Photocatalytic degradation of butanoic acid
Influence of its ionisation state on the degradation pathway: comparison with O_3/UV process

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Abstract

In an attempt to improve our understanding on the basic mechanisms of the degradation of aqueous organic pollutants by TiO_2-based photocatalysis, butanoic acid was selected, especially because it does not react with $O_2^{\bullet-}$ and it has several hydrogen atoms able to be abstracted by $OH^{\bullet}$ radicals. This study has been based on the identification and the quantification of the intermediate products of butanoic acid either by TiO_2 photocatalysis (pH=3.6 and 6.9) or by a homogeneous process (O_3/UV, pH=3.6) which forms $OH^{\bullet}$ radicals. In the latter case, acetic and butanedioic acids are the two main intermediates detected and, in a lesser extent, 3- and 2-oxobutanoic, oxalic and formic acids. TiO_2-based photocatalysis also yielded acetic acid, but an abstraction of one hydrogen atom, preferentially in β position, and a decarboxylation reaction also occurred giving 35% of 3-oxobutanoic acid and 10% of propanoic acid, after 10 min. The surface of titania and the holes (h^+) are suggested to explain the differences observed between photocatalysis and O_3/UV processes. TiO_2-based photocatalysis at neutral pH showed an increase in formic and butenoic acids formation as well as that of 2-oxobutanoic and oxalic acids which were not observed at acidic pHs. These results with the comparison of the kinetics at both pH have confirmed the participation of h^+ species and the role of the adsorption step in photocatalytic processes. The role of surface hydrogen atom was suggested by taking into account the decrease in the formation of propane and the formation of butenoic acid at pH=6.9. A mechanistic route is proposed for the photocatalytic degradation of butanoic acid. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

A large number of heterogeneous photocatalytic studies for air and water decontamination has been recently reviewed [1,2]. Concerning active species, can the hydroxyl radicals formed at the surface of TiO_2 totally account for the degradation of aromatic pollutants? Do other oxidative pathways also occur [1,3–4]? In our previous works, participation of active species other than $OH^{\bullet}$ has been demonstrated either by using enzyme [5,6] or by comparing the intermediates formed during the quinoline degradation using photocatalysis and Fenton processes [7].

Simple aliphatic acids are often found among oxidation products. Several publications about C_1–C_2 acids photodegradation have been studied in the presence of TiO_2 or Pt/TiO_2 with or without oxygen [8–12]. The formation of CO_2 and alkanes (methane and ethane in the case of acetic acid) has been indicated. A direct attack by photogenerated holes was proposed to explain the photo-Kolbe decarboxylation reactions observed. However, only a few studies have been done on the aqueous photocatalytic degradation of aliphatic acids, containing more than two carbon atoms [13–16]. These studies have been mainly performed in deaerated aqueous solution [14,15]. The influence of several parameters such as pH, amount of TiO_2, initial concentrations of pollutant, temperature, etc. have been examined [13]. In deaerated solutions, the formation of alcohols, acids, aldehydes (or ketones) and alkanes have been observed as intermediates during the photocatalytic degradations of C_2–C_4 acids [14] and of 4-oxopentanoic acid [15]. Sakata has proposed a mechanism with the participation of the holes h^+ and H_2O [14]. Nozik has suggested the attack by the hole or by $OH^{\bullet}$ radicals without specifying any mechanism [15]. In aerated solutions, Schwitzgebel et al. has found the formation of heptanol and heptanoic acid during octanoic acid degradation [16]. He has proposed the intervention of h^+ or of $OH^{\bullet}$ to produce $R^{\bullet}$ which could react with O_2. If

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all these studies have showed that acids are decarboxylated, only a few authors have indicated the oxidation reaction before decarboxylation, without any determination of the carbon atom preferentially oxidised in the molecule.

One of the aims of this work was to determine (i) the part of decarboxylation versus oxidation in aerated solutions and (ii) which carbon atom is preferentially oxidised by photocatalysis. In the second part, the role of adsorption and the nature of active species have been investigated. Subsequently the degradation intermediates obtained in the photocatalytic process at two pHs have been compared to those obtained with OH$^\bullet$ radicals generated by the O_3/UV process.

2. Experimental

2.1. Materials

Butanoic acid and the degradation intermediate products were obtained from Aldrich. Sulphuric acid (Merck, 96%), hydrochloric acid (Riedel-De-Haën), ether (Fluka, >99.8%), magnesium sulphate (Aldrich, 99%), sodium chloride (Prolabo, 99%), BSTFA with 1% TMCS (Supelco), diazomethane (home made) were employed as eluents, or as agents to set the pH values, to dry, to extract and to derivatise the aqueous samples. The photocatalyst was TiO_2 Degussa P-25 (mainly anatase, $50\,m^2\,g^{-1}$, non-porous).

2.2. Reactor and light source

The magnetically stirred aqueous suspensions were UV-irradiated in a cylindrical flask (total volume: ca. 90 ml), open to the air, with a bottom optical window whose surface was approximately $11\,cm^2$. In the case of O_3/UV degradation, the reactor was closed and ozonised oxygen was circulated in the reactor at a flow rate of $4\,ml\,min^{-1}$. For gas analyses, the reactor was closed and directly connected to a GC/FID apparatus (Varian 3400). Before introduction of butanoic acid, the air was saturated by oxygen. Irradiation was provided by a high-pressure mercury lamp (Philips HPK, 125 W) and the infrared radiations were filtered by a circulating water cell (thickness, 2.2 cm) equipped with a Pyrex cut-off filter. The radiant flux, entering the photoreactor, was measured with a power meter (UDT, model 21A), and found equal to $55\pm2\,mW\,cm^{-2}$. The corresponding number of photons per second potentially absorbable by TiO_2 was $(5.06\pm0.08)\times10^{17}$.

2.3. Initial conditions

A solution of 20 ml (3.77×10^{-3} or $5\times10^{-3}\,mol\,l^{-1}$) of butanoic acid was magnetically stirred, respectively, in the presence of TiO_2 ($3.5\,g\,l^{-1}$) or of ozonised oxygen (2.4%). During photocatalysis, the solution was kept 15 min in the dark in order to reach adsorption equilibrium. When degradation was performed at pH=6.9, KOH was added to adjust the pH. For the identification of the degradation intermediates by GC/MS, the initial concentration was $1.14\times10^{-2}\,mol\,l^{-1}$ (1005 ppm) and the suspensions were UV irradiated for 240 min. Before analyses, samples were acidified at pH=1 with HCl, then NaCl was added until saturation. Organic compounds were extracted 3 times with 20 ml of ether and the solution dried on $MgSO_4$, filtered and concentrated to 0.2 ml or to dryness. To silylate the organic acids sample, 30 ml of the concentrated solution was added to 100 µl of BSTFA. The vial was then closed with a teflon cap and the solution was let to react in a water bath at 333 K for over 30 min. An other silylation was made in the same condition with the dry sample. For the methylation, diazomethane was used as a derivatisation agent for organic acids.

2.4. Analyses

Millipore discs (0.2 µm) were used to remove particulate matter before HPLC analysis. The HPLC system was an LDC/Milton Roy Constametric 3000 isocratic pump, a waters 486 tunable absorbance detector adjusted at 210 nm and a Shimadzu C-R5A chromatopack integrator. The two columns used were either a Sarasep CAR-H, stainless steel of $300\,mm\times7.8\,mm$ with a flow rate of $0.7\,ml\,min^{-1}$ with a mobile phase of H_2SO_4 pH=2.5, or a Biorad Aminex HPX-87H of $300\,mm\times7.8\,mm$, with a flow rate of $0.27\,ml\,min^{-1}$ and a mobile phase of H_2SO_4 pH=2.0 as mobile phase.

GC/MS analysis were performed with an HP5890 chromatograph coupled to an HP5971 mass detector (electronic ionisation (EI)). The capillary column (length: 25 m, inner diameter: 0.25 mm) was packed with CPSil 5CB (thickness: 1.2 µm). The injection was made in the splitless mode. The temperature of the column was raised from 313 to 321 K ($20\,K\,min^{-1}$), then to 373 K ($5\,K\,min^{-1}$) for underivatised or methylated sample analysis, and from 313 to 413 K ($60\,K\,min^{-1}$) maintained for 4 min and to 553 K ($10\,K\,min^{-1}$) for silylated sample analysis. The analyses of alkane products was performed using an Intersmat OIGC 120 FB chromatograph equipped with a GS-Q $30\,m\times0.543\,mm$. The column temperature was kept at 333 K.

3. Results

3.1. Photocatalytic degradation of butanoic acid

3.1.1. Adsorption of butanoic acid onto TiO$_2$

At pH=3.6 (natural pH) there are 2.22×10^{-6} moles of dissociated butanoic acid (pK_a=4.83), corresponding to 3% of total acid amount, whereas TiO_2 is positively charged (pZc=6.5). Accordingly, we can estimate that all the molecules of butanoic acid which are dissociated, would

be adsorbed (i.e. ca. 0.38 molecules nm^{-2} of TiO_2). Analyses indicated an adsorption of $0.52+0.06$ molecules which implies the adsorption of 27% of the non-dissociated acid molecules.

This adsorption corresponded approximately to that observed with benzofuran [17] which is a molecule very poorly soluble in water. If we consider (i) that one molecule is adsorbed on one OH surface group and (ii) that there are 5×10^{18} $OH\,m^{-2}$ of TiO_2, there is a surface coverage of only 10%.

When the degradation was carried out at pH=6.9, all the butanoic acid molecules were dissociated, whereas the TiO_2 surface was approximately neutral. In this conditions, the number of adsorbed molecules was smaller than at pH=3.6 and only 0.27 molecules nm^{-2} were adsorbed. At pH=6.9, the surface of titania has as many positive charges as negative charges. According to the dissociated form of butanoic acid at this pH, the adsorption on negative charge is impossible and only half of the sites are available. This explains why only about half of butanoic acid molecules were adsorbed at pH=6.9 compared to pH=3.6.

3.1.2. Kinetics of the photocatalytic disappearance of butanoic acid

The kinetics of disappearance of butanoic acid correspond to an apparent first-order kinetic at both pH. The rate constant, k_{app}, is 8.9×10^{-3} and 1.2×10^{-2} min^{-1} at pH=3.6 and 6.9, respectively. These results suggest that the dissociated form is slightly more active than the neutral one, which is in agreement with the influence of pH found by Inel and Ökte [13] and with the observations of Sclafani et al. about acetic

acid degradation on different solids [9]. He has found that basic solids were the most active and he has suggested that monodentate acetate was the photoactive species.

3.1.3. Identification and evolution of organic intermediates at pH=3.6 and 6.9

At pH=3.6, three major intermediates were detected: acetic and 3-oxobutanoic acids and, in a lesser extent propanoic acid. Owing to the calibration of their HPLC peaks, these compounds represented about 35, 35 and 10% of, respectively, butanoic acid degraded within 10 min. Their evolutions are drawn in Fig. 1. Traces of 2-butenoic acid and of formic acid were also detected. These intermediates were identified using two HPLC columns and then confirmed by GC/MS without derivatisation and after methylation or silylation.

Using silylation and comparing with authentic compounds, 3- and 4-hydroxybutanoic acids were observed. These two compounds should be present at low concentration because of their absence in HPLC analysis. Several other peaks were detected after silylation and their mass spectrum are described further. At tr=10.3 min, a mass spectrum was recorded (Fig. 2) with fragments at $m/z=73$ and 147 corresponding to $(CH_3)_3Si^+$ and $(CH_2)_2=O-Si(CH_3)_3{}^+$, respectively. This last fragment indicates multisilylated compound. The parent peak was equal to $m/z=232$ and the fragmentation pattern corresponded to that of 3-oxopropanoic acid. Two other important peaks (tr=6.4 and 7 min) were obtained (Fig. 3a and b). In both cases, the same peaks appeared at 73 and 75, corresponding to $(CH_3)_3Si^+$ and $(CH_3)_2SiOH^+$, respectively. Moreover, we also know that
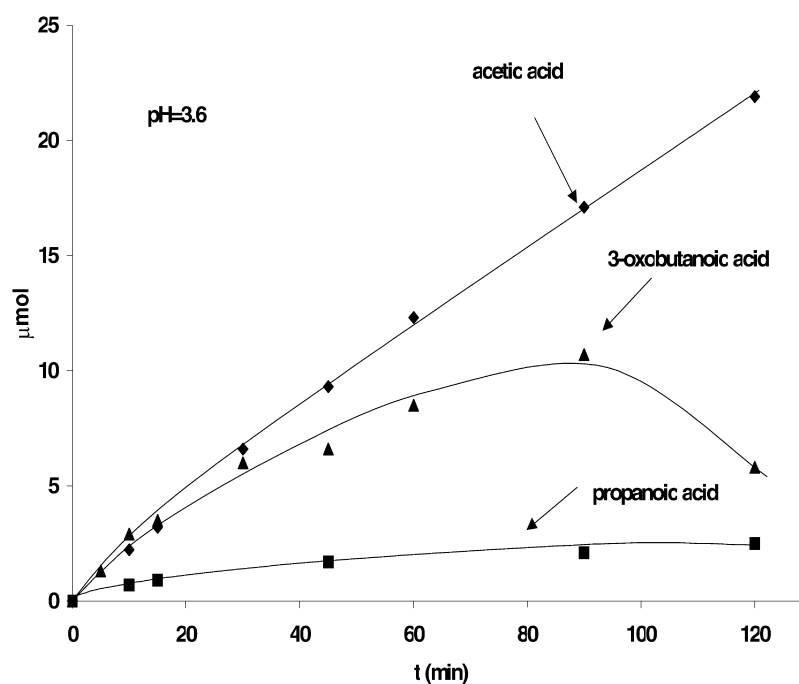

Fig. 1. Appearance and disappearance of main intermediates detected during the butanoic acid photodegradation on TiO_2 at pH=3.6.
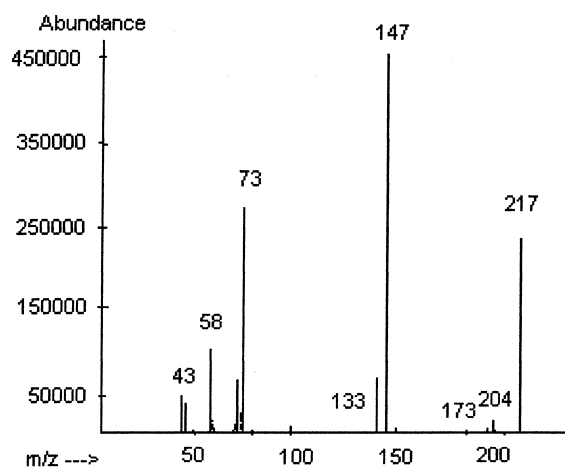
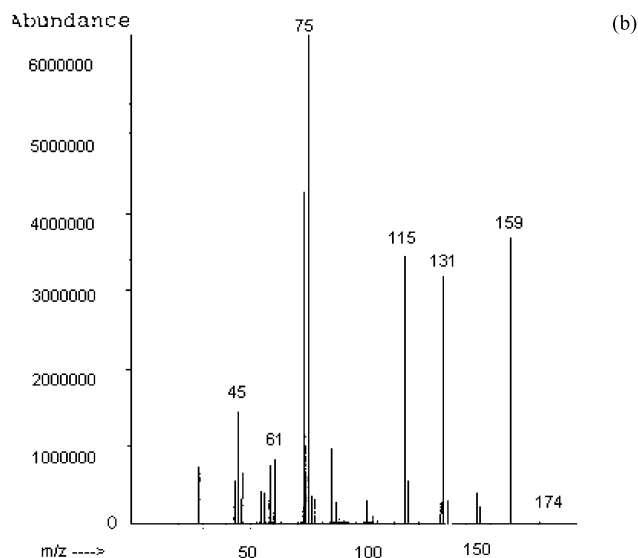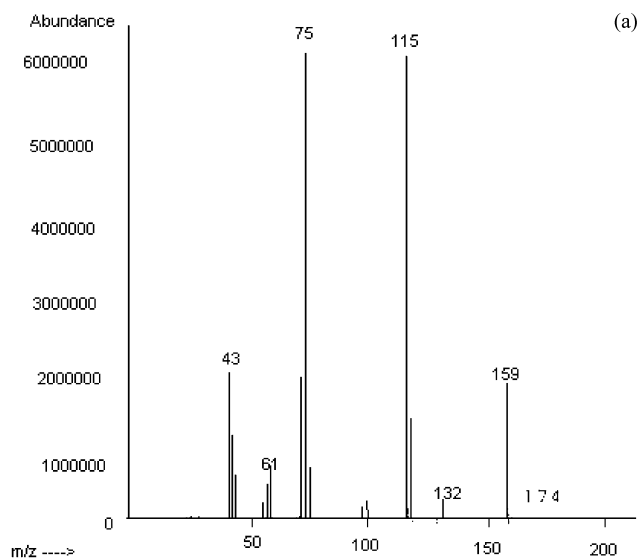Fig. 2. Mass spectrum of intermediate eluted at 10.3 min.

Fig. 3. Mass spectrum of intermediates eluted at (a) 6.4 and (b) 7 min.

there is only one silyl group in the molecule, since there are no peaks at $m/z=147$. For both peaks, isotopic contribution leads to the general formula $C_8H_{18}SiO_2$. Assuming that the compound is an acid, and subtracting the trimethylsilyl group, one gets the general formula C_4H_9COOH. For samples evaporated to dryness before silylation, we observed also similar fragmentations with a peak detected at 8.6 min. The conclusion was that the three isomers (pentanoic, 2-methylbutanoic and 3-methylbutanoic acids) were formed. With the same procedure, we observed also a peak at tr=8.8 min which corresponds to 3-hydroxypropanoic acid according to the library mass spectra. Two other peaks at tr=9.3 and 9.75 min were also obtained, which had a mass of 200 and with only one silyl group. Subtracting the trimethylsilyl group, we got $C_7H_{20}O_2$. These peaks could be due to condensation of two molecules of butanoic acid before decarboxylation and creation of a double bond.

The GC/FID analysis of gas phase showed the presence of two alkanes (ethane and propane) and two alkenes (ethene and propene) (Fig. 4). Although no calibration of these compounds were made, their overall concentration was lower than 20% for an irradiation period below 50 min. The percentage of organic carbon atoms left in the solution as a function of irradiation time is given in Fig. 5.

At pH=6.9, the main compounds are the same as at pH=3.6, i.e. acetic and 3-oxobutanoic acids. Their percentages are the same as those observed at pH=3.6. Meanwhile, propanoic, 2-butenoic and formic acid concentrations, are strongly increased, and represent 15, 7 and 7%, respectively within 10 min. Moreover, two other intermediates, oxalic acid and 2-oxobutanoic acids, appeared at pH=6.9. The last one corresponds to about 1% of butanoic acid degraded within 10 min and oxalic acid concentration increases as a function of time representing about 3% within 120 min. The evolution of all these organic compounds detected by HPLC are drawn in Fig. 6a and b.

No GC/MS analyses were made. Therefore, only the major intermediates were detected in these conditions. GC/FID gas phase analysis revealed also the presence of alkanes (ethane and propane) and alkenes (ethene and propene). An important decrease in propane concentration was observed when compared to experiments at pH=3.6, whereas other hydrocarbons increased (Fig. 7).

3.2. Degradation of butanoic acid by O_3/UV

3.2.1. Kinetics and intermediate formation

The butanoic acid disappearance by O_3/UV process corresponds to an apparent first order reaction. Its apparent rate constant ($1.4\,min^{-1}$) is slightly higher than k_{app} observed for the photocatalytic degradation.

Two major intermediates were detected: acetic and butanedioic acids. Their evolution are presented in Fig. 8.
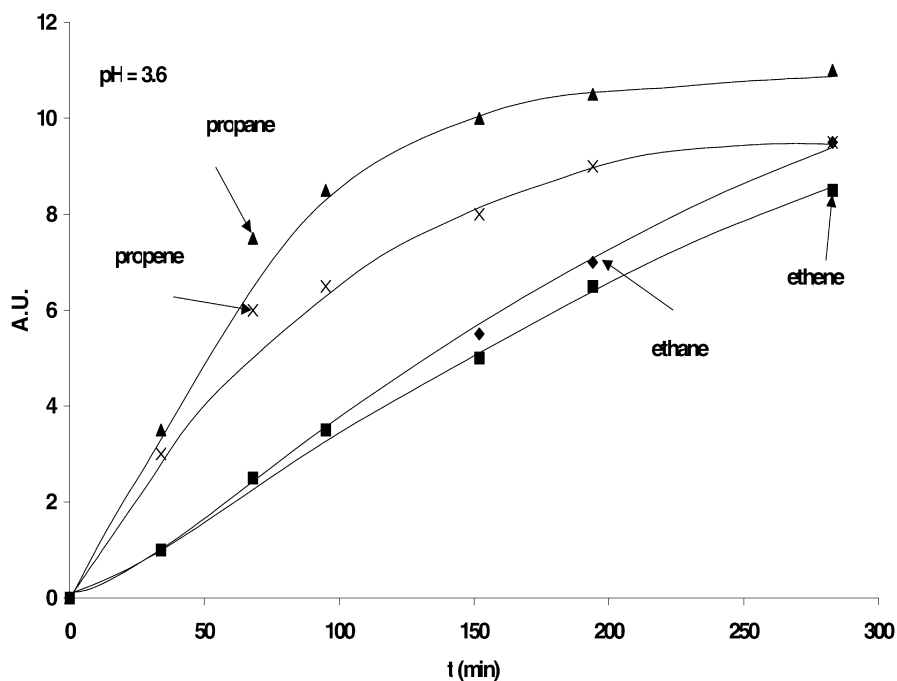
Fig. 4. Appearance and disappearance of alkane and alkene during photocatalysis at pH=3.6.
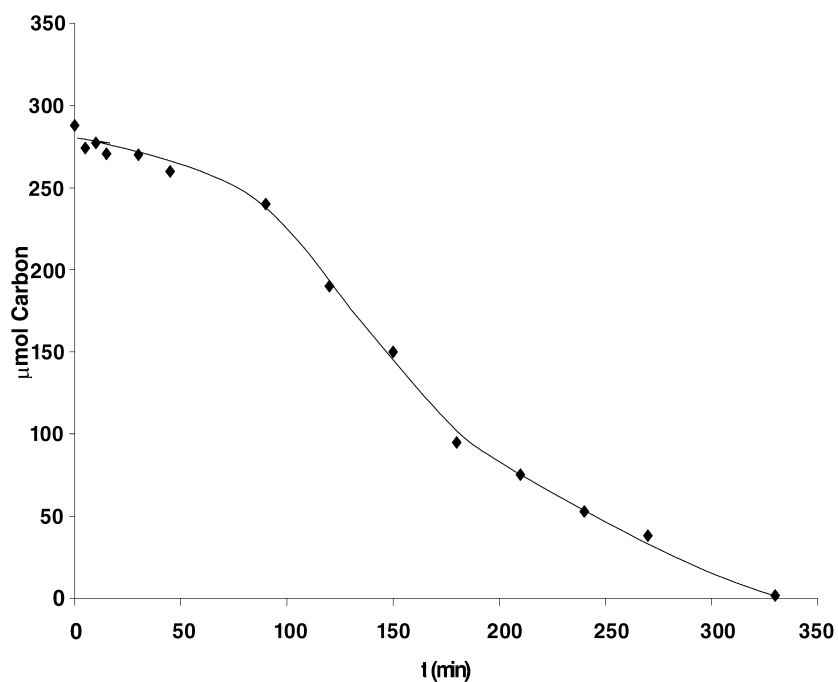
Fig. 5. Calculated organic carbon present in the solution as a function of time.

Traces of 2- and 3-oxobutanoic, propanoic and formic acids were also detected.

4. Discussion

A summary of all the intermediates identified for photocatalysis at both pHs and for O_3/UV are given in Table 1.

4.1. Comparison of photocatalytic degradation at pH 3.6 and 6.9

In the present study, the number of molecules adsorbed per square nanometer in the dark does not control the kinetics. The rate constant obtained at pH=6.9 is slightly higher than that observed at pH=3.6 while adsorption is smaller.
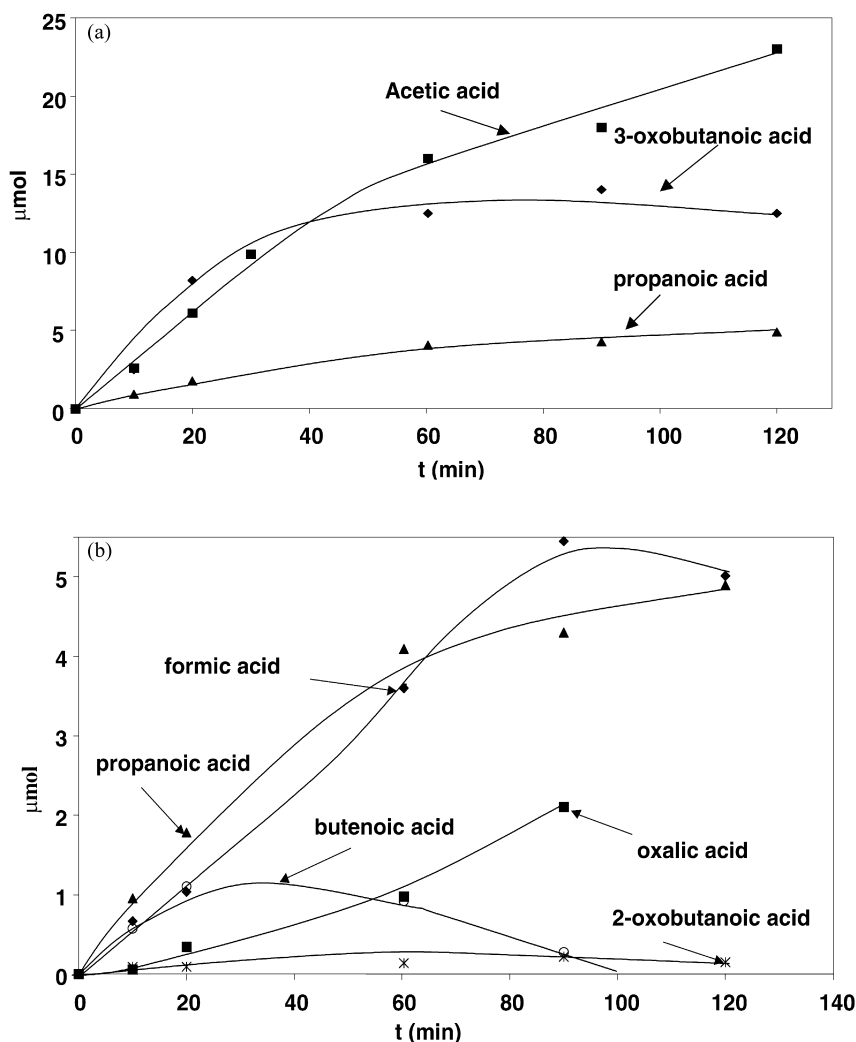
Fig. 6. Appearance and disappearance of intermediates during the butanoic acid photodegradation on TiO_2 at pH=6.9 (a) major intermediates and (b) other intermediates.

This result is opposite to the reactivity of OH$^\bullet$ on dissociated and on non-dissociated butanoic acid in homogeneous phase [18]. The reactivity of OH$^\bullet$ onto dissociated butanoic acid is 1.1 times higher than reactivity of OH$^\bullet$ onto dissociated butanoic acid. We assume that these species are not the only ones involved in the mechanism.

It is known that decarboxylation can occur in the photocatalytic degradation of acids by the transfer of h$^+$ to the carboxylic group [19–20]. It will be easier to decarboxylate dissociated acids as previously observed according to the reaction [13,21]:

This result agrees with the increase in propanoic acid formation at pH=6.9.

$$R-COO^- + h^+ \rightarrow R^\bullet + CO_2$$
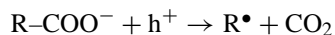
Whereas the main intermediates detected at both pH are the same, we observed the apparition of 2-oxobutanoic acid at neutral pH. The extent of H-abstraction by OH$^\bullet$ radicals in the α position at basic pH (or neutral) has already been noticed in homogeneous phase by radiolysis of aliphatic

acid [22]. However, the abstraction of H atoms by OH$^\bullet$ in α position appears more probable in homogeneous phase (around 12% at pH=2 and 25% at pH=9) than in heterogeneous phase (in our condition around 1% is detected at pH=6.9)

An hypothesis to explain the different reactivities of the C–H bonds in $CH_3-CH_2-CH_2-COOH$ and in $CH_3-CH_2-CH_2-COO^-$ towards OH$^\bullet$ radicals could be a difference in the extent of the inductive effect of the COOH and COO$^-$ groups. The smaller abstraction of a hydrogen atom in α position by photocatalysis could be due to the adsorption of COO$^-$ on TiO_2 which modifies the inductive effect.

The appearance of oxalic acid, at pH=6.9 could be explained by the formation of 2-oxobutanoic acid at this pH (Scheme 1).

Another difference observed when varying the pH is a decrease of the formation of propane at pH=6.9 (Fig. 7) which could be due to surface hydroxyl groups of TiO_2 as given by Eqs. (1) and (2).
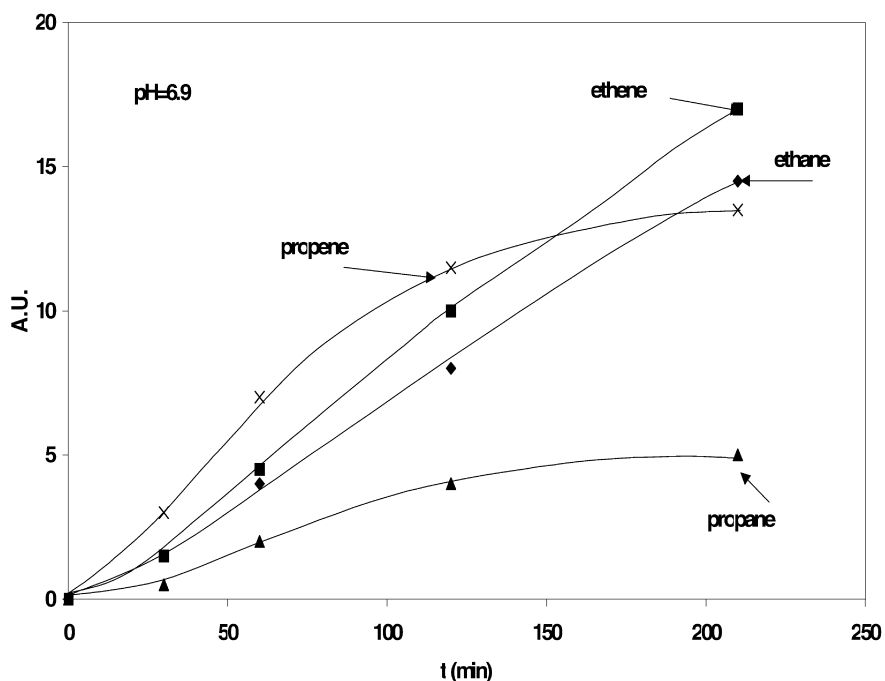
Fig. 7. Appearance and disappearance of alkane and alkene during photocatalysis at pH=6.9.

$$Ti{-}^{+}OH_2 + C_3H_7^{\bullet} + e^{-} \rightarrow Ti{-}OH + C_3H_8 \qquad (1)$$

$$Ti{-}OH + C_3H_7^{\bullet} + e^{-} \rightarrow Ti{-}O^{-} + C_3H_8 \qquad (2)$$
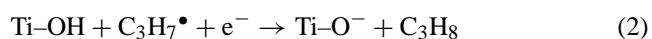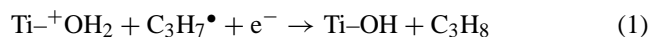
Positively charged (Ti–OH$_2^+$) and/or neutral surface hydroxyls (Ti–OH) could act as hydrogen sources. These sites are more important at acidic pH. This phenomenon has already been observed by Miyoshi et al. on Fe$_2$O$_3$ microcrystals [23]. No decrease of ethane content was observed at pH=6.9 probably because it can also be formed by reaction between two methyl radical coming from acetic acid. The formation of butenoic acid can also be explained by the decrease of hydrogen atom on the TiO$_2$ surface area.
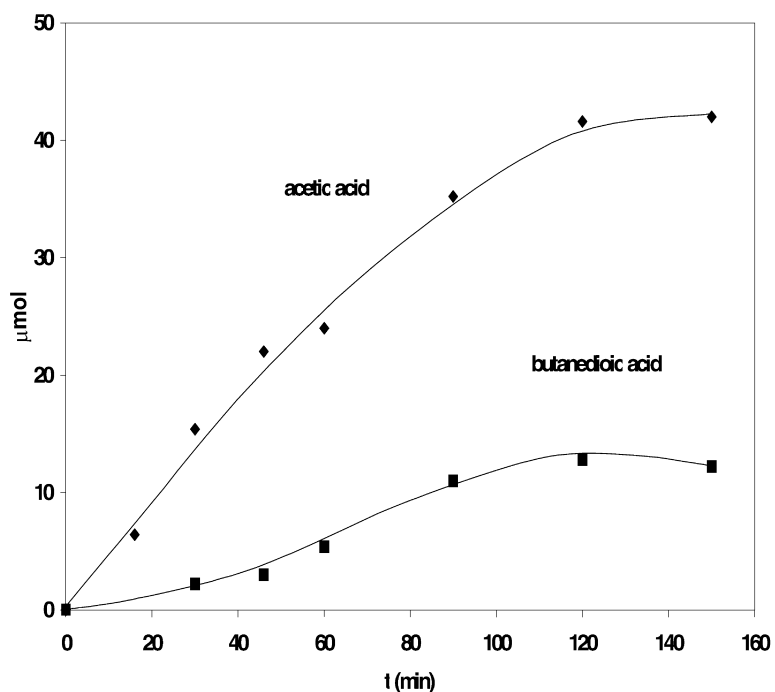
Fig. 8. Evolution of main intermediates observed by O$_3$/UV.

Table 1
Sum up of all intermediates identified in photocatalysis at both pH and in O_3/UVprocess and amount of main intermediates observed at 20% of butanoic acid conversion

Compounds	In photocatalysis		In O_3/UV
	pH=3.6 (μmol)	pH=6.9 (μmol)	pH=3.6 (μmol)
H–COOH	Trace[a]	0.8[a]	Trace[a]
CH_3–COOH	5[a,b]	5[a]	10[a]
HOOC–COOH	No	0.2[a]	Trace[a]
CH_3–CH_2–COOH	0.8[a,c]	1.3[a]	Trace[a]
HO–CH_2–CH_2–COOH	Trace[d]	–	–
HCO–CH_2–COOH	Trace[d]	–	–
CH_3–CH_2–CO–COOH	No	0.15[a]	0.05[a]
CH_3–CO–CH_2–COOH	4[a,b]	5.5[a]	0.07[a]
CH_3–CH_2–CH(OH)–COOH	Trace[e]	–	–
CH_2(OH)–CH_2–CH_2–COOH	Trace[e]	–	–
HOOC–CH_2–CH_2–COOH	Trace[a,e]	–	2.5[a]
CH_3–CH=CH–COOH	Trace[a,b]	0.8[a]	–
CH_3–$(CH_2)_3$–COOH	Trace[d]	–	–
CH_3–CH(CH_3)–CH_2–COOH	Trace[d]	–	–
CH_3–CH_2–CH(CH_3)–COOH	Trace[d]	–	–
Condensation of two molecules of butanoic acid	Trace[d]	–	–

[a] HPLC/UV analysis, comparison of retention time and UV spectrum.

[b] GC/MS analysis without derivatisation.

[c] GC/MS analysis after silylation and comparison with authentic compound.

[d] GC/MS analysis after silylation and identification by either own interpretation or with library manager (NBS49K).

[e] GC/MS analysis after methylation; in the case of the degradation realised by photocatalysis at pH=6.9 and by O_3/UV, no GC/MS analysis has been done. So the signal (–) means these compounds are not present by HPLC.

4.2. Comparison between photocatalytic and O_3/UV degradations

The kinetics of disappearance of butanoic acid is faster with O_3/UV than with photocatalysis. However (i) photocatalysis is not optimised and (ii) ozone is consumed whereas TiO_2 is a catalyst and can be recycled. Moreover, ozone photolysis is not a cheap process: three ozone molecules and one UV quantum are required for the production of merely two OH$^\bullet$ radicals [28]. Another advantage of photocatalysis is the possibility to use the solar energy [29].

In both cases acetic acid is an important intermediate, likely because (i) it is formed by different pathways and (ii) it reacts slowly with OH$^\bullet$ radicals. Its rate constant is in average $1.6 \times 10^7 \, l \, mol^{-1} \, s^{-1}$, although it is $2.2 \times 10^9 \, l \, mol^{-1} \, s^{-1}$ with butanoic acid [19]. Moreover the main intermediate detected with O_3/UV or with photocatalysis corresponds to an oxidation either in γ-position (butanedioic acid) or in β-position (3-oxobutanoic acid), respectively.

In O_3/UV process, O_3 is photolysed into O_2 plus one oxygen atom, which forms H_2O_2. Subsequently H_2O_2 reacts with O_3 to give OH$^\bullet$ radicals [28]. The abstraction of one hydrogen atom preferentially occurs at the farthest position, even with a carbon atom in sp^3 configuration. This phenomenon has already been observed in homogeneous phase by Dixon et al. [24]. He showed by RPE the presence of $^\bullet CH_2$–CH_2–COOH originating from propanoic acid.

Two hypotheses can explain the abstraction of a γ-hydrogen atom: (i) the presence of the COOH deactivating group or (ii) more likely, an intramolecular H-abstraction by the carboxyl radical. In the case of photocatalysis, the adsorption of butanoic acid via its carboxyl group at the surface of TiO_2 would explain the absence of the abstraction of a γ-hydrogen atom. Therefore, in photocatalysis the H-abstraction will mainly occur on the farthest sp^2 carbon atom, because of the deactivating effect of the COOH group.

The formation of propanoic acid is more important by photocatalysis than by O_3/UV, according to the reaction of COO$^-$ with hole (h$^+$) photogenerated by photocatalysis. Nevertheless, decarboxylation is not the only way for the photocatalytic degradation of acid compounds, as suggested by several authors [12,25–27]. The differences come from the use of Pt/TiO_2 [11,12] instead of TiO_2 in deaerated solution and the study of aromatic acid [12,30] or acetic acid [9,26] which have no hydrogen in β position.

The formation of the 2-oxobutanoic acid by the O_3/UV process at acidic pH corresponds to the abstraction of an H atom in α position. Since it is absent at the same pH in photocatalytic degradation, this confirms that adsorption modifies the inductive effect of COOH.

4.3. Proposition of photocatalytic degradation pathways for butanoic acid

The butanoic acid degradation occurs in two steps, first, the formation of an alkyl radical either by OH$^\bullet$ radical attack or by a hole h$^+$, and secondly, the reaction of this alkyl radical either with O_2 or with RH or $(Ti–OH_x)^{(x-1)+}$ surface species (Scheme 1). Depending on the presence of non-dissociated or dissociated butanoic acid, the H-abstraction will occur via an attack by an OH$^\bullet$

A- FORMATION OF ALKYL RADICAL

(a) Reaction with OH°

$$H_3C-CH_2\cdot CH_2\cdot COOH$$
$$\downarrow OH°$$
$$H_3C-CH_2\cdot CH°\cdot COOH \ + \ H_3C-CH°\cdot CH_2\cdot COOH \ +°H_2C-CH_2\cdot CH_2\cdot COOH$$

(b) Reaction with h$^\pm$

$$H_3C-CH_2\cdot CH_2\cdot COO^- \ \xrightarrow{h^+} \ H_3C-CH_2\cdot CH_2° \ + \ CO_2$$

B- REACTION WITH O$_2$

$$H_3C-CH_2-CH°-COOH \ \xrightarrow{O_2} \ H_3C-CH_2-\underset{\underset{OH}{|}}{CH}-COOH \ + \ H_3C-CH_2-CO-COOH$$
$$(trace) \qquad\qquad (trace)$$

$$\textbf{H}_3\textbf{C-CH}_2\textbf{ COOH} \ + \ \textbf{H}_3\textbf{C-COOH} \ + \ HOOC-COOH$$

$$H_3C-CH°-CH_2-COOH \ \xrightarrow{O_2} \ H_3C-\underset{\underset{OH}{|}}{CH}-CH_2-COOH \ + \ \textbf{H}_3\textbf{C-CO-CH}_2\textbf{-COOH}$$
$$(trace)$$

$$OHC-CH_2\cdot COOH \quad + \quad \textbf{H}_3\textbf{C-COOH}$$
$$(trace)$$

$$°H_2C-CH_2-CH_2-COOH \ \xrightarrow{O_2} \ HOH_2C-CH_2-CH_2-COOH \ + \ HOOC-CH_2-CH_2-COOH$$
$$(trace) \qquad\qquad\qquad (trace)$$

$$H_3C-CH_2-CH_2° \ \xrightarrow{O_2} \ \textbf{H}_3\textbf{C-CH}_2\textbf{-COOH} \quad + \quad H_3C-CH_2-CH_2OH$$

C- REACTION WITH RH or TiO$_2$-SURFACE

$$H_3C-CH_2\cdot CH_2° \ \xrightarrow{RH \ or \ TiOH \ or \ (TiOH_2)^+} \ H_3C-CH_2\cdot CH_3$$

$$H_3C-CH_2\cdot CH_2° \ \xrightarrow{TiO^-} \ CH_3\cdot CH=CH_2$$

Scheme 1. Photocatalytic degradation pathway of butanoic acid photodegradation on TiO$_2$. The main intermediate products detected are drawn in bold.

radical, or by a hole (h$^+$). Radicals can react with O$_2$ adsorbed on TiO$_2$ and form a tetroxide which degrades following the mechanism proposed by von Sonntag and Schuchmann [31]. This mechanism is presented in the case of a β H-abstraction in Scheme 2. The obtention of traces of 2-oxobutanoic and 4-hydroxybutanoic acids shows that H-abstraction is pr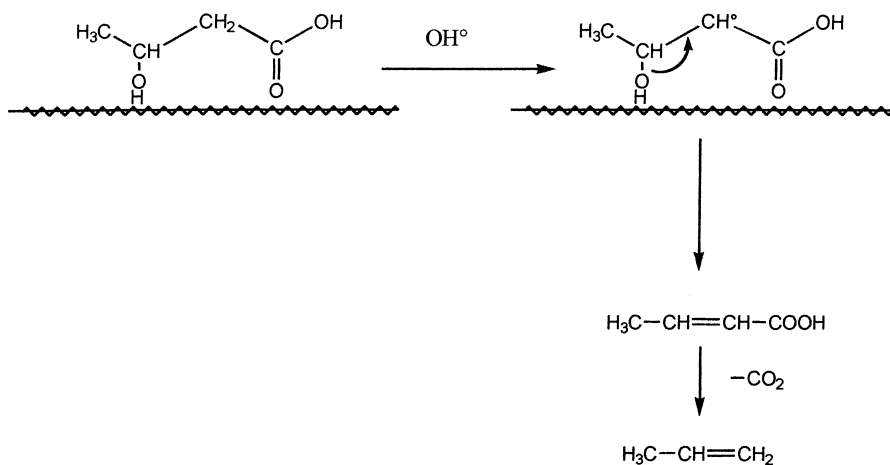omoted in β position by photocatalysis. In our case, 3-oxobutanoic and acetic acids are the main intermediates and only small amount of 3-hydroxybutanoic acid is detected. The major pathways are a, or c in order to form 3-oxobutanoic and acetic acids by oxidation of acetaldehyde. Nevertheless, alcohol can be formed and be dehydroxylated on TiO$_2$ surface to give 2-butenoic acid. This latter acid can give propene by decarboxylation (Scheme 3). Oxoacid can also be formed by reaction between R$^\bullet$ and O$_2$ and then by H-abstraction of a new butanoic acid molecule

$$H_3C-CH^\circ-CH_2-COOH$$

$$\downarrow O_2$$

$$H_3C-CH(OO^\circ)-CH_2-COOH$$

$$\textbf{(A)}$$

$$\textbf{(A)} \longrightarrow \begin{array}{c} CH_2-COOH \\ | \\ H_3C-CH-O_4-CH-CH_3 \\ | \\ CH_2-COOH \end{array}$$

a	b	c	d
$2\ H_3C-CO-CH_2-COOH$	$H_3C-CO-CH_2-COOH$	$2\ CH_3-COH$	$2\ H_3C-CHO^\circ-CH_2-COOH$
$+$		$+$	
H_2O_2	$H_3C-CHOH-CH_2-COOH$	O_2	
	$+$	$+$	
	O_2	$2\ CH_2{}^\circ-COOH$	
		$(or\ 2\ OHC-CH_2-COOH$	
		$+\ O_2+2\ CH_3{}^\circ\ )$	

Scheme 2. Oxidation mechanism of butanoic acid by formation of tetroxide (scheme proposed by von Sonntag and schuchmann [31]).

Scheme 3. Dehydroxylation and decarboxylation photoassisted on TiO_2 surface.

to form a peroxide which, by further oxidation, will give an oxocompound.

Alkyl radicals formed after decarboxylation can give either propene or propane by reaction with RH or with surface of TiO_2 or propanoic acid by reaction with O_2.

The same mechanisms can also be used for the degradation of intermediate compounds. The formations of pentanoic, 2- and 3-methylbutanoic acids are explained by attack of $CH_3{}^\bullet$ radicals on butanoic acid. $CH_3{}^\bullet$ radicals can also dimerise and form ethane.

5. Conclusions

In contrast with the faster reaction of non-dissociated acid with $OH^\bullet$ radicals in homogeneous phase, photocatalytic degradation provides 1.3 times smaller reaction rate. This phenomenon is probably due to the participation of hole in the photocatalytic reaction mechanism.

At pH=6.9, 2-oxobutanoic, oxalic and formic acids are formed, whereas they are not present at pH=3.6 (or as traces: in the case of formic acid). The extent of H-abstraction by

OH$^\bullet$ radical in α position at pH more basic has already been observed in homogeneous phase [22]. However, it was less important in the photocatalytic degradation. This difference is explained by the modification of $-I$ effect of COO^- when it is adsorbed. The decrease of butane formed at pH=6.9 is probably due to the involvement of surface hydroxyls of TiO_2.

The comparison of intermediates issued from the degradation of butanoic acid by photocatalysis and by O_3/UV shows the participation of h$^+$ in the photocatalytic mechanism, involving the formation of propanoic acid, and of alkanes and alkenes. The participation of OH$^\bullet$ seems at least equivalent. However, the H-abstraction appears to be modified by the adsorption of the acid. In homogeneous phase, intramolecular H-abstraction by the carboxyl radical can occur, forming butanedioic acid while, in photocatalytic degradation, the adsorption of butanoic acid via its carboxyl group prevents the intramolecular H-abstraction and favours the H-abstraction on the farthest sp^2 carbon atom because of the presence of the deactivating carboxyl group. A mechanism involving h$^+$, OH$^\bullet$ and titania's surface are proposed to explain all the intermediates detected by photocatalysis. This work has allowed us to have a better knowledge of the reactions involved in the photocatalytic degradation of acids.

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