

cyano-2-phenylethylene respectively (DMCPE). The proposed reaction mechanism was confirmed.

New polysulfide synthesized by terpolymerization of dibenzoylmethane, carbon disulfide, and α,α' -dichloro-*p*-xylene in the presence of benzyltriethylammonium chloride as a phase transfer catalyst shows reasonably higher yield and molecular weight than that obtained in previous report.³

The optimum reaction conditions for the terpolymerization were found to be 7.5 mmol of phase transfer-catalyst (quaternary ammonium salt type), 10% of NaOH solution, 60 °C-70 °C of reaction temperature, and 6 hours of reaction time in chloroform. Among the reaction variables, concentration of base and reaction temperature were considered to be the most important ones.

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Photolysis of Chlorobenzene in Aqueous Solution

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As the environmental pollution caused by halogenated aromatic compounds increased, these materials have been the hot subject of investigation in recent years.¹⁻³ Among the halogenated aromatic compounds, chlorobenzene is the simplest, best-utilized chloroaromatic compound. Chlorobenzene is a colorless, volatile liquid with an aromatic almond-like odor under standard environmental conditions. It is used primarily as a solvent (e.g. resins, dyes, rubbers, pesticides, and perfumes), a degreasing agent, and a chemical intermediate. Because chlorobenzene enters the environment from industrial and municipal discharge, it can be concentrated in the tissues and internal organs of fishes, animals and humans and it can pose significant human health hazards to large populations by its possible toxicity and carcinogenicity. Since the potential hazards of chlorobenzene on human health had been reported,⁴ considerably large number of investigations concerning photochemical behavior, transformation routes and accumulation in environment were carried out.⁵⁻¹¹ It is therefore important to investigate the photochemical reaction of chlorobenzene, because the waste water containing chloroaromatic pollutants could be purified or some organic compounds could be also synthesized by photochemical reaction.

Most of the photochemical behavior of chlorobenzene was investigated only in organic solvents such as cyclohexane,⁵ isopropanol⁶ and methanol.^{7,8} Sometimes methanol/water⁹ or acetonitrile/water mixtures^{10,11} were used, but photochemical studies on aqueous chlorobenzene solution have not been

studied so extensively because of its low solubility in water (510 mg/L at 25 °C).¹² Tissot *et al.* reported that photolysis of chlorobenzene in water-acetonitrile gives phenol via the shorted-lived (30 ns) triplet state and they proposed a mechanism involving photohydrolysis from the triplet state.¹³ It is important to measure the quantum yield, assess the effects of aerated and degassed solvent in order to clarify the reaction mechanism. The purpose of this study is to elucidate the mechanism concerning the photolysis reaction of aqueous chlorobenzene based on the products analysis.

Experimental

Reagents and General. Chlorobenzene, dichloromethane and methanol (Aldrich Chemical Co., 99.9% A.C.S HPLC grade) were used as commercial compounds without further purification. All other chemicals were reagent grade and used as received. Irradiations were carried out at 25 ± 0.1 °C using low pressure Hg lamp (Osram HNS 10W/U OFR). Low pressure Hg lamp is classified into two types depending on the method of its emitting wavelength; ozone generating lamp and ozone-free lamp.¹⁴ The ozone-free lamp used in this study emits only 253.7 nm UV light, but on the other hand ozone generating lamp emits two monochromatic lights of 184.9 and 253.7 nm. The irradiation vessel was of cylindrical shape fitted with a magnetic stirrer and a waterbath circulator maintained the solution temperature at 25 ± 0.1 °C. The intensity of the 253.7 nm light was

determined by monochloroacetic acid actinometer.^{15,16} The yield of chloride ion (Cl^-) formed after irradiation of aqueous monochloroacetic acid was measured by spectrophotometric method. The lamp intensity was found to be 2.07×10^{19} quanta $\cdot \text{mL}^{-1} \cdot \text{min}^{-1}$ at 25 °C from the known quantum yield, $Q(\text{Cl}^-) = 0.32$.^{15,16} No change in the intensity of the lamp was observed over the period of the experiments.

Aqueous chlorobenzene 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 order to prepare the air-free aqueous chlorobenzene solution, each of the compounds (distilled water and chlorobenzene) was first saturated by bubbling for about 60 minutes with Ar (99.999%) and then 3.54×10^{-3} M aqueous chlorobenzene solution was prepared. 80 mL of the freshly prepared solution was transferred into the irradiation vessel and bubbled again for about 3 minutes with Ar gas before the irradiation. Absorbance and UV-spectrum were recorded on Uvikon (model 943) spectrophotometer.

Products Analysis. In order to obtain the mass spectra of the products in the irradiated aqueous chlorobenzene solution, the sample was prepared by extraction of the irradiated solution using dichloromethane as an extractant. The sample prepared was then analyzed using a GC-MS system (HP 5890 II GC and JEOL SX-102A MS, DB-5, 30 m \times 0.25 μm capillary column, EI method); [product: m/z (relative intensity)]. phenol: 55(10), 65(22), 66(30), 94(100). benzene: 52(19), 63(4), 78(100). 2-phenylphenol: 63(5), 115(20), 141(30), 169(80), 170(100). 3-phenylphenol: 115(10), 141(20), 169(20), 170(100). 4-phenylphenol: 63(5), 115(15), 141(20), 179(100). biphenyl: 51(5), 76(15), 115(5), 152(30), 153(50), 154(100). The identifications were carried on comparison of fragmentation patterns with those of known amounts of the pure substances. The identified products from MS spectra were reconfirmed by comparison with retention times of the separated GC peaks of standard chemicals using a Varian Model 3700 gas chromatography (splitless mode, 60 °C/1 min., 10 °C/min., 270 °C/20 min., cp-sil 60 m \times 0.25 m capillary column). The quantitative analysis of the products identified from MS spectra was performed by estimating the area ratio of the products and methanol chosen as an internal standard material. The amount of the chloride ion¹⁷ was determined by spectrophotometric method and it was not interfered by the presence of the other chlorinated organic compounds.

Results and Discussion

The photolysis of 3.54×10^{-3} M deoxygenated aqueous chlorobenzene solution was studied as a function of the number of quanta. The solution in the presence of air was also investigated under the same experimental conditions. The results of the experiments were presented in Figure 1. During the irradiation of the solutions, phenol and chloride ion were mainly produced with benzene, 2-phenylphenol, 3-phenylphenol, 4-phenylphenol and biphenyl. The yield of the phenol and chloride ion as a function of the number of quanta was presented in Figure 2 and Figure 3, respectively. As shown in the Figures, the decomposition of chlorobenzene and the product yields were not increased in

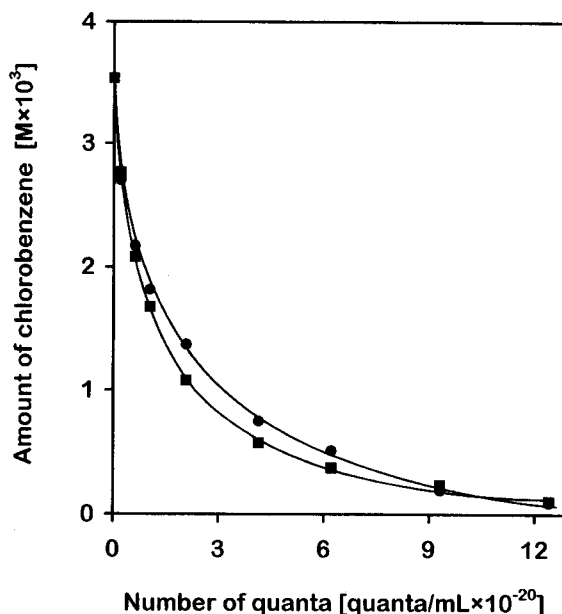


Figure 1. Amount of chlorobenzene after irradiation of 3.54×10^{-3} M aqueous chlorobenzene solution as a function of the number of quanta: (●) in the absence of air, (■) in the presence of air.

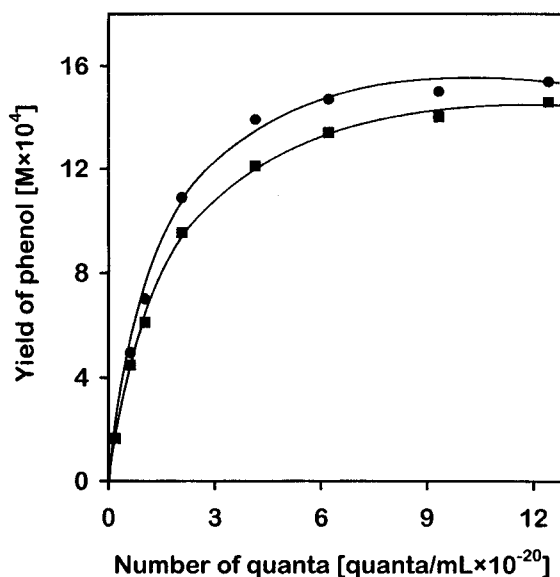


Figure 2. Formation of phenol after irradiation of 3.54×10^{-3} M aqueous chlorobenzene solution as a function of the number of quanta: (●) in the absence of air, (■) in the presence of air.

proportion to the number of quanta. This behavior indicates that some secondary reactions, which contributes to the formation of the other products, occurred in the system and that the obtained product was also decomposed by the absorption of the UV light or by an attack of the radicals formed during the photochemical reaction. Therefore, to avoid the interference of secondary reactions, we determined the initial quantum yields (Q_i), obtained from the slope of tangent line of the curve shown in the Figures and the results are summarized in Table 1.

In the irradiation of aqueous chlorobenzene solution by 253.7 nm UV light, H_2O did not absorb the light¹⁸ and only

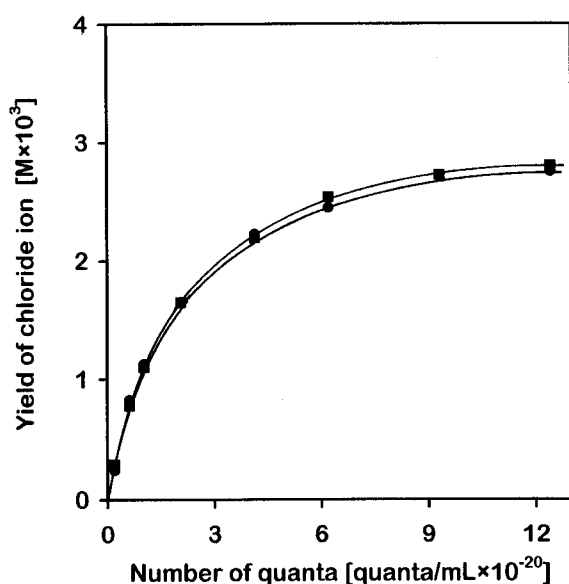


Figure 3. Formation of chloride ion after irradiation of 3.54×10^{-3} M aqueous chlorobenzene solution as a function of the number of quanta: (●) in the absence of air, (■) in the presence of air.

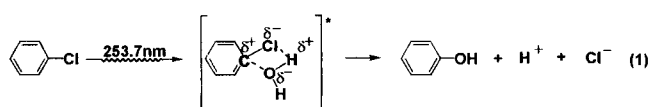
Table 1. Initial quantum yield (Q_i) of the compounds after irradiation ($\lambda=253.7$ nm) of 3.54×10^{-3} M aqueous chlorobenzene solution in the absence and presence of air

| Compounds | Q_i when saturated with | |
|----------------------------|---------------------------|-----------------------|
| | Ar | Air |
| Chlorobenzene ^a | 2.44×10^{-2} | 2.27×10^{-2} |
| Chloride ion | 9.16×10^{-3} | 8.92×10^{-3} |
| Phenol | 5.62×10^{-3} | 5.53×10^{-3} |
| 2-phenylphenol | 8.20×10^{-5} | 7.37×10^{-5} |
| 3-phenylphenol | 1.31×10^{-3} | 1.27×10^{-4} |
| 4-phenylphenol | 3.87×10^{-6} | 2.54×10^{-6} |
| Benzene | 9.45×10^{-6} | 3.39×10^{-6} |
| Biphenyl | Trace | Trace |

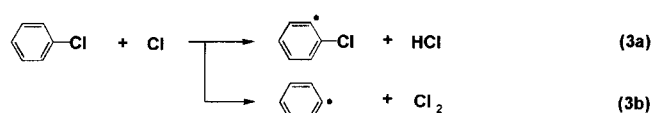
^aThese values indicate the initial quantum yield of chlorobenzene decomposed. The others indicate the initial quantum yield of the products.

chlorobenzene absorbed all of the light at the initial process of the reaction. It means that the photochemical decomposition of aqueous chlorobenzene begins with absorption of the light by chlorobenzene. As the number of quanta increased, the UV light could also be absorbed by the products. As a result, the secondary photochemical reactions would be carried out. The photolysis pathway of the electronically excited chlorobenzene by the absorption of 253.7 nm can be probably divided into two types; one is attack the electronically excited chlorobenzene by the water in the solution as in process (1) and the other is its photofragmentation into Cl and phenyl radical as in process (2). Since the bond dissociation energy of C-H bond (about 411 kJ) is greater than that of C-Cl bond (about 327 kJ),¹⁹ the photofragmentation into H and chlorophenyl radical could be negligible.

During the irradiation of the 3.54×10^{-3} M deoxygenated aqueous chlorobenzene solution, phenol and chloride ion were produced mainly, and only small amount of benzene and biphenyl (Q_i are below 10^{-5}) were detected. Moreover,

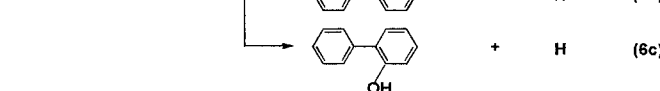
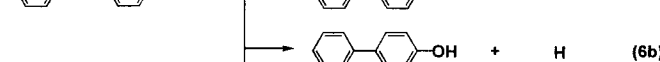
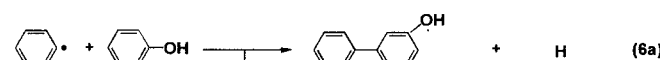
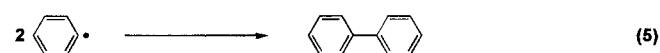
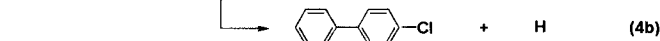
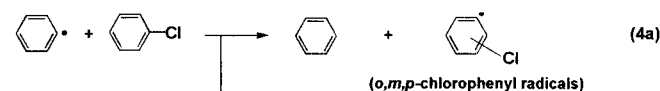


the fact that chlorinated aromatic compounds were not formed indicates that the process (1) is more favorable than process (2). Generally, the electronically excited states of aromatic compounds possess larger dipole moment (μ^*) than that in the ground state (μ). Hence, water can easily attack chloro combined carbon atom in the electronically excited chlorobenzene. If the electronically excited chlorobenzene is splitted into Cl and phenyl radical as in process (2), the formed Cl radical can attack chlorobenzene as in reaction (3), and thereby much more phenyl or chlorophenyl radicals are produced. As a result, large amount of benzene, biphenyl or chlorinated aromatic compounds should be produced as main products and phenol should not be detected. But the experimental results are just opposite to these interpretations. This result is quite similar to the photochemical reaction mechanism of the chlorobenzene in methanol reported by the Nagaoka *et al.*⁸



The fact that the initial quantum yield of the decomposed chlorobenzene has nearly same value regardless of the absence and the presence of air, is another evidence supporting that the process (1) is more favorable.

The formation of benzene, 2-phenylphenol, 3-phenylphenol, 4-phenylphenol and biphenyl can be explained by the photofragmentation of the electronically excited chlorobenzene as presented in process (2). Even so most of the electronically excited chlorobenzene undergoes by the process (1), a small part of this can also splitted into the radicals as in process (2). Thereby some of the phenyl and chlorophenyl radicals produced, and the radicals take part in the formation of the benzene, 2-phenylphenol, 3-phenylphenol, 4-phenylphenol and biphenyl as in reaction (4)-(6).



However chlorodiphenyl compounds were not detected by the analytical method used in this study. It indicates that greater amount of phenyl radical is produced than chlorophenyl radical in the reaction by attack of Cl radical to chlorobenzene as in reaction (3).

In summary, phenol and chloride ion were produced as main products along with benzene, 2-phenylphenol, 3-phenylphenol, 4-phenylphenol and biphenyl in the irradiation of 3.54×10^{-3} M deoxygenated aqueous chlorobenzene solution using 253.7 nm UV light. The initial quantum yield of the products was found to be nearly same regardless of the absence or presence of air. Most of the electronically excited chlorobenzene by the absorption of 253.7 nm UV light was decomposed to phenol by the attack of the water in the solution. In addition to this photochemical decomposition process, small part of the electronically excited chlorobenzene can also be split into the phenyl and chlorophenyl radicals, and the radicals produced take part in the formation of the benzene, 2-phenylphenol, 3-phenylphenol, 4-phenylphenol and biphenyl. During the reaction by attack of Cl radical to chlorobenzene, Cl atom is more easily abstracted from the chlorobenzene molecule rather than H atom.

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Reductive Amination of Aldehydes and Ketones with Dimethylamine Using Borohydride Exchange Resin (BER)

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The synthesis of amines is an important theme in chemical research because of their versatile utility as intermediates for drugs and agrochemicals.¹ The *N,N*-dimethylalkylamines are particularly useful as ligands² in homogeneous catalytic asymmetric transformations, and as buffers³ in sequential analysis of proteins and peptides among other applications.⁴ The most direct approach for the synthesis of *N,N*-dimethylated tertiary amines is the reductive amination of appropriate aldehydes or ketones. Among the reducing reagents, sodium cyanoborohydride⁵ has been widely used to effect this transformation. However, it is expensive and highly

toxic, and also risks the presence of residual cyanide in the product. Therefore, borane pyridine (BAP),⁶ sodium triacetoxyborohydride⁷ and borohydride exchange resin (BER)⁸ were reported as alternatives, less expensive, and less toxic reagents. Recently an efficient method for the reductive amination of aldehydes and ketones was reported using the combination of titanium(IV) isopropoxide and sodium borohydride.⁹ However, this system needs titanium(IV) isopropoxide as Lewis acid and requires a considerably long reaction time. This prompted us to apply our earlier method⁸ for the synthesis of *N,N*-dimethylalkylamines. Previously we