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Photodecomposition of o-Chloroaniline in Aqueous Solution with Low Pressure Mercury Lamp

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Pollution of organochloric compounds has been a world-wide problem because of their toxicity, resistance to biodegradation and potential for accumulation in biological organisms. Several kinds of organochloric compounds had been detected in environmental samples and biological organisms. About 300 t of o-chloroaniline(o-CA) is produced in Japan annually(The Chemical Daily Co Ltd 1983). o-CA had been detected in river water and sediment(Japan Environment Agency 1977). o-CA has -Cl and $-NH_2$ groups in molecule. Decomposition by sunlight is a possible route for the environmental degradation of organochloric compounds and ultra violet ray(UV) irradiation is a effective treatment of them in natural water or wastewater(Crosby and Hamadmad 1971; Ishikawa et al. 1985; Tissot et al. 1984). The transformation between $-NH_2$ and $-NO_2$ groups is said to be performed in environment(Uchimura and Kido 1987). Therefore we are interested in the photochemical behavior of o-CA in aqueous solution. Then the disappearance of substrate and photodecomposition products by using of a low pressure mercury lamp were examined.

MATERIALS AND METHODS

o-CA was purchased from Tokyo Chemical Co. Japan. All solvents were reagents for pesticide residue analysis. Purified water was prepared using a Yamato Model WA-715 auto-still. The reactor used in this experiment was a Taika Kogyo Model HLV-A photochemical reactor equipped with a 15 W low pressure mercury lamp having an energy output of 90% at 254 nm as shown in Figure 1. Gas chromatograph(GC) was a Shimazu Model GC-9A GC equipped with a flame ionizing detector(FID). The GC conditions were as follows: 0.35 mm id x 25 m of WCOT OV-1701 capillary column; injector temperature, 290 °C; column temperature, 50-280 °C at 10 °C/min; carrier gas, 50 mL/min of nitrogen gas; detector temperature, 300 °C. Gas chromatograph/mass spectrometer(GC/MS) was a Nihon

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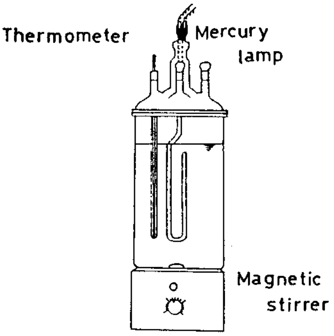

Figure 1. Apparatus for UV irradiation.

Denshi Model JMS-DX303 GC/MS. The helium flow rate was 10 mL/min. Ionizing energy was 70 eV. Other conditions were the same as those of GC. Inorganic carbon(IC) and total organic carbon(TOC) were measured with a Beckman Model 915A TOC analyzer. Total nitrogen(T-N) was measured with a Yanako Model TN-7 micro nitrogen analyzer. UV spectra were recorded on a JASCO Model UVIDEL-505 spectrophotometer.

Two liters of purified water was placed in 3 L separatory funnel. o-CA was added at the concentration of 2.5×10^{-3} M and the separatory funnel was vigorously shaken for 1 hr. The aqueous solution was placed in the reactor, the system was allowed to reach equilibrium by stirring for 0.5 hr and the mercury lamp was switched on. A hundred milliliters of the irradiated solution was periodically withdrawn during irradiation and analyzed. UV intensity was checked by using an UVP Model UVX radiometer having 254, 297 and 365 nm sensors. pH, IC, TOC and T-N were measured by the method of Japanese Industrial Standard(Japan Industrial Standards Committee 1986). Chlorine ion, NO_2^- ion, NO_3^- ion and phenols were measured by the Mohr Method(Japanese Society of Water Supply 1978), the Sulfanilamid-naphtylethylenediamine Method(Japanese Society of Water Supply 1978), the Brucine Method(Japanese Society of Sewerage 1974) and the 4-Aminoantipirine Method(Japanese Society of Water Supply 1978), respectively. Residual chlorine was measured by the o-Tolidine Method with a Shibata residual chlorine measuring equipment.

Ten milliliters of the sample withdrawn was adjusted pH to 9 with NaOH, 5 g of NaCl was added and o-CA was extracted with 3 mL of dichloromethane. The dichloromethane layer was dried over anhydrous Na_2SO_4 , filled up to 3 mL with dichloromethane and the concentration of o-CA was measured by GC.

Acetylation of photodecomposition products of o-CA was performed as follows. Zero point seven grams of K_2CO_3 was added to 50 mL of the sample and thoroughly mixed at

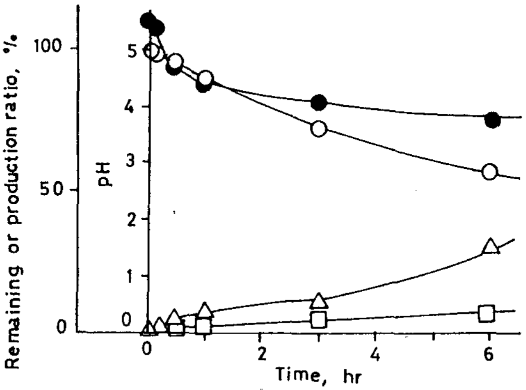

Figure 2. Changes of each item during UV irradiation. Initial concentration of o-CA was 2.5 x 10^{-3} M. UV intensities were 6.620-6.750 mW/cm^2(254nm), 0.135-0.145 mW/cm^2(297 nm) and 0.154-0.167 mW/cm^2(365 nm). -○- o-CA, -●- pH, -△- Cl^- ion, -□- phenols.

room temperature. After a few minutes, the acetylated compounds and other compounds were extracted with 5 mL of n-hexane and the hexane layer was analyzed by GC or GC/MS(Krijgsman and Kamp 1977).

RESULTS AND DISCUSSION

Figure 2 shows changes of each item. o-CA was decreased exponentially with time and the rate of o-CA disappearance was nearly represented by a first-order

$$-d[o\text{-}CA]/dt = k\ [o\text{-}CA]$$

process. The value of pseudo-first-order rate constant k determined from the plot of data points($[o\text{-}CA]/[o\text{-}CA]_0$ vs time) was 0.107/hr. The scission of a C-Cl bond, leading to Cl^- ion was observed. This transformation is accompanied by the formation of the same quantity of H^+ ions and the formation of H^+ ion leads to the decrease of pH value. The pH value after 6 hr irradiation(3.55) was higher than the value(3.15) calculated from Cl^- ion concentration because of the influence of $-NH_2$ group. As NH_4^+, NO_2^- and NO_3^- ions were not observed almost even after 6 hr irradiation, the scission of a C-N bond would have been hardly occurred. Phenols were detected in each sample. Phenols would have been produced by the photohydrolysis in the position of -Cl group on the ring or the homolytical attack of ·OH radical(Tissot et al. 1977). TOC and T-N values were not changed and IC and CN^- ion were not detected. o-CA was not converted into CO_2, N_2 and other volatile low molecular carbon and nitrogen compounds. Color of the irradiated solution became brown and brown deposit was produced. About 12% of TOC and about 11% of T-N were removed where the 6 hr irradiated solution had been centrifuged at 3500 rpm.

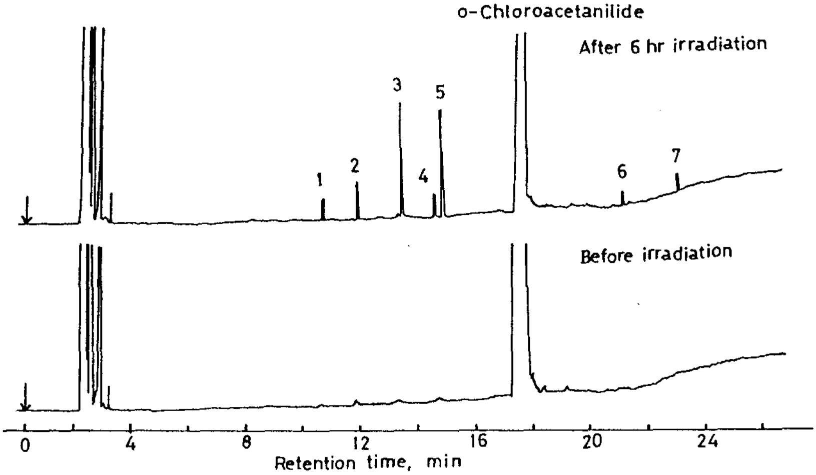

Figure 3. FID-GC chromatograms of acetylated samples. Column was 0.35 mm id x 25 m of WCOT OV-1701 capillary column and column temperature was programmed 50 to 280°C at 10°C/min.

Consequently, for the Cl atomic number of initial o-CA, 45% of o-CA was converted into 29% of non Cl-contained compounds and 16% of the Cl-contained compounds. About

Table 1. Identification of peaks in Figure 3 by FID-GC retention time and EI/MS spectrum.

Peak	Retention time, min	Retention time of standard reagent, min	EI/MS spectrum, m/z	compound
1	10.72	10.76	136(M^+),94,77,66,65,51,43	Phenol acetate
2	12.02	12.08	129,127(M^+),100,92,91,65,64,63,52	o-Chloroaniline
3	13.25	13.25	172,170(M^+),130,128,113,111,101,99,92,75,73,65,64,63,50,43	o-Chlorophenol acetate
4	14.56	-	165,163,161,135,133,127,126,125,101,99,91,90,81,73,65,63,62,52,45	Unidentified
5	14.74	14.76	159,157(M^+),143,141,129,127,113,111,101,99,87,85,75,63,62,51,50	o-Chloronitrobenzene
6	21.09	-	-	Unidentified
7	22.99	-	-	Unidentified

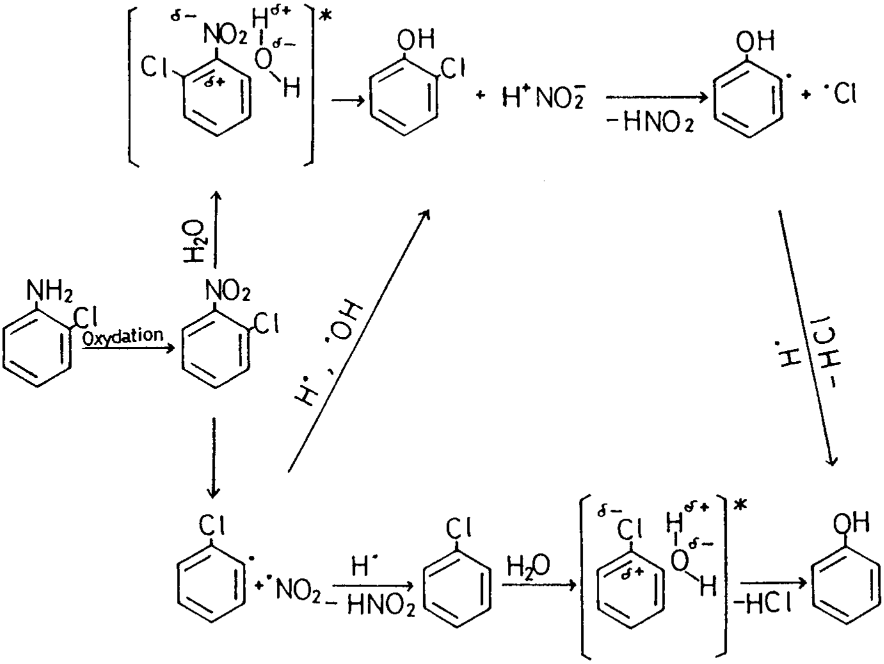

Figure 4. Reaction mechanisms of the production of phenols.

4% of phenols(as phenol) and 12%(as TOC) or 11%(as T-N) of undissolved compounds were produced after 6 hr irradiation. Photodecomposition of o-CA into CO_2, N_2, NH_4^+ ion, CN^- ion and volatile low molecular carbon and nitrogen compounds were not occurred.

In order to identify the produced phenols precisely, acetylation of the solution irradiated for 6 hr was done. Figure 3 shows FID-GC chromatograms of the acetylated samples. Peaks 1-5 were identified by electron impact(EI)/MS(Budzikiemicz et al. 1973; Stenhagen et al. 1974) and each retention time was consisted with that of standard reagent as shown in Table 1. Peak 5 was that of o-chloronitrobenzene. Amino group was photooxydized. Peaks 1 and 3 were those of phenol acetate and o-chlorophenol acetate, respectively. For example, these phenols would have been formed by heterolytic or homolytic mechanism as shown in Figure 4. These concentrations are estimated to be very low from each peak hight. o-Hydroxyaniline was not detected. The photohydrolysis of o-CA in the position of $-Cl^-$ group on the ring would be hardly occurred because of the electrostatic effect of $-NH_2$ group. Peak 2 was that of unacetylated o-CA.

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