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A Novel Oxidation Model with Photolysis for Degradation of Trichlorobenzenes (TCBs)

Jae-Hyoun Kim

Department of Health Science, School of Natural Science, Dongduk Women's University Sungbuk-Gu, Wolkogdong 23-1, Seoul, Korea

ABSTRACT

First- and second-order kinetic oxidation rates of trichlorobenzenes (TCBs) were obtained and compared by a chemical activation system (CAS) which mimics mixed functional oxidase activity. The system consists of EDTA, ferrous sulfate, ascorbic acid, and H_2O_2 in potassium phosphate buffer (monobasic at pH 7.4). The rate of transformation in CAS was enhanced in the presence and absence of catalase in the sequence 1, 2, 3-TCB < 1, 2, 4-TCB < 1, 3, 5-TCB. In general, the rates of degradation were greater in the test media with catalase. The effect of photolysis on the degradation of the TCBs with the CAS were examined. Sensitized photolysis with nitrite, Fenton's reagent, TiO_2 and triethylamine (TEA) studied in concert with the CAS demonstrated significant enhancement of the degradation rate of TCBs. Disappearance rates of TCBs in CAS with prior photolysis or prior photosensitization were at least 10-fold higher than the sum of the rate for each single experiment. This study proves that the combination of the CAS and photolysis can be used as a suitable technique for enhancing degradation of TCBs in aqueous systems.

INTRODUCTION

The high persistence and hazards of TCBs, which are considered relatively stable and biologically inert in the environment, make TCBs difficult for disposal in an environmentally safe manner. Although 1, 2, 3- and 1, 2, 4-TCB eventually undergo mineralization, the more resistant 1, 3, 5-TCB undergoes microbial transformation with greater difficulty[1, 2].

TCBs are also known to undergo photodegradation mechanisms *via* isomerization, reductive dechlorination, or PCB formation from the aqueous environment[3)-5)]. While there is an indication that TCBs undergo photoreactions under sunlight exposures, direct photolysis of these compounds shows half-lives in the order of years[6)]. The influence of sensitizers such as humic acid, shows considerable enhancement of the photoreaction shortening the half-lives to days[7)]. The introduction of strong oxidants such as hydroxyl radicals ($OH^{\cdot}$), superoxide radicals($O_2^{\cdot -}$) or a reducing agent such as TEA as photosensitizers may provide a means of destroying TCBs in the environment. Photochemical processes for generating strong oxidants in aqueous solutions for degradation of chlorobenzenes inclu-

de the use of TiO_2[8)-12)], Fenton's reagent[13)], nitrite in gaseous state[14)] or aqueous phase[15)-17)]. Other processes using TEA[18)-20)] also show degradation of TCBs.

A sequential treatment process using a brief photolysis period followed by microbial treatment may offer a potential and effective removal process for environmental pollutants. There have been positive reports of combined photochemical degradation in the presence of microbial treatment for some xenobiotic compounds. Xenobiotics such as chloroanilines[21)], chlorophenols[22),23)], benzo[a]pyrene[24)], PCBs[25)] and pesticides[26)] were observed to undergo photolytic and microbial breakdown when a photolytic treatment followed by microbial treatment were employed.

A chemical activation system (CAS) to mimic a biochemical oxidation model via hydroxyl radical production was shown previously to oxidize a variety of compounds[27)]. Two oxidation models (Fenton's reagent and Udenfriend's system) are of interest in relation to the CAS study. Fenton's reagent consists essentially of Fe^{++} and H_2O_2 to form the OH radical. Udenfriend's system consists of Fe^{++}, EDTA, ascorbic acid, and O_2[28)]. A model of a mixed-function oxidase consisting of Fe_2^{++}, O_2 and ascorbic acid has been also proposed[29)]. Later, the mechanism of hydroxylation of aromatic compounds by Fenton's reagent and its analogs was examined in detail[30),31)]. An integration of the Udenfriend hydroxylation system containing molecular oxygen, ascorbic acid, ferrous ion, EDTA in monophosphate buffer was also developed[32)]. The products for the Fe^{++}-H_2O_2-substrate systems in dry acetonitrile are characteristic of dehydrogenation (characteristic of oxidase) or monooxygenation reactions[33),34)]. So the CAS, a mixture of hydrogen peroxide, ascorbic acid, ferrous ion, EDTA in monophosphate buffer in the presence or absence of catalase was found to activate a wide variety of oxidations with a broad substrate specificity on different target compounds in the CAS, and provided a sensitive and quantitative oxidation system.

One of the objectives of this study is to examine the degradation pathwys for each TCB isomer using the CAS. The application of the CAS incubation system is expected to demostrate for the identification of products formed from oxidative reaction.

MATERIALS AND METHODS

1. Reagents

Catalase (Lot#, 88F-7185) and TiO_2 (anhydrous, anatase) were obtained from Sigma Chemical Co. (St. Louis, Mo 63178) and Fisher Scientific Co. (Fair Lawn, NJ 07081) respectively. H_2O_2 (30%, analytical reagent) was obtained from Mallinckrodt Chemical Works (St. Louis, MO 63160). Solvents (Baker Resi-analyzed) were purchased from J. T. Baker Chem. Co. (Philipsburg, NJ 08865). All other organic chemicals including TCBs were purchased from Aldrich Chemical Co. (Milwaukee, WI 53233). The chemicals obtained were of the highest purity available confirmed by gas chromatography/mass spectrometry and were used without further purification.

2. Sample Preparation and Photodegradation Kinetics

The degradation study of TCBs in CAS was initiated with CAS, a hydroxyl radical-generating system, that consists of chemicals described below. Concentrations of the exposed, control and other samples were prepared with authentic standards provided by EPA (Cincinnati, OH 45268). The stock solution (5,000 mg/L in methanol) for each TCB obtained was directly diluted in 1% aqueous

acetonitrile solution to make 4.73×10^{-5} M 1, 2, 3-TCB, 4.01×10^{-5} M 1, 2, 4-TCB, and 9.89×10^{-6} M 1, 3, 5-TCB stock-solutions.

For the photosensitization study, different concentrations of sensitizers such as TEA (1.5×10^{-3} M), TiO_2, Fenton's reagent and sodium nitrite (3.97×10^{-4} M) were added to individual stock solutions of TCBs in dark 1-L bottles and stirred before transfer into test tubes to be used for the exposure experiments. 3 mL of 1, 2, 3-, 1, 2, 4- and 1, 3, 5-TCB stock solutions, and sensitizers in different concentrations were added into the same tubes. Fenton's reagent consisted of EDTA (1.0×10^{-3} M), H_2O_2 (1.13×10^{-3} M) and $FeSO_4.7H_2O$ (1.25×10^{-3} M). The TiO_2 (anatase) consisted of 99.9% anatase, 0.3 mm grain size and 20 m^2/g BET surface. To avoid any possibility of contaminant interference, the TiO_2 was washed several times with distilled water and dried in the oven at 50°C. TiO_2 (0.5 g/L) was added into 2 L volumetric flask and stirred with a magnetic stirrer for 30 min and the flask was kept at room temperature for 3 h to precipitate TiO_2 particles, followed by filtration of the supernatant through a 0.45 μm glass fiber filter (Beckmann). The supernatant was then used to make a 2 L sample for both the kinetics and photoproduct studies. Samples in the flasks were equilibrated with air at room temperature for 20 min. All of the exposure tests were performed in Pyrex culture tubes (Thomas Scientific, Swedesboro, NJ 08085-0099): 10 mL, 13 mm O.D (9826-13) with Teflon screw caps. The exposure solutions were filled up to not less than 2 mm from the top. Sample tubes were sealed with Teflon tape and capped tightly with Teflon-lined caps. Sufficient test samples were prepared for the duration of the exposure period. Additional tubes for each exposure solutions were wrapped in aluminum foil as dark controls. Photolysis experiments were performed with a merry-go-round Rayonet photoreactor with 10 20-watt photochemical lamps (The Southern New England Co., Middletown, CT 06457) with major output at 3500Å. After photolysis, the samples were then kept in the cold room for 2 h to minimize the reactivity and volatility of the compound. Then the assay solutions were added to the photolyzed solution for further incubation.

3. Batch Study of CAS Assay

A large-scale product-accumulation experiment was conducted to isolate sufficient quantities of metabolites in a batch mode using test samples. Blanks, and controls were prepared simultaneously. 500 mL of an assay mixture of the CAS reagents in 500 mL Erlenmeyer flasks sealed under an atmosphere of oxygen were incubated at 20°C for 5 days. The same concentration of reagents of CAS were used as those used for the kinetic study. Batch samples were each spiked with TCB stock solutions to make up 1.42×10^{-4} M 1, 2, 3-TCB, 1.1×10^{-4} M 1, 2, 4-TCB and 1.0×10^{-4} M 1, 3, 5-TCB. Aliquots samples were withdrawn at designated time intervals for 5 days for analysis. The CAS medium at pH 7.4 was extracted twice with equal volumes of diethyl ether for analysis of the parent compound and its products. The aqueous fraction was acidified to pH 3 with H_2SO_4 for quantitative identification of carboxylic acids and phenolic compounds, and then extracted with diethyl ether. The solution after ether extraction was reextracted with hexane to check for other remaining compounds. Some organic carboxylic acids in this fraction (2 mL) were esterified with 2 mL methanol, 1 drop of concentrated H_2SO_4 and 2 mL diethyl ether over Na_2SO_4 with stirring for 24 h and then extracted with diethyl ether. The extracts were then concentrated to approxima-

tely 1 mL by evaporation under a gentle stream of nitrogen and analyzed for TCBs and metabolites by GC/MS.

ANALYTICAL METHODS

1. Gas Chromatography/Mass Spectrometry (GC/MS)

Each test sample was prepared by the procedures described previously and was analyzed by GC/MS for structural elucidation. The GC/MS consists of a Varian 3000 GC (Varian, New Walk, Connecticut) with a Finnigan 800 Ion Trap Detector (Finnigan, San Jose, California 95134-1991) interfaced to an IBM computer with DOS system (version 3.3) of ITDS application software program. A 30 m (0.25 mm ID) DB-5 fused silica capillary column was used for the GC. 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 1 mL/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 3 min and programmed at 8°C/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 to the GC mass spectrometer.

2. Product Identification (Batch Study)

Large-scale batch experiments using CAS, described in the experimental section were conducted in order to have enough samples for product identification. Table 1 shows the comparison of the degradation products in the presence and absence of catalase in CAS.

The CAS assay, after a 5-day incubation at 20°C, produced the following products: 2, 4-dichlorophenol (DCP), 2, 6-dichlorophenol, 2, 3, 4-trichlorophenol (TCP) and 1, 3-dichloro-4, 6-diolbenzene from 1, 2, 3-TCB. Incubation with CAS in monophosphate buffer (pH 7.4) in the presence of catalase, also led

Table 1. Retention time (min) and products of 1, 2, 3-TCB after a 5-day incubation in CAS with or without catalase. The number in parentheses indicates the peak number of products in Figures 7 through 8.

	R.T. (min)	Products	
		w/o catalase	w/ catalase
1, 2, 3-TCB			
	13.12 (1)	2, 4-Dichlorophenol	2, 4-Dichlorophenol
	13.53 (2)	2, 6-Dichlorophenol	-
	16.37 (3)	1, 3-Dichloro-4, 6-benzenediol*	1, 3-Dichloro-4, 6-benzenediol*
	16.82 (4)	2, 3, 4-Trichlorophenol*	2, 3, 4-Trichlorophenol*
1, 2, 4-TCB			
	9.42 (1)	1, 4-Dichlorobenzene	1, 4-Dichlorobenzene
	9.80 (2)	1, 2-Dichlorobenzene	1, 2-Dichlorobenzene
	13.47 (3)	1, 2, 3-Trichlorobenzene	1, 2, 3-Trichlorobenzene
1, 3, 5-TCB			
	12.44	1, 2, 4-Trichlorobenzene	1, 2, 4-Trichlorobenzene

* represent major products.

to the formation of 2, 3, 4-TCP in ether extracts of the assay culture at pH 7 and pH 3 for this isomer. The primary degradative event for 1, 2, 3-TCB in both experiments appears to involve the hydroxylation of the ring at the *ortho* position that showed a

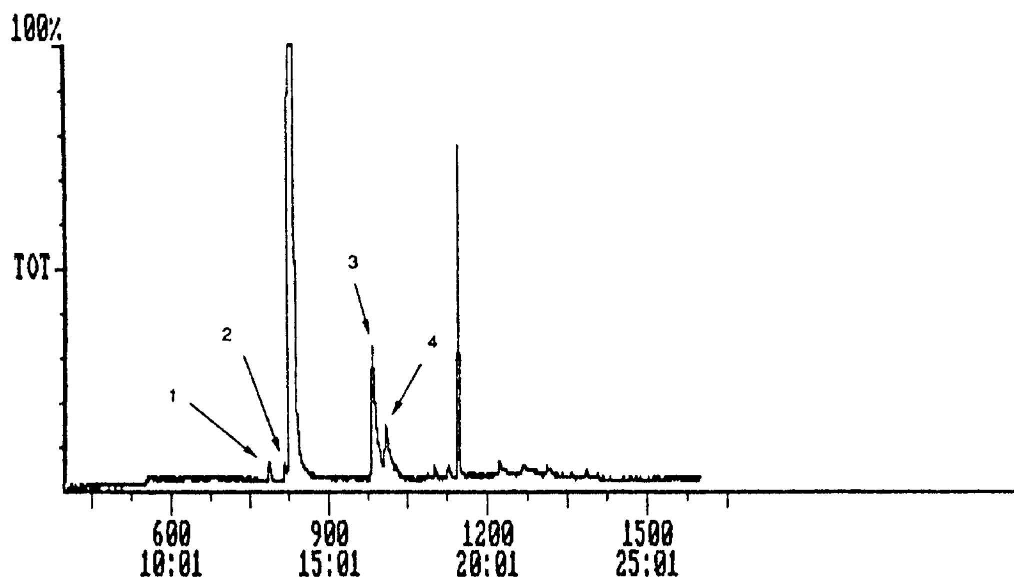

Fig. 1. Total ion chromatogram of 1, 2, 3-TCB after a 5-day incubation in CAS (chemical activation system) without catalase.

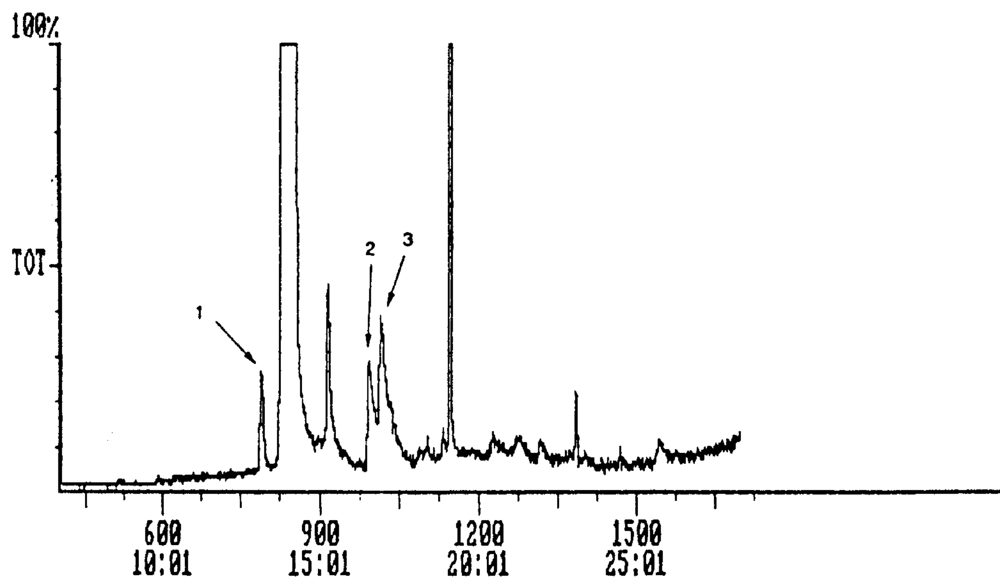

Fig. 2. Total ion chromatogram of 1, 2, 3-TCB after a 5-day incubation in CAS (chemical activation system) with catalase.

retention time identical to that of a known standard 2, 3, 4-TCP. Fig. 7 and 8 show chromatograms of 1, 2, 3-TCB incubated in CAS in the absence or presence of catalase.

Mass spectral analysis of the metabolite (peak 3) conclusively identified it as a dichlorodiol compound (Fig. 1). The GC/MS analysis of a dichlorodiol compound revealed that the dechlorination mechanism is dominant in the CAS without catalase, resulting from the fact that the peak of dichlorodiol formation (peak 3) is dominant over the formation of TCP (peak 4). However, more accumulation of TCB, and hydroxylated compound, occurred in the presence of catalase for the same test systems (Fig. 2).

Oxidation mechanisms of 1, 2, 3-TCB have been studied mainly in the field of biological metabolism by bacteria (36~38). The oxidation mechanism has been shown to occur with absolute specificity involving the *ortho* position as most vulnerable for attack in oxidative environments.

Among the products, dichlorophenols yielding virtually identical mass spectra were constantly found at pH 3 and pH 7.4 extracts in the presence or absence of catalase. It appears that the most probable pathway for the

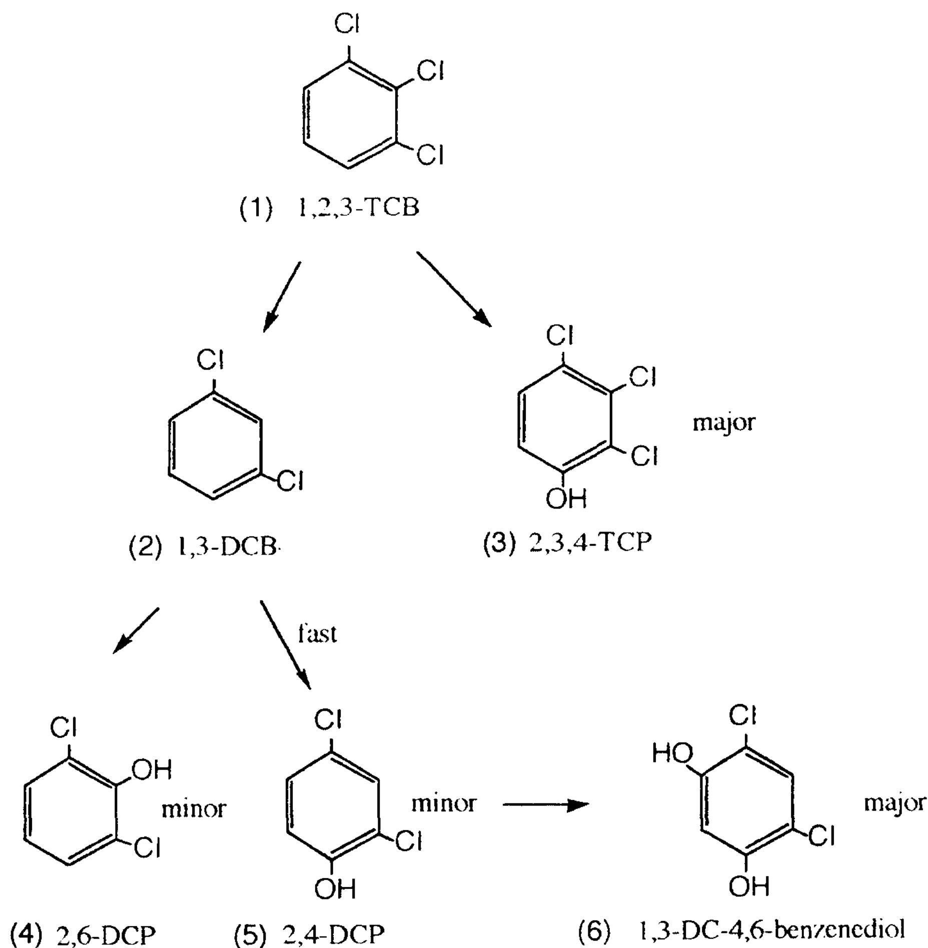

Fig. 3. A proposed pathway for the metabolism of 1, 2, 3-TCB in CAS.

production of 2, 6-dichloro-1, 4-diolbenzene is *via* reductive dechlorination of 1, 2, 3-TCB first and then hydroxylation, demonstrating that biodegradation may have been responsible for the reductions mostly in 1, 2, 3-TCB. Identification of 1, 3-dichloro-4, 6-diol benzene which was deduced from mass spectra, but for which no authentic samples are available, are indicated as tentatively identified. Subsequent steps in the degradation of hydroxylated intermediate are unclear. Another experiment was conducted by the incubation of 2, 3, 4-TCP in CAS to prove whether or not the dichlorodiol compound is dechlorinated from 2, 3, 4-TCP. The result indicates that dechlorination of 2, 3, 4-TCP is not a major process to yield dichlorodiol compound. No other, chlorinated esters or acid were found. Based on GC/MS evidence, the effects of catalase in CAS suggest that catalase is likely to be a specific for the enzymatic oxidation of TCBs. For the investigation of the possible degradation of 2, 3, 4-TCP, the compound was incubated in CAS. It is reasonable to conclude that the product dichlorodiol found in CAS results from the hydroxylation of 1, 3-DCB and 2, 4-DCP which are reductively dechlorinated from the parent compounds.

The above findings indicate the involvement of 1, 2, 3-TCB with some form of metabolic. interaction. Taking into account all the above facts, the mechanism of the biodegradation of 1, 2, 3-TCB in CAS shown in (1)-(6) is proposed (Fig. 3).

The comparison of 1, 2, 4-TCB with incubated control (absence of CAS) demonstrates that 1, 2, 4-TCB was reductively transformed by dechlorination mechanism (Fig. 4).

Relatively low concentrations of an isomerized product (1, 2, 3-TCB), 1, 2- and 1, 4-dichlorobenzene (DCBs) were observed in the 1, 2, 4-TCB sample incubated in CAS for the same incubation periods (Fig. 5 and 6).

1, 2, 4-TCB seems to be dechlorinated with ease based on the structural properties of the compound. No products were found in 1, 3, 5-TCB sample, indicating that the 1,3,5-TCB is easily degraded in the CAS.

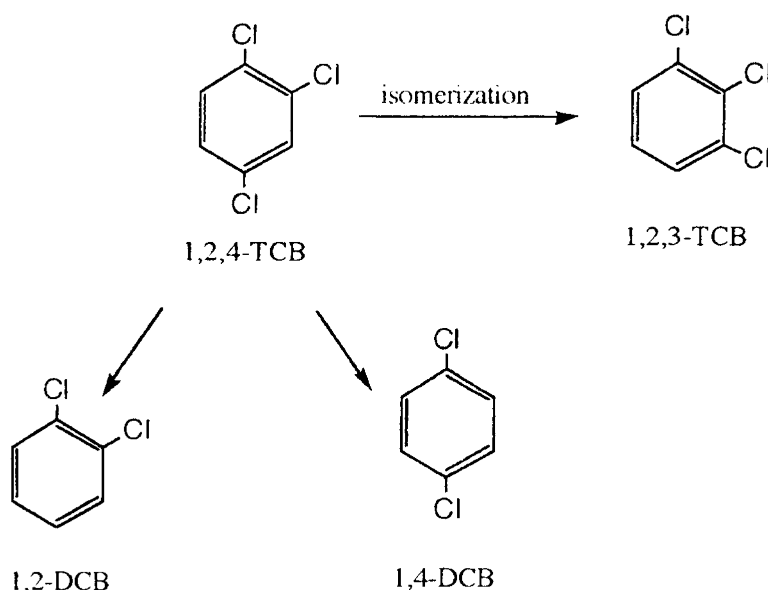

Fig. 4. A proposed pathway for the metabolism of 1, 2, 4-TCB in CAS.

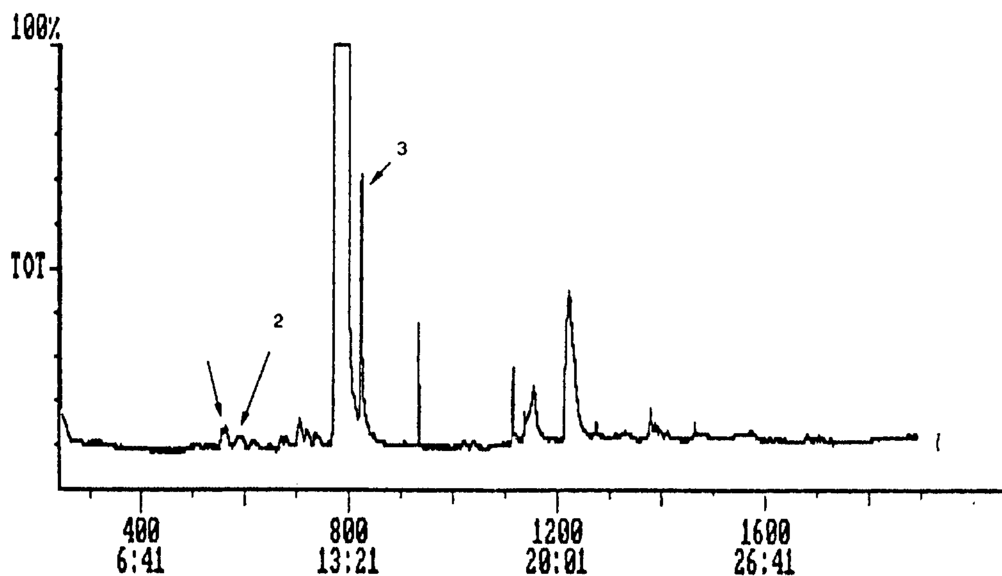

Fig. 5. Total ion chromatogram of 1, 2, 4-TCB after a 5-day incubation in CAS (chemical activation system) without catalase.

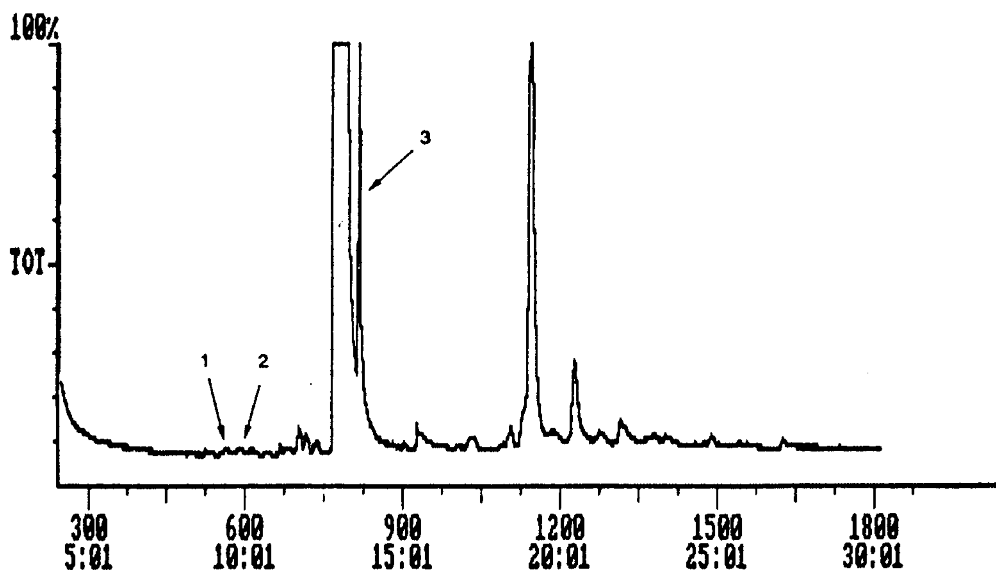

Fig. 6. Total ion chromatogram of 1, 2, 4-TCB after a 5-day incubation in CAS (chemical activation system) with catalase.

GC/MS analysis indicated that no chlorinated acids were present in the extracts at pH 1. Some additional peaks without numbers on the chromatograms were identified as fatty acids or as their esters, which are presumed to be extracted from CAS solutions.

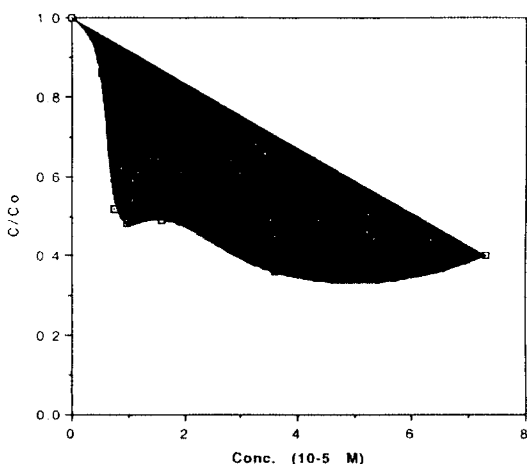

Fig. 7. Degradation profile of 1, 2, 3-TCB in CAS incubated for 3 days.

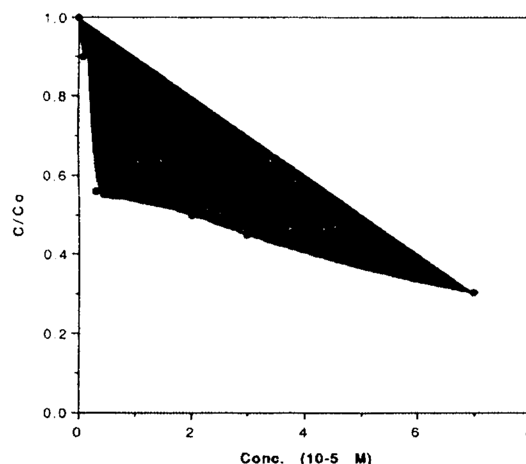

Fig. 9. Degradation profile of 1, 3, 5-TCB in CAS incubated for 3 days.

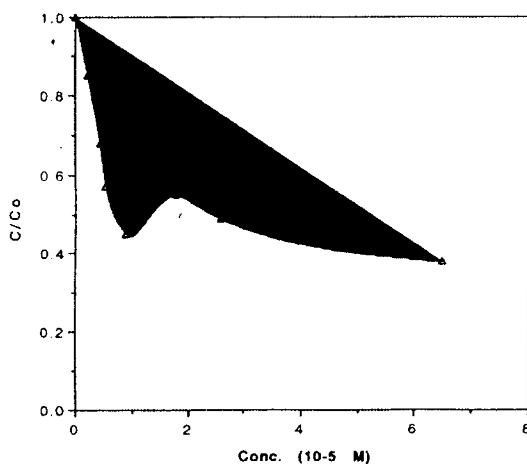

Fig. 8. Degradation profile of 1, 2, 4-TCB in CAS incubated for 3 days.

3. Influence of Concentration on Degradation of TCBs

The CAS kinetic studies showed higher disappearance rates with 1, 2, 4- or 1, 3, 5-TCB than that with 1, 2, 3-TCB. Possible reasons for the different results are that the initial concentrations of TCBs used were different. Subsequent experiments were designed to determine the influence of concentration on the kinetic rates. As shown in Fig. 7-9, a sharp decrease of C/Co in concentration from 0 to approximately 1.0×10^{-5} M, and relatively small change in degradation above 1.0×10^{-5} M for each TCB is observed.

4. Photolysis and Photosensitization Mediated Degradation Using the CAS

Having shown that TCBs were photodegraded with different kinetic rates in the presence or absence of photosensitizers in a previous study[39], we then exploited the results of the photolysis study and combined photolysis with the use of the CAS to compare disappearance rates. In this part of the study, experiments were carried out to test whether photolysis combined with CAS affect the degradation of TCBs. The CAS experiment performed with prior photolysis demonstrates that the rate of degradation is much more enhanced compared to the experiment conducted by photolysis or CAS assay only. Comparison of the two tables reflects that significant differences in TCB degradation due to the effect of light were observed (Table 2) and similar results were obtained from the study using the CAS

Table 2. Disappearance kinetic rates ($k_{p,d}$) and half-lives ($t_{1/2}$) of TCBs in CAS with photolysis in the absence of sensitizers.

	Exposure time (days) Photolysis	CAS assay	Photolysis and CAS assay $k_{p,d}$ (day^{-1})	$t_{1/2}$ (days)
1, 2, 3-TCB	1	1.5	0.14 (± 0.02)	4.85 (±0.63)
	2	2	0.74 (± 0.18)	0.93 (±0.22)
1, 2, 4-TCB	2	1	1.02 (± 0.04)	0.68 (±0.06)
	2	2	1.09 (± 0.10)	0.63 (±0.18)
	1	1.5	2.43 (± 0.67)	0.29 (±0.06)
	4	2	7.71	0.09
1, 3, 5-TCB	2	0.5	2.93 (± 6.68)	0.24 (±0.55)
	2	1.5	4.12 (±11.07)	0.17 (±0.45)

The confidence intervals in ( ) are calculated at 95% significance level.

Table 3. Disappearance kinetic rates (kps, d) and half-lives ($t_{1/2}$) of TCBs in CAS with photolysis in the presence of sensitizers.

	Exposure time (days) Photolysis	CAS assay	Photolysis and CAS assay kps, d (day^{-1})	$t^{1/2}$ (days)
TiO_2				
TCBs	5 h	1	ND	ND
NO_2				
1, 2, 3-TCB	2	2	2.75 (± 2.98)	0.25 (±0.27)
1, 2, 4-TCB	2	2	1.90 (± 0.29)	0.37 (±0.06)
1, 3, 5-TCB	2	0.5	4.38 (± 5.64)	0.16 (±0.22)
Fenton's reagent				
1, 2, 3-TCB	2	2	6.82 (±11.92)	0.10 (±0.18)
1, 2, 4-TCB	2	2	8.34 (±30.49)	0.08 (±0.27)
1, 3, 5-TCB	2	0.5	12.64	0.03
TEA				
1, 2, 3-TCB	2	2	1.30 (± 0.24)	0.53 (±0.10)
1, 2, 4-TCB	2	2	1.49	0.46
1, 3, 5-TCB	2	0.5	3.20 (± 1.18)	0.22 (±0.08)

* 1, 3, 5-TCB sample disappeared during exposure. The confidence intervals were calculated at 95% significance level. ND indicates that the parent compound completely disappeared.

assay with prior photosensitization (Table 3).

Incorporation of photolysis into the CAS assay promoted the highest degradation of 1, 3, 5-TCB followed by 1, 2, 4-TCB and then 1, 2, 3-TCB (Table 2). If the measured rate constant of photolysis (k_p) or of CAS assay (k_d) only are summed up and compared to the rate constant ($k_{p,d}$) of the CAS with prior photolysis in the absence of sensitizers, it is possible to derive approximate effectiveness of the sequential experiment in terms of the TCB degradation studied in combination with CAS and photolysis in this work. The results for the 2-day photolysis of 1, 2, 3-TCB showed that $t_{1/2}$ (0.93±0.11 days) of CAS assay with prior 2-day photolysis of 1, 2, 3-TCB in CAS is about 40-fold shorter than the sum of $t_{1/2}$ in CAS and photolysis. The half-life (0.63±0.09 days) of 1, 2, 4-TCB in CAS after 2-day with prior photolysis is 13 times shorter than the sum of $t_{1/2}$ of CAS assay (1.39±0.10) and direct photolysis (6.8

$\pm$1.2). Similarly, photolysis for 2 days and subsequent CAS assay of 1, 3, 5-TCB could bring the half-life from approximately 3 days to 0.24$\pm$0.28 days or 0.17($\pm$0.45) days respectively. It is also evident in Table 5, that $k_{p,d}$ is enhanced over longer exposure time with photolysis. Similarly, kinetic rates of the combined effect of photosensitization and CAS assay were compared (Table 6). The dramatic effect of photosensitizers on the degradation of TCBs is shown, as evidenced by the fact that the overall change in $t_{1/2}$ of 1, 2, 3-TCB in nitrite solution is 47 times, 176 times in Fenton's reagent solution, and 12 times shorter in triethylamine (TEA) solution. For 1, 2, 4-TCB, $t_{1/2}$ in nitrite solution was enhanced 12 times, around 100 times in Fenton's Reagent solution, and 10 times shorter in TEA solution. For 1, 3, 5-TCB enhancement of 16 times for nitrite solution, 19 times in Fenton's Regent solution, and 13 times in TEA solution were observed. The enhancement of all TCBs in TiO_2 suspension was observed.

The observed disappearance rates of TCBs in the presence of sensitizers (Table 3) during the photo-assisted biodegradation in 2-day photolysis, for 1, 2, 3-TCB and 1, 2, 4-TCB, and 2-day photolysis for 1, 3, 5-TCB respectively were generally much faster than those in the absence of sensitizers. The control used for these experiments was conducted without sensitizers. TiO_2 and Fenton's reagent were the most effective sensitizers that exhibited remarkable enhancement of kp_s,d when they are used in combination with CAS. Of the sensitizers, the TiO_2 is the most effective since the parent compound completely disappeared after incubation with a 2-day photolysis. The disappearance rate of 1, 2, 4- and 1, 3, 5-TCB in the presence or absence of sensitizers, was much higher than that of 1, 2, 3-TCB.

As compared to the sum of the kinetic rates of the direct photolysis and CAS assay, kp,d of combined photolysis and CAS assay shows much higher disappearance rates, as shown in Table 2. The conspicuous difference may be mainly due to the combined effect, although some of substrates loss can be accounted for in terms of the volatility during addition of CAS assay medium. Similar results were obtained from the CAS assay combined with photosensitization. These results demonstrate that the photolysis can be an effective process to assist in the degradation of TCBs in aqueous environments. Regarding the loss by the volatility of TCBs, a separate experiment was conducted to determine the reduction before and after adding the CAS assay mixtures. TCBs for the experiment underwent the same procedures such as sample preparation, photolysis and transfer of photoproducts into CAS mixture described in the Method Section before the CAS assay,

Table 4. The % change ($\pm$SD) by volatilization of TCBs during addition of CAS mixtures.

	% changes before and after adding CAS mixture	
	before (%)	after (%)
1, 2, 3-TCB	100	92.6$\pm$6.7
1, 2, 4-TCB	100	91.5$\pm$7.3
1, 3, 5-TCB	100	90.1$\pm$6.6

and the initial concentrations of TCBs were determined by GC and then extracted with hexane. The % changes are shown in Table 4.

The % reduction obtained is approximately 7~10%, which is a relatively small indicating that the calculated enhancement factors by the combined experiments are reliable. Thus, most of the loss in the kinetic rates ($k_{p,d}$) is caused by the combined effects of the CAS and photolysis (or photosensitization) and only

a minor part of the loss is due to volatilization or other processes.

In summary, the most significant result of the study is the preliminary demonstration that (i) an oxidative degradation using the CAS is a potentially effective process for the removal of TCBs, (ii) the combination of the CAS assay and photolysis in the presence or absence of sensitizers was effective for degradation of TCBs, (iii) TiO_2 was the most efficient sensitizer to degrade TCBs not only in photosensitization experiment (39) but also when combined with CAS assay. Batch experiments provided structure-activity behavior information under oxidative environments, demonstrating that 1, 2, 3-TCB was the most degradable one in combination with photosensitization and CAS assay. Future experiments will involve the identification of photoproducts with CAS assay combined with photosensitization, and also will probe mechanistic pathways for the study.

Registry No.

1, 2, 3-TCB, 87-61-6; 1, 2, 4-TCB, 120-82-1; 1, 3, 5-TCB, 108-70-3.

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