than $\dot{C}HCl_2$ radical in the reactions (2) and (3). The formation of 1,1,2-trichloroethane can be explained by the combination of $\dot{C}H_2Cl$ and $\dot{C}HCl_2$ radicals as in reaction (6).

$$\dot{C}H_2Cl + \dot{C}H_2Cl \longrightarrow ClC_2H_4Cl \qquad (4)$$

$$\dot{C}HCl_2 + \dot{C}HCl_2 \longrightarrow Cl_2CHCHCl_2 \qquad (5)$$

$$\dot{C}H_2Cl + \dot{C}HCl_2 \longrightarrow ClCH_2CHCl_2 \qquad (6)$$

H atom and ȮH radical attack both dichloromethane and products with increasing the number of quanta. As a result, the products are decomposed, producing some secondary


Figure 1. Formation of the products after irradiation of deaerated 0.15 M CH_2Cl_2 aqueous solution as a function of the number of quanta; A: 1.2-dichloroethane, B: 1,1,2-trichloroethane, C: chloride ion, D: 1,1,2,2- tetrachloroethane.

Table 1. Initial quantum yield (Q_i) of the compounds after irradiation at 184.9 nm of 0.15 M CH_2Cl_2 aqueous solution in the absence and presence of O_2

Compounds	Q_i when saturated with		
	Ar	Air	O_2
Chloride ion	2.3×10^{-2}	4.6×10^{-2}	6.4×10^{-2}
1,2-dichloroethane	8.6×10^{-3}	8.1×10^{-3}	6.7×10^{-3}
1,1,2-trichloroethane	7.3×10^{-3}	6.8×10^{-3}	5.6×10^{-3}
1,1,2,2-tetrachloroethane	4.4×10^{-3}	3.9×10^{-3}	3.2×10^{-3}
1,2,3-trichloropropane	$<10^{-4}$	$<10^{-4}$	$<10^{-4}$
1,1,2,2,3-pentachloropropane	$<10^{-4}$	$<10^{-4}$	$<10^{-4}$
1,1,2,3,3-pentachloropropane	$<10^{-4}$	$<10^{-4}$	$<10^{-4}$
1,3-dichloropropane	$<10^{-4}$	$<10^{-4}$	$<10^{-4}$
1,1,2,2,3,3-hexachloropropane	$<10^{-4}$	$<10^{-4}$	$<10^{-4}$

radicals such as $ClĊ_2H_4$, $ClĊ_2H_3Cl$, $Cl_2CHCHCl$, $Cl_2CHĊCl_2$, $ClCH_2ĊHCl$, $ĊH_2CHCl_2$, $ClCH_2ĊCl_2$ and $ClĊHCHCl_2$ radicalsc as in reactions (7)-(12). This is the reason why the formation of the products was not linearly proportional to the number of quanta. 1,1,2,2,3-Pentachloropropane, 1,3-dichloropropane, 1,2,3-trichloropropane, 1,3-dichloro-1-propene, 1,1,2,3,3-pentachloropropane, and 1,1,2,2,3,3-hexachloropropane can be formed by the combination of these secondary radicals, although the initial quantum yields of these products are very small as shown in Table 1.

$$ClC_2H_4Cl + H \longrightarrow \begin{cases} ClĊ_2H_4 + HCl & \text{(7a)} \\ ClĊ_2H_3Cl + H_2 & \text{(7b)} \end{cases}$$

$$ClC_2H_4Cl + ȮH \longrightarrow \begin{cases} ClĊ_2H_4 + HOCl & \text{(8a)} \\ ClĊ_2H_3Cl + H_2O & \text{(8b)} \end{cases}$$

$$Cl_2CHCHCl_2 + H \longrightarrow \begin{cases} Cl_2CHĊHCl + HCl & \text{(9a)} \\ Cl_2CHĊCl_2 + H_2 & \text{(9b)} \end{cases}$$

$$Cl_2CHCHCl_2 + ȮH \longrightarrow \begin{cases} Cl_2CHĊHCl + HOCl & \text{(10a)} \\ Cl_2CHĊCl_2 + H_2O & \text{(10b)} \end{cases}$$

$$ClCH_2CHCl_2 + H \longrightarrow \begin{cases} ClCH_2ĊHCl + HCl & \text{(11a)} \\ ĊH_2CHCl_2 + HCl & \text{(11b)} \\ ClCH_2ĊCl_2 + H_2 & \text{(11c)} \\ ClĊHCHCl_2 + H_2 & \text{(11d)} \end{cases}$$

$$ClCH_2CHCl_2 + ȮH \longrightarrow \begin{cases} ClCH_2ĊHCl + HOCl & \text{(12a)} \\ ĊH_2CHCl_2 + HOCl & \text{(12b)} \\ ClCH_2ĊCl_2 + H_2O & \text{(12c)} \\ ClĊHCHCl_2 + H_2O & \text{(12d)} \end{cases}$$

The hydrogen atom can react with each other to produce hydrogen molecules as in reaction (13). But, it can predominantly react with dichloromethane producing $ĊH_2Cl$ and $Ċ$ HCl_2 radicals in reactions (2) because the reaction probability of the reactions (2), defined by product of concentration and rate constant, is greater than that of the reaction (13).

$$H + H \longrightarrow H_2 \; (k=1\times10^{10} \; M^{-1}s^{-1})^{16} \tag{13}$$
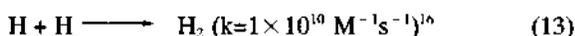
To test this hypothesis, we attempted to detect hydrogen molecules produced by the irradiation, but the yield of hydrogen molecules formation was too small to be detected and is considered to be negligible. This result supports that the hypothesis described above is reasonable.

The formation of chloride ion can be rationalized by attack of H atom to dichloromethane as in reaction (2). The HCl molecule produced by the irradiation of aqueous dichloromethane 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, dichloromethane also absorbs the 184.9 nm light. It is expected that the electronically excited dichloromethane by the absorption of 184.9 nm light is splitted mainly into $Ċl$ and $ĊH_2Cl$ radicals or H and $ĊHCl_2$ radicals as in reaction (14).

$$CH_2Cl_{2(aq)} \xrightarrow{h\nu} (CH_2Cl_{2(aq)})^* \longrightarrow \begin{cases} Ċl + ĊH_2Cl & \text{(14a)} \\ H + ĊHCl_2 & \text{(14b)} \end{cases}$$
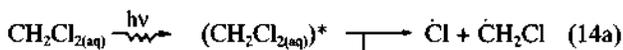
The $ĊH_2Cl$ and $ĊHCl_2$ radicals produced by direct pho-
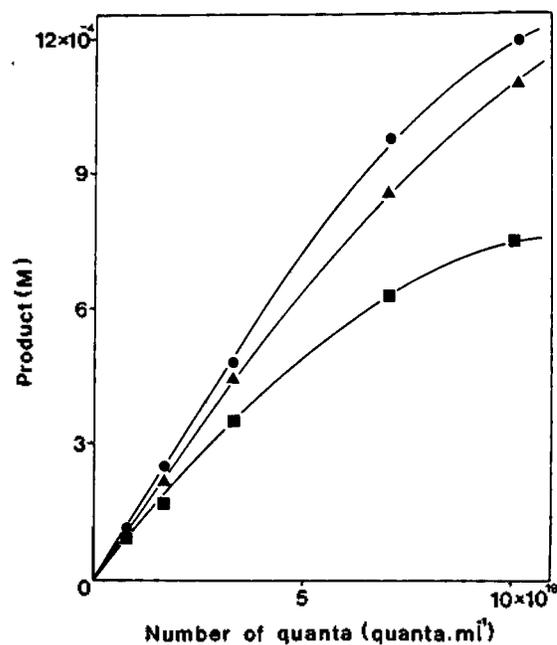
Figure 2. Formation of 1,2-dichloroethane after irradiation of 0. 15 M CH_2Cl_2 aqueous solution as a function of the number of quanta: (●) in the absence of O_2, (▲) in the saturation with air, (■) in the saturation with O_2.

tolysis of dichloromethane as shown in reaction (14) also take part in the formation of 1,2-dichloroethane, 1,1,2,2-tetrachloroethane and 1,1,2-trichloroethane as in reactions (4)-(6). The $Ċl$ and H atoms react with each other or attack dichloromethane and the other products. As a result, much more HCl molecules and $ĊHCl_2$ or $ĊH_2Cl$ radicals can be produced.

In the presence of oxygen. In the irradiation of 0.15 M aqueous dichloromethane saturated with air, the formation of 1,2-dichloroethane and 1,1,2,2-tetrachloroethane decreased as compared with the case of air-free aqueous dichloromethane as shown in Figures 2 and 3. The initial quantum yields of 1,2-dichloroethane, 1,1,2,2-tetrachloroethane and 1,1,2-trichloroethane decreased as compared with the case of air-free aqueous dichloromethane as shown in Table 1. These behaviors indicate that oxygen affects the photochemical process of aqueous dichloromethane. Formation of 1,2-dichloroethane, 1,1,2,2-tetrachloroethane and 1,1,2-trichloroethane could be initiated mainly by H and ȮH radical attack, produced by photolysis of water. In the presence of oxygen, however, the produced H atoms may participate not only in the reaction (2) but also in the combination with oxygen very rapidly as in reaction (15). Therefore, in the aqueous dichloromethane solution saturated with air, dichloromethane was less attacked by H atom than in the air-free solution.

$$H + O_2 \longrightarrow HȮ_2 \; (k=2.5\times10^{10} \; M^{-1}s^{-1})^{17} \tag{15}$$
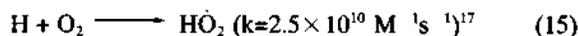
Since reactions (2) and (15) are competitive, less $ĊH_2Cl$ and $ĊHCl_2$ radicals formed in the irradiation of aqueous dichloromethane saturated with air. As a result, 1,2-dichloroethane and 1,1,2,2-tetrachloroethane formed by their dimerization process give lower yields. Furthermore, the $ĊH_2Cl$
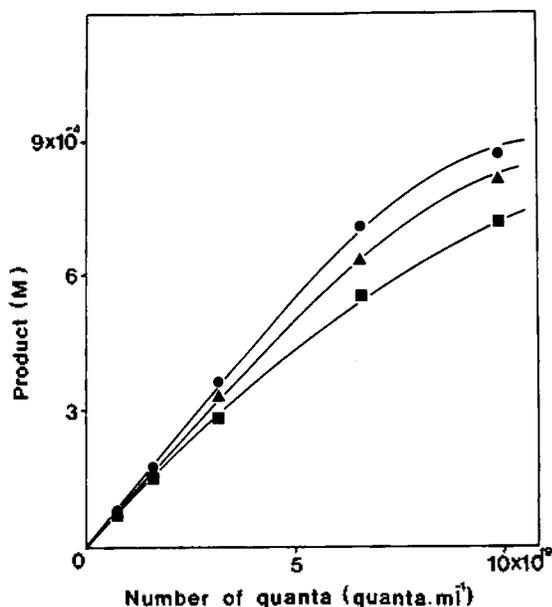
Figure 3. Formation of 1,1,2-trichloroethane after irradiation of 0.15 M CH_2Cl_2 aqueous solution as a function of the number of quanta: (●) in the absence of O_2, (▲) in the saturation with air, (■) in the saturation with O_2.


Figure 4. Formation of Chloride ion after irradiation of 0.15 M CH_2Cl_2 aqueous solution as a function of the number of quanta: (●) in the absence of O_2, (▲) in the saturation with air, (■) in the saturation with O_2.

and $\dot{C}HCl_2$ radicals can also react with oxygen very rapidly to produce chloromethylperoxide radicals such as $CH_2ClO\dot{O}$ and $CHCl_2O\dot{O}$ because oxygen reacts generally with radicals very well.[18] This fact can explain the reason why the formation of 1,2-dichloroethane and 1,1,2,2-tetrachloroethane in the air saturation condition decreased as compared with the case of air-free aqueous dichloromethane solution. Especially, 1,2-dichloroethane and 1,1,2,2-tetrachloroethane in the presence of oxygen were the least produced as shown in Figures 2 and 3. This result supports that the hypothesis described above is reasonable.

Asmus *et al.* reported[19] that peroxide radicals are so unstable in aqueous solution that they are hydrolyzed. Recently, Catoire and coworkers suggested in kinetic study of $CH_2ClO\dot{O}$ radicals in gas phase that the radicals converted into $\dot{C}H_2ClO$ species and then HCl is eliminated from the $CH_2Cl\dot{O}$ radical.[20] Therefore, we postulate that chloromethylperoxide radicals such as $CHCl_2O\dot{O}$ and $CH_2ClO\dot{O}$ converted to chloride ion *via* the reactions (16)-(19). The formation of chloride ion in the irradiation of aqueous dichloromethane saturated with air or oxygen greater than in the irradiation of air-free aqueous dichloromethane as shown in Figure 4 can be explained by these reactions.

$$CHCl_2O\dot{O} \longrightarrow \dot{O}H + OCCl_2 \tag{16}$$

$$OCCl_2 + H_2O \longrightarrow CO_2 + 2H^+ + 2Cl^- \tag{17}$$

$$2CH_2ClO\dot{O} \longrightarrow 2CH_2Cl\dot{O} + O_2 \tag{18}$$

$$CH_2Cl\dot{O} \longrightarrow H\dot{C}O + H^+ + Cl^- \tag{19}$$

The $H\dot{O}_2$ radical formed in reaction (15) is so unstable that it may convert to hydrogen peroxide and oxygen *via* a disproportionation process as shown in reaction (20).

$$2H\dot{O}_2 \longrightarrow H_2O_2 + O_2 \ (2k=3.7\times10^6 \ M^{-1}s^{-1})[21] \tag{20}$$
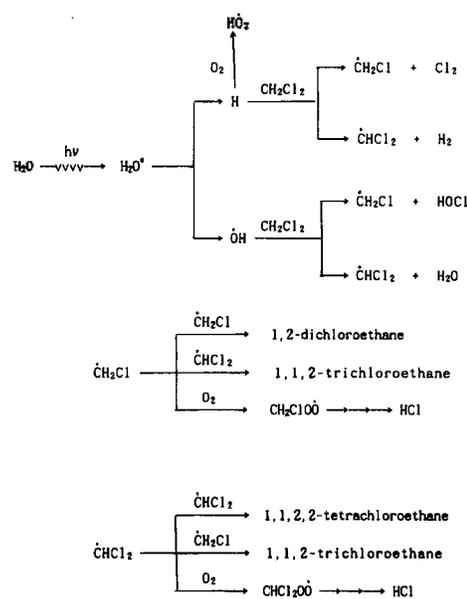
Scheme 1.

To prove this, the amount of hydrogen peroxide formed by the irradiation of aqueous dichloromethane was analyzed by the spectrophotometric method. In the irradiation of aqueous dichloromethane saturated with air and oxygen, hydrogen peroxide was detected. However, in the irradiation of air-free aqueous dichloromethane, 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 summary, in the irradiation of 0.15 M aqueous dichloromethane solution using 184.9 nm UV light, photochemical decomposition of dichloromethane was mainly initiated by attack of the H and $\dot{O}H$ radicals formed during

the photolysis of water. 1,2-Dichloroethane, 1,1,2-trichloro-ethane, 1,1,2,2-tetrachloroethane and chloride ion were produced as major products. Probable reaction mechanisms for the photochemical reaction were presented in Scheme 1.

The fact that 1,2-dichloroethane was the predominant product among the chlorinated organic products implies that the reaction producing $\dot{C}H_2Cl$ radical occurs at a faster rate than that producing $\dot{C}HCl_2$ radical by attack of H and $\dot{O}H$ radicals. With increasing the concentration of oxygen, while the formation of the chlorinated organic products diminished, the formation of chloride ion increased. This is because the primary radicals, formed during the photolysis of aqueous dichloromethane, combined competitively with oxygen. In particular, chloromethylperoxide radicals such as $CHCl_2O\dot{O}$ and $CH_2ClO\dot{O}$, which were produced by combination of oxygen either with $\dot{C}HCl_2$ radical or with $\dot{C}H_2Cl$ radical, increased the formation of chloride ion.

Acknowledgment. We thank Prof. N. Getoff in the University of Vienna, Austria for helpful discussions. KBSI (Korea Basic Science Institute) is acknowledged for the use of HP 5890II GC and 5988 MS spectroscopy.

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Monte Carlo Simulation on the Adsorption Properties of Methane in Zeolite L

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The adsorption of methane in K^+ ion exchanged zeolite L has been studied using grand canonical ensemble Monte Carlo simulation. Average number of molecules per unit cell, number density of molecules in zeolite, distribution of molecules per unit cell, average potential per sorbate molecule, and isosteric heats of adsorption were calculated, and these results were compared with experimental results. The simulation results agreed fairly well with experimental ones. All methane molecules were located in the main channel, and the average potential of sorbate molecule was almost constant regardless of average number of molecules per unit cell and the amounts sorbed in zeolite.

Introduction

Grand canonical ensemble Monte Carlo (GCMC) simu-

lation has been used to investigate adsorption in zeolites. Thermodynamic adsorption properties of hard sphere,[1] xenon,[2,3] methane[3] in zeolite X and Y have been reported.