



Bis(2-chloroethoxy)methane degradation by TiO₂ photocatalysis: Parameter and reaction pathway investigations

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ABSTRACT

Haloethers are widely used in industry, and the release of these species into the environment is of great concern because of their toxicity and carcinogenicity. The present study deals with the photocatalytic degradation of the haloether, bis(2-chloroethoxy)methane (BCEXM), in the presence of TiO₂ particles and UV-A ($\lambda = 365$ nm) radiation. About 99.5% of BCEXM was degraded after UV irradiation for 16 h. Factors such as solution pH, TiO₂ dosage, and the presence of anions were found to influence the degradation rate. To obtain a better understanding of the mechanistic details of this TiO₂-assisted photodegradation of BCEXM with UV irradiation, the intermediates of the processes were separated, identified, and characterized by the solid-phase microextraction (SPME) and gas chromatography/mass spectrometry (GC/MS) technique. To the best of our knowledge, this is the first report on the degradation pathways of BCEXM. The first step in the destruction of BCEXM is thought to be abstraction of a hydrogen by $\cdot\text{OH}$ to form a carbon-centered radical which then reacts with O₂ to form a peroxy radical. Peroxy radicals react with one another and produce an alkoxy radical. The β -bond fragmentation of the alkoxy radical produces different intermediates.

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1. Introduction

Haloethers are widely used in many industries [1,2] as solvents during fiber processing, in medicines, ion-exchange resins, pesticides, and polymers. They are also used in dry-cleaning to remove stains. The release of haloethers into the environment is of great concern because of their toxicity and carcinogenicity [1,3]. They have been detected in river water and drinking water in the United States and abroad. Five haloethers were classified as priority pollutants by the US Environmental Protection Agency (EPA) in 1979 [4,5]. Haloethers are stable in aqueous media and non-biodegradable in river water; exposure to the general population is expected to occur through the consumption of contaminated drinking water.

Bis(2-chloroethoxy)methane (BCEXM) is classified as a haloether. Its chemical structure is shown in Fig. 1. It is used primarily as the starting compound in the production of polysulfide elastomers. Over 95% of polysulfide polymers are made from BCEXM and sodium polysulfide. These polysulfides are used extensively in a variety of sealant applications because of their resistance to degradation by many solvents and resistance to high temperature

[6]. BCEXM is reported to be produced in very significant quantities, 25–50 million pounds per year [7] and the chemical is on the Environmental Protection Agency's list of high production volume chemicals [8]. Bis(2-chloroethoxy)methane was found in the industrial wastes of metal finishing, plastics, and chemical manufacturers, and in those of steam electric power industries that discharge effluents to the combined sewerage system along the lower Passaic River in New Jersey [9]. Samples taken from a synthetic rubber plant's treated effluent revealed BCEXM levels of 140 mg L⁻¹ [10]. In the Chef Menteur River that flows from Lake Pontchartrain, Louisiana, to the Gulf of Mexico, clams had BCEXM levels of 12 ng g⁻¹ (ppb), wet weight in tissue [11].

Degradation by photolysis is not a significant factor in surface waters since BCEXM does not contain chromophores that absorb light in the visible or ultraviolet regions of the electromagnetic spectrum. Hydrolysis is relatively slow, and BCEXM has a minimum calculated half-life in water of six months to several years. Haag and Mill [12] showed that the minimum half-life of BCEXM in water was two years.

Conventional water treatment methods based on adsorption or reverse osmosis principles can be used, but these methods involve only phase transfer of pollutants without degradation. Accordingly, a subsequent waste treatment has to follow [13]. Biological treatment is highly effective for the removal of most contaminants. A study by Patterson and Kodukala [14] showed that when the influ-

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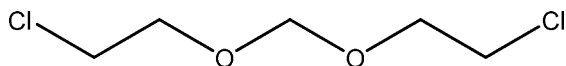


Fig. 1. Chemical structure of BCEXM.

ent of a sludge treatment facility was spiked with 0.24 g L^{-1} of BCEXM, 60% of the pollutant was removed. Despite the success and cost effectiveness of biodegradation processes, they are inherently slow, do not allow for high degrees of removal, and are not suitable for removing compounds toxic to microorganisms. The disposal of sludge formed during biological treatment can pose additional expenses and environmental problems [15].

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 [16]. The TiO_2 -mediated photocatalysis process has been successfully used to degrade pollutants during the past few years [17–21]. TiO_2 is broadly used as a photocatalyst because of its non-toxicity, photochemical stability, and low cost [22]. The initial step in TiO_2 -mediated photocatalysis degradation is proposed to involve the generation of an (e^-/h^+) pair, leading mainly to the formation of hydroxyl radicals ($\cdot\text{OH}$), superoxide radical anions ($\text{O}_2^{\cdot-}$), and hydroperoxyl radicals ($\cdot\text{OOH}$) as shown below [23–25]



These radicals are the oxidizing species in the photocatalytic oxidation processes. Among them, hydroxyl radicals are the most powerful oxidizing species that TiO_2 photocatalysis produces and can attack organic contaminants present at or near the surface of TiO_2 [26].

To the best of our knowledge, no studies on the photocatalytic degradation of haloethers have been published yet, in particular not for BCEXM. In this paper, we report the photocatalytic degradation of BCEXM for the first time. We investigate various parameters that may affect the photodegradation of BCEXM in the presence of TiO_2 suspensions, in order to better understand TiO_2 photocatalysis. This study also focuses on the identification of the reaction intermediates and understanding of the mechanistic details of the photodegradation of BCEXM in the TiO_2/UV light process as a foundation for future application of the technology for degradation of haloether compounds.

2. Experimental

2.1. Materials and reagents

Bis(2-chloroethoxy)methane (99.5%) and 2-chloroethanol (98%) were obtained from ChemService. Standard solutions containing 50 mg L^{-1} of BCEXM in water were prepared, protected from light, and stored at 4°C . Other chemicals were of reagent grade and were used as such without further purification. The 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 $1.8 \times 10^7 \Omega \text{ cm}$.

2.2. Apparatus and instruments

The apparatus for studying the photocatalytic degradation of BCEXM has been described elsewhere [27]. The C-75 Chromatovue cabinet of UVP provides a wide area of illumination from the 15-W UV-365 nm tubes positioned on two sides of the cabinet interior. Solid-phase microextraction (SPME) was utilized for the analysis of BCEXM and intermediates resulting from the photocatalytic degradation process. SPME holder and fiber-coating divinylbenzene-carboxen-polydimethyl-siloxane (DVB-CAR-PDMS 50/30 μm) 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. Analysis of ionic byproducts was performed by ion chromatography (IC) with a Dionex ICS-90 instrument. The mineralization of BCEXM was monitored by measuring the total organic carbon (TOC) content with a Dohrmann Phoenix 8000 Carbon Analyzer, which employs a u.v./persulfate oxidation method by directly injecting the aqueous solution.

2.3. Procedures and analysis

BCEXM solution (50 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 0.1N NaOH or 0.1N 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 W). An average irradiation intensity of 0.2 mW/cm^2 was maintained throughout the experiments and was measured by internal radiometer. After each irradiation cycle, the amount of BCEXM was thus determined by SPME-GC/MS. The aqueous TiO_2 dispersion was sampled (5 mL) and centrifuged to separate the TiO_2 particles. The clear solution was then transferred into a 4-mL sample vial. The SPME fiber was directly immersed into the sample solution to extract BCEXM 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 24 min. Separation was carried out in a DB-5 capillary column (5% diphenyl/95% dimethyl-siloxane), 60 m, 0.25-mm i.d., and 1.0- μm 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 , 8°C/min to 240°C (0.5 min). Electron impact (EI) mass spectra were monitored from 20 to 350 m/z . The ion source and inlet line temperatures were set at 220 and 250°C , respectively.

The ionic byproducts from BCEXM degradation were analyzed using a Dionex ICS-90 ion chromatograph. The column was an IonPac[®] AS4A-SC (4 mm \times 250 mm) for chloride (Cl^-) analysis. The flow rate was 1.0 mL/min, and the injection volume was 100 μL of the filtered reaction samples. The eluent consisted of a mixture of 3.5 mM Na_2CO_3 and 1 mM NaHCO_3 for the anion analysis. For these operating conditions, the retention time for chloride ion was 2.2 min. For quantitative studies, standard solutions and a calibration curve for chloride ion were prepared in the range from 1 to 25 mg L^{-1} .

3. Results and discussion

3.1. Blank experiments

To confirm the role of TiO_2 in the photocatalysis reaction, three sets of experiments were performed to compare BCEXM

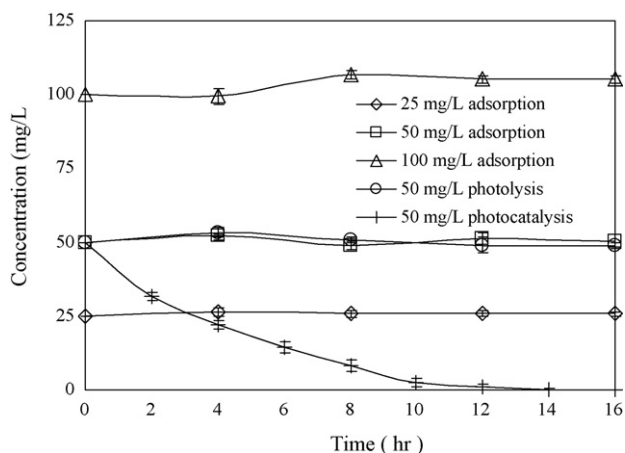


Fig. 2. BCEXM degradation under control conditions (TiO_2 only and UV only) and photocatalytic conditions (experimental conditions: BCEXM = 50 mg L^{-1} , $\text{TiO}_2 = 0 \text{ g L}^{-1}$ in photolysis, 0.5 g L^{-1} in photocatalysis, UV-365 nm = 0.2 mW/cm^2 in photolysis and photocatalysis conditions). Error bars represent the standard deviations of triplicates.

degradation rates with and without catalysts. One set was performed with BCEXM ($25\text{--}100 \text{ mg L}^{-1}$) exposed to TiO_2 (0.5 g L^{-1}) but no UV (the TiO_2 -only condition). The second set was performed by exposing BCEXM (50 mg L^{-1}) to UV without TiO_2 (the photolysis condition). Then, the third set was performed by exposing BCEXM (50 mg L^{-1}) to TiO_2 (0.5 g L^{-1}) in the presence of UV illumination (the photocatalysis condition). The results are presented in Fig. 2. First, blank experiments in the dark (without exposure to UV light) revealed that the change of initial BCEXM concentrations after 16 h of mixing with TiO_2 was less than 5%, so the adsorption of BCEXM on TiO_2 is insignificant and can 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 BCEXM. Photolysis was found to be negligible in overall degradation process. Third, the results of the photocatalytic experiments showed that BCEXM could be degraded efficiently in aqueous TiO_2 dispersions by UV light irradiation. After UV irradiation for 16 h, ca. 99.5% of BCEXM was degraded.

3.2. pH effect

Many studies have indicated that the pH of a solution is an important parameter in the photocatalytic degradation of organic compounds [28,29]. This is because pH influences the surface charge of the semiconductor, thereby affecting the interfacial electron transfer and the photoredox process [30]. The influence of the initial pH value on the photodegradation rate of BCEXM for the TiO_2 suspensions is demonstrated in Fig. 3. The results indicated that the degradation rate increased with an increase in pH in the studied range of 4–8. The effect of pH on a photocatalytic reaction is 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 is taking place, and these events consequently enhance or inhibit, respectively, the photodegradation rate [31]. Since BCEXM is a unionizable compound, the observed increase of the degradation rate with an increase in pH can be attributed to the high hydroxylation of the photocatalyst's surface due to the presence of a large quantity of OH^- ions. Consequently, a higher concentration of $\cdot\text{OH}$ species is formed, and the overall rate is enhanced [26,32].

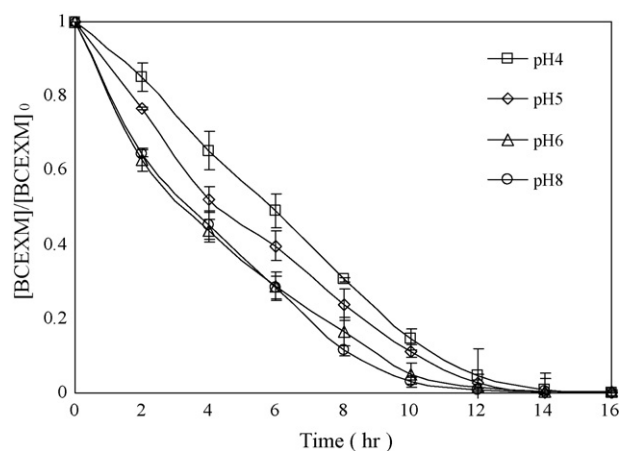


Fig. 3. pH effect on the photocatalytic degradation rate of BCEXM. Experimental conditions: BCEXM concentration 50 mg L^{-1} ; TiO_2 concentration 0.5 g L^{-1} . Error bars represent the standard deviations of triplicates.

3.3. Effect of TiO_2 dosage

It is important from both the mechanistic and application point of view to study the dependence of the photocatalytic reaction rate on the concentration of TiO_2 . Hence, the effect of TiO_2 dosage on the photodegradation rate of BCEXM was investigated by employing different concentrations of TiO_2 varying from 0.1 to 1.0 g L^{-1} . The photocatalytic degradation rate was found to increase with increasing TiO_2 dosages, but the reaction was retarded at high TiO_2 dosages (Fig. 4). The higher degradation rate with increase in catalyst dosage can be attributed to the increase in catalyst surface area, increase of light absorption, and consequently the creation of a higher number of active species. However, when TiO_2 was overdosed, 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 [33].

3.4. Effect of substrate concentration

When the initial BCEXM concentration was varied from 25 to 100 mg L^{-1} at constant TiO_2 dosage (0.5 g L^{-1} , pH 6), degradation

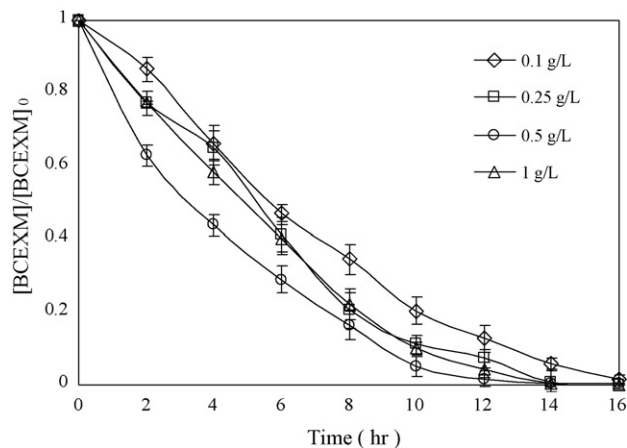


Fig. 4. Effect of TiO_2 dosage on the photocatalytic degradation rate of BCEXM. Experimental conditions: BCEXM concentration 50 mg L^{-1} ; pH 6. Error bars represent the standard deviations of triplicates.

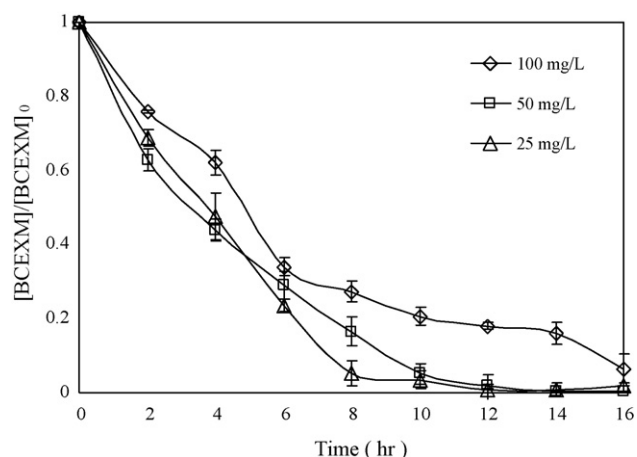


Fig. 5. Effect of initial substrate concentration on the photocatalytic degradation rate of BCEXM. Experimental conditions: TiO_2 concentration 0.5 g L^{-1} ; pH 6. Error bars represent the standard deviations of triplicates.

efficiency was inversely affected by BCEXM concentration (Fig. 5). This can be explained as follows: as the BCEXM concentration increased, the equilibrium adsorption of the BCEXM on the catalyst surface increased, and the competitive adsorption of OH^- on the same adsorption sites decreased, resulting in a lower formation rate of $\cdot\text{OH}$ radical, the principal oxidant necessary for high degradation efficiency [26].

3.5. Effects of anions

The study of the effects of anions on the photocatalytic degradation of BCEXM is important because anions are rather common in natural water and industrial wastewater. The effects of Cl^- and NO_3^- ions on the degradation rate of BCEXM were examined individually by adding NaCl and NaNO_3 to the system until the resultant solution contained 0.1 M of Cl^- and NO_3^- ions before the irradiation had begun. The results showed that anions inhibit the degradation considerably (see Fig. 6). These substances may compete for the active sites on the TiO_2 surface or deactivate the photocatalyst and, subsequently, decrease the degradation rate of BCEXM. Also, inhibition effects of anions can be explained as the reaction of positive holes (h^+) and hydroxyl radicals ($\cdot\text{OH}$) with anions that behaved as h^+ and $\cdot\text{OH}$ scavengers resulting in prolonged BCEXM

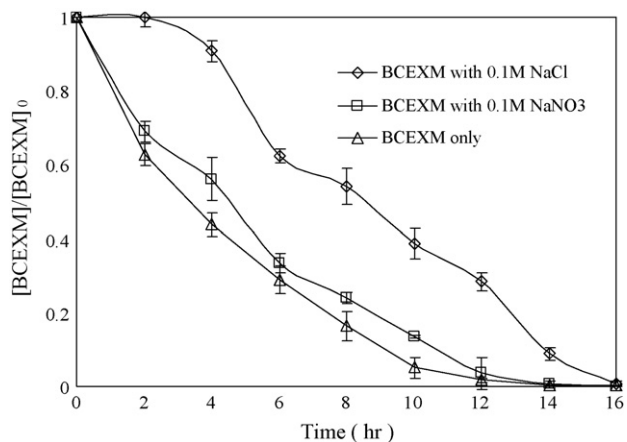


Fig. 6. Effect of anions on the photocatalytic degradation rate of BCEXM. Experimental conditions: BCEXM concentration 50 mg L^{-1} ; TiO_2 concentration 0.5 g L^{-1} ; pH 6. Error bars represent the standard deviations of triplicates.

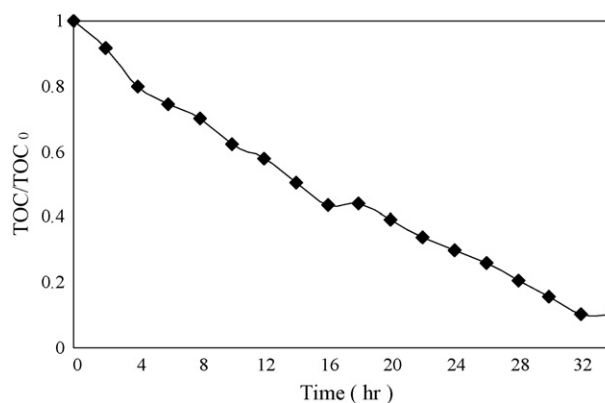


Fig. 7. Depletion in TOC measured as a function of irradiation time for an aqueous solution of BCEXM (50 mg L^{-1}) in the presence of TiO_2 (0.5 g L^{-1}).

removal [34]. A major drawback resulting from the high reactivity and non-selectivity of $\cdot\text{OH}$ is that it also reacts with non-target compounds present in the background water matrix, i.e. inorganic anions present in water. This results in a higher $\cdot\text{OH}$ demand to accomplish the desired degree of degradation [35]. Similar results have been reported previously by Chen et al. [36], suggesting that inorganic anions were capable of inhibiting the photocatalytic degradation of dichloroethane in an aqueous suspension of TiO_2 .

3.6. 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_2 and of the heteroatoms into inorganic anions that remain in solution. In order to study the total mineralization of BCEXM, the determination of total organic carbon (TOC) was carried out as a function of the irradiation time. The decrease in the TOC percentage of BCEXM during the photocatalytic degradation is depicted in Fig. 7. The complete removal of 50 mg L^{-1} of BCEXM was achieved after 16 h of treatment, and the corresponding carbon mineralization was 56%. The treatment was prolonged to 34 h to test whether mineralization could be completed as well. Approximately 90% of BCEXM was mineralized within 34 h of photocatalytic reaction time. Complete mineralization of BCEXM was not achieved after 34 h of oxidation although BCEXM disappeared after 16 h. The great difference between degradation efficiency and miner-

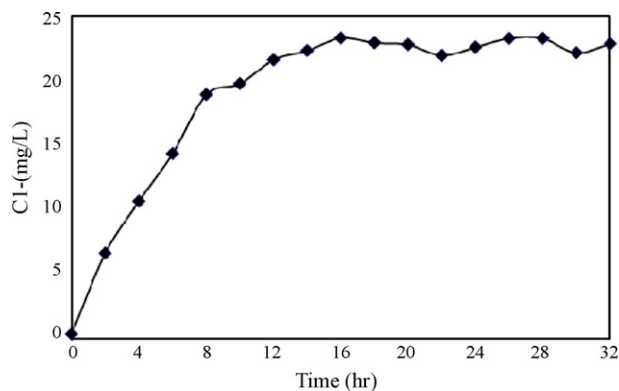


Fig. 8. Evolution of chloride ion originating from BCEXM photocatalytic degradation. Experimental conditions: BCEXM concentration 50 mg L^{-1} ; TiO_2 concentration 0.5 g L^{-1} ; pH 6.

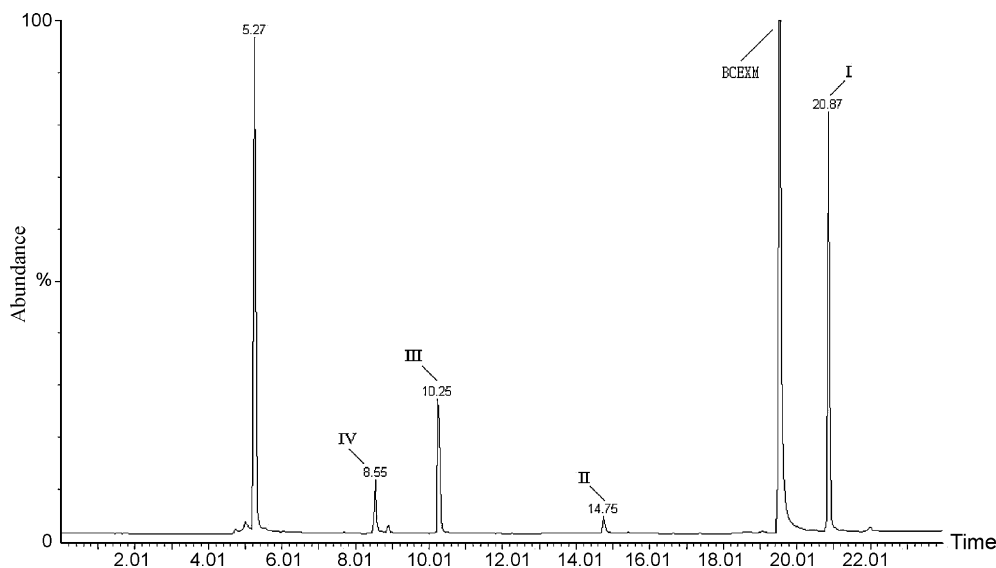


Fig. 9. GC/MS chromatogram obtained for BCEXM solution after 8 h of irradiation with UV light in the presence of TiO_2 .

alization efficiency implied that the products of BCEXM oxidation mostly stayed at the intermediate product stage under the present experimental conditions.

3.7. Formation of ionic byproduct

Since bis(2-chloroethoxy)methane is a haloether compound containing chlorine atoms, the chloride ion (Cl^-) is a potential ionic degradation byproduct. An alternative approach to tracking the progress of the TiO_2 photocatalytic degradation of BCEXM is to monitor the chloride ion formed in the solution. Therefore,

we measured the ionic byproduct produced during photocatalysis. The evolution of chloride ion as a function of irradiation time is shown in Fig. 8. Ion chromatography analysis shows the increase of chloride concentration in the reaction mixture as the photocatalysis progressed. The increase indicates that chlorine atoms are transformed into chloride ions after they are released from the BCEXM molecule. The stoichiometric formation of chloride ions was achieved in 16 h. The complete disappearance of BCEXM also occurs after 16 h while complete carbon mineralization requires an irradiation period longer than 34 h under the same working conditions. Thus, de-chlorinated organic intermediates are likely to be

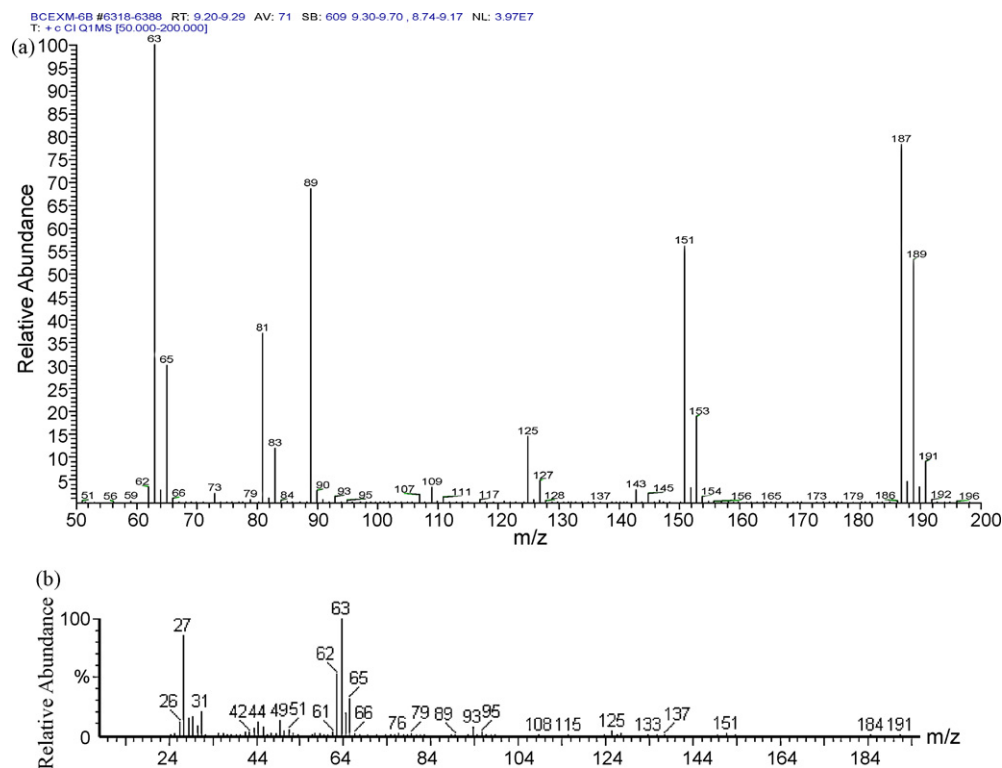


Fig. 10. Mass spectra of compound I formed during the photodegradation of the BCEXM (a) CI mass spectra, and (b) EI mass spectra.

present in the reaction system after the complete destruction of BCEXM.

3.8. Separation and identification of the intermediates

A search of the cited literature has led us to conclude that no prior study has investigated the photocatalytic transformations of haloethers and that very little is known about the use of TiO_2 to treat haloethers in aqueous solution. In this paper, the photocatalytic degradation mechanisms of haloether are

reported for the first time. A relatively low intensity UV-365 lamp (15 W) was used in our study to identify organic intermediates. This enabled us to obtain slower degradation rates and provide favorable conditions for the determination of intermediates. Additionally, the initial BCEXM concentration (50 mg L^{-1}) was selected to be high enough to facilitate the identification of intermediate products.

In photocatalytic degradation process the concentration of reaction intermediates is low and thus the intermediates have to be pre-concentrated before the application of an appropriate analytical

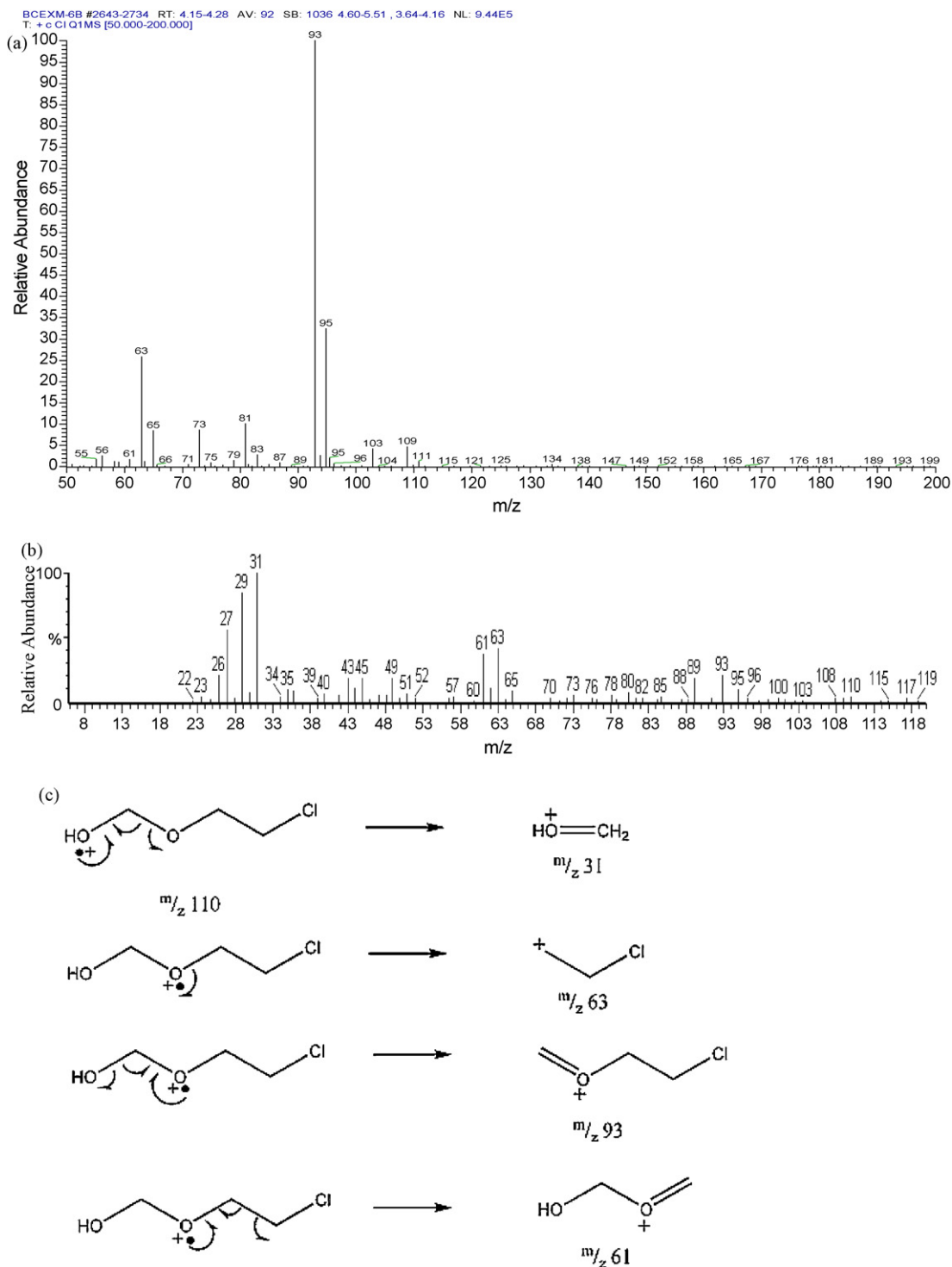


Fig. 11. Mass spectra of compound II formed during the photodegradation of the BCEXM (a) CI mass spectra, (b) EI mass spectra, and (c) proposed fragmentation pathway of compound II obtained from mass spectra analysis.

procedure. Prior to GC–MS analysis; the samples were pre-concentrated 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 BCEXM solution during the photocatalytic degradation process with UV irradiation were examined with SPME–GC/MS. Fig. 9 displays the chromatogram of the reacted solution after irradiation for 8 h in the presence of TiO_2 . At least five compounds were identified at retention times of less than 24 min. One of the peaks was the initial BCEXM; the other four (new) peaks were the intermediates formed. We denoted the related intermediates as species I–IV. Except for the initial BCEXM, 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.

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 taking into account both the relative intensity of the $^{35}\text{Cl}/^{37}\text{Cl}$ signals and the mass differences between the two masses.

The positive ion CI and EI mass spectra of compound I eluting at 20.87 min are shown in Fig. 10. Compound I was identified as bis(2-chloroethyl)carbonate by a library search with a fit value of 96%. The molecular mass was determined from the CI mass spectrum to be $m/z = 186$ by the observation of an $[\text{M}+\text{H}]^+$ ion of 187. The triple signals of protonated molecular ion 187/189/191 appear to be in a ratio of 9:6:1, and the double signals of basic peak 63/65 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 two chlorine atoms.

The positive ion CI and EI mass spectra of compound II, which was eluted at 14.75 min, are shown in Fig. 11. The protonated molecular ion ($m/z = 111$) for this intermediate was not obviously detected by the GC/MS, but three characteristic fragments were found in high abundance for the EI mass spectrum. The mass spectrum showed the characteristic ions at $m/z = 93$, $m/z = 63$, and $m/z = 31$ that correspond to the groups $[\text{CH}_2=\text{OCH}_2\text{CH}_2\text{Cl}]^+$, $[\text{CH}_2\text{CH}_2\text{Cl}]^+$ and $[\text{CH}_2=\text{OH}]^+$, respectively. Both the fragment ions 93/95 and 63/65 appear 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. The proposed fragmentation pathway of compound II matches quite well with the mass spectrum shown in Fig. 11. According to mass spectrometric anal-

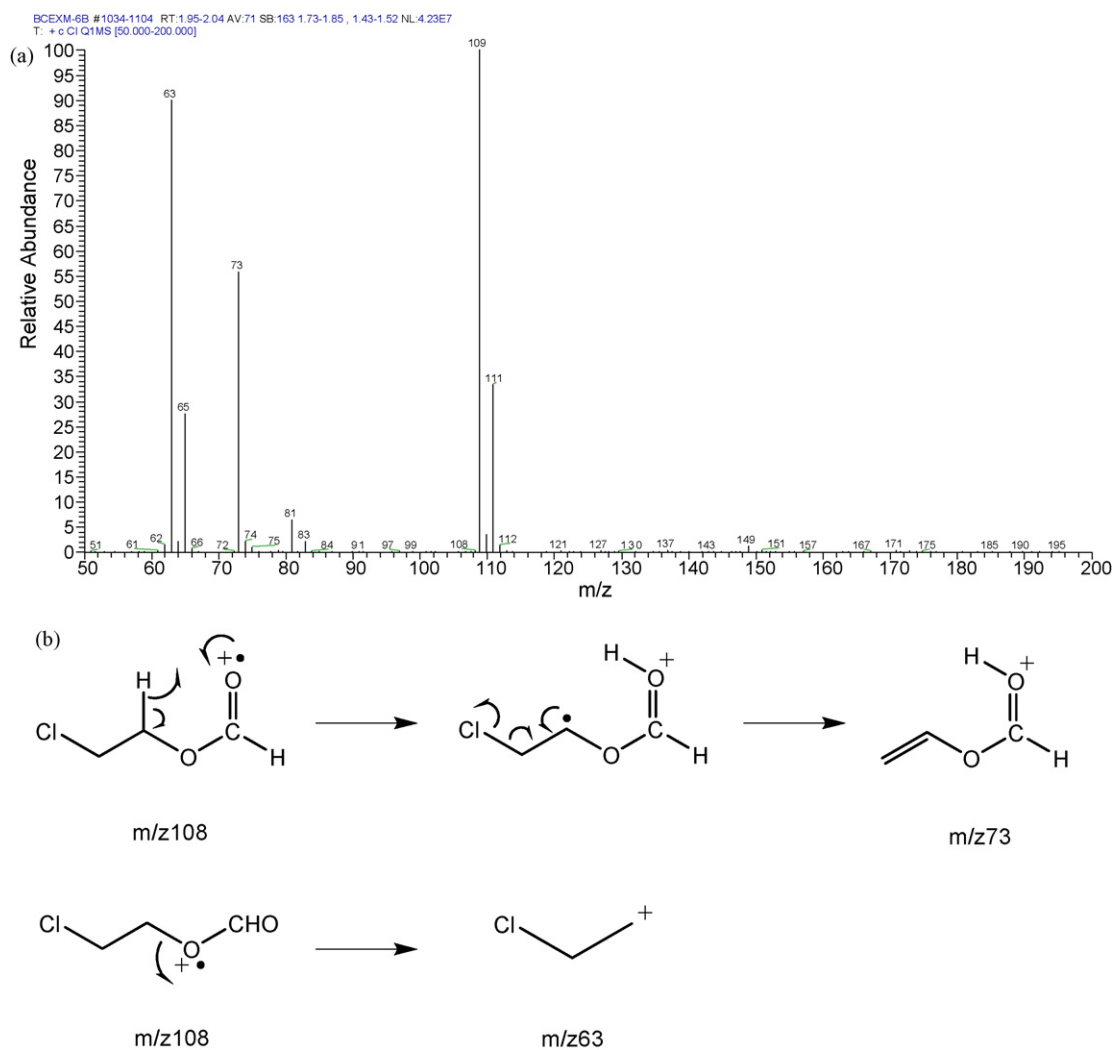


Fig. 12. Mass spectra of compound III formed during the photodegradation of the BCEXM (a) CI mass spectra, and (b) proposed fragmentation pathway of compound III obtained from mass spectra analysis.

yses, compound II was tentatively identified as (2-chloroethoxy)methanol.

The molecular mass of compound III was determined from the CI mass spectrum to be $m/z = 108$ by the observation of an $[M+H]^+$ ion of 109 (Fig. 12). The mass spectrum showed the characteristic ions at $m/z = 73$ and $m/z = 63$ that correspond to the groups $[CH_2=CHOCHOH]^+$ and $[CH_2CH_2Cl]^+$, respectively. The fragment ion 63/65 appears 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 III was tentatively identified as (2-chloroethoxy)methanol. As the pure compounds II and III are not commercially available, a more conclusive identification is difficult.

A search of the mass spectra library selected 2-chloroethanol as a good match (90%) for compound IV, whose retention time on

GC was 8.55 min. The positive ion CI and EI mass spectra of compound IV are shown in Fig. 13. Neat 2-chloroethanol, purchased from ChemService and dissolved in methanol, yielded the same GC retention time (~ 8.5 min) and mass spectrum as that of the suspected 2-chloroethanol found in the irradiated samples of the BCEXM photocatalytic experiment.

3.9. Initial photooxidation pathway

It is well established that conduction band electrons (e^-) and valence band holes (h^+) are generated when an aqueous TiO_2 suspension is irradiated with light energy greater than its band gap energy (3.2 eV). Hydroxyl radicals can be produced by the oxidation of water by these holes and are recognized as one of the most powerful oxidants [26]. Nakamura and Nakato [37] proposed a mechanism of water oxidation that involved a nucle-

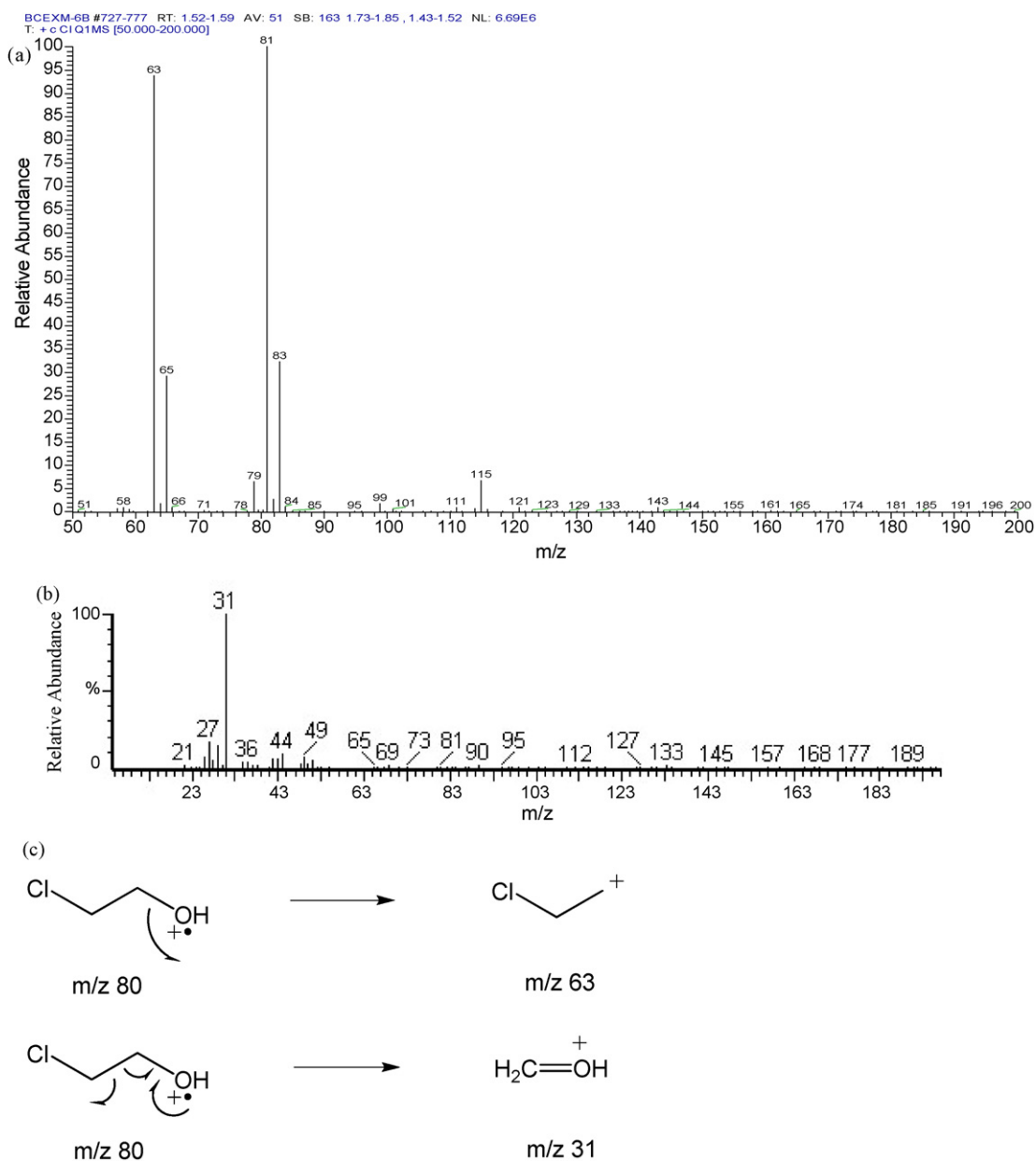
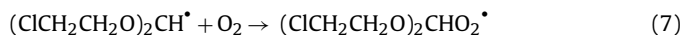


Fig. 13. Mass spectra of compound IV formed during the photodegradation of the BCEXM (a) CI mass spectra, (b) EI mass spectra, and (c) proposed fragmentation pathway of compound IV obtained from mass spectra analysis.

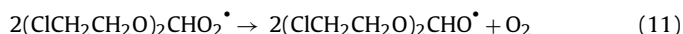
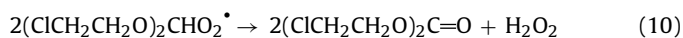
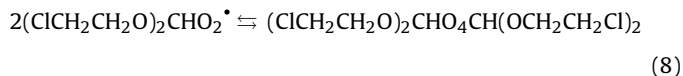
ophilic attack on a surface-trapped hole at a bridged O site. Murakami et al. [38] reported that when the O–O bond in Ti–O–OH breaks, the hydroxyl radicals can be formed from the bridge OH groups.

The instability of any carbon atom possessing two functional groups is well-known [39]. Therefore, it is particularly noteworthy that a single carbon atom situated between two heteroatoms (e.g., oxygen in the case of BCEXM) might be a reactive center susceptible to attack. Additionally, it is well known that the $\cdot\text{OH}$ radical is an electrophile and that C–H bonds adjacent to oxygen are responsible for a pronounced stereoelectronic effect that produces high rates of H-atom abstraction [40]. Therefore, the H atoms attached to the carbon atom situated between two oxygen atoms in BCEXM are the most prone to radical attack. The molecular structure of the degradation intermediates and the tentative photocatalytic degradation pathway of BCEXM are presented in Schemes 1 and 2.

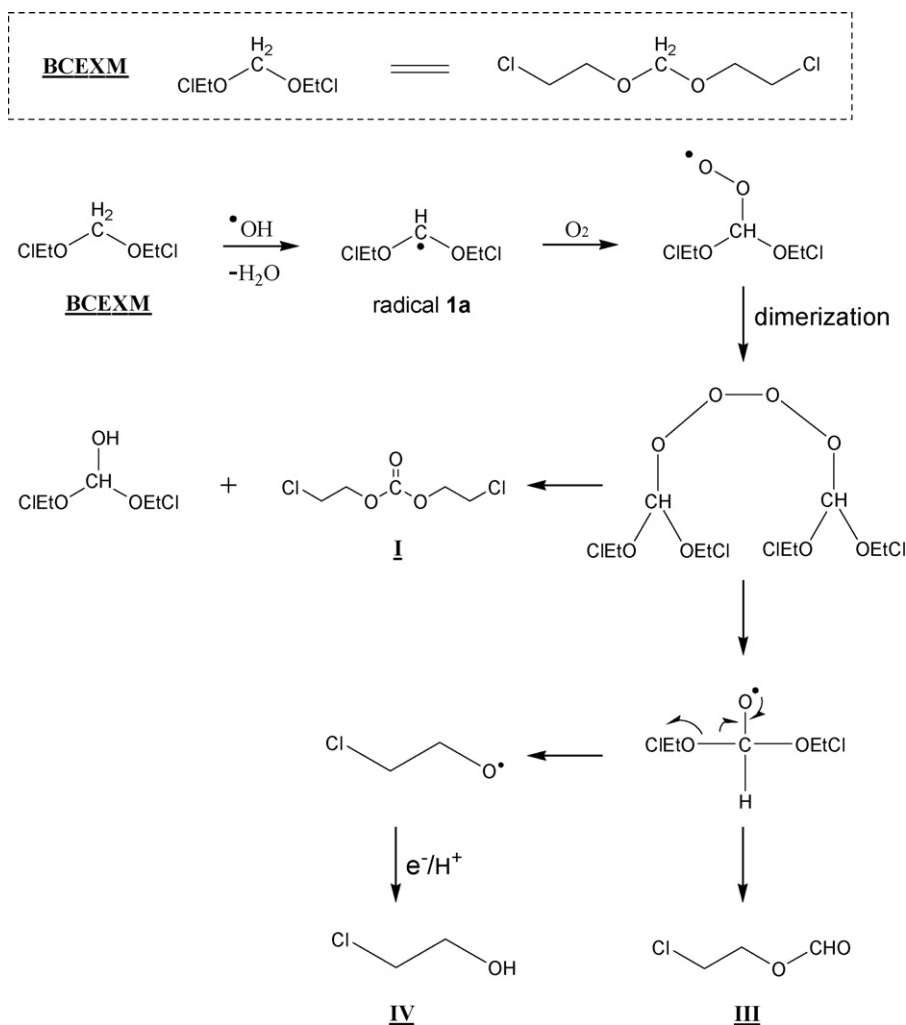
Initial attack by $\cdot\text{OH}$ radicals on BCEXM may involve hydrogen atom abstraction from the carbon atom situated between two oxygen atoms and results in the formation of carbon-centered radical **1a** (Scheme 1). The carbon-centered radical reacts at diffusion-controlled rate with oxygen, forming a peroxy radical [41] (reactions (6) and (7)).



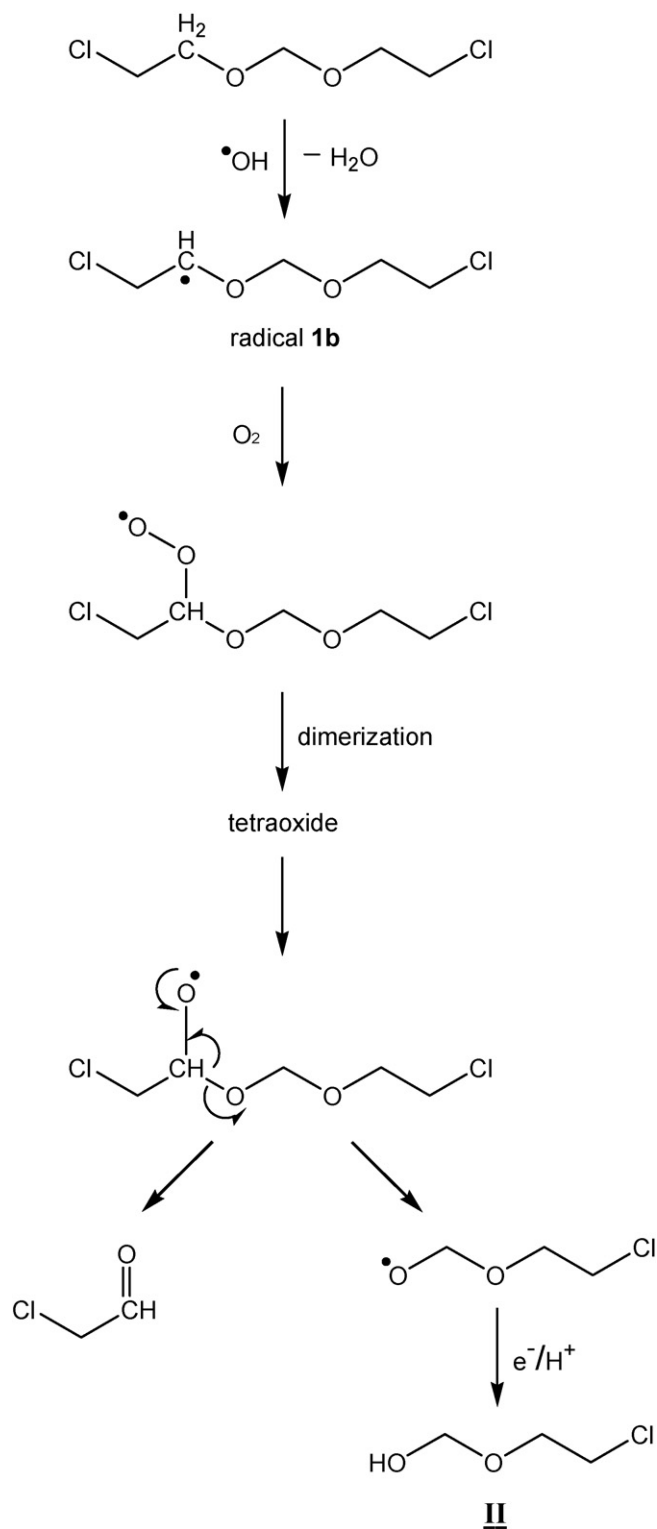
Dimerization of peroxy radicals yields the corresponding tetroxide, which can undergo a number of competing reaction pathways leading to different intermediates [42] as shown schematically in reactions (8)–(11).



Reaction (9), the so-called Russell mechanism [43], leads to the production of bis(2-chloroethyl)carbonate (compound I) and bis(2-chloroethoxy)methanol. Reaction (10) results in the direct formation of hydrogen peroxide and two equivalents of bis(2-chloroethyl)carbonate. Reaction (11) leads to the formation of two alkoxy radicals and a molecule of oxygen. The alkoxy radical produced by this sequence may react further by β -bond fragmentation (reaction (12)) leading to (2-chloroethoxy)methanal

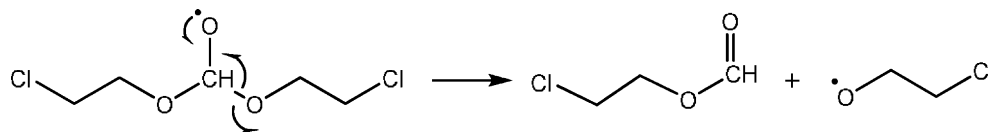


Scheme 1. Proposed pathways of photocatalytic degradation of BCEXM: route A.



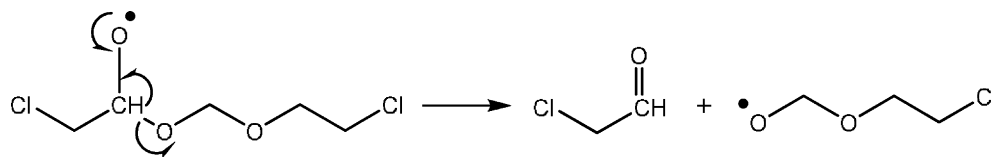
Scheme 2. Proposed pathways of photocatalytic degradation of BCEXM: route B.

(compound III) and a $\text{ClCH}_2\text{CH}_2\text{O}^\bullet$ radical that is the precursor of 2-chloroethanol (compound IV). The H atom necessary for O–H bond formation was proposed to have originated from the proton reduction by photogenerated electron $\text{H}^+ + \text{e}^- \rightarrow \text{H}^\bullet$ as already observed in the degradation of the insecticide fenitrothion by Kerzhentsev et al. [44]



(12)

Another possible degradation route was based on hydrogen abstraction from the carbon atom, which is located between the oxygen and chlorine atoms, and leads to the formation of carbon-centered radical **1b** (Scheme 2). The carbon-centered radical reacts with O_2 to produce a peroxy radical that subsequently transforms into an alkoxy radical through the bimolecular Russell mechanism [43]. The β -bond fragmentation of the alkoxy radical produces 2-chloroacetaldehyde and a $\text{ClCH}_2\text{CH}_2\text{OCH}_2\text{O}^\bullet$ radical that is the precursor of (2-chloroethoxy)methanol (compound II) as shown schematically in reaction (13)



(13)

Once the intermediates are formed, they can be degraded further by hydroxy radical attack until the final products of carbon dioxide and water are formed. Pace et al. [45] indicated that the photooxidation of 2-chloroethanol yielded intermediates such as acetic, glycolic, and formic acids and acetaldehyde. It has been shown previously that these organic acids and acetaldehyde can be photocatalytically oxidized by oxygen in contact with TiO_2 into CO_2 and water [46].

4. Conclusion

BCEXM could be successfully degraded by TiO_2 under UV irradiation. After a 0.2 mW/cm^2 light intensity (365 nm UV) irradiation for 16 h, ca. 99.5% of BCEXM was degraded. The photodegradation rate of BCEXM was found to increase with increasing pH. The photodegradation rate was found to increase with increasing TiO_2 dosages, but the reaction was slower at high dosages. In addition, the presence of inorganic ions such as Cl^- and NO_3^- , which are often present in natural water and industrial wastewater, decreased the photocatalytic degradation rate of BCEXM. Establishment of the reaction pathway was made possible by a thorough analysis of the reaction mixture identifying the main intermediate products generated. BCEXM was degraded to bis(2-chloroethyl)carbonate, (2-chloroethoxy)methanol, (2-chloroethoxy)methanal, and 2-chloroethanol. Results suggest that possible transformation pathways may include hydrogen abstraction and oxidation reactions. The hydroxyl radical extracts hydrogen from the carbon atom producing a carbon-centered radical; this radical reacts with O_2 to form a peroxy radical; two peroxy radicals dimerize to form a tetraoxide, which could produce different intermediates. The reaction pathway investigation provides a better understanding and new insights on the mechanism of degradation of bis(2-chloroethoxy)methane with TiO_2 .

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