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Identification of the degradation pathways of alkanolamines with TiO_2 photocatalysis

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ABSTRACT

The present study deals with the photocatalytic degradation of the alkanolamine, 2-dimethylamino-2-methyl-1-propanol (DMAMP), in the presence of TiO_2 particles and UV-A ($\lambda = 365$ nm) radiation. The obtained results show complete oxidation of DMAMP after 20 h, and a little over 90% of DMAMP was mineralization after 64-h of treatment. The effects of the solution pH, catalyst loading, and anions on the photocatalytic degradation of DMAMP were investigated, as well as the reaction intermediates that were formed during treatment. To the best of our knowledge, this is the first time that reports the degradation pathways of DMAMP. A number of intermediates were identified by GC/MS techniques during the treatment of DMAMP, following three tentative degradation routes. The first one is based on the oxidation of the primary alcohol group leading to the formation of corresponding aldehyde and carboxylic acid. The second route is based on the rupture of the N–C bond to form 2-methylpropanal and acetone. The last degradation route is based on the cyclization of the β-amino alcohol group to form the oxazolidine derivatives.

1. Introduction

Alkanolamines are organic compounds that possess the chemical properties of both amines and alcohols. These versatile chemicals are used extensively by chemical and pharmaceutical industries as lubricants, corrosion protection, emulsifying agents, and as ingredients of various pharmaceutical preparations. Furthermore, they are often utilized for metal surface finishing, natural gas purification, and as additives and dyes in cleaning solutions [1]. In 1993, approximately 20 million kg of alkanolamines were used for natural gas purification in the United States [2]. Because alkanolamines are used in many ways, and since they have been identified as pollutants in certain wastewater effluents [1,3], the development of a simple and effective removal method is necessary.

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 [4]. Biological wastewater treatments combining nitrification and denitrification processes often leave one or more nitrogen species in the effluent stream [5]. Moreover, the use of these biological processes to remove organic pollutants from wastewater is limited to low concentration. Diluting wastewater to a suitable concentration for the microorganisms leads to economically unfeasible volumes. Furthermore, selected contaminants can harm the bacteria populations used, resulting in a decrease of their biological activity. The slow reaction rates and need to dispose of activated sludge are large drawbacks of biological treatment methods [6,7].

Titanium dioxide (TiO_2)-based photocatalytic oxidation is a promising technology in water and wastewater treatment because TiO_2 is a cheap, stable, and nontoxic catalyst [8]. It has been shown that solar radiation can be used in photocatalysis, which would make it economically competitive for water and wastewater treatment [9]. The TiO_2-mediated photocatalysis process has been successfully used to degrade pollutants during the past few years [10–13]. 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 (${}^\bullet OH$), as well as superoxide radical anions ($O_2{}^{\bullet -}$), and hydroperoxyl radicals (${}^\bullet OOH$), and these radicals are the oxidizing species in the photocatalytic oxidation processes [14–16]. 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 [17].

2-Dimethylamino-2-methyl-1-propanol (DMAMP) was selected as the model compound for photocatalytic studies

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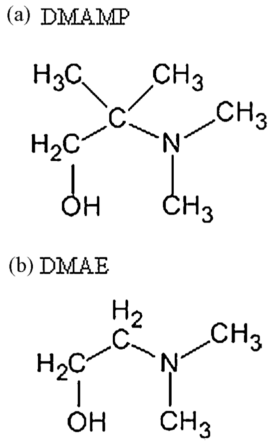


Fig. 1. Chemical structures of DMAMP (a) and DMAE (b).

since it is extensively used as an emulsifying agent, corrosion inhibitor, resin solubilizer, and catalyst for the production of foams, a stabilizer for finishes, and raw material for chemical synthesis [18]. In our study, we investigated various parameters that may affect the photodegradation of DMAMP in the presence of TiO_2 suspensions, in order to obtain a better understanding on TiO_2 photocatalysis. To the best of our knowledge, this is the first study that reports the degradation pathways of DMAMP. This study focused on the identification of the reaction intermediates and understanding of the photodegradation pathways of DMAMP in the TiO_2/UV light process. To obtain a better understanding on the mechanistic details of this TiO_2-assisted photodegradation of alkanolamine with UV irradiation, the photocatalytic degradation of structurally similar 2-dimethylaminoethanol (DMAE) was also examined and compared with that of DMAMP.

2. Experimental

2.1. Materials and reagents

2-Dimethylamino-2-methyl-1-propanol and 2-dimethylaminoethanol were obtained from Sigma–Aldrich and Acros, respectively. The chemical structures of both alkanolamines are shown in Fig. 1. Other chemicals used were of reagent grade and used as received without further purification. The TiO_2 nanoparticles (P25, ca. 80% anatase, 20% rutile; particle size, ca. 20–30 nm; BET area, ca. 55 $m^2\,g^{-1}$) 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 conductivity of 1.8×10^7 Ω-cm.

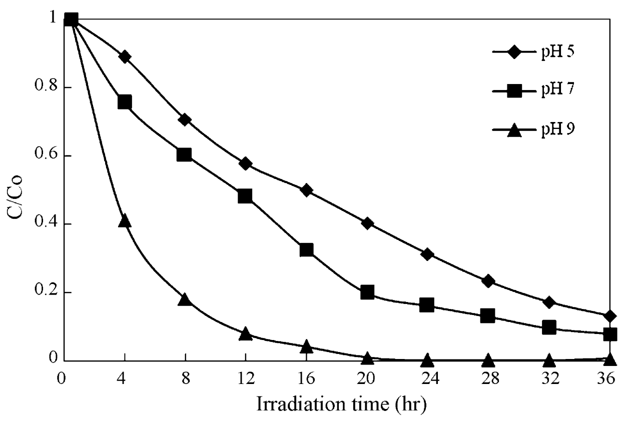


Fig. 2. pH effect on the photocatalytic degradation rate of DMAMP. Experimental conditions: DMAMP concentration 8.5×10^{-4} M; TiO_2 concentration 0.5 $g\,L^{-1}$.

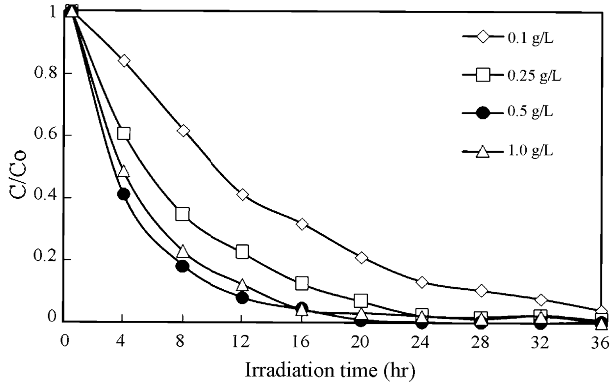


Fig. 3. Effect of TiO_2 dosage on the photocatalytic degradation rate of DMAMP. Experimental conditions: DMAMP concentration 8.5×10^{-4} M; pH 9.

2.2. Apparatus and instruments

The apparatus for studying the photocatalytic degradation of DMAMP has been described elsewhere [19]. The C-75 Chromato-Vue 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 DMAMP and intermediates resulting from the photocatalytic degradation process. SPME holder and fiber-coating divinylbenzene-carboxen-polydimethylsiloxane (DVB-CAR-PDMS 50/30 μm) were supplied from Supelco (Bellefonte, PA). GC/MS analyses were conducted with a PerkinElmer AutoSystem-XL gas chromatographer interfaced to a TurboMass selective mass detector. The mineralization of DMAMP 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 into the aqueous solution.

2.3. Procedures and analysis

DMAMP solution (8.5×10^{-4} M) 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 either NaOH or $HClO_4$ solutions. Prior to irradiation, the suspensions were magnetically

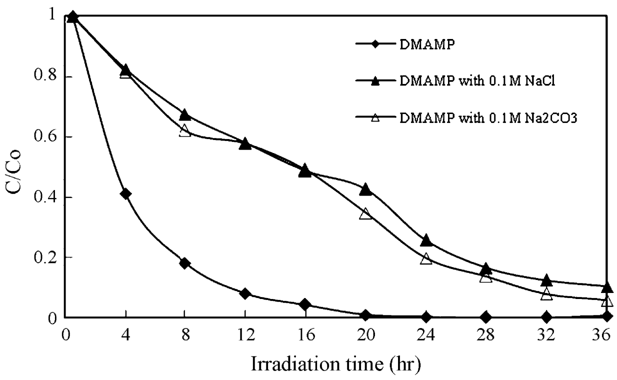


Fig. 4. Effect of anions on the photocatalytic degradation rate of DMAMP. Experimental conditions: DMAMP concentration 8.5×10^{-4} M; TiO_2 concentration 0.5 $g\,L^{-1}$; pH 9.

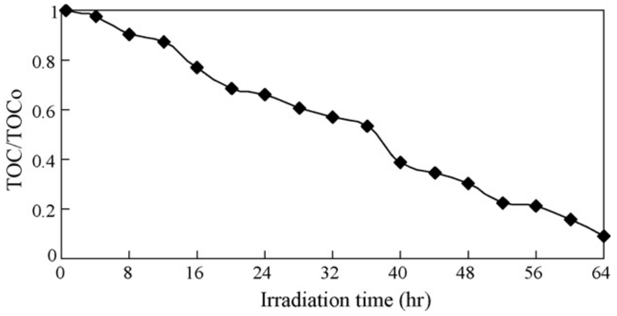


Fig. 5. Depletion in TOC measured as a function of irradiation time for an aqueous solution of DMAMP (8.5×10^{-4} M) in the presence of TiO_2 ($0.5\,g\,L^{-1}$).

stirred in the dark for ca. 30 min to ensure the establishment of the adsorption/desorption equilibrium. Irradiations were carried out using two UV-365 nm lamps (15 W). After each irradiation cycle, the amount of DMAMP was thus determined by SPME–GC/MS. The aqueous TiO_2 suspension was sampled (5 mL) and centrifuged to separate the TiO_2 particles. The clear solution was then transferred into 4 mL sample vial. The SPME fiber was directly immerged into the sample solution to extract DMAMP and its intermediates for 30 min at room temperature, with magnetic stirring at 550 ± 10 rpm on the Corning stirrer/plate (Corning, USA). Finally, the compounds were thermally desorbed from the fiber to the GC injector for 25 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 and split flow 10 mL/min. The helium carrier gas flow was 1.5 mL/min. The oven temperature program was 1.0 min at 40 °C and 8 °C/min to 200 °C (4.0 min). Electron impact (EI) mass spectra were monitored from 10 to 350 *m*/*z*. The ion source and inlet line temperatures were set at 220 and 250 °C, respectively.

3. Results and discussion

3.1. Effect of pH

Many studies have indicated that the pH of a solution is an important parameter in the photocatalytic degradation of organic compounds [20,21]. This is due to the fact that pH influences the surface charge of the semiconductor, thereby affecting the interfacial electron transfer and the photoredox process [22]. The photodegradation rate of the DMAMP as a function of reaction pH is shown in Fig. 2. The results indicated that the degradation rate decreased with a decrease in pH, and it proceeded much faster under an alkaline pH. 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 [23].

The zero point charge (pHzpc) of TiO_2 is 6.25 and so its surface is predominately positively charged below pHzpc (i.e., $Ti\text{-}OH + H^+ \leftrightarrows TiOH_2{}^+$) and negatively charged above pHzpc (i.e., $Ti\text{-}OH + OH^- \leftrightarrows TiO^- + H_2O$). The pK_a value of DMAMP is about 10.2 [24], so this alkanolamine is mostly protonated at pH 9 or below. Under an acidic condition (pH 5), the protonated DMAMP is difficult to adsorb onto the positively charged TiO_2 surface. As a result, active species like hydroxyl radical have such small possibilities of contacts with DMAMP that the overall degradation rate becomes lower. Similar result has been reported previously by Antoniou and Dionysiou [25]. They studied on the photocatalytic degradation of creatinine and showed that both catalyst and primary contaminant (creatinine) were positively charged at acidic pH. Hence the adsorption on the surface of the titania was limited and the photodegradation of creatinine occurred slowly. At a basic initial pH (pH 9), photocatalytic degradation is enhanced due to electrostatic attraction between the negatively charged surface and the protonated DMAMP. In addition, more hydroxide ions (OH^-) in the solution induce the generation of hydroxyl free radicals ($^\bullet OH$), which come from the photooxidation of OH^- by holes forming on the TiO_2 surface [17,26]. Since hydroxyl free radical is the dominant oxidizing species in the photocatalytic process, the photodegradation of DMAMP is therefore accelerated in an alkaline medium.

3.2. 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 degradation of DMAMP was investigated using TiO_2 at different concentrations, keeping all other parameters stable. The photocat-

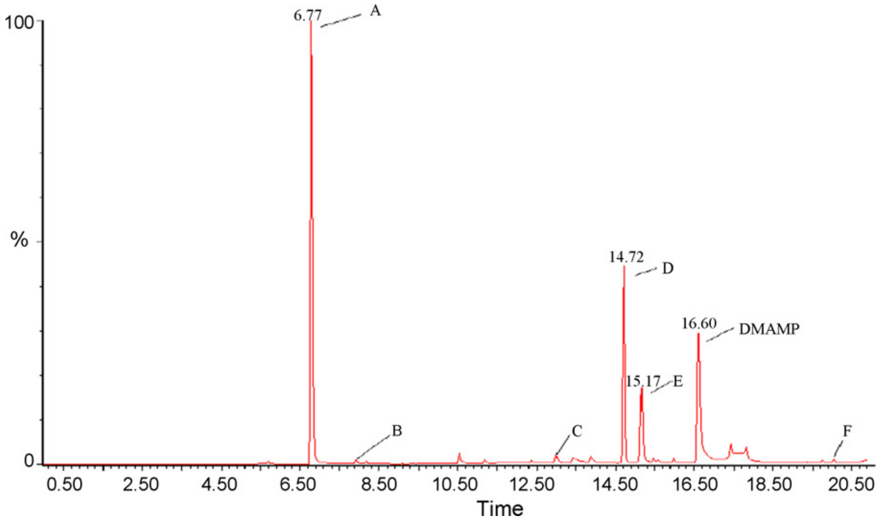
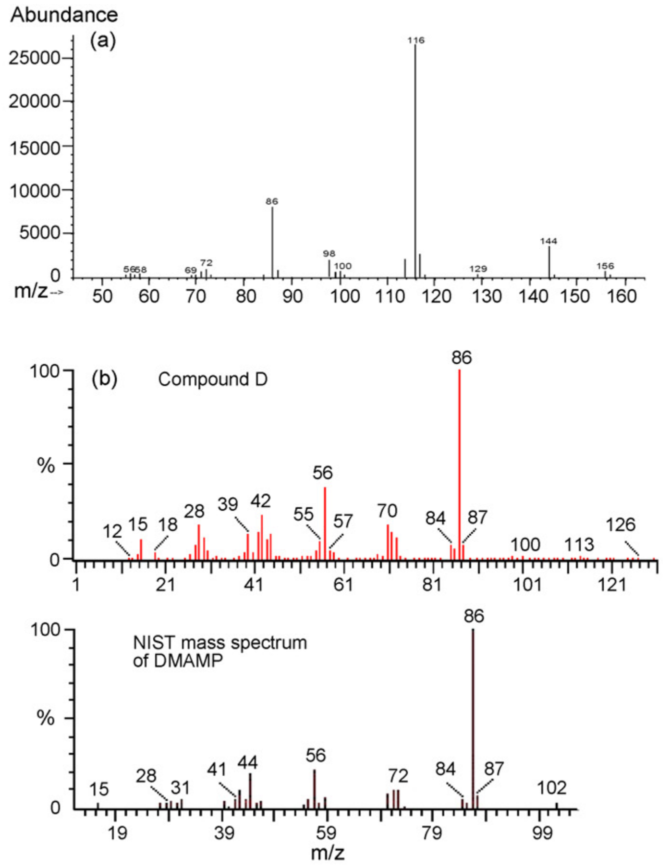
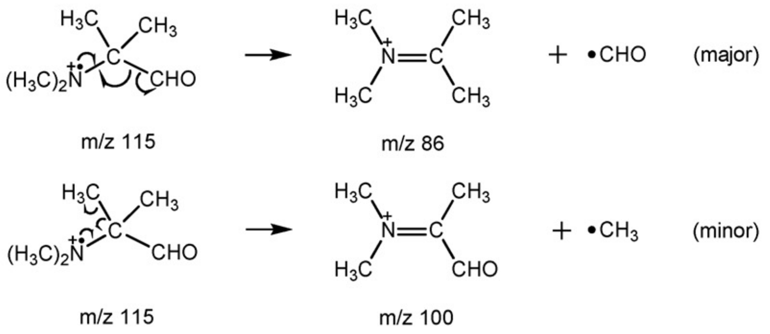


Fig. 6. GC/MS chromatogram obtained for DMAMP solution after 8 h of irradiation with UV light in the presence of TiO_2.



(c) Fragmentation pathway of compound **D**



+ Fragmentation pathway of DMAMP

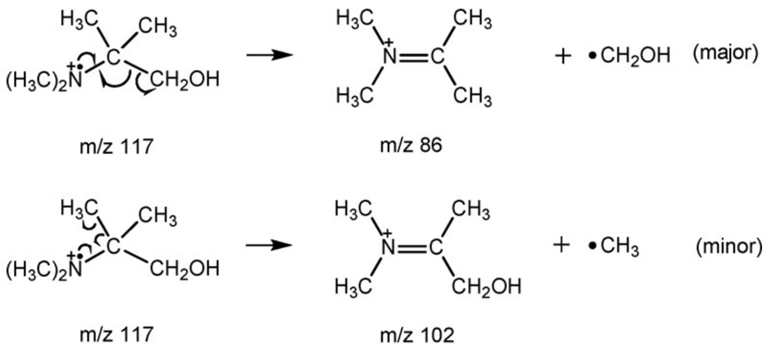


Fig. 7. Mass spectra of compound **D** formed during the photodegradation of the DMAMP (a) CI mass spectra, (b) EI mass spectra of compound **D** and DMAMP, and (c) proposed fragmentation pathways of compound **D** and DMAMP obtained from EI mass spectra analyses.

Table 1
Identification of the intermediates from the photodegradation of DMAMP by GC–MS.

Peaks	Photodegradation intermediates	RT (min)	MS peaks (*m*/*z*)
A	Acetone	6.77	58,43,15
B	2-Methylpropanal	7.96	72,43,41,29,27
C	4,4-Dimethyloxazolidine	12.97	101,86,71,58,56,42
D	2-Dimethylamino-2-methylpropanal	14.72	115,86,72,70,56,44,42
E	3,4,4-Trimethyloxazolidine	15.17	115,100,85,72,70,56,42
DMAMP	2-Dimethylamino-2-methyl-1-propanol	16.60	117,86,72,70,56,44,42
F	2-Dimethylamino-2-methylpropanoic acid	20.08	131,86,72,70,56,44,42

alytic degradation rate was found to increase with increasing TiO_2 dosages, but the reaction was slower at higher TiO_2 dosages (Fig. 3). 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 therefore reduced the overall performance [27].

3.3. *Effects of anions*

The presence of anions such as chloride and carbonate is common in industrial effluents. These ions act as hydroxyl radical scavengers and also absorb UV light, which affects the photocatalytic degradation [28,29]. Therefore, studying the effects of anions on the photocatalytic degradation of DMAMP is important. The effects of Cl^- and $CO_3{}^{2-}$ ions on the degradation rate of DMAMP were examined individually, by adding NaCl and Na_2CO_3 to the system until the resultant solution contained 0.1 M of Cl^- and $CO_3{}^{2-}$ ions. The results showed that anions inhibited the degradation considerably (see Fig. 4). Inhibition effects of anions can be explained as the reaction of hydroxyl radical with anions that behaved as $^{\bullet}OH$ radical scavengers (Eqs. (1) and (2)) resulting in prolonged DMAMP removal. Formation of inorganic radical anions (e.g. $Cl^{\bullet}$, $CO_3{}^{\bullet -}$) under these circumstances is possible.

$$Cl^- + {}^{\bullet}OH \rightarrow Cl^{\bullet} + OH^- \qquad (1)$$

$$CO_3{}^{2-} + {}^{\bullet}OH \rightarrow CO_3{}^{\bullet -} + OH^- \qquad (2)$$

However, these radicals have a lower oxidation potential than hydroxyl radicals ($E_0(CO_3{}^{\bullet -}/CO_3{}^{2-}) = 1.85\,V$, $E_0(Cl^{\bullet}/Cl^-) = 2.47\,V$, $E_0(OH^{\bullet}/H_2O) = 2.80\,V$), they are not as reactive as $^{\bullet}OH$ and thus the rate of photocatalytic degradation is reduced [30,31]. Similar results have been reported previously by Chen et al. [32], suggesting that inorganic anions were capable of inhibiting the photocatalytic degradation of dichloroethane in aqueous suspensions of TiO_2.

3.4. *TOC removal*

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 DMAMP, the determination of total organic carbon (TOC) was carried out as a function of the irradiation time. The decrease in the TOC percentage of DMAMP during the photocatalytic degradation is depicted in Fig. 5. Approximately, 90% of DMAMP was mineralized within 64 h of photocatalytic reaction time. The TOC data confirms that all of the organic compounds were mineralized when the TiO_2/UV process was applied for sufficient reaction time.

Table 2
Identification of the intermediates from the photodegradation of DMAE by GC–MS.

	Photodegradation intermediates	RT (min)	MS peaks (*m*/*z*)
a	Ethanal	5.57	44,43,29
b	2-Dimethylaminoethanal	10.44	87,58,44,42,30
DMAE	2-Dimethylaminoethanol	11.95	89,58,44,42,30
c	3-Methyloxazolidine	12.04	87,86,57,42
d	2-Dimethylaminoacetic acid	15.14	103,58,44,42,30

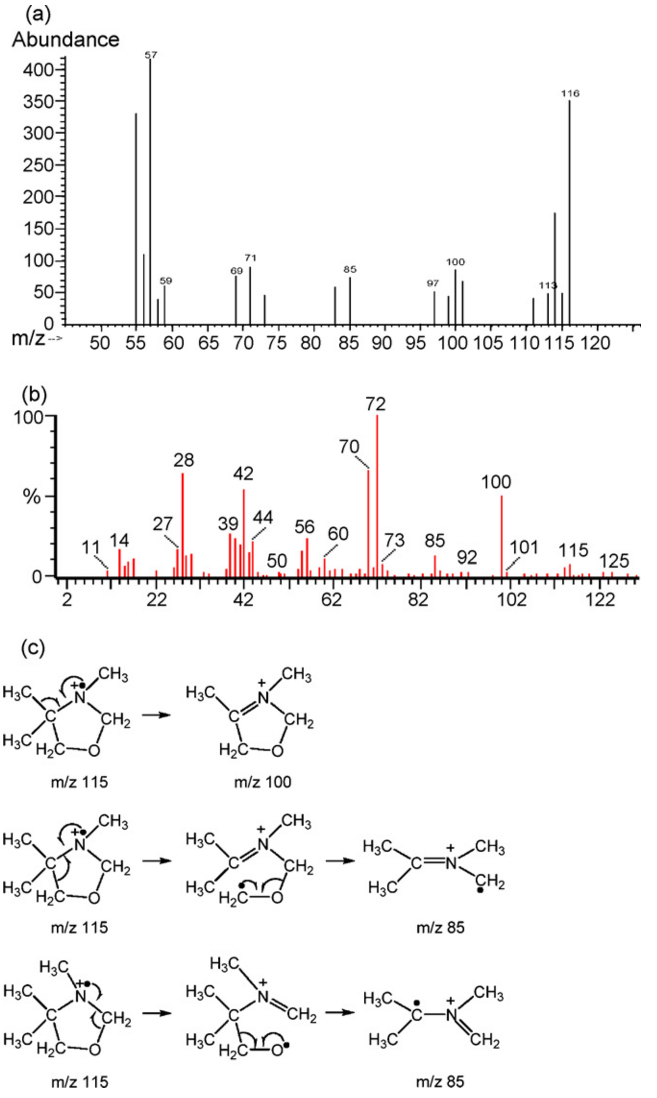


Fig. 8. Mass spectra of compound **E** formed during the photodegradation of the DMAMP (a) CI mass spectra, (b) EI mass spectra, and (c) proposed fragmentation pathway of compound **E** obtained from EI mass spectra analysis.

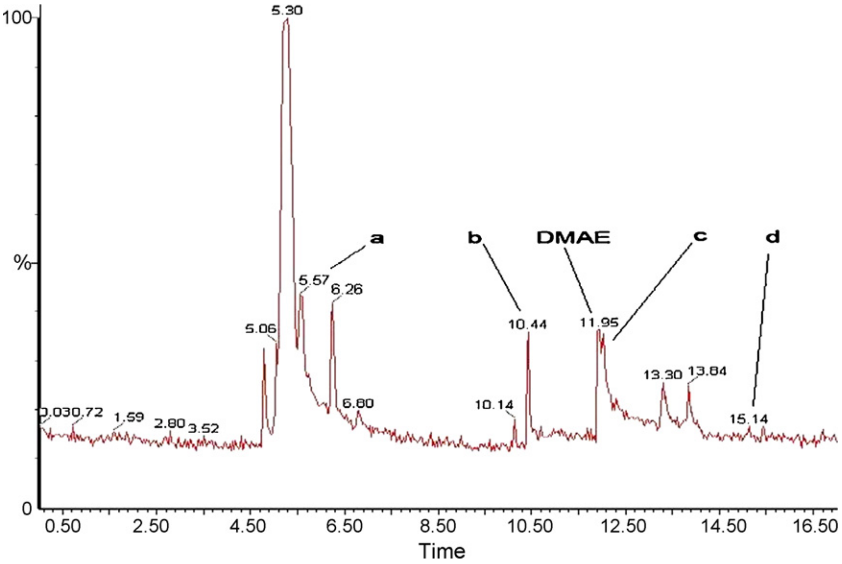


Fig. 9. GC/MS chromatogram obtained for DMAE solution after 12 h of irradiation with UV light in the presence of TiO_2.

3.5. Separation and identification of the intermediates

After searching the cited literature and to the best of our knowledge we have come to the conclusion that no prior study has investigated the photocatalytic transformations of alkanolamines and that very little is known about the use of TiO_2 in the treatment of alkanolamines in aqueous solution. In this paper, the photocatalytic degradation mechanisms of alkanolamines are reported for the first time. A low intensity UV-365 lamp (15 W) was used in our study for the identification of organic intermediates. This enabled us to obtain slower degradation rates and provide favorable conditions for the determination of intermediates. Additionally, the initial DMAMP concentration (8.5×10^{-4} M) was selected to be high enough to facilitate the identification of intermediate products. To obtain a better understanding on the mechanistic details of this TiO_2-assisted photodegradation of alkanolamine with UV irradiation, the photocatalytic degradation of structurally similar 2-dimethylaminoethanol (DMAE) was also examined and compared with that of DMAMP.

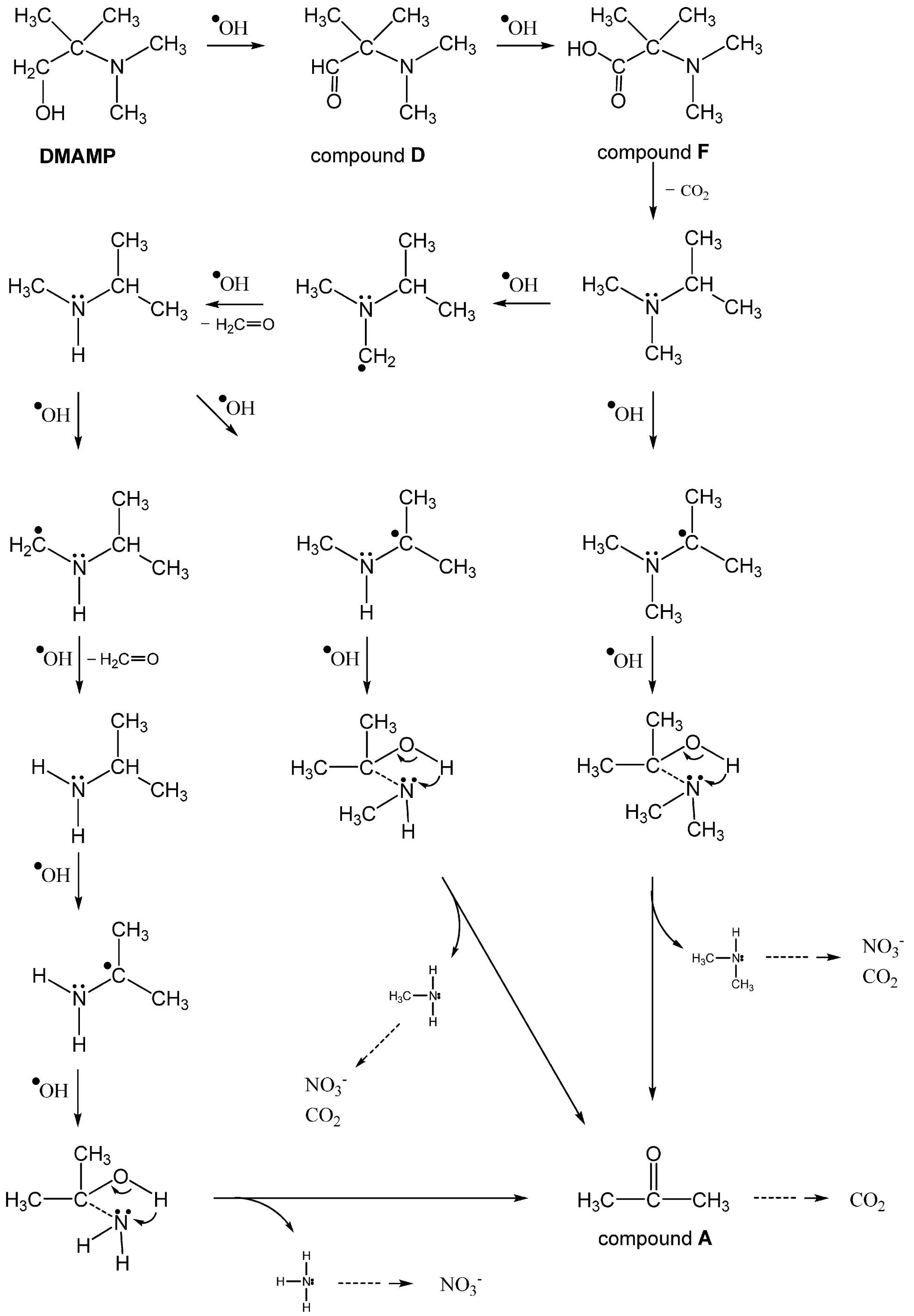
The intermediate products generated in the DMAMP solution during the photocatalytic degradation process with UV irradiation were examined with SPME–GC/MS. Fig. 6 displays the chromatogram of the reacted solution after irradiation for 8 h in the presence of TiO_2. At least seven compounds were identified at retention times less than 25 min. One of the peaks was the initial DMAMP; the other six new peaks were those of the intermediates formed. We denoted the related intermediates as species **A**–**F**. Except for the initial DMAMP, 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.

Table 1 summarizes the identified intermediates of DMAMP along with their retention times and the characteristic ions of the mass spectra. The peaks eluting at 6.77 min [compound **A**] and 7.96 min [compound **B**] during GC/MS analysis of DMAMP solution were identified as acetone and 2-methylpropanal with fit values of 94% and 96%, respectively, with the mass spectra library. Both compounds were further identified by matching their retention times and mass spectra with those of standards of acetone and 2-methylpropanal. They exhibit the exact retention times and similar mass spectra. A search of the mass spectra library selected 4,4-dimethyloxazolidine with a fit value of 76% for compound **C**, the retention time of which on GC/MS was 12.97 min. Unfortunately, the pure compound is not commercially available, making it difficult to reach a conclusive identification of this intermediate.

Three compounds (**D**, **E** and **F**) not included in the library were identified by interpretation of the mass spectra. The molecular mass of these compounds was determined using positive ion chemical ionization (CI) mass spectrometry through the abundant protonated molecule and the characteristic $[M+C_2H_5]^+$ and $[M+C_3H_5]^+$ adducts, and then structural data were obtained from the electron impact (EI) fragmentation patterns.

The positive ion CI and EI mass spectra of compound **D** eluting at 14.72 min are shown in Fig. 7. The molecular mass was determined from the CI mass spectrum to be $m/z = 115$ by the observation of an $[M+H]^+$ ion of 116, an $[M+C_2H_5]^+$ ion of 144, and an $[M+C_3H_5]^+$ ion of 156 (Fig. 7a). The EI mass spectrum of compound **D** shows high similarities with that of DMAMP. Both spectra showed the characteristic ions at $m/z = 86$ and $m/z = 56$ that correspond to the groups $[(CH_3)_2N{=}C(CH_3)_2]^+$ and $[CH_3N{\equiv}CCH_3]^+$, respectively (Fig. 7b and c). Compound **F** exhibited a molecular ion peak at $m/z = 131$ and a fragmentation pattern similar to compound **D** and DMAMP. Based on these data, the structures of compounds **D** and **F** are consistent with the 2-dimethylamino-2-methylpropanal and 2-dimethylamino-2-methylpropanoic acid, formed by photocatalytic oxidation of the alcohol group of DMAMP, leading to aldehyde and carboxylic acid products.

The positive ion CI and EI mass spectra of compound **E**, which eluted at 15.17 min, are shown in Fig. 8. The molecular mass was determined from the EI mass spectrum to be $m/z = 115$, which was confirmed by the observation of an $[M+H]^+$ ion of 116 using positive ion CI mass spectrometry (Fig. 8a). The product ion at $m/z = 100$ in the mass spectrum of compound **E** corresponded to the dimethyloxazolidine species produced following the loss of a methyl radical from the molecular ion of $m/z = 115$. The mass spectrum showed the characteristic ions at $m/z = 85$ and $m/z = 70$ that correspond to the groups $[(CH_3)_2C{=}N(CH_3)(CH_2)]^{\bullet+}$ and $[(CH_3)_2C{=}N(CH_2)]^+$, respectively (Fig. 8b and c). According to mass spectrometric analyses, compound **E** was tentatively identified as 3,4,4-trimethyloxazolidine. The oxazolidine derivatives have been reported to be transformation products formed from *N*-methyl substituted β-alkanolamines through oxidation and cyclization [33].

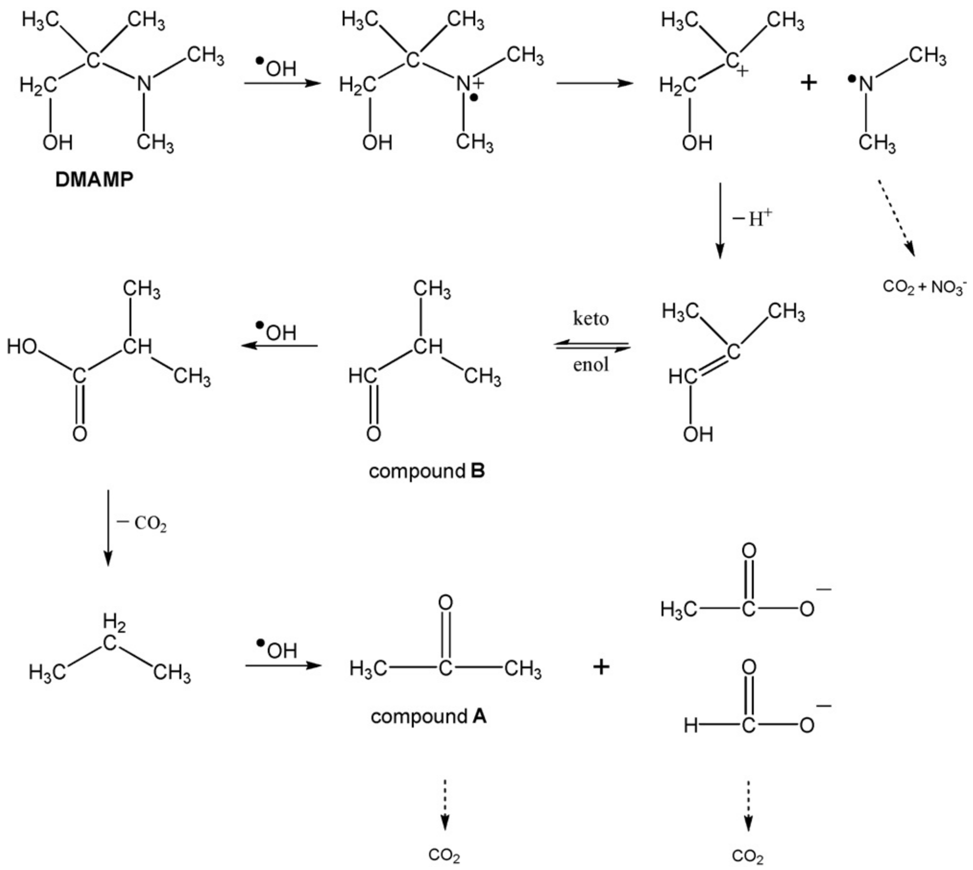


Scheme 1. Proposed pathway of the oxidation of the primary alcohol group of the DMAMP under UV irradiation in aqueous TiO_2 dispersions (Route I).

Fig. 9 displays the chromatogram of the DMAE solution during irradiation in the presence of TiO_2. One of the peaks was the initial DMAE; the other four new peaks are those of the intermediates formed. We denoted the related intermediates as species **a**–**d** (see Table 2 for detail). Compound **a** eluting during GC/MS analysis of DMAE solution at 5.57 min was identified as ethanal with a fit value of 93%. This compound was further identified by matching its retention time and mass spectra with that of an authentic standard. They exhibit the exact retention times and similar mass spectra.

The molecular mass of compound **b** was determined from the CI mass spectrum to be $m/z = 87$ by the observation of an $[M+H]^+$ ion of 88. The EI mass spectrum of compound **b** shows high similarities with that of DMAE. Both spectra showed the characteristic ions at $m/z = 58$ and $m/z = 30$ that correspond to the groups $[(CH_3)_2N{=}CH_2]^+$ and $[H_2N{=}CH_2]^+$, respectively. Based on these data, the structure of compound **b** is consistent with the 2-dimethylaminoethanal, formed by photocatalytic oxidation of the alcohol group of DMAE, leading to aldehyde product.

Compound **d** was identified by searching the mass spectra library as 2-dimethylaminoacetic acid, with a fit value of 86%. It exhibited a molecular ion peak at $m/z = 103$ and product ions ($m/z = 58$ and 30) similar to those of DMAE.



Scheme 2. Proposed pathway of the cleavage of the N–C bond of the DMAMP under UV irradiation in aqueous TiO_2 dispersions (Route II).

A search of the mass spectra library revealed 3-methyloxazolidine to be a good match (96%) for compound **c**, the retention time of which on GC/MS was 12.04 min. Compound **c** exhibits a peak at $m/z = 87$, which corresponds to the molecular ion $[M+H]^+$ and the characteristic ions at $m/z = 57$ and $m/z = 42$ that correspond to the groups $[CH_2{=}N(CH_3)CH_2]^{\bullet+}$ and $[CH_2{=}NCH_2]^{\bullet+}$, respectively.

From the above results, several families of intermediates can be distinguished:

- The first one arises from the oxidation of the primary alcohol group and includes compounds **D**, **F**, **b** and **d**.
- The second family of intermediates (compounds **B** and **a**) comes from the rupture of the N–C bond.
- The last family of intermediates (compounds **C**, **E** and **c**) is the result of the cyclization of the β-amino alcohol groups, leading to oxazolidines derivatives.

3.6. *Initial photooxidation pathway*

Most organic molecules undergo photocatalytic degradation when irradiated in the presence of a photocatalyst. This occurs through a multistep process involving the attack of the substrate by radical species, among which the •OH radical was recognized to be the most powerful oxidant [17]. Nakamura and Nakato [34] proposed a mechanism of water oxidation by a nucleophilic attack to a surface-trapped hole at a bridged O site. Murakami et al. [35] reported when the O–O bond in Ti–O–OH breaks the hydroxyl radicals can be formed from the bridge OH groups.

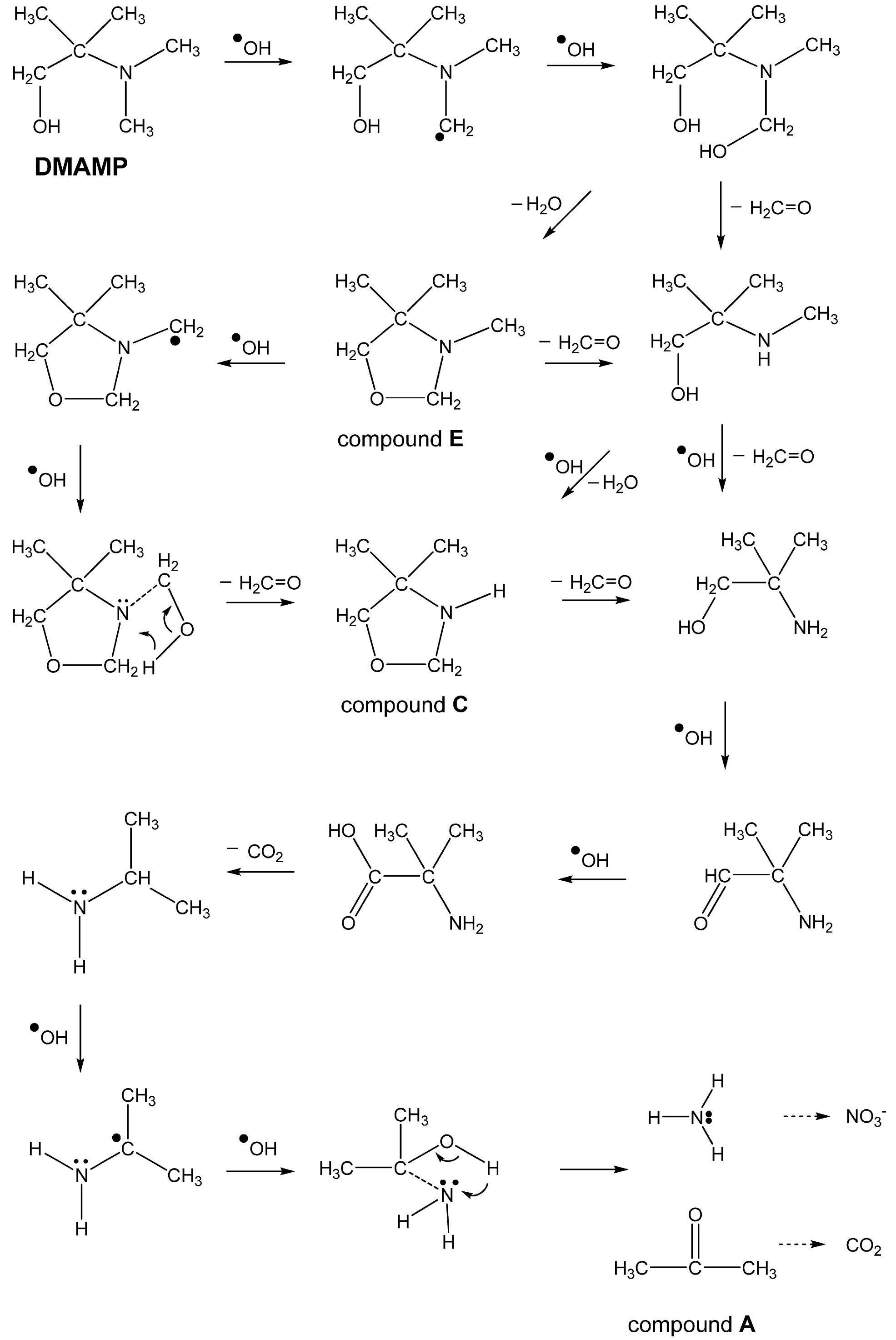
Schemes 1–3 show the proposed mechanisms for the generation of the primary detected intermediates, which involve three different pathways (routes I, II and III, respectively), corresponding to the three possible reaction sites on the DMAMP molecule. Route I is based on the oxidation of the primary alcohol group leading to the formation of 2-dimethylamino-2-methylpropanal (compound **D**) and 2-dimethylamino-2-methylpropanoic acid (compound **F**). Many researchers have indicated that the photocatalytic degradation of aliphatic alcohols may occur through direct reaction with holes or •OH radicals to yield the corresponding aldehydes [36,37]. Alcoholates or aldehydes generated in these reactions may respectively react with $O_2^{\bullet-}$ or •OH radicals, to yield the corresponding carboxylates or carboxylic acids [38,39]. The sequential reactions in the oxidation process are shown in Scheme 1. In this scheme, 2-dimethylamino-2-methylpropanoic acid (compound **F**) is further transformed via decarboxylation, hydrogen abstraction and reaction with hydroxyl radicals to produce the acetone (compound **A**) and finally to be mineralized.

The second possible pathway (Scheme 2) is based on the rupture of the N–C bond resulting in the formation of 2-methylpropanal (compound **B**) and acetone (compound **A**). Previous studies indicated that the oxidation of aliphatic amines involves a one-electron transfer to form a cation radical which almost entirely decomposes to a carbonium ion and amidogen radical [40].

$$\mathrm{RCH_2NH_2} \rightarrow \mathrm{RC\overset{+\bullet}{H}_2NH_2} + e^- \tag{3}$$

$$\mathrm{RC\overset{+\bullet}{H}_2NH_2} \rightarrow \mathrm{R\overset{+}{C}H_2} + {}^\bullet\mathrm{NH_2} \tag{4}$$

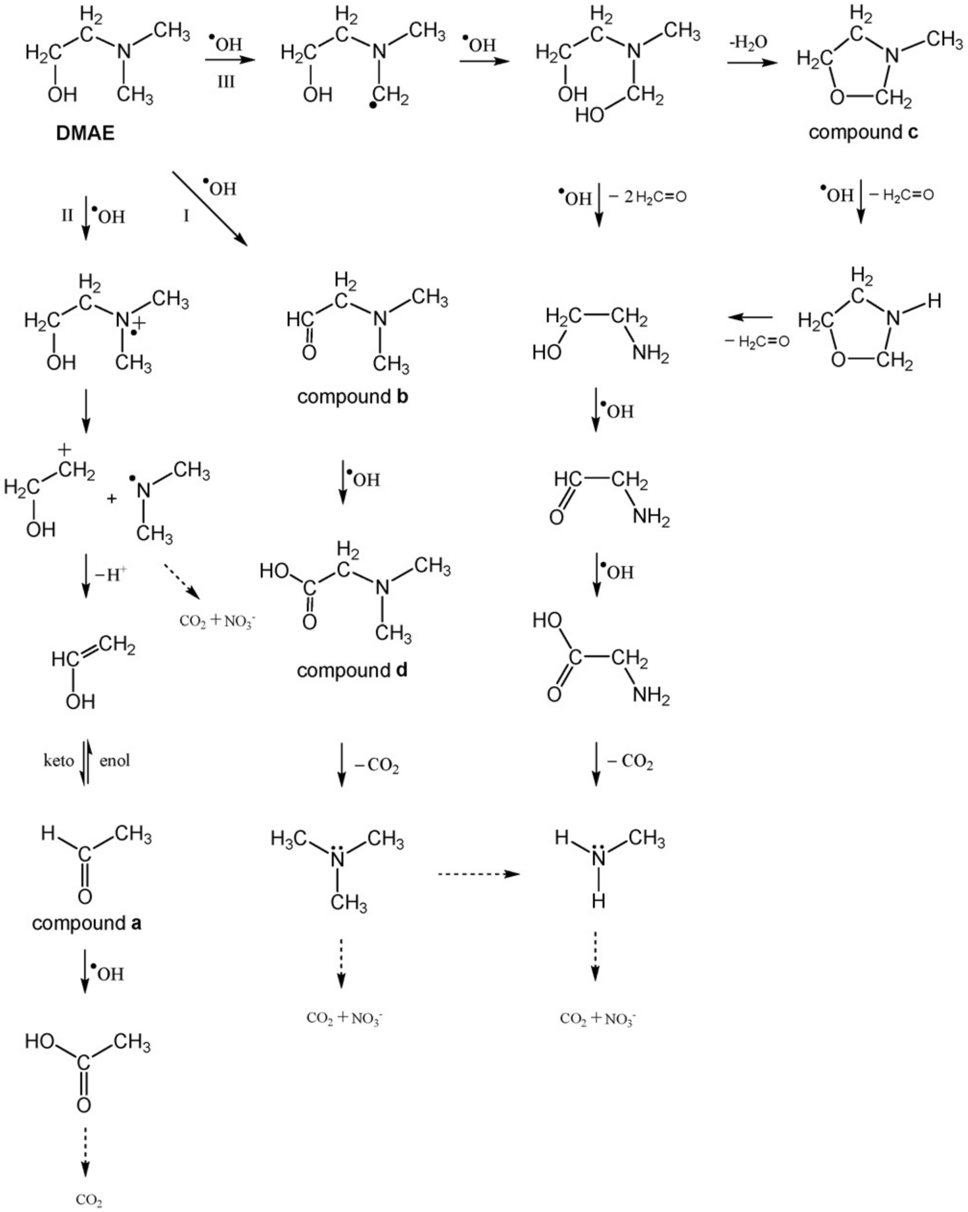
$$\mathrm{R\overset{+\bullet}{C}H_2} \rightarrow \mathrm{H^+} + \text{hydrocarbons} \tag{5}$$



Scheme 3. Proposed pathway of the cyclization of the β-amino alcohol group of the DMAMP under UV irradiation in aqueous TiO_2 dispersions (Route III).

A plausible mechanism (route II) for the formation of degradation intermediates (**B** and **A)** involving electron transfer reactions and reaction with hydroxyl radicals formed in the photocatalytic system is proposed in Scheme 2. In this scheme, hydroxyl radical reacts with the lone-pair electron on the N atom to generate a cationic radical, which subsequently decomposes to a carbonium ion $[(CH_3)_2C(CH_2OH)]^+$ and dimethyl-substituted amidogen radical $[(CH_3)_2N^\bullet]$. The deprotonation of the carbonium ion produces the 2-methyl-1-propenol, which converts into 2-methylpropanal (compound **B**) through the keto-enol tautomerism. 2-Methylpropanal generated in these reactions may respectively react with $O_2^{\bullet -}$ or $^\bullet OH$ radicals to yield the corresponding 2-methylpropanoic acid. Decarboxylation of the carboxylic acid produces the propane, which converts into acetone (compound **A**), formate and acetate [41].

Finally, in the degradation route III the detected intermediates (compounds **C** and **E**) are rationalized as being formed by the cyclization of the β-amino alcohol groups during photooxidation



Scheme 4. Proposed reaction pathways for photocatalytic degradation of DMAE.

of DMAMP. In the Scheme 3, hydroxyl radical yields a (hydroxy-tert-butyl)-methylaminomethyl radical upon the H-atom abstraction from the methyl group attached to the nitrogen. The corresponding aminomethyl radical reacts with hydroxyl radical to generate a di-hydroxylated intermediate that subsequently transforms into 3,4,4-trimethyloxazolidine (compound **E**) through the cyclo-dehydration mechanism [42]. Analog cyclization transformation products were also found in the oxidation of *N*-aryl-*N*-methyl substituted β-alkanolamines using pyridinium dichromate [33]. The mechanism for the hydrolysis of oxazolidines has been reported by Walker et al. [43], suggesting that oxazolidines were capable of undergoing facile hydrolysis in aqueous media to produce the β-amino alcohol and carbonyl compound. In the Scheme 3, the 4,4-dimethyloxazolidine (compound **C**) is further transformed via hydrolysis, oxidation of the primary alcohol group, decarboxylation and dealkylation leading to the formation of acetone (compound **A**) and finally to the mineralization.

Similar photooxidation pathways can be observed also in the photocatalytic degradation of DMAE. In the Scheme 4, route I is based on the oxidation of the primary alcohol group leading to the formation of 2-dimethylaminoethanal (compound **b**) and 2-dimethylaminoacetic acid (compound **d**). The carboxylic acid is subsequently decarboxylated into trimethylamine and further mineralized. Route II involves a one-electron transfer to form a cation radical, which subsequently decomposes to a carbonium ion $[CH_2CH_2OH]^+$ and dimethyl-substituted amidogen radical $[(CH_3)_2N^\bullet]$. Vinyl alcohol is formed via deprotonation but quickly tautomerize to ethanal (compound **a**) that sequentially react with $O_2^{\bullet-}$ or $^\bullet OH$ to form acetic acid and to be mineralized. Route III is based on the cyclization of the β-amino alcohol groups leading to the formation of 3-methyloxazolidine (compound **c**). Following one $^\bullet OH$ radical abstracting a hydrogen atom from the methyl group attached to the nitrogen, and another $^\bullet OH$ radical attacking the corresponding aminomethyl radical, forming a di-hydroxylated intermediate, the subsequent cyclo-dehydration of this intermediate yields the 3-methyloxazolidine (compound **c**). The corresponding 3-methyloxazolidine is further transformed via dealkylation, hydrolysis, oxidation of the primary alcohol group and decarboxylation leading to the formation of methylamine and finally to the mineralization.

4. Conclusion

Photodegradation using TiO_2 as a catalyst is an efficient method of degrading DMAMP. At optimal operating parameters, its degradation efficiency could reach 99% in 20 h. The photodegradation rate of DMAMP was found to increase with increasing value of pH. The photodegradation rate was found to increase with increasing TiO_2 dosages, but the reaction was slower at higher TiO_2 dosages. In addition, the presence of inorganic ions such as Cl^- and ${CO_3}^{2-}$ that are often presented in industrial effluents decreased the photocatalytic degradation rate of DMAMP. The photodegradation mechanism proposed consists of three main competitive pathways: the oxidation of the primary alcohol group, the rupture of the N–C bond and the cyclization of the β-amino alcohol group. The reaction mechanisms of TiO_2/UV proposed in this research would be useful for future application of the technology for degradation of alkanolamine compounds.

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References

[1] D.A. Dobberpuhl, D.C. Johnson, Pulsed electrochemical detection of alkanolamines separated by multimodal high-performance liquid chromatography, J. Chromatogr. A 694 (1995) 391–398.

[2] S.B. Hawthorne, A. Kubätovä, J.R. Gallagher, J.A. Sorensen, D.J. Miller, Persistence and biodegradation of monoethanolamine and 2-propanolamine at an abandoned industrial site, Environ. Sci. Technol. 39 (2005) 3639–3645.

[3] R.B. Butwell, D.J. Kubek, P.W. Sigmund, Hydrocarbon Processing, Gulf Publishing Co., 1982, pp. 108–116.

[4] I.K. Konstantinou, T.M. Sakellarides, V.A. Sakkas, T.A. Albanis, Photocatalytic degradation of selected s-triazine herbicides and organophosphorus insecticides over aqueous TiO_2 suspensions, Environ. Sci. Technol. 35 (2001) 398–405.

[5] M. Klare, J. Scheen, K. Vogelsang, H. Jacobs, J.A.C. Broekaert, Degradation of short-chain alkyl- and alkanolamines by TiO_2- and Pt/TiO_2-assisted photocatalysis, Chemosphere 41 (2000) 353–362.

[6] E. Pelizzetti, V. Maurino, C. Minero, V. Carlin, E. Pramauro, O. Zerbinati, M. Tosato, Photocatalytic degradation of atrazine and other s-triazine herbicides, Environ. Sci. Technol. 24 (1990) 1559–1565.

[7] K.H. Wang, Y.H. Hsieh, M.Y. Chou, C.Y. Chang, Photocatalytic degradation of 2-chloro and 2-nitrophenol by titanium dioxide suspensions in aqueous solution, Appl. Catal. B: Environ. 21 (1999) 1–8.

[8] M.I. Litter, Heterogeneous photocatalysis: transition metal ions in photocatalytic systems, Appl. Catal. B: Environ. 23 (1999) 89–114.

[9] K. Nagaveni, G. Sivalingam, M.S. Hegde, G. Madras, Solar photocatalytic degradation of dyes: high activity of combustion synthesized nano TiO_2, Appl. Catal. B: Environ. 48 (2004) 83–93.

[10] C.S. Lu, C.C. Chen, F.D. Mai, Y.C. Wu, Photocatalytic degradation of Michler's Ethyl Ketone in titanium dioxide dispersions under UV irradiation, J. Photochem. Photobiol. A: Chem. 187 (2007) 167–176.

[11] C.C. Chen, F.D. Mai, K.T. Chen, C.W. Wu, C.S. Lu, Photocatalyzed N-demethylation and degradation of crystal violet in titania dispersions under UV irradiation, Dyes Pigment 75 (2007) 434–442.

[12] I.K. Konstantinou, T.A. Albanis, TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: a review, Appl. Catal. B: Environ. 49 (2004) 1–14.

[13] N. Watanabe, S. Horikoshi, A. Kawasaki, H. Hidaka, N. Serpone, Formation of refractory ring-expanded triazine intermediates during the photocatalyzed mineralization of the endocrine disruptor amitrole and related triazole derivatives at UV-irradiated TiO_2/H_2O interfaces, Environ. Sci. Technol. 39 (2005) 2320–2326.

[14] N. Daneshvar, D. Salari, A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water: investigation of the effect of operational parameters, J. Photochem. Photobiol. A: Chem. 157 (2003) 111–116.

[15] D.D. Dionysiou, M.T. Suidan, E. Bekou, I. Baudin, J.M. Laîné, Effect of ionic strength and hydrogen peroxide on the photocatalytic degradation of 4-chlorobenzoic acid in water, Appl. Catal. B: Environ. 26 (2000) 153–171.

[16] C.G. Da Silva, J.L. Faria, Photochemical and photocatalytic degradation of an azo dye in aqueous solution by UV irradiation, J. Photochem. Photobiol. A: Chem. 155 (2003) 133–143.

[17] P.A. Bianco, M. Vincenti, A. Banciotto, E. Pramauro, Photocatalytic and photolytic transformation of chloramben in aqueous solutions, Appl. Catal. B: Environ. 22 (1999) 149–158.

[18] ANGUS Chemical Company Technical Data Sheet, JCR-Form No. 31900021, 2000.

[19] C.C. Chen, C.S. Lu, F.D. Mai, C.S. Weng, Photooxidative *N*-de-ethylation of anionic triarylmethane dye (sulfan blue) in titanium dioxide dispersions under UV irradiation, J. Hazard. Mater. B 137 (2006) 1600–1607.

[20] E. Evgenidou, K. Fytianos, I. Poulios, Photocatalytic oxidation of dimethoate in aqueous solutions, J. Photochem. Photobiol. A: Chem. 175 (2005) 29–38.

[21] A. Piscopo, D. Robert, J.V. Weber, Influence of pH and chloride anion on the photocatalytic degradation of organic compounds. Part I. Effect on the benzamide and *para*-hydroxybenzoic acid in TiO_2 aqueous solution, Appl. Catal. B: Environ. 35 (2001) 117–124.

[22] X. Zhu, C. Yuan, Y. Bao, J. Yang, Y. Wu, Photocatalytic degradation of pesticide pyridaben on TiO_2 particles, J. Mol. Catal. A 229 (2005) 95–105.

[23] E. Evgenidou, K. Fytianos, I. Poulios, Semiconductor-sensitized photodegradation of dichlorvos in water using TiO_2 and ZnO as catalyst, Appl. Catal. B: Environ. 59 (2005) 81–89.

[24] M. Sandin, S. Allenmark, L. Edebo, Selective toxicity of alkanolamines, Antimicrob. Agents Chemoth. 34 (1990) 491–493.

[25] M.G. Antoniou, D.D. Dionysiou, Application of immobilized titanium dioxide photocatalysts for the degradation of creatinine and phenol, model organic contaminants found in NASA's spacecrafts wastewater streams, Catal. Today 124 (2007) 215–223.

[26] Y. Cao, J. Chen, L. Huang, Y. Wang, Y. Hou, Y. Lu, Photocatalytic degradation of chlorfenapyr in aqueous suspension of TiO_2, J. Mol. Catal. A 233 (2005) 61–66.

[27] C.C. Wong, W. Chou, The direct photolysis and photocatalytic degradation of alachlor at different TiO_2 and UV sources, Chemosphere 50 (2003) 981–987.

[28] K. Pujara, S.P. Kamble, V.G. Pangarkar, Photocatalytic degradation of phenol-4-sulfonic acid using an artificial UV/TiO_2 system in a slurry bubble column reactor, Ind. Eng. Chem. Res. 46 (2007) 4257–4264.

[29] S.P. Kamble, S.B. Sawant, V.G. Pangarkar, Heterogeneous photocatalytic degradation of *p*-toluenesulfonic acid using concentrated solar radiation in slurry photoreactor, J. Hazard. Mater. 140 (2007) 149–154.

[30] A. Lair, C. Ferronato, J.-M. Chovelon, J.-M. Herrmann, Naphthalene degradation in water by heterogeneous photocatalysis: an investigation of the influence of inorganic anions, J. Photochem. Photobiol. A: Chem. 193 (2008) 193–203.

[31] T. Hirakawa, Y. Nosaka, Properties of $O_2^{\bullet-}$ and $OH^{\bullet}$ formed in TiO_2 aqueous suspensions by photocatalytic reaction and the influence of H_2O_2 and some ions, Langmuir 18 (2002) 3247–3254.

[32] H.Y. Chen, O. Zahraa, M. Bouchy, Inhibition of the adsorption and photocatalytic degradation of an organic contaminant in an aqueous suspension of TiO_2 by inorganic ions, J. Photochem. Photobiol. A: Chem. 108 (1997) 37–44.

[33] J.T. Yli-Kauhaluoma, C.W. Harwig, P. Wentworth Jr., K.D. Janda, Unexpected 1,3-oxazolidine formation in the attempted oxidation of N-aryl-N-methyl substituted β-amino alcohols using pyridinium dichromate, Tetrahedron Lett. 39 (1998) 2269–2272.

[34] R. Nakamura, Y. Nakato, Primary intermediates of oxygen photoevolution reaction on TiO_2 (rutile) particles, revealed by in situ FTIR absorption and photoluminescence measurements, J. Am. Chem. Soc. 126 (2004) 1290–1298.

[35] Y. Murakami, E. Kenji, A.Y. Nosaka, Y. Nosaka, Direct detection of OH radicals diffused to the gas phase from the UV-irradiated photocatalytic TiO_2 surfaces by means of laser-induced fluorescence spectroscopy, J. Phys. Chem. B 110 (2006) 16808–16811.

[36] J. Chen, D.F. Ollis, W.H. Rulkens, H. Bruning, Photocatalyzed oxidation of alcohols and organochlorides in the presence of native TiO_2 and metallized TiO_2 suspensions. Part (II). Photocatalytic mechanisms, Water Res. 33 (1999) 669–676.

[37] J. Araña, J.M. Doña-Rodríguez, J.A. Herrera Melián, E. Tello Rendón, O. González Díaz, Role of Pd and Cu in gas-phase alcohols photocatalytic degradation with doped TiO_2, J. Photochem. Photobiol. A: Chem. 174 (2005) 7–14.

[38] J.M. Herrmann, H. Tahiri, C. Guillard, P. Pichat, Photocatalytic degradation of aqueous hydroxy-butandioic acid (malic acid) in contact with powdered and supported titania in water, Catal. Today 54 (1999) 131–141.

[39] J. Araña, J.M. Doña-Rodríguez, O. González-Díaz, E. Tello Rendón, J.A. Herrera Melián, G. Colón, J.A. Navío, J. Pérez Peña, Gas-phase ethanol photocatalytic degradation study with TiO_2 doped with Fe, Pd and Cu, J. Mol. Catal. 215 (2004) 153–160.

[40] K.K. Barnes, C.K. Mann, Electrochemical oxidation of primary aliphatic amines, J. Org. Chem. 32 (1967) 1474–1479.

[41] T. van der Meulen, A. Mattson, L. Österlund, A comparative study of the photocatalytic oxidation of propane on anatase, rutile, and mixed-phase anatase–rutile TiO_2 nanoparticles: role of surface intermediates, J. Catal. 251 (2007) 131–144.

[42] Y. Yang, P.-G. Duan, Y.-Y. Wang, L.-Y. Dai, Additives assisted catalytic cyclodehydration of diethylene glycol in near-critical water, Chem. Eng. Process. 47 (2008) 2402–2407.

[43] R.B. Walker, M.-J. Huang, J. Leszczynski, An investigation of isomeric differences in hydrolytic rates of oxazolidines using computational methods, J. Mol. Struct. (Theochem) 549 (2001) 137–146.