

## 휴믹산용액과 삼염화벤젠의 광분해 반응에 관한 연구

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Photosensitized Decomposition of  
Trichlorobenzenes(TCBs) in Humic Acid(HA)  
Solution

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## ABSTRACT

The photodegradation of TCBs in humic acid solutions at pH 7 was evaluated under laboratory sunlight simulated irradiation for 8 and 42 days. The irradiation to TCBs in solution in the presence of humic acid produced trichlorophenols, dichlorophenols in addition to the minor photodegraded products such as dichlorobutadiene, dichlorobenzaldehyde and pentachlorobiphenyls. The formation of photodegradation products indicate that the excited singlet oxygen and solvated electrons play a major contributors to the photodegradation process.

## INTRODUCTION

In the environment, humic substances are ubiquitous and may show effects on the environmental chemicals namely(Choudhry, 1983; Kopinke *et al.*, 1995): photosensitizing and quenching effects, sorptive and catalytic effects on hydrolysis. Many surface waters and soil solutions contain humic and fulvic substances, that strongly absorb light(Boggs *et al.*, 1985; Choudhry, 1984). A further developed model of humic acids was proposed which consists of aromatic rings joined by alkyl chains which are substituted by

oxygen-containing functional groups(COOH, OH), CH<sub>3</sub>, and C N groups(Schulten, 1994). It is considered that aromatic rings substituted by various functional groups play an important role in the energy absorption. In general, humic materials(HM) general uncharacteristic spectra in the visible(400 to 800 nm) and ultraviolet(200 to 400 nm) regions. Absorption spectra of alkaline and neutral aqueous solutions of HM's show no maxima or minima(Fig. 1).

In general, light absorption of humic materials appears to increase with (a) the degree of condensation of the aromatic rings

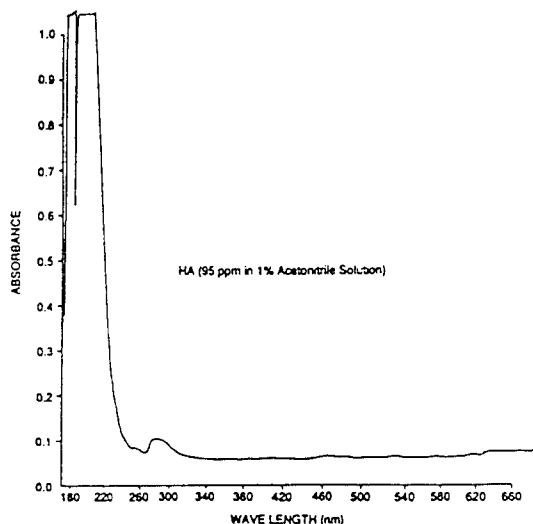


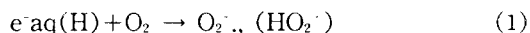
Fig. 1. Absorption spectrum of humic acid(Aldrich) solution.

which they contain, (b) the ratio of carbon in aromatic "nuclei" to carbon in aliphatic or alicyclic side chains, (c) total carbon content, and (d) molecular weight(Choudhry, 1984).

Recently, humic acid was shown to sensitize dechlorination of pentachlorobenzene in deionized water(van Noort *et al.*, 1988). Choudhry *et al.*(1987) reported that chlorobenzenes with humic monomers gave some minor photoproducts in water/acetonitrile mixtures. All chlorobenzenes except hexachlorobenzene gave minor yields of photoproducts formed by the reaction of the polychlorobiphenyl radicals with the individual humic monomers. Furthermore, a number of papers have been published to date on the photochemical incorporation of these compounds with humic macromolecules(Faust and Hoigne, 1987). Some reports have shown that humic material seems to accelerate photo-transformation of chlorinated aromatic compounds by indirect process(Zepp *et al.*, 1975; Mill *et al.*, 1981; Zepp *et al.*, 1981a; Zepp *et al.*, 1981b; Zepp *et al.*, 1984; Zepp *et al.*, 1985; Dulin *et al.*, 1986; Choudhry *et al.*,

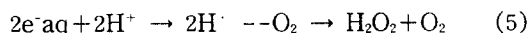
1987; Jensen-Korte *et al.*, 1987; Kotzias *et al.*, 1987). In this process, oxygen plays a major role in the reaction involving energy transfer mechanism that produces singlet state oxygen through the excited state. Haag *et al.*(1984) reported that quantum yields for production of singlet oxygen for some organic materials(DOM) in natural water showed a decrease with increasing wavelength.

Zepp *et al.*(1985), Power *et al.*(1987) and Fisher *et al.*(1987) have provided evidence that polyhydroxy aromatic compounds and aromatic carboxylic acids of humic or fulvic substances photoproduce hydrated(solvated) electrons( $e^-_{aq}$ ) and organic pollutants are believed to be photosensitized either by solvated electrons or by energy transfer mechanisms. In the presence of oxygen,  $e^-_{aq}$  and H are transformed to  $HO_2$  radicals.



The hydrated electrons seem to form a transient exciplex(or radical ion pair) with triplet and radical anions of an oxidizing substrate to generate excited singlet oxygen, then ejected electrons from humic acids react with oxidizing substrates. Secondly, singlet oxygen( $^1O_2$ ) is generated via direct energy transfer mechanism from triplet excited states of the humics to ground-state oxygen(Blough, 1988). Ejected electrons from humic acids react with oxidizing substrates. Hydrated electrons may play a significant role in the photosensitization of chlorobenzenes through the processes suggested in Eq.(2-5) (Zepp *et al.*, 1985; Power *et al.*, 1987; Fisher *et al.*, 1987):





Organic pollutants may be photoreacted by an energy transfer mechanism mediated by humic substances whose triplet energy level is around 57kcal/mol. (Fisher *et al.*, 1987). However, the triplet energy of 1,3,5-trichlorobenzene is 79kcal/mol(at 361nm) and the lifetime of chlorobenzene is about 30ns (nanosecond) in the triplet state with an energy of 86 kcal/mole(Tissot *et al.*, 1983). The triplet state energy of hexachlorobenzene is approximately 95kcal/mol(Augustyniak, 1978). So it is unlikely that energy transfer will occur between humic substances and trichlorobenzenes.

A redox potential of a reactive transient produced by humic substances can be the other indicator of the possibility of photo-reaction of xenobiotics. If the value of a redox potential of a transient is higher than that of a xenobiotic, then the xenobiotic may be oxidized, provided the reaction is kinetically favored. Reduction potential values of two peaks of Cl of 1,3,5-trichlorobenzene were reported as -2.16 and -2.45(eV) respectively(Sugimoto *et al.*, 1987). Oxidation-reduction potential of  $O_2$  is -0.33eV and excitation energy of singlet oxygen is as follows: first singlet( $^1\Sigma_g$ )=0.98eV, second singlet( $^1\Delta_g$ )=1.63eV. From these data 1,3,5-TCB is susceptible to oxidation processes.

In the case of chlorobenzenes the excited singlet(e.g., benzene, biphenyl, and naphthalene systems) usually possesses sufficient energy to undergo C-Cl bond homolysis, but the triplet state formed by intersystem crossing is generally too low in energy to react in this manner without additional thermal energy, exciplex formation, or strain relief(Bunce *et al.*, 1980). No reports have been published to date on the positive photochemical incorporation of highly chlorinated benzenes with humic macromolecules.

## MATERIALS AND METHODS

### 1. Chemicals

1,2,3-TCB(99%), 1,2,4-TCB(98%), 1,3,5-TCB(99+%), hexane(distilled in glass), humic acid and p-nitroacetophenone(97%) were purchased from Aldrich Chemical Co, (Milwaukee, WI). Acetonitrile(HPLC grade) was obtained from Mallinckrodt Chem Works, (St. Louis, Mo). Sodium sulfate(anhydrous) was Baker analyzed reagent.

### 2. Procedures

Solutions of trichlorobenzenes were prepared by dissolving with continuous stirring a weighed amount of trichlorobenzene compound(29mg/L for 1,2,3-TCB, 25mg/L for 1,2,4-TCB, and 6mg/L for 1,3,5-TCB) in 1%(v/v) acetonitrile solution in water with mixing overnight. TCBS were added into distilled water and then tightly capped and agitated.

### 3. Photoproduct Identification Experiments

Test solutions were prepared in a large batch for the photoproduct identification study. One L-in 1% aqueous acetonitrile (AN) solution(v/v) were irradiated in a 2 L Pyrex roundbottom flask, on a rack, inside the photoreactor using black lamps( $\lambda_{max}$  =360nm). Acetonitrile was chosen as an ideal co-solvent because CH-abstraction from acetonitrile by free radicals hardly occurs(Choudhry and Hutzinger, 1984). The control samples were contained in the same type of vessels but kept in a dark chamber. Another set of samples were irradiated using a sunlamp( $\lambda_{max}$ =313nm) over selected time periods based on the results of the kinetic studies. The exposed and dark samples were extracted twice with equal volumes (30mL) of hexane. All extracts were dried

using  $\text{Na}_2\text{SO}_4$  and the solvents were concentrated using Kuderna-Danish(K-D) concentrators to 1mL aided with a stream of nitrogen gas. An amount of the extracted sample was then taken for GC/MS analysis of TCBs and their photoproducts. Identification and confirmation of the products were made with authentic standards.

#### 4. Actinometry

PNA/pyridine in 1% acetonitrile solution was used as the chemical actinometer and the solutions were irradiated alongside the samples to determine the rate of photolysis of PNAP as a measure of the intensity of the radiation source(Dulin and Mill, 1982).

#### 5. Gas Chromatography/Mass Spectrometry(GC/MS) Analysis

Each test sample was prepared by the procedures described previously and was analyzed by GC/MS(Finnigan, San Jose, California 95134-1991) for structural identification. GC/MS was performed on a Varian 3000GC/MS(Finnigan ITD800). 1.6 $\mu\text{L}$  of the 1mL extracts were injected in the gas chromatography for GC/MS analysis. GC/MS was performed with a Finnigan Ion Trap Detector interfaced to an IBM computer with DOS system(version 3.3) of ITDS application software program and coupled to a Varian 3000 Gas Chromatograph(Varian, New Walk, Connecticut) equipped with a 30 m(0.25mm ID) DB-5 fused silica capillary column. Injections were done in the splitless mode. The capillary column was introduced directly in the mass spectrometer source. Helium was the carrier gas at a flow rate of 1mL/min. The GC injector and GC/MS interface were maintained at 290°C and 250°C respectively. The analyses were performed at an initial temperature of 60°C maintained for 3min and programmed at 8C/min to 285

°C. The operating conditions for the mass spectrometer were the following: scan speed was 1 scan/sec from 50 to 500 amu. The electron multiplier was operated at 50-80 eV. An internal standard, m-chlorotoluene was added to each sample prior to injection into the GC mass spectrometer.

#### 6. UV Spectrophotometry

The UV-Visible spectra of TCBs and humic acid were obtained with a Cary 219 spectrophotometer from Varian Associates Inc.,(Sugar Land, TX 77478) operated in the zero suppression mode, using 1% acetonitrile (v/v) in doubly distilled water for the blank. The spectra were recorded on a Beckman 25.4 cm stripchart recorder.

## RESULTS AND DISCUSSION

### 1. Photoproducts Formation on Photolysis of Trichlorobenzenes in Humic Acid Solution

When a solution of 1,2,3-TCB with humic acids was irradiated using a black lamp for 3 weeks, 2,3,4-trichlorophenol was the major product. At least 6 other products including PCBs were also detected(Table 1). The GC chromatogram showed several distinctive photoproducts compared to the dark control samples(Appendix A). The photoproducts identified are shown in Fig. 1.

Among the compounds identified in the irradiated samples, the most significant peak was 2,3,4-trichlorophenol at 16.51 min with a base peak of m/e 198. A significant amount of the 1,2,4-TCB isomer was produced in this experiment. It is evident from the data in Table 1 that a variety of photoproducts resulted from the exposure of 1,2,3-TCB in humic acid(Aldrich) solution for 6 weeks based on a 12-h day time exposure. Present results do not show any hybrid products from chlorination of actual

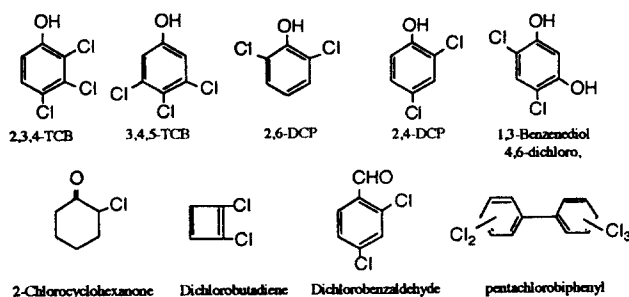
**Table 1.** Summary of Proposed and Identified Photoproducts of Trichlorobenzenes with Humic Acid.

Experiment 1 (6 days)		Experiment 2 (**)	
1,2,3-TCB	1,2,3-TCB		(13.26) [6]
1,3-dichlorobenzene		1,3-dichlorobenzene	(9.16) [1]
		2-chlorocyclohexanone	(10.14) [2]
		1,3-butadiene	
		1,4-dichloro	(12.41) [3]
2,4-dichlorophenol		2,4-dichlorophenol	(12.53) [4]
3,4-dichlorophenol			
2,6-dichlorophenol		2,6-dichlorophenol	(13.32) [5]
		1,2,3-trichlorobenzene	(13.24) [6]
2,3,4-trichlorophenol		2,4-dichlorobenzaldehyde	(15.09) [7]
1,3-benzenediol,		1,3-benzenediol,	
4,6-dichloro		4,6-dichloro	(16.22) [8]
2,3,4-trichlorophenol		2,3,4-trichlorophenol	(16.51) [9]
		3,4,5-trichlorophenol	(20.34) [10]
		pentachlorobiphenyl	(27.30) [11]*
		pentachlorobiphenyl	(28.08) [12]*
		pentachlorobiphenyl	(29.08) [13]*
1,2,4-TCB	1,2,4-TCB		(12.42) [2]
no product		1,4-dichlorobenzene	(9.47) [1]
1,3,5-TCB	1,3,5-TCB		(11.29) [1]
		1,2,4-trichlorobenzene	(13.14) [2]
no product		2,4-dichlorophenol	(9.32) [3]

The figures in ( ) and number in [ ] indicate retention times of products and number of peaks shown in chromatograms.

\* represents proposed photoproducts.

\*\* 42 days exposure for 1,2,3-TCB, 8 days for 1,2,4-TCB and 1,3,5-TCB.

**Fig. 1.** Photoproducts identified during photolysis of 1,2,3-TCB in humic acid solution.

humic acid. A quantitative evaluation was not possible owing to the lack of reference standards. The total mass balance obtained from a solution irradiated for 42 days accounts for up to a conversion to 76 % for 1,2,3-TCB.

The result shows that as the exposure

time increased from 6 days to 42 days, the number of photoproducts increased.

The PCBs produced by light were pentachlorobiphenyls (PPCBs), suggesting that the formation of PPCBs can be explained via free radical mechanisms. In the photolysis of TCB, light excited molecules of TCB

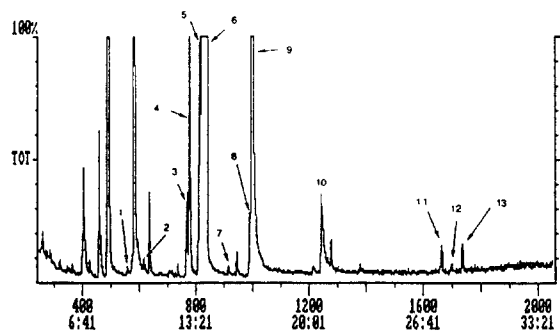


Fig. 2. Total Ion Chromatogram of the Photolyzed 1,2,3-TCB in Humic Acid Solution(42-hr Photolysis).

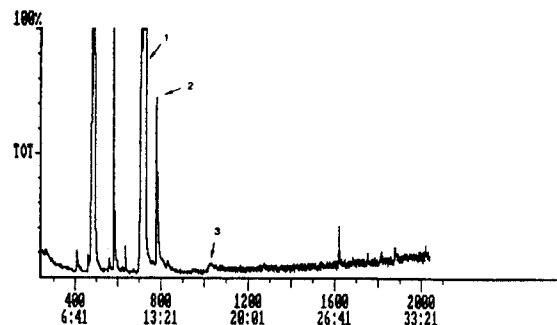


Fig. 5. Total Ion Chromatogram of the Photolyzed 1,3,5-TCB in Humic Acid Solution(42-hr Photolysis).

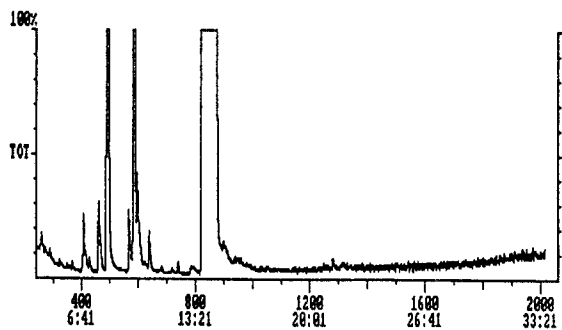


Fig. 3. Total Ion Chromatogram of the Dark-controlled 1,2,3-TCB in Humic Acid Solution (42-hr Photolysis).

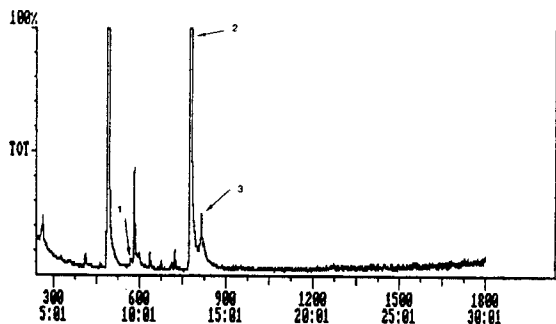


Fig. 4. Total Ion Chromatogram of the Photolyzed 1,2,4-TCB in Humic Acid Solution(42-hr Photolysis).

yield dechlorinated phenyl radicals(i), which then attack ground state of molecules(ii) to produce complex intermediate(iii). Interme-

diates then lose the H atom to yield the PPCB(iv).

However, 1,2,4- and 1,3,5-TCB were observed to have little susceptibility upon photoirradiation(Fig. 4 and 5). The result can be explained by the fact that the oxidation reaction of 1,2,4- and 1,3,5-TCB is sterically inhibited by two adjacent Cl atoms in terms of structure-activity relationship.

## CONCLUSION

The photolysis study gives detailed information about the photodegradability of 3 different TCBS and their photoproducts. The results demonstrate that the presence of oxygen was essential for oxidation of TCBS and the experiment requires more time to degrade TCBS, especially 1,2,4- and 1,3,5-TCB, which are regarded recalcitrant.

These studies account for the contribution of oxygen and light energy to degrade TCBS and HA vice versa but still neglect the effect of solvated electrons in the absence of oxygen to get a clear picture of the reductive dechlorination mechanism.

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