

## Thiobencarb Degradation by TiO<sub>2</sub> Photocatalysis: Parameter and Reaction Pathway Investigations

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The present study deals with the photocatalytic degradation of the thiocarbamate herbicide, thiobencarb (TBC), in the presence of TiO<sub>2</sub> particles and UV-A ( $\lambda = 365$  nm) radiation. Results show rapid and complete oxidation of TBC after 90 min, and slightly over 70% of TBC was mineralized after 32-h treatment. Factors such as solution pH, TiO<sub>2</sub> dosage, and the presence of anions are found to influence the degradation rate. The establishment of the reaction pathway is made possible by a thorough analysis of the reaction mixture identifying the main intermediate products generated. Results suggest that possible transformation pathways may include hydroxylation, dealkylation and C–S bond cleavage processes. The possible degradation pathways are proposed and discussed on the basis of the evidence of oxidative intermediate formation.

**Keywords:** Photocatalysis; Titanium dioxide; Thiocarbamate herbicide; Thiobencarb; Intermediate; Reaction pathway.

### INTRODUCTION

Thiobencarb (TBC, S-4-chlorobenzyl diethylthiocarbamate) is a thiocarbamate herbicide used in rice production, at a worldwide (40 countries) rate of approximately 18,000 tons per year.<sup>1</sup> It may contaminate surface waters as a result of releases of rice paddy water soon after field application, or from spray drift associated with aerial or ground spray application. TBC is resistant to degradation by hydrolysis and has been detected in river waters. It is moderately toxic to aquatic invertebrates and fish in acute toxicity tests.<sup>2,3</sup> The US Environmental Protection Agency (USEPA) researchers have reported the reference doses in publicly accessible databases such as the Integrated Risk Information System, which contained 0.01 mg/kg/d of TBC. The Ministry of the Environment in Japan released the Environmental Quality Standards for Water Pollutants, which included 0.02 mg/L of TBC.<sup>4</sup> Because of the importance of this compound, an urgent need for more enhanced technologies to reduce its presence in the environment has become evident.

Degradation and purification processes for the organic compound in polluted water include adsorption on

various adsorbents,<sup>5,6</sup> chemical oxidation,<sup>7</sup> biodegradation,<sup>8,9</sup> photolysis<sup>10,11</sup> and photocatalysis.<sup>12–16</sup> However each has limitations and disadvantages. The adsorption method involves only a phase transfer of pollutants without degradation; the chemical oxidation method is unable to mineralize all organic substances; and in biological treatment methods, the slow reaction rates and the disposal of activated sludge are the drawbacks.<sup>17,18</sup> The photocatalytic processes have received increasing attention in recent years because they are not burdened by the above disadvantages. Since organic pollutants can be completely degraded into harmless matter by photocatalysis under ambient temperature and pressure, scientists predict that it will soon be recognized as one of the most effective means of dealing with various kinds of wastewater.<sup>19</sup>

Titanium dioxide (TiO<sub>2</sub>)-based photocatalytic oxidation is a promising technology in water and wastewater treatment because TiO<sub>2</sub> is a cheap, stable, and nontoxic catalyst.<sup>20</sup> The initial step in TiO<sub>2</sub>-mediated photocatalysis degradation is proposed to involve the generation of an (e<sup>-</sup>/h<sup>+</sup>) pair, leading mainly to the formation of hydroxyl radicals (<sup>•</sup>OH), as well as superoxide radical anions (O<sub>2</sub><sup>•-</sup>)

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and hydroperoxyl radicals ( $\cdot\text{OOH}$ ), and these radicals are the oxidizing species in the photocatalytic oxidation processes.<sup>21–23</sup> Among them hydroxyl radicals are the most powerful oxidizing species that  $\text{TiO}_2$  photocatalysis produces and can attack organic contaminants present at or near the surface of  $\text{TiO}_2$ .<sup>24</sup>

Sturini et al.<sup>25</sup> investigated the degradation of thiocarbamate herbicides in a  $\text{TiO}_2$  heterogeneous aqueous system. Their results indicated that thiobencarb degraded to 4-chlorobenzaldehyde and S-4-chlorobenzyl acetyl(ethyl)thiocarbamate. However, only two photodegradation intermediates of TBC have been separated and identified, and the detailed mechanisms are still unclear. Considering the environmental concerns regarding TBC and very limited information in the literature with regard to the photodegradation intermediates and reaction mechanisms, a thorough intermediate study on the degradation of TBC in dilute aqueous solution using the  $\text{TiO}_2/\text{UV}$  process was undertaken. Moreover, some potential factors likely to influence the photodegradability of TBC have not been well documented. In this study, various parameters that may affect the photodegradation of TBC in the presence of  $\text{TiO}_2$  suspensions are also analyzed to obtain a more complete knowledge of  $\text{TiO}_2$  photocatalytic efficiency.

## EXPERIMENTAL

### Materials

Thiobencarb (99.8%) was obtained from Sigma-Aldrich. Standard solutions containing  $5 \text{ mg L}^{-1}$  of TBC in water were prepared, protected from light, and stored at  $4^\circ\text{C}$ . Other chemicals were of reagent grade and were used as such without further purification. The  $\text{TiO}_2$  nanoparticles (P25, ca. 80% anatase, 20% rutile; particle size, ca. 20–30 nm; BET area, ca.  $55 \text{ m}^2 \text{ g}^{-1}$ ) were supplied by Degussa. De-ionized water was used throughout this study. The water was purified with a Milli-Q water ion-exchange system (Millipore Co.) to give a resistivity of  $1.8 \times 10^7 \Omega\text{-cm}$ .

### Apparatus and instruments

The apparatus for studying the photocatalytic degradation of TBC has been described elsewhere.<sup>26</sup> The C-75 Chromato-Vue cabinet of UVP provided a wide area of illumination from the 15-Watt UV-365 nm tubes positioned on two sides of the cabinet interior. A Waters LC system, equipped with a binary pump, an autosampler, and a photodiode array detector, was used for the determination of the

amount of TBC in the aqueous solution. Solid-phase microextraction (SPME) and gas chromatography/mass spectrometry (GC/MS) were utilized for the analysis of intermediate products resulting from the photocatalytic degradation process. SPME holder and fiber-coating divinylbenzene-carboxen-polydimethylsiloxane (DVB-CAR-PDMS 50/30  $\mu\text{m}$ ) were supplied from Supelco (Bellefonte, PA). GC/MS analyses were run on a Perkin-Elmer AutoSystem-XL gas chromatograph interfaced to a TurboMass selective mass detector. The mineralization of TBC was monitored by measuring the total organic carbon (TOC) content with a Dohrmann Phoenix 8000 Carbon Analyzer, which employed a u.v./persulfate oxidation method by directly injecting the aqueous solution.

### Procedures and analyses

TBC solution ( $5 \text{ mg L}^{-1}$ ) with the appropriate amount of photocatalyst was mixed and used in photocatalytic experiments. For reactions in different pH media, the initial pH of the suspensions was adjusted by the addition of a few drops of either 0.1 N NaOH or 0.1 N  $\text{HNO}_3$  solutions. Prior to irradiation, the dispersions were magnetically stirred in the dark for 30 min to ensure the establishment of the adsorption/desorption equilibrium. Irradiations were carried out using two UV-365 nm lamps (15 watt). An average irradiation intensity of  $0.1 \text{ mW/cm}^2$  was maintained throughout the experiments and was measured by internal radiometer. At given irradiation time intervals, the aqueous  $\text{TiO}_2$  dispersion was sampled (5 mL) and centrifuged to separate the  $\text{TiO}_2$  particles. After each irradiation cycle, the amount of residual TBC was determined by HPLC. Two different kinds of solvents were prepared in this study namely, solvent A, 25 mM aqueous ammonium acetate buffer (pH 6.9) and solvent B, methanol. LC was carried out on an Atlantis dC18 column (250 mm  $\times$  4.6 mm i.d.,  $\text{dp} = 5 \mu\text{m}$ ). The flow rate of the mobile phase was set at 1.0 mL/min. A linear gradient was run as follows:  $t = 0, A = 95, B = 5$ ;  $t = 20, A = 50, B = 50$ ;  $t = 35\text{--}40, A = 10, B = 90$ ;  $t = 45, A = 95, B = 5$ . The elution was monitored at 220 nm.

The analysis of organic intermediates was accomplished by SPME-GC/MS. The SPME fiber was directly immersed into the sample solution to extract TBC and its intermediates for 30 min at room temperature, with magnetic stirring at  $550 \pm 10 \text{ rpm}$  on the Corning stirrer/plate (Corning, USA). Finally, the compounds were thermally desorbed from the fiber to the GC injector for 45 min. Sepa-

ration was carried out in a DB-5 capillary column (5% diphenyl/95% dimethyl-siloxane), 60 m, 0.25-mm i.d., and 1.0- $\mu\text{m}$  thick film. A split-splitless injector was used under the following conditions: injector temperature 250 °C, split flow 10 mL/min. The helium carrier gas flow was 1.5 mL/min. The oven temperature program was 1.0 min at 60 °C then it was increased at 8 °C min<sup>-1</sup> until reaching 240 °C. It was kept at this temperature for 21.5 min, the total run time being 45 min.

Mass spectrometric detection was performed in full-scan conditions for both electron impact (EI) and chemical ionization (CI) using isobutane as reagent gas. The ion source and inlet line temperatures were set at 220 and 250 °C, respectively. Electron impact mass spectra were obtained at 70 eV of electron energy, and monitored from 20 to 350  $m/z$ . The mass spectrometer was tuned regularly with perfluorotributylamine using the fragment ions at  $m/z$  69, 131, 219 and 502. EI mass spectra were identified using the NIST 2008 Library and the analytes were automatically identified by the NIST MS-Search 2.0 software. Chemical ionization mass spectrometry was operated in the positive ionization mode, isobutane was used as reagent gas at an apparent pressure of  $4.4 \times 10^{-4}$  Torr in the ionization source. The full scan mode with a mass range of  $m/z$  40-350 was used to confirm the analytes. The autotuning software performed the reagent gas flow adjustment, and the lens and electronic tuning.

## RESULTS AND DISCUSSION

### Blank experiments

To confirm the role of TiO<sub>2</sub> in the photocatalysis reaction, three sets of experiments were performed to compare TBC degradation rates with and without catalysts. One set was performed with TBC (5 mg L<sup>-1</sup>) exposed to TiO<sub>2</sub> (0.5 g L<sup>-1</sup>) but no UV (the TiO<sub>2</sub>-only condition). The second set was performed by exposing TBC (5 mg L<sup>-1</sup>) to UV without TiO<sub>2</sub> (the photolysis condition). Then, the third set was performed by exposing TBC (5 mg L<sup>-1</sup>) to TiO<sub>2</sub> (0.5 g L<sup>-1</sup>) in the presence of UV illumination (the photocatalysis condition). The results are presented in Fig. 1. First, blank experiments in the dark (without exposure to UV light) revealed that the change of initial TBC concentrations after 90 min of mixing with TiO<sub>2</sub> was less than 4% that the adsorption of TBC on TiO<sub>2</sub> was insignificant and could be neglected.

Next, blank experiments conducted in the presence of UV radiation, but in the absence of photocatalyst, did not result in any measurable degradation of TBC. Photolysis was found to be negligible in overall degradation process. Third, the results of the photocatalytic experiments showed that TBC could be degraded efficiently in aqueous TiO<sub>2</sub> dispersions by UV light irradiation. After UV irradiation for 90 min, ca. 99.8% of TBC was degraded.

### pH effect

According to previous studies, pH appears to play an important role in the photocatalytic process of various pollutants.<sup>27,28</sup> This is because pH influences the surface charge of the semiconductor, thereby affecting the interfa-

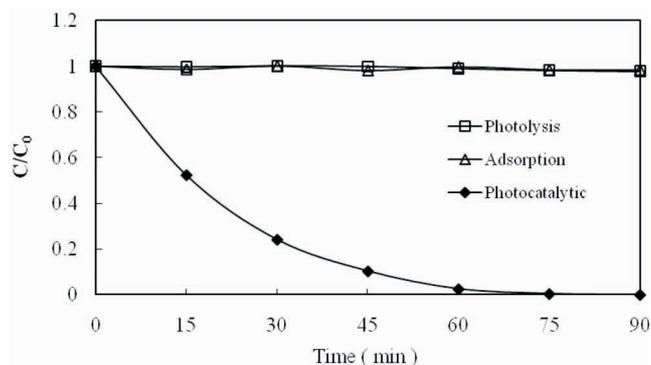


Fig. 1. TBC degradation under control conditions (TiO<sub>2</sub> only and UV only) and photocatalytic conditions (experimental conditions: TBC = 5 mg L<sup>-1</sup>, TiO<sub>2</sub> = 0 g L<sup>-1</sup> in photolysis, 0.5 g L<sup>-1</sup> in photocatalysis, UV-365 nm = 0.1 mW/cm<sup>2</sup> in photolysis and photocatalysis conditions).

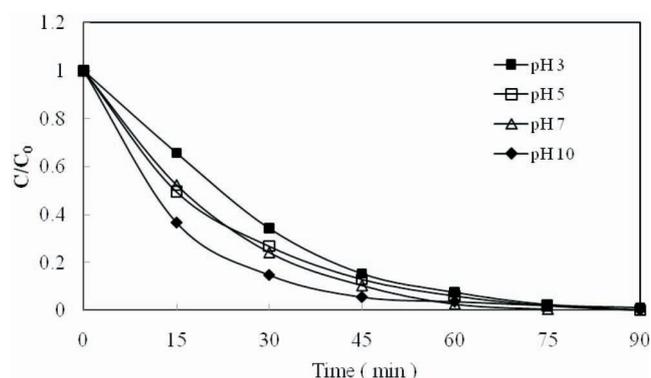


Fig. 2. pH effect on the photocatalytic degradation rate of TBC. Experimental conditions: TBC concentration 5 mg L<sup>-1</sup>; TiO<sub>2</sub> concentration 0.5 g L<sup>-1</sup>.

cial electron transfer and the photoredox process.<sup>29</sup> The influence of the initial pH value on the photodegradation rate of TBC for the TiO<sub>2</sub> suspensions is demonstrated in Fig. 2. The results indicated that the degradation rate increased with an increase in pH in the studied range of 3–10. The effect of pH on a photocatalytic reaction was generally ascribed to the surface charge of the photocatalyst and its relation to the ionic form of the organic compound (anionic or cationic). Electrostatic attraction or repulsion between the photocatalyst's surface and the organic molecule was taking place, and these events consequently enhanced or inhibited, respectively, the photodegradation rate.<sup>30</sup> Due to the non-ionic property of TBC, the observed increase in the degradation rate under an alkaline pH can be ascribed to the high hydroxylation of the photocatalyst's surface due to the presence of a large quantity of OH<sup>-</sup> ions. Consequently, a higher concentration of <sup>•</sup>OH species was formed, and the overall rate was enhanced.<sup>24,31</sup>

#### Effect of TiO<sub>2</sub> dosage

In photocatalytic processes, the amount of photocatalyst is an important parameter that can affect the degradation rate of organic compounds. In order to obtain the optimum catalyst dosage, the relationship between the dosage and degradation rate was investigated as shown in Fig. 3. The photocatalytic degradation rate was found to increase with increasing TiO<sub>2</sub> dosages, but the reaction was retarded at high TiO<sub>2</sub> dosages. The increase in the rate was likely due to the increase in the total surface area (or number of active sites) available for photocatalytic reaction as the dosage of TiO<sub>2</sub> increased. However, when TiO<sub>2</sub> was over-

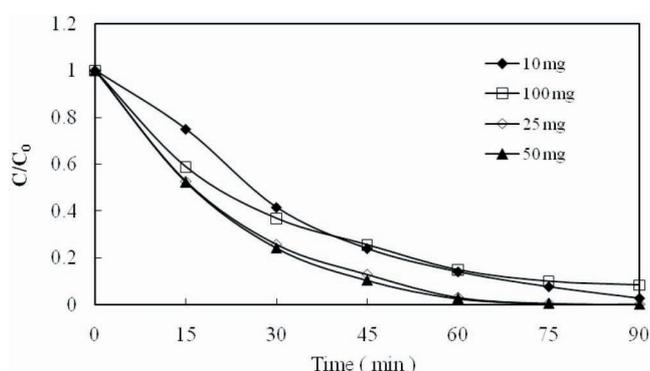


Fig. 3. Effect of TiO<sub>2</sub> dosage on the photocatalytic degradation rate of TBC. Experimental conditions: TBC concentration 5 mg L<sup>-1</sup>; pH 7.

dosed, the intensity of incident UV light was attenuated because of the decreased light penetration and increased light scattering, which counteracted the positive effect coming from the dosage increment and reduced the overall performance.<sup>32</sup>

#### Effects of anions

Studying the effects of anions on the photocatalytic degradation of TBC is important because anions are often present in natural water and industrial wastewater. The effects of the presence of various anions such as chloride, bicarbonate, carbonate and sulfate were studied using 0.05 M solutions of their sodium salts and an initial concentration of 5 mg L<sup>-1</sup> of TBC with a 0.5 g L<sup>-1</sup> of TiO<sub>2</sub>. The results showed that all these anions inhibited the degradation significantly (see Fig. 4). These substances might compete for the active sites on the TiO<sub>2</sub> surface or deactivate the photocatalyst and, subsequently, decrease the degradation rate of TBC. Also, inhibition effects of anions could be explained as the reaction of positive holes (h<sup>+</sup>) and hydroxyl radicals (<sup>•</sup>OH) with anions that behaved as h<sup>+</sup> and <sup>•</sup>OH scavengers resulting in prolonged TBC removal.<sup>33</sup> A major drawback resulting from the high reactivity and non-selectivity of <sup>•</sup>OH was that it also reacted with non-target compounds present in the background water matrix, i.e. inorganic anions present in water. This resulted in a higher <sup>•</sup>OH demand to accomplish the desired degree of degradation.<sup>15</sup> Similar results were reported previously by Chen et al.,<sup>34</sup> suggesting that inorganic anions were capable of inhibiting the photocatalytic degradation of dichloroethane in an aqueous

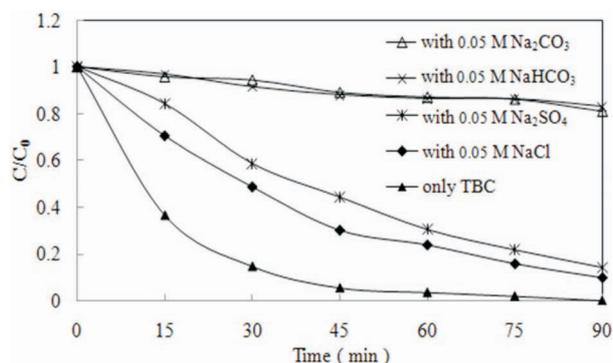


Fig. 4. Effect of anions on the photocatalytic degradation rate of TBC. Experimental conditions: TBC concentration 5 mg L<sup>-1</sup>; TiO<sub>2</sub> concentration 0.5 g L<sup>-1</sup>; pH 10.

suspension of TiO<sub>2</sub>.

### Evolution of TOC

The complete degradation of an organic molecule by photocatalysis normally leads to the conversion of all its carbon atoms to gaseous CO<sub>2</sub> and of the heteroatoms into inorganic anions that remain in solution. In order to study the mineralization during TBC photocatalysis, total organic carbon (TOC) measurement was performed. The results are shown in Fig. 5. It was found that approximately 71% of the TBC was mineralized within 32 h by the photocatalytic reaction. Complete mineralization of TBC was not achieved after 32 h of oxidation although TBC disappeared after 90 min. The great difference between degradation efficiency and mineralization efficiency implied that the products of TBC oxidation mostly stayed at the intermediate product stage under the present experimental conditions.

### Separation and identification of the intermediates

Since thiobencarb is sparingly soluble in water, it is therefore a challenge to study its photodegradation in dilute aqueous solutions in the absence of any organic solvents, and to identify its degradation products. A relatively low intensity UV-365 lamp (15 watt) was used in this study to identify organic intermediates. This made it possible to obtain slower degradation rates and provide favorable conditions for the determination of intermediates. Additionally, the initial TBC concentration (100 mg L<sup>-1</sup>) was selected to be high enough to facilitate the identification of intermediate products. In photocatalytic degradation process, the

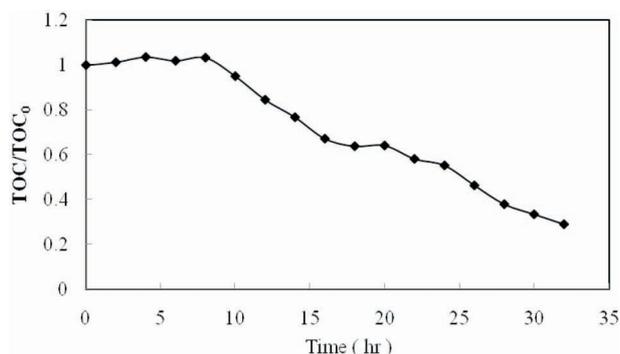


Fig. 5. Depletion in TOC measured as a function of irradiation time for an aqueous solution of TBC (5 mg L<sup>-1</sup>) in the presence of TiO<sub>2</sub> (0.5 g L<sup>-1</sup>).

concentration of reaction intermediates was low and thus the intermediates had to be preconcentrated before the application of an appropriate analytical procedure. Prior to GC/MS analysis; the samples were preconcentrated using a solid-phase microextraction (SPME) method, a selective tool for the trace analysis of organic compound in water samples. Therefore, the intermediates generated in the TBC solution during the photocatalytic degradation process with UV irradiation were examined with SPME-GC/MS.

Fig. 6 displays the chromatogram of the reacted solution after irradiation for 280 min in the presence of TiO<sub>2</sub>. At least eight compounds were identified at retention times of less than 45 min. One of the peaks was the initial TBC; the other seven (new) peaks were the intermediates formed. We denoted the related intermediates as species I-VII. Except for the initial TBC, the other peaks increased at first and subsequently decreased, indicating formation and subsequent transformation of the intermediates. Some other minor peaks were present, but mass fragment information did not allow elucidation of their structures.

Intermediate identification is usually carried out on the basis of EI mass spectra, mainly because their structure can be elucidated by comparing the unknown compound spectrum with published spectra from spectra databases or research papers. Otherwise, from the knowledge of the molecular weight and the interpretation of fragmentation patterns according to well-known mass spectroscopy rules, it is possible to hypothesize a molecular structure.<sup>35</sup> Table 1 summarizes the identified intermediates of TBC along with their retention time and the characteristic ions of the mass spectra. Four intermediates (compounds I-IV) were identified by the molecular ion and mass fragment ions and also through comparison with NIST library data. The similarities of these compounds to the NIST library data were more than 89%. Three intermediates (compounds V-VII) not included in the library were identified by the molecular ion and the interpretation of the mass spectra. The molecular mass of these intermediates was determined using positive ion chemical ionization (CI) mass spectrometry through the abundant protonated molecules, and then structural data was obtained from the electron impact (EI) fragmentation patterns. The presence and number of chlorine atoms in the suspected intermediates can be easily attained by taking into account both the relative intensity of the <sup>35</sup>Cl/<sup>37</sup>Cl

Table 1. Identification of the intermediates from the photodegradation of thiobencarb by GC/MS

Peaks	Photodegradation intermediates	R.T. (min)	MS peaks ( $m/z$ )
<b>I</b>	4-chlorobenzaldehyde	16.21	140,139,111,75,50
<b>II</b>	4-chloro-2/3-hydroxybenzaldehyde	17.89	156,155,99,63,39
<b>III</b>	4-chlorobenzyl alcohol	18.31	142,107,79,77,51
<b>IV</b>	4-chlorobenzyl mercaptan	19.39	158,125,89,63,45
<b>V</b>	S-4-chlorobenzyl ethylthiocarbamate	31.60	229,158,125,89,72
TBC	S-4-chlorobenzyl diethylthiocarbamate	34.40	257,125,100,72,44,29
<b>VI</b>	S-4-chlorobenzyl acetyl(ethyl)thiocarbamate	36.47	271,156,146,125,89,43
<b>VII</b>	S-4-chloro-2/3-hydroxybenzyl diethylthiocarbamate	41.45	273,141,100,72,44,29

signals and the mass differences between the two masses.

The EI and CI mass spectra of the identified intermediates are shown in Fig. 7 and Fig. 8, respectively. Compound **I** was identified as 4-chlorobenzaldehyde with a fit value of 99%, found by searching the mass spectra library. The molecular mass was determined from the CI mass spectrum to be  $m/z = 140$  by the observation of an  $[M + H]^+$  ion of 141. The double signal of protonated molecular ion 141/143 appeared to be in a ratio of 3:1 due to the natural ratio of the chlorine isotope. Based on this, the intermediate product can be confirmed to contain one chlorine atom.

The peak eluting at 17.89 min (compound **II**) during

GC/MS analysis of TBC solution was identified as 4-chloro-2/3-hydroxybenzaldehyde with the mass spectra library. The molecular mass was determined from the CI mass spectrum to be  $m/z = 156$  that corresponded to the hydroxylated derivative of 4-chlorobenzaldehyde (addition of OH group,  $m/z = [M + 16]^+$ ). However, even an EI mass spectrum did not provide secure information about the position of the hydroxyl group in this hydroxylated derivative.<sup>35</sup> As the pure compound **II** is not commercially available, a more conclusive identification is difficult.

A search of the mass spectra library selected 4-chlorobenzyl alcohol with a fit value of 89% for compound **III**,

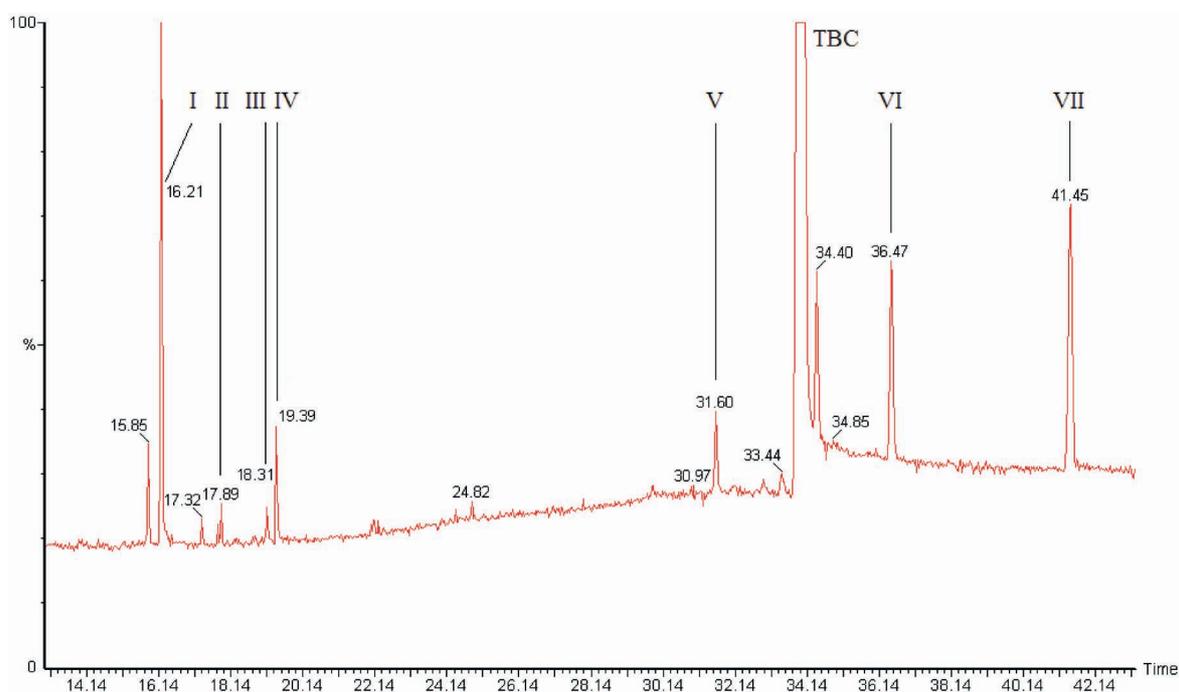


Fig. 6. GC/MS chromatogram obtained for TBC solution ( $100 \text{ mg L}^{-1}$ ) after 280 min of irradiation with UV light in the presence of  $\text{TiO}_2$ .

whose retention time on GC/MS was 18.31 min. The molecular mass was determined from the CI mass spectrum to be  $m/z = 142$  by the observation of  $[M + H]^+$  ion of 143. The peak eluting at 19.39 min (compound IV) during GC/MS analysis of TBC solution was identified as 4-chlorobenzyl mercaptan with a fit value of 99%, with the mass spectra library. The protonated molecular ion ( $m/z = 159$ ) for compound IV was not obviously detected by the GC/MS, but

two characteristic fragments were found in high abundance for the CI mass spectrum. The mass spectrum showed the characteristic ions at  $m/z = 125$  and  $m/z = 47$  that correspond to the groups  $[C_6H_4CH_2]^+$  and  $[CH_2SH]^+$ , respectively. The fragment ion 125/127 appears to be in a ratio of 3:1 due to the natural ratio of the chlorine isotope. It can be

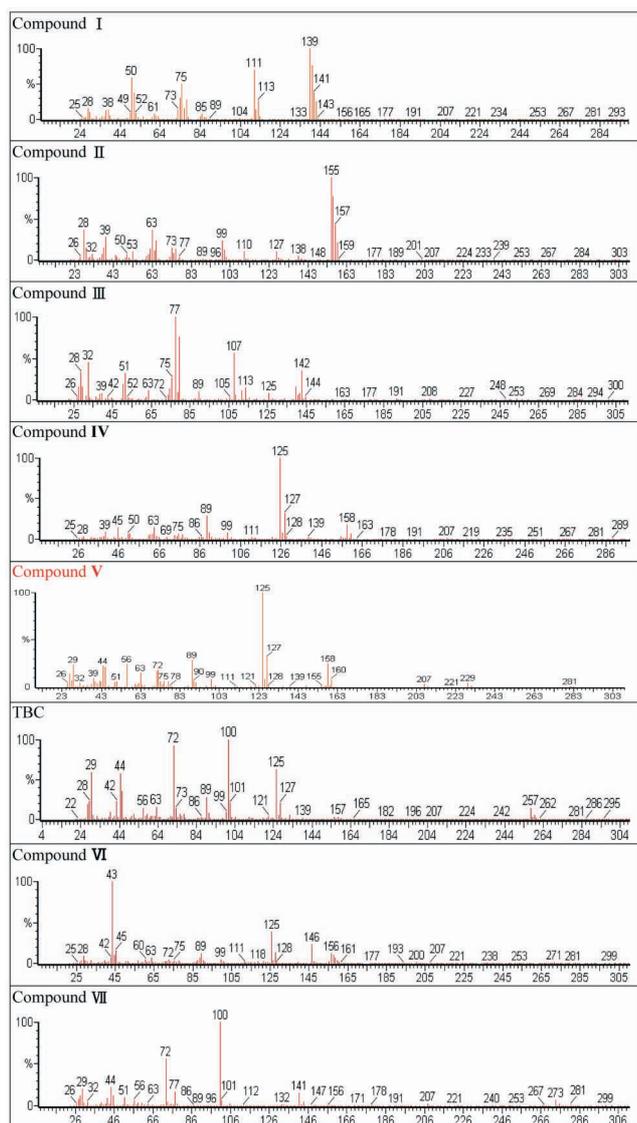


Fig. 7. EI mass spectra of intermediates formed during the photodegradation of TBC after they were separated by GC/MS method. Spectra are denoted I-VII and correspond to the I-VII species in Fig. 6, respectively.

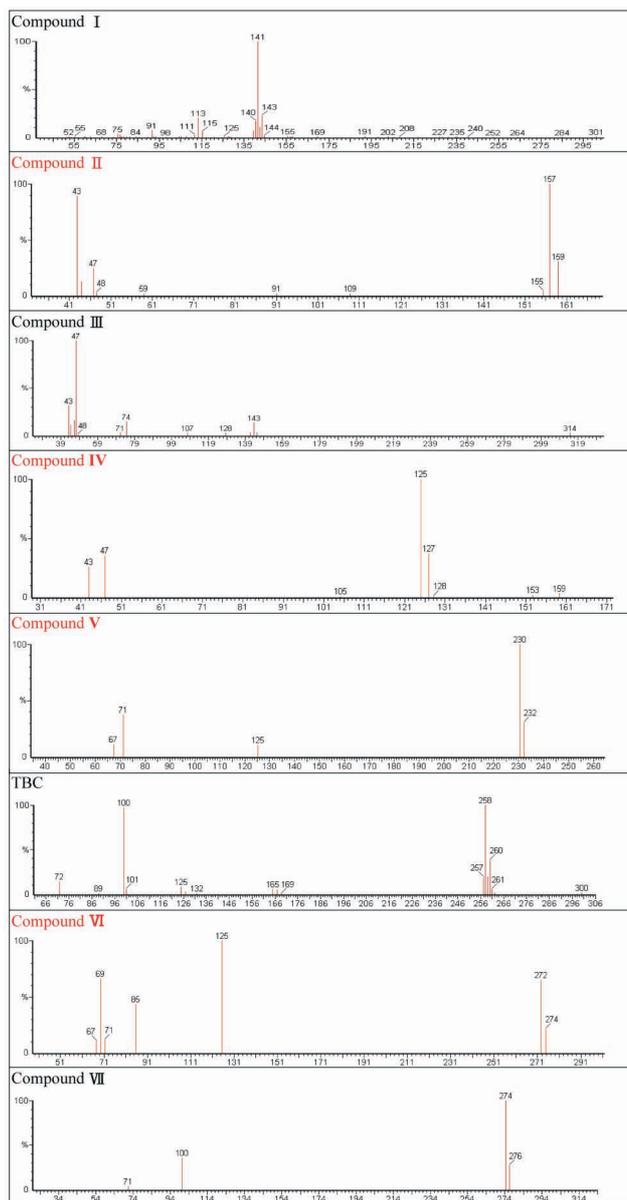


Fig. 8. CI mass spectra of intermediates formed during the photodegradation of TBC after they were separated by GC/MS method. Spectra are denoted I-VII and correspond to the I-VII species in Fig. 6, respectively.

deduced that a chlorine atom is present in the molecular ion of this intermediate.

Compound **V** had a molecular ion at  $m/z = 229$  and major fragments at  $m/z = 125$  and  $72$ , which were common ions with thiobencarb. The molecular mass difference of 28 amu, compared to the initial thiobencarb molecule, indicated that a de-ethylated product was formed. According to mass spectrometric analyses, compound **V** was tentatively identified as S-4-chlorobenzyl ethylthiocarbamate. *N*-Dealkylation of thiobencarb to compound **V** was previously reported as a process mediated by hydroxyl radicals.<sup>36</sup>

The molecular mass of compound **VI** was determined from the CI mass spectrum to be  $m/z = 271$  by the observation of an  $[M + H]^+$  ion of 272. The EI mass spectrum showed the characteristic ions at  $m/z = 125$  and  $m/z = 43$  that correspond to the groups  $[ClC_6H_4CH_2]^+$  and  $[CH_3CO]^+$ , respectively. According to mass spectrometric analyses, compound **VI** was tentatively identified as S-4-chlorobenzyl acetyl(ethyl)thiocarbamate. This compound was further identified by comparing the mass spectrum with previous reported spectrum. The fragments of the studied compound match with the previous spectrum of the literature.<sup>25</sup>

Compound **VII** was attributed as the ring-hydroxylated derivative of thiobencarb. It exhibited the same characteristic ions ( $m/z = 100, 72, 44$ ) with thiobencarb and its molecular ion  $M^+$  at  $m/z = 273$  corresponded to the addition of  $-OH$  group to the phenyl ring. The main difference was the presence of an  $m/z = 141$  ion which corresponded to the  $[ClC_6H_3(OH)CH_2]^+$  group. This means that the hydroxylation takes place in the aromatic moiety because the mass spectra shows the peak at  $m/z = 141$  that correspond to the ring-hydroxylated analog of  $[ClC_6H_4CH_2]^+$  ( $m/z = 125$ ), a fragment common to thiobencarb (addition of OH group,  $m/z = [M + 16]^+$ ). The double signal of protonated molecular ion 274/276 appeared to be in a ratio of 3:1 due to the natural ratio of the chlorine isotope. It can be deduced that a chlorine atom is present in the molecular ion of this intermediate. According to mass spectrometric analyses, compound **VII** was tentatively identified as S-4-chloro-2/3-hydroxybenzyl diethylthiocarbamate. As the pure compounds **V-VII** are not commercially available, a more conclusive identification is difficult.

Fig. 9 shows the evolution profiles of the reaction in-

termediates detected during photocatalysis. By describing the typical bell-shaped profiles in most of the cases, we clearly observed the change in the distribution of each intermediate during the photocatalytic degradation of TBC ( $5 \text{ mg L}^{-1}$ ). Compounds **I**, **VI** and **VII** may be considered as the main intermediates, due to their high concentration compared with other intermediates detected. Their concentrations increase with time of irradiation and go through maximum at 30 min and then decline gradually. Compounds **II-V** were present at lower concentrations, but they were considered as main intermediates, because they increased at first and subsequently decreased.

### Initial photooxidation pathway

Irradiation of  $TiO_2$  suspension with photons, the energy of which is equal to or higher than that of the band gap energy of the semiconductor (e.g. 3.2 eV for  $TiO_2$ ), results in the formation of conduction band electrons ( $e^-$ ) and valence band holes ( $h^+$ ). Hydroxyl radicals can be produced by the oxidation of water by these holes and are recognized as one of the most powerful oxidants.<sup>24</sup> Nakamura and

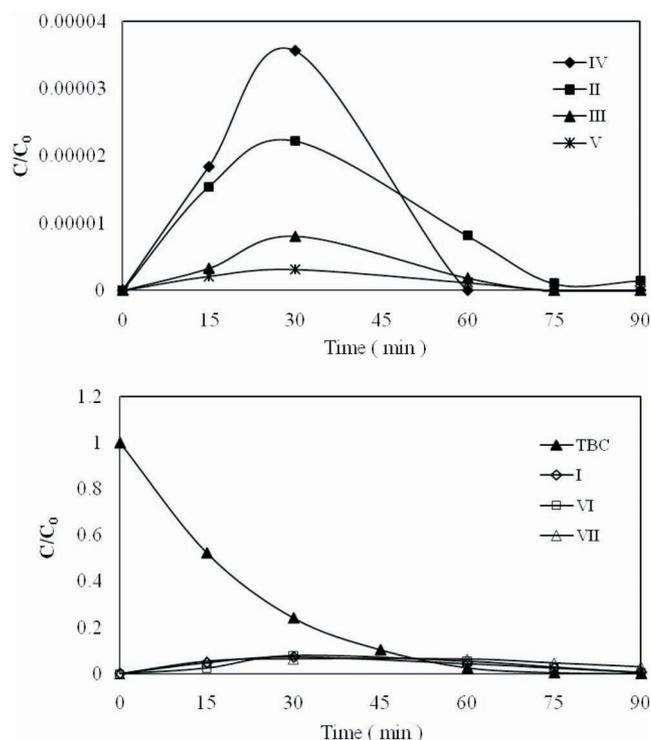


Fig. 9. Evolution profiles of the reaction intermediates detected during the photocatalytic degradation of TBC ( $5 \text{ mg L}^{-1}$ ).

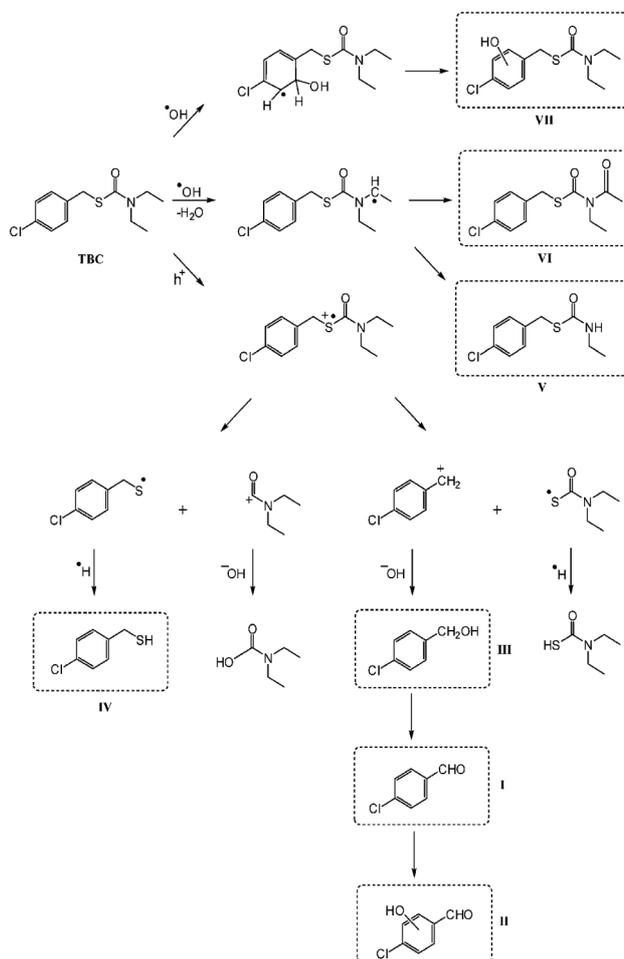
Nakato<sup>37</sup> proposed a mechanism of water oxidation that involved a nucleophilic attack on a surface-trapped hole at a bridged O site. Murakami et al.<sup>38</sup> reported that when the O-O bond in Ti-O-OH broke, the hydroxyl radicals could be formed from the bridge OH groups.

Various aromatic intermediates were identified by GC/MS techniques during the treatment, which were involved into three tentative degradation routes. One was based on the initial attack of the aromatic ring by  $\cdot\text{OH}$  leading to the formation of hydroxylated derivative. The second route was based on the abstraction of hydrogen atoms of the *N*-alkyl group followed by the addition of oxygen resulting in dealkylated derivative. Finally, the third possible degradation route was based on the oxidative cleavage of the C-S bond of the substrate molecule. The molecular structure of the degradation intermediates and the tentative photocatalytic degradation pathway of TBC are presented in Scheme I.

Aromatic hydroxylation is a typical reaction of hydroxyl free radicals ( $\cdot\text{OH}$ ) and involves hydroxycyclohexadienyl radical intermediates that are oxidized by molecular oxygen to the phenolic products.<sup>39</sup> Hydroxyl radicals attacked preferentially the aromatic moiety due to their electrophilic character to form the ring-hydroxylated product (compound VII) but also attacked the *N*-alkyl chain to form the de-alkylated product (compound V). It is well known that the  $\cdot\text{OH}$  radical is an electrophile and that C-H bonds adjacent to nitrogen are responsible for a pronounced stereoelectronic effect that produces high rates of H-atom abstraction. Therefore, the  $\alpha$ -hydrogen atoms in the *N*-ethyl group of TBC molecule were the most prone to radical attack. Hydroxyl radicals yielded carbon-centered radicals upon the H-atom abstraction from the *N*-ethyl group, or they reacted with the lone-pair electron on the N atom to generate cationic radicals, which subsequently converted into carbon-centered radicals.<sup>40</sup> The carbon-centered radical generated after addition of oxygen forming the peroxy radical decomposed to different intermediates (compounds V and VI).

In addition to the degradation routes of hydroxylation and *N*-de-ethylation, an alternative pathway was also identified. First, oxidation of the thiobencarb molecule to form the thiobencarb cation radical took place when positive holes attacked it, initiating a series of reactions. The formation of cation radicals had also been observed in the photo-

**Scheme I** Proposed photodegradation pathway of TBC under UV irradiation in aqueous TiO<sub>2</sub> dispersions



catalytic degradation of organophosphorus pesticides<sup>41</sup> and thioethers.<sup>42</sup>

The interfacial transfer of a single electron from the sulfur atom led to the formation of thiobencarb cation radical. The scission of the C-S bond in this cation radical led to the formation of a  $\text{ClC}_6\text{H}_4\text{CH}_2\text{S}\cdot$  radical that was the precursor of 4-chlorobenzyl mercaptan (compound IV). The H atom necessary for S-H bond formation was proposed to have originated from the proton reduction by photogenerated electron  $\text{H}^+ + \text{e}^- \rightarrow \text{H}\cdot$  as already observed in the degradation of the insecticide fenitrothion by Kerzhentsev et al.<sup>43</sup> Similarly, the scission of the C-S bond in the TBC cation radical led to the formation of (4-chlorophenyl)methyl cation. The carbocation was extremely unstable and un-

derwent rapid hydrolysis. Hydrolysis of (4-chlorophenyl)-methylion yielded 4-chlorobenzyl alcohol (compound **III**). Subsequently, 4-chlorobenzyl alcohol underwent oxidation to 4-chlorobenzaldehyde (compound **I**) and 4-chloro-2/3-hydroxybenzaldehyde (compound **II**).

## CONCLUSION

Photodegradation using TiO<sub>2</sub> as a catalyst is an efficient method of degrading TBC. After a 0.1 mW/cm<sup>2</sup> light intensity (365 nm UV) irradiation for 90 min, ca. 99.8% of TBC is degraded. The photodegradation rate of TBC is found to increase along with increasing pH and to increase, and then decrease, along with increasing catalyst concentration. In addition, the presence of inorganic ions such as chloride, bicarbonate, carbonate and sulfate, which are often present in natural water and industrial wastewater, decrease the photocatalytic degradation rate of TBC. Seven intermediate products are detected by the solid-phase microextraction (SPME) and gas chromatography/mass spectrometry (GC/MS) technique, giving insight into the early steps of the degradation process. The analysis of the intermediate products reveals the presence of hydroxylation, dealkylation and C–S bond cleavage pathways. The reaction pathway investigation provides a better understanding and new insights on the mechanism of degradation of thio-bencarb with TiO<sub>2</sub>.

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